



UNIVERSITY OF NOVI SAD
FACULTY OF TECHNICAL SCIENCES „MIHAILO PUPIN“
ZRENJANIN, REPUBLIC OF SERBIA
in cooperation with
POLITEHNICA UNIVERSITY,
TIMISOARA, ROMANIA

PROCEEDINGS



2nd INTERNATIONAL
CONFERENCE

„ECOLOGY OF URBAN AREAS 2012“

Zrenjanin, October 15th, 2012
Serbia



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TIMISOARA, ROMANIA

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„ECOLOGY OF URBAN AREAS 2012“

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INTRODUCTION

Science has a very important role in raising awareness of the importance of responsible use of natural resources and environmental protection. We, as scientists and individuals, should have a mission to find new ways for prevention of damage caused by rising levels of pollution, nuclear waste, depletion of non-renewable natural resources and to find a balance between rapid scientific and technological progress, on one hand, and protection of environment and health, on the other.

The Faculty of Technical Sciences “Mihajlo Pupin“ from Zrenjanin, as a part of the University of Novi Sad, in cooperation with the Politechnica University from Timisoara, Romania, has organized the Second International Conference “Ecology of Urban Areas 2012” (URBANECO 2012).

The conference is organized bearing in mind the importance of the ecological aspect in the sustainability of urban areas and its activities are aimed at the presentation of issues related to protection and development of urban areas in the region and beyond.

It aims to enable and expand regional and international cooperation between the University of Novi Sad and other educational institutions and businesses, especially the Politechnica University from Timisoara, thus increasing the level of professional and scientific activities at the Faculty of Technical Sciences “Mihajlo Pupin“ from Zrenjanin. We wish to engage research capacities in the region to solve the problems of protection of urban environment, to enhance the level of research in this area, and the interest of the economy for the introduction of new technologies.

The indirect aim of the project is the promotion of the Faculty of Technical Sciences from Zrenjanin as one of the bearers of economic and social development in the Banat region.

The aims of the International Conference “Ecology of Urban Areas 2012” are in full accordance with the priorities of the adopted Strategy for Sustainable Development as well as the Scientific and Technological Development Strategy of the Republic of Serbia.

Topics which will be dealt with at this year’s conference are: Air quality, Management of solid urban waste, Water quality in urban areas (ground water, drinking water, waste water and facilities), System of ecological management (ISO 14000), Economics of sustainable development of urban areas, Noise and vibrations in urban areas, Electro and electro- magnetic pollution in urban areas, Climate changes and urban pollution, Transfer stations in the system of management of solid communal waste, Spatial planning and greening in urban areas, Development of urban ecology through educative and information activities, ICT in the ecology of urban areas, Accidents in urban areas, Environmental aspects of traffic in urban areas, Impact of agricultural activities to urban area and Public health and the ecology of urban areas.

We would like to express our gratitude to the Ministry of Environment, Mining and Spatial Planning of Serbia, the Ministry of Education and Science of Serbia, the Ministry of Economy and Regional Development of Serbia, Serbian Chamber of Commerce, Provincial Department of Science and Technology and Provincial Secretariat for Environmental Protection and Sustainable Development.

Finally, we wish to thank all the authors of papers and participants in the Conference in hope that we will continue our cooperation successfully in the future and that each new year will bring better ideas and solutions to help raise awareness of the responsibility we hold today for the well-being of future generations.

President of the Organizing Committee
Ph.D Vjekoslav Sajfert

Zrenjanin, October 2012.

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We wish to thank **Ministry of Education and Sciences**, Republic of Serbia
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II International Conference „ECOLOGY OF URBAN AREAS 2012“

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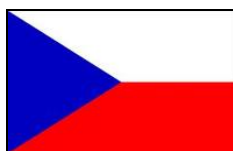
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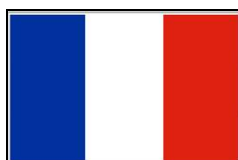
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AIR QUALITY

**II International Conference
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**STUDY ON ATMOSPHERIC WATER VAPOR CONTENT,
COMPARING DATA COLLECTED FROM WEATHER STATION AND
SUN PHOTOMETER DIRECT MEASUREMENTS**

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ABSTRACT

The paper gives the amount of water vapor above Timisoara, Romania. Data used to calculate the amount of water vapor is taken from sun photometer and weather station located at “Politehnica” University of Timisoara (45.74 N; 21.22 E). The study was achieved for March - December 2011. The extraction of water vapor amount from sun photometer measurements relies on a measurement in the region of water vapor absorption at 940 nm. To apply the empirical models, the temperature, barometric pressure and humidity content has been taken from weather station.

Key words: sun photometer, weather station, water vapor, AERONET, temperature, humidity.

INTRODUCTION

Earth’s atmosphere contains roughly 78.08% nitrogen, 20.95% oxygen, 1.247% water vapor (a variable amount), 0.93% argon, 0.038 carbon dioxide and other gases. This value was determined by National Center for Atmospheric Research (<http://ncar.ucar.edu/>). This water vapor makes up less than 0.001% of all the water on the Earth and this is important to our climate.

Aerosols play important roles in global climate change by increasing backscattered solar radiation and by absorbing solar and longwave radiation and also, by altering cloud properties.

Sun photometry has the capability to describe characteristic features of different air masses and the aerosol sources that affect the climate. Aerosol optical depth and size distributions can be derived remotely through solar direct beam measurements at a range of wavelengths and zenith angles (Kanfman et al., 2002; Dubovnik et al., 2002; Dubovnik et al., 2000; Popescu et al., 2010). From aerosol optical depth can remove the required amount of water vapor.

A sun photometer is an optical instrument for the measurement of the spectral solar radiation. The spectral resolution depends on the number of channels. The range of wavelength is between 340 - 1640 nm. The 940 nm channel is used for column water abundance determination.

The Aerosol RObotic NETwork (AERONET) is a global network of sun photometers. In this network exists over 700 instruments, 5 of them being in Romania (AERONET-NASA; Holben et al., 1998). The network hardware consists of identical automatic Sun–sky scanning spectral radiometers owned by national agencies and universities. AERONET provides not only spectral aerosol optical depth, but also derived aerosol properties, such as, single-scattering albedo, asymmetry parameter, phase function, and size distributions of aerosol particles at a given location.

This paper presents the results of continuous measurements of aerosol optical properties from whence is extracted amount of water vapor over Timisoara for almost 1 year. And, from values recorded by the weather station, using several methods is deduced the amount of water in the atmosphere.

The measurements taken from weather station and used in this paper include temperature, barometric pressure and humidity.

This analysis is very important, because water vapor is the most potent greenhouse gas.

EXPERIMENTAL

The sun photometer and weather station is located on the roof of the Mechanical Engineering Faculty of “Politehnica” University of Timisoara (figure 1), with coordinates: 45.74 N; 21.22 E.

The sun photometer from Timisoara is connected at AERONET site (<http://aeronet.gsfc.nasa.gov>), ranking #645.

Figure 1 left presents the components of sun photometer. This is composed of an optical head, an electronic box and a robot (Sunphotometer, 2010).



Figure 1. Sun photometer and weather station located at “Politehnica” University of Timisoara

The optical head has two channel systems: the sun collimator and the sky collimator. The sun tracking is equipped with a 4- quadrant detector. The electronic box contains two microprocessors for real time operation for data acquisition and motion control. In automatic mode, a ‘wet sensor’ detects precipitation and forces the instrument to park and to protect the optics. The robot is moved by step-by-step motors in two directions: in the zenith and azimuth planes. The sun photometer accomplishes two basic measurements, either direct sun or sky, both within several programmed sequences. The direct sun measurements are made in nine spectral bands (340, 380, 440, 500, 670, 870, 940, 1020 and 1640 nm) requiring approximately 10 seconds. The 940 nm channel is used for column water abundance determination. Sky measurements are performed at 440 nm, 670 nm, 870 nm, and 1020 nm. Two basic sky observation sequences are recorded: the “almucantar” and the “principal plane”.

RESULTS AND DISCUSSIONS

Sun photometer measures the spectral extinction of the direct solar radiation. This is expressed in the Beer-Lambert-Bouguer law:

$$V_{\lambda} = V_{0\lambda} \left(\frac{d_0}{d} \right)^2 \exp(-\tau \cdot m) \quad (1)$$

where:

- V is the digital voltage, in V,
- V_0 - extraterrestrial voltage, in V,
- λ - wavelength, in nm,

m – optical air mass,
 d_0 - the average Earth - Sun distance, expressed in astronomical units (AU),
 d - the Earth - Sun distance on the day of observation, expressed in astronomical units (AU),
 τ_t - total atmospheric optical thickness.

The air mass is calculated as function of the solar zenith angle. Absorption by water vapor is restricted to narrow spectral bands. The extraction of water vapor amount from sun photometer measurements generally relies on a measurement in the region of water vapor absorption at 940 nm. The aerosol effect is removed by extrapolating the value based on an adjacent band outside the absorption or, by interpolation between two adjacent bands. Equation 1 is not valid since exponential attenuation applies strictly to monochromatic radiation and is invalid across the broad region of water vapor absorption.

Transmission in the water vapor band (T_w) can be modeled as:

$$T_w = \exp(-am^bW^b) \tag{2}$$

where:

T_w is transmission in the water vapor,
 W - vertical column abundance
 a, b - constants depend on the wavelength position, width and shape of the sun-photometer filter function, and the atmospheric conditions.

Figure 2 presents the variation of water vapor depending to the Julian day. In this paper the range for Julian day is between March – December 2011. Value for the amount of water vapor is given in cm. Under normal pressure, atmospheric height standard is 8 km of which enter 1 - 7 cm represents the variation in the amount of water vapor. In figure can be see the variation amount of water vapor from spring to winter. The amount of water vapor presents the maximum during summer.

The average amount of water vapor in the studied period has a value of 1.405 cm, with an error of 1.0039 % (table 1).

Table 1: The average water vapor from Timisoara station during March – December

Month	Mar	Apr	May	Jun	Jul
w	0.979	1.251	1.844	2.368	2.453
Month	Aug	Sep	Oct	Nov	Dec
w	2.493	2.192	1.066	0.915	0.786

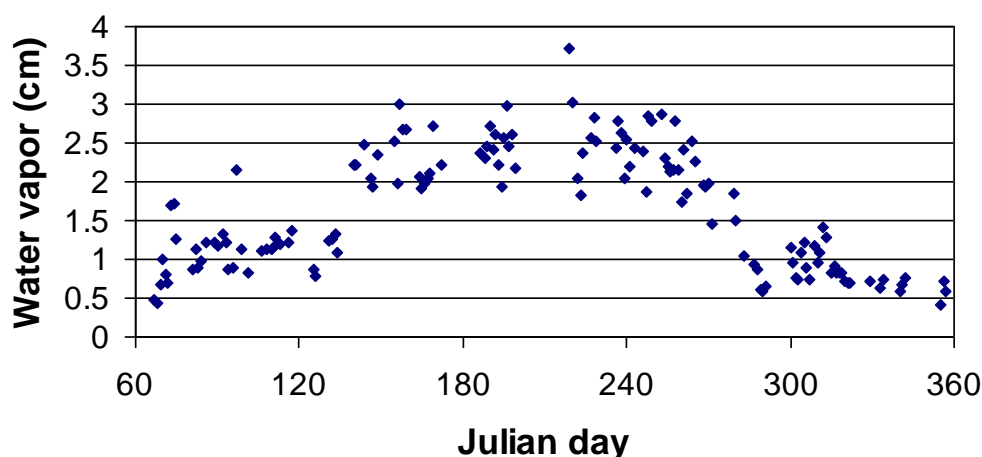


Figure 2. Water vapor during March to December 2011 at Timisoara

From figure 3 can be observed that frequency distribution the amount of water vapor is over 14 % for 0.75 – 1.25 cm. In intervals 0.50 – 0.75 cm and 2.00 – 2.25 cm, occupation frequency is 12 %.

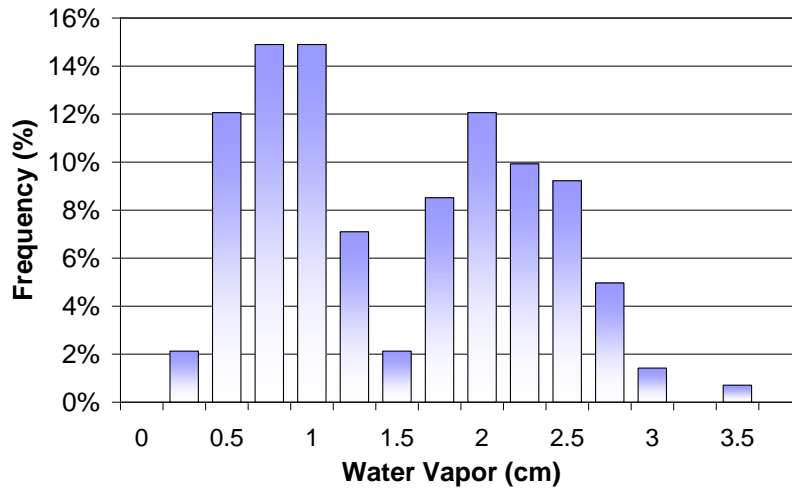


Figure 3. Frequency distribution of water vapor during March to December 2011 at Timisoara

Another way to calculate the water column content is using Hann's equation 3 (Hann, 1991):

$$w = 0.25 \cdot p_{sat} \cdot RH \quad (3)$$

where:

- w is water vapor column, in g/cm²,
- p_{sat} – saturation pressure of water vapor, in (hPa),
- RH - relative humidity of the air, %.

The saturation pressure of water vapor is given in equation 4:

$$p_{sat} = e^{77.3450 + 0.0057T - 7235/T} / T^{8.2} \quad (4)$$

where: T is temperature, in K.

Inserting equation 4 into 3 is obtained water vapor, knowing the temperature and the relative humidity. Precipitable water product consists of column water-vapor amounts. An alternative method often used to calculate the amount of precipitable water is given by Lencker (Lekner, 1978). Lencker's correlation expresses the precipitable water in terms of relative humidity:

$$w_L = 49.3 \frac{RH p_{sat}^L}{T} \quad (5)$$

$$p_{sat}^L = 0.01 \exp\left(26.23 - \frac{5416}{T}\right) \quad (6)$$

Knowing the RH and inserting the equation (6) into (5) is obtained another value of water vapor. More recently, Gueymard (Gueymard, 1993) introduced a new relationship between w and the surface temperature and relative humidity given by equation (7).

$$w_G = 21.67 H_v \frac{RH * p_{sat}^G}{T} \quad (7)$$

Where:

- w_G is precipitable water given by Gueymard,
- p_{sat}^G - saturation pressure of water vapor given by Gueymard.

$$\ln p_{sat}^G = 22.33 - 49.14 \frac{100}{T} - 10.922 \left(\frac{100}{T}\right) - 0.3902 \frac{T}{100} \quad (8)$$

$$H_v = 0.4976 + 1.5265 \frac{T}{273.15} + \exp\left(13.6897 * \frac{T}{273.15} - 14.9188 \left(\frac{T}{273.15}\right)^3\right) \quad (9)$$

In the absence of an atmospheric sounding or solar spectral measurements, the linear relationship between the logarithm of w and dew point temperature T_d , has been often used to calculate precipitable water with Iqbal equation (3) (Lecker, 1978):

$$\ln w = a + bT_d \tag{10}$$

where:

a and b is parameters, being calculated for every place and for a specific sampling time, T_d - dew point temperature, in °C.

The values for a and b parameters was calculated by Wright (Wright et al., 1989). Which were suitable for estimating precipitable water under cloudless.

Figure 4 represent the different empirical models of calculation of water vapor. Values obtained by the method used to calculate amount of water vapor from 940 nm wavelength of sun photometer are between the four empirical models of calculation whit data from weather station.

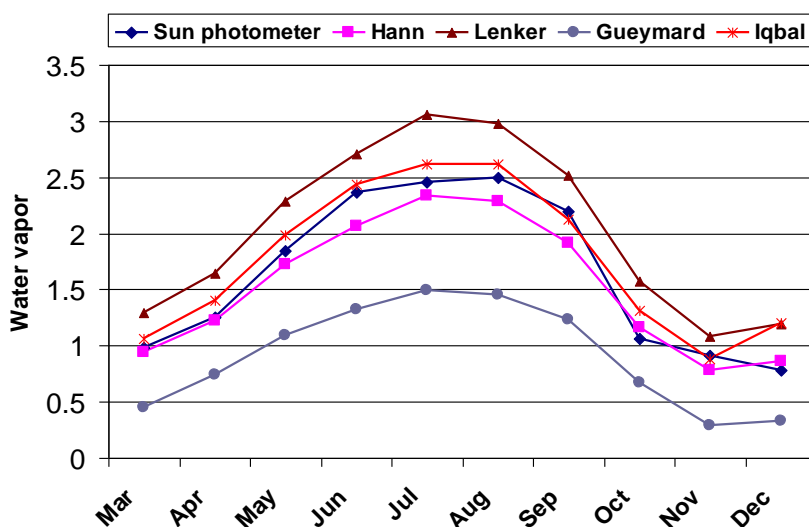


Figure 4. Different methods for calculating atmospheric water during March to December 2011

Table 2 represents the monthly average for water vapor calculated with several equations: Hann, Lenker, Gueymard and Iqbal.

Table 2: The average water vapor from Timisoara during March – December using several methods

	Hann	Lenker	Gueymard	Iqbal
Mar	0.942	1.289	0.455	1.064
Apr	1.227	1.645	0.739	1.403
May	1.723	2.285	1.090	1.982
Jun	2.064	2.706	1.324	2.439
Jul	2.340	3.057	1.496	2.614
Aug	2.285	2.982	1.458	2.614
Sep	1.919	2.517	1.231	2.124
Oct	1.164	1.570	0.667	1.310
Nov	0.779	1.079	0.290	0.885
Dec	0.863	1.194	0.329	1.206

CONCLUSIONS

This paper analyzes data from sun photometer for 940 nm wavelength and weather station during March to December 2011. Recorded data from sun photometer and weather station were used to investigate water vapor in the atmosphere. Water vapor amount calculated for Timisoara (45° N) was 1.405 cm, which is comparable with U.S. Standard Atmosphere (45° N) value of 1.419 cm (ISO 9845-1).

ACKNOWLEDGEMENT

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II International Conference
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**THE EXAMINATION OF THE SEASONAL INFLUENCE ON THE
GROUND-LEVEL OZONE BUILD-UP AND DECAY KINETIC, BASED
ON THE URBAN AIR MONITORING**

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ABSTRACT

In this paper is examined the kinetik of ozone and sulphur dioxide trasport in urban air during achieving of the stationary state in the minimum of the Gibbs free energy : in the period of the build up of the ground level ozone and decay of sulphur dioxide kinetic with equal rate constant , as well as after achieved stationary state during the opposite reacion direction, with the ozone decay and sulphur dioxide build up Based on the results of the urban air monitoring it was found: - in summer, nitrogen oxide immision lower than $40 \mu\text{gm}^{-3}$ does not increase Gibbs free energy at equal rate constants of direct and opposite direction of the relaxation un-polarisable process; -in November increasing nitrogen oxides immision up to MAC for rural area $70 \mu\text{gm}^{-3}$ favor increasing the free Gibbs energy of the polarizable relaxation process.

Keywords: *Urban air, Transport kinetic, Seasonal influence, Reversible processes, Catalytic influence of NO_x .*

INTRODUCTION

Urban human activities have increased the concentration of ground-level ozone [Hough A.M., Derwent R.G., 1990]. Particulate matter and acid aerosols are fine solid or liquid particles produced by the combustion of fossil fuel, including emissions from diesel engines, coal-burning power plants, cement plants, mining operations, residential wood combustion, and dust emissions from fields and roads. The coal-fired electric stations are major emitters of pollutants such as sulfur dioxide, nitrogen oxides, particulate matter, mercury and carbon dioxide. Acid aerosols e.g. sulfates are often referred to as particulate sulfates from the combustion of fuels, mainly from transportation vehicles such as heavy-duty diesel vehicles, but also from coal-burning power plants and natural gas processing. The increased amounts of nitrogen oxides - the chemicals that cause smog - and more sulfur dioxide, is a key precursor of acid rain and acid aerosols. Sulfate and other fine particles scatter and absorb light, thus reducing visibility. Models and measurements besides corrosion of materials show that visibility in southern Ontario and Quebec is lowest where sulfate deposition is highest [Stieb D.M, Pengelly L D. et al 1995]. The area of generally reduced visibility coincides with the area receiving most acid deposition. The sulfur levels in gasoline and diesel in Ontario are the highest in the country and among the highest in the developed world at 579 parts per million (ppm) in gasoline and diesel fuels of 2620 ppm off-road [Health Canada, 1997]. By comparison, California, a state that has acted aggressively to reduce air pollution, limits sulfur in gasoline to 30 ppm. High-sulfur gasoline leads to the production of more sulfates, extremely small acidic particles that can become imbedded deep in lung tissue [Mittelstaedt M.1998]. Environment Canada issues smog advisories advise the public on the possible health risks associated with smog exposure, when ozone levels are expected to exceed a specified level $82 \mu\text{gm}^{-3}$. According to the previously obtained results the values of the ozone content velocity changes, depending on the content of other pollutants indicated on the middle SO_2 influence on the the ground-level ozone build up or decay velocity (Pavlović, M., Ionel J. Popescu F. Ševaljević M., Đurić, A., 2012). The increased amounts of pollutant examined in this paper are

limited up to average value measured during 24 h, with the law regulative (SI Glasnik RS): ground-level ozone 65-85 μgm^{-3} , Sulphur- dioxide 100 -150 μgm^{-3} and nitrogen oxides (70-85) μgm^{-3} .

The objective in this work is the study of the seasonal influence on the ozone build up and on the SO_2 decay kinetic, depending and NO_x content, where $y = \ln (c/c_0)$ and $\text{tg}\alpha = k, \text{day}^{-1}$, based on the monitoring data (Milan Pavlović, Joana Jonel, Francisc Popescu, Alexandar Đurić, 2010-2011).

$$\ln \frac{c_\tau}{c_0} = -k\tau + \ln\left(\frac{c_{\tau 0}}{c_0}\right)_0.$$

EXPERIMENTAL RESULTS

The seasonal influence is examined on the build –up and decay kinetic of the pollutants, based on the results of the urban air monitoring in the six days, in the summer 2011., (Timisoara I, Pančevo), as well as in November 2011, (Timisoara II , Turn Severin, and Resita) obtained with the mobile laboratory:

- O_3 measured with Environment O341M instrument based on the UV photometry, with the reference method: EN 14625:2005. The combined measurement uncertainty is $U = 6.98 \%$
- SO_2 measured with Environment AF21M instrument based on the UV fluorescence, with the reference method: EN 14212:2005. The combined measurement uncertainty is $U = 1.76 \%$
- NO_x measured with Environment AC31M instrument based on the chemi-luminescence, with the reference method: EN 14211:2005. The combined measurement uncertainty is $U = 2.06 \%$

Table 1: The O_3 , SO_2 and NO_x monitoring results and average NO_x content variation coefficient, ρ , % and calculated pollutants transport rate constants based on the functional dependences in the figure 2 and figure 3

	Timisoara I June, July	Pančevo August	Timisoara II November	Turn Severin November	Resita November	MAC μgm^{-3}
$\text{O}_3, \mu\text{gm}^{-3}$	16,1-22,36	27-53	12-16,4	14-33	34,5-48	65-85
$\text{SO}_2, \mu\text{gm}^{-3}$	4,6-5,4	6,3-8,5	19,3-23,7	9-15,6	5,2-13,3	100-150
$\text{NO}_x, \mu\text{gm}^{-3}$ Average v.	35,45-40,69 38 ; $\rho = 6,2 \%$	15, 87-28,8 20; $\rho=21 \%$	42,2-58,2 49,3; $\rho=14\%$	33,2-73 55,5; $\rho= 31 \%$	46,6 -71,9 59; $\rho=22\%$	70-120
$k_{\text{O}_3}, \text{day}^{-1}$	0,058	0,08	-0,075	-0,18	-0,076	
$k_{\text{SO}_2}, \text{day}^{-1}$	-0,041	-0,076	0,05	0,19	-0,085	

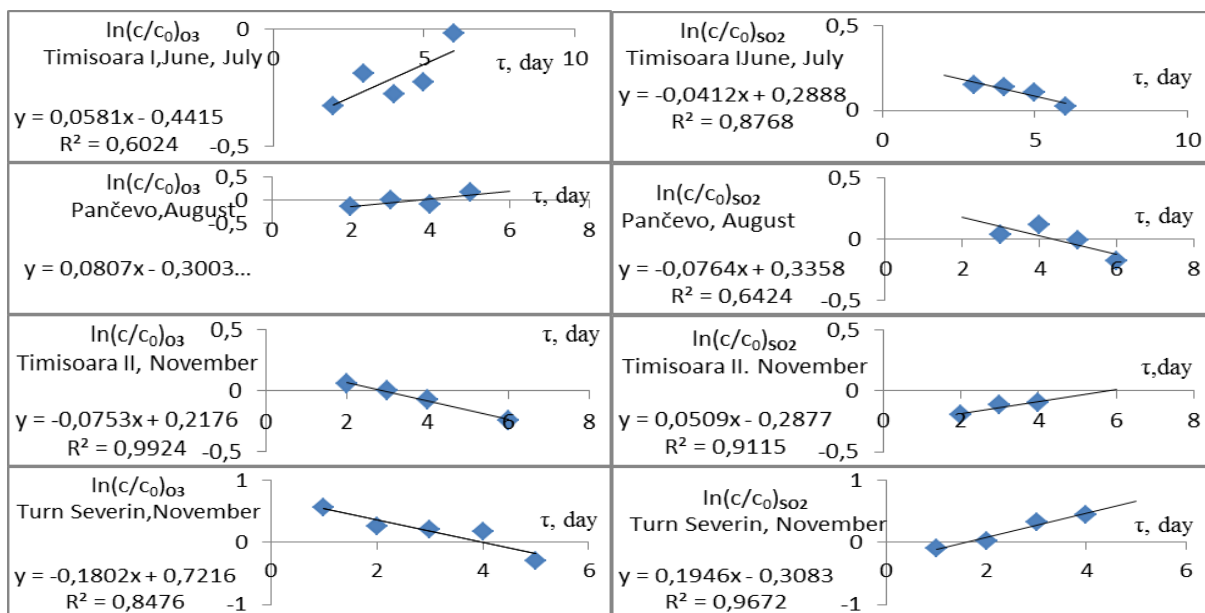


Figure 1. The determination of the ozone and sulfur dioxide transport kinetic in summer (Timisoara I and Pančevo) and November (Timisoara 2, Turn-Severin and Resita)

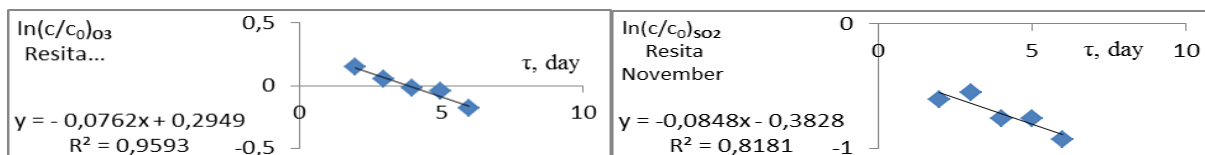


Figure 2. The determination of the seasonal O₃ and SO₂ decay kinetic on the urban location in Resita

The equal O₃ and SO₂ transport rate constants (determine the slope in the obtained linear functional dependences which indicate on the stationary processes with the equal rate constants of the O₃ build up and SO₂ decay in summer (Timisoara I , Pančevo) and opposite in November (Timisoara II, Turn Severin) (Figure 2) and twice faster decay transport rate constants of the both pollutants in the urban area in Resita (Figure 3).

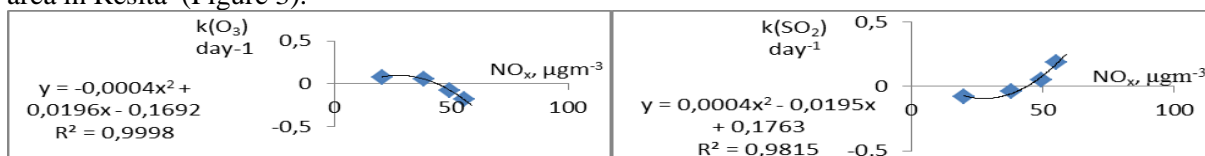


Figure 3. The transport rate constants of the O₃ and SO₂, depending on the seasonal average NO_x content

The seasonal NO_x average content in Timisoara I, in summer from (28,8 – 40, 69) µgm⁻³ and in Timisoara II, in November ((42 – 58) the equal rate constants of the direct and of the opposite directions of the O₃ and of the SO₂ indicate un-polarisable reaction keep the stationary state in the minimum of the Gibbs free energy.

The increased NO_x content in and Turn Severin (33-73) µgm⁻³ in November favor the twice faster rate constant of the opposite direction compared to summer period: $k(O_3) = -k(SO_2) = -0,18 \text{ day}^{-1}$

In Resita with the increased NO_x (47-72) µgm⁻³ in November favor decay of the both reactants with equal decay rate constants, $k(O_3) = k(SO_2) = -0,08 \text{ day}^{-1}$.

CONCLUSION

Based on the monitoring results it can be concluded:

1. The ground-ozone and sulphur-dioxide levels were lower than MAC and NO_x achieves MAC in November
2. In summer, in the content range of NO_x , 30 - 40 μgm^{-3} does not influence on the transport rate constant $k(\text{O}_3) = (0,06-0,08) \text{ day}^{-1}$ and opposite in summer, the SO_2 decay with transport rate constant $k(\text{SO}_2) = -0,04$ to $-0,076 \text{ day}^{-1}$ of the reversible processes
3. In November at the less the content range of NO_x , 40 - 60 μgm^{-3} in Timisoara II, favor the opposite direction compared to summer, ground-ozone level decay and the SO_2 build-up with rate constant $k(\text{O}_3) = -0,075 \text{ day}^{-1}$ $k(\text{SO}_2) = 0,05 \text{ day}^{-1}$
4. The increasing of NO_x content up to 70 μgm^{-3} in November increased the pollutants transport process rate constants:
 - in Turn-Severin of the ozone decay $k(\text{O}_3) = -0,18 \text{ day}^{-1}$ and SO_2 build-up, $k(\text{SO}_2) = 0,19 \text{ day}^{-1}$
 - in Resita the parallel decay of the both transport rate constant is found: $k = k(\text{O}_3) + k(\text{SO}_2) = -0,161 \text{ day}^{-1}$

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THE STUDY OF THE SEASONAL INFLUENCE ON SUSPENDED PARTICLES PM10 ELECTRO-KINETIC POTENTIAL, BASED ON THE URBAN AIR MONITORING

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ABSTRACT

Elektrokinetic potentials of the suspended matter fraction with diameter less than 10 μm is studied as indicator of the electrochemical gasification, immision levels of ground-ozone level, sulphur dioxide and nitro-oxides due reactions between specifically and (or) un-specifically adsorbed ions in active transition intermediate complexes, in the diffusion layer of contact surface with the solid phase. Concentration polarizations of active complexes between polutants are identified which define the elektro-kinetic potentials in resonance with energy quant with characteristic vibration of the active transition complexes of adsorbed polutants causing un-stability and degradation. The transport rate constant of reactants and products in air of urban area determine the rate constant of processes which control the achieving of the stationary state of producing and degradation energy of the polutants active transition complex: - in summer period, at the lower electric polarizations of PM 10 than thermal values where polutants PM10 concentrations are twice lower than maximal allowed contents (MAC) limited by law regulative for total suspended matter (TSM); - in november, at concentrations of polutants PM10 achieved the MAC of the TSM for urban areas, the electro-kinetic potentials of PM 10 was corresponding to the thermal energy of gas particles.

Keywords: *Fraction of the suspended matter PM10, Spontaneous polarization, Electrochemical gasification, Electro-kinetic potential, Stationary states.*

INTRODUCTION

The law regulative (Sl Glasnik RS) define maximal allowed contents, MAC of air pollutant average values measured during 24 h, which are studied in this paper: the total suspended particles of 70 μgm⁻³ in rural up to 120 μgm⁻³ in the urban areas, sulfur dioxide 100 -150 μgm⁻³, ground-level ozone 65-85 μgm⁻³ and nitrogen oxides (70-85) μgm⁻³. Based on the urban air monitoring and previously kinetic study (Pavlović, M., Jonel J. Popescu F. Ševaljević M., Đurić, A., 2012) in this paper is calculated the electro-kinetic potential of the PM 10 in the double layer:

1. In the June, July and August, 2011. on location in Timisoara I and in town Pančevo
2. In the November 2011., on the location Timisoara II, Turn Severin, and Resita

The transport of the pollutants after stationary state is achieved determines the stationary electro kinetic potential, η of the slowest successive polarization steps: chemical reaction, diffusion, or the possible successive adsorption or desorption or secondary chemical reaction:

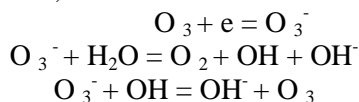
$$k = -\frac{1}{\Delta\tau} \cdot \frac{F\eta}{RT}$$

The polarization, ΔE of the slowest step determine pollutants adsorbed specifically and un-specifically in the active transition intermediate complexes depending on its Gibbs free energy, determining the pollutants transport rate constant in air, equal to its electrochemical gasification rate constant. After achieving thermodynamic equilibrium the characteristic vibration energy which can cause un-stability and spontaneous degradation of the activated intermediate determine electrochemical gasification

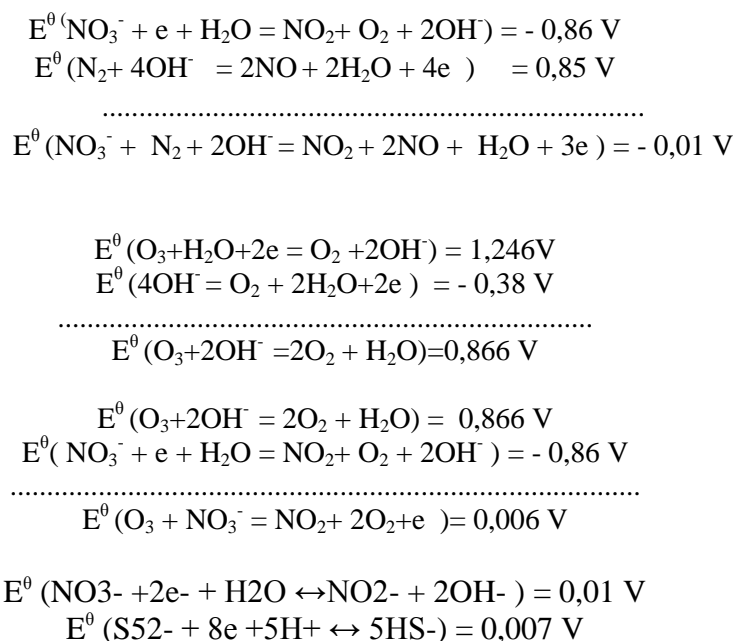
kinetic (R. W. Coughlin, M. Farooque, 1980) determining in the stationary state the transport kinetic, $\Delta E = \eta$.

$$\Delta E = -k\Delta\tau \frac{RT}{F}$$

The successive ozone build-up processes are limited with an electron transfer step, which polarize the reaction surface with the adsorbed water, as well as with the second reaction of ozonide and radical:



The standard potentials enabling electrochemical gasification after the period of the electro kinetic polarization, $\eta = -0,016$ to $-0,022V$, determining the adsorbed pollutants dissolution rate constants are given in the data tables (Bard, 1983):



Based on the monitoring data (Milan Pavlović, Ioana Ionel, Francisc Popescu, Alexandar Đurić, 2010-2011), the objective in this paper is the determination of the electro kinetic potentials of the suspended matter fraction, with diameter less than $10\mu m$ as indicator of the electrochemical gasification of air with ground – ozone level, sulphur-dioxide level and nitro-oxides, in reactions between specifically and (or) un-specifically adsorbed ions in active transition intermediate complexes, These reactions in the diffusion layer of contact surface with the solid phase, with the depth of diffusion layer about $10\mu m$ enable polarization between cathode hydrating and anode oxidation (Mirjana M. Ševaljević, 2000).

EXPERIMENTAL RESULTS

The seasonal influence is examined on the build-up and decay pollutants electrochemical polarization based on the results of the urban air monitoring in the six days, in the summer 2011., (Timisoara I, Pančevo), as well as in November 2011, (Timisoara II, Turn Severin, and Resita) obtained with the mobile laboratory:

- PM10 (suspended particles, fraction PM10), based on the principle is laser light scattering .
- SO₂ measurement with Environment AF21M instrument based on the UV fluorescence, with the reference method: EN 14212:2005. The combined measurement uncertainty is $U = 1.76 \%$
- O₃ measurement with Environment O341M instrument based on the UV photometry, with the reference method: EN 14625:2005. The combined measurement uncertainty is $U = 6.98 \%$

- NO_x measurement with Environment AC31M instrument based on the chemi-luminescence, with the reference method: EN 14211:2005. The combined measurement uncertainty is $U = 2.06\%$

The results (table 1) present the suspended particles PM 10 , the electro-kinetic potentials determined on the base transport rate constants, k (PM 10) (Figure 1) calculated in the previously paper (Pavlović M., Ionel I., Popescu F., Ševaljević M., Đurić, A., 2012), also for O₃ and SO₂.

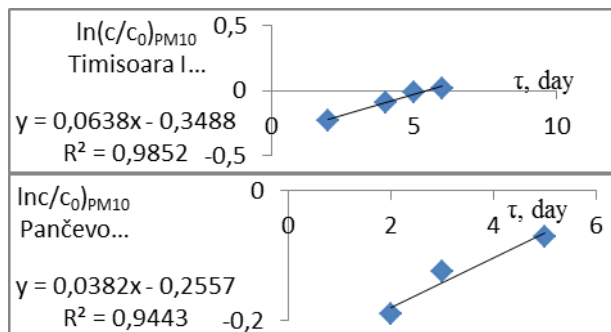


Figure 1a. The suspended particles PM10 transport rate constant in the summer months in urban areas with the least NO_x content range (15, 9-40) μgm⁻³ and PM 10 content (37-50) μgm⁻³

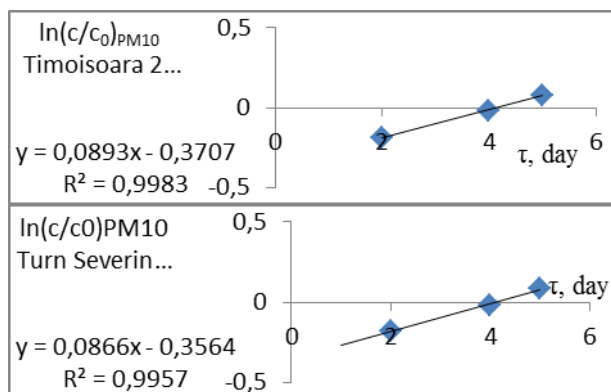


Figure 1b. The suspended particles PM10 transport kinetic, in November in urban areas with the middle PM 10 content (38-69) μgm⁻³

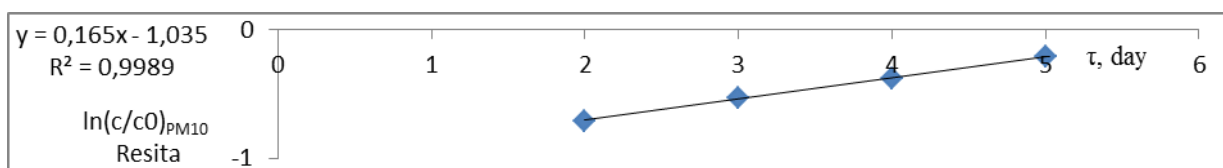


Figure 1c. The suspended particles PM10 transport kinetic in November in Resita with the PM 10 content (48,4-98,77) μgm⁻³ (greater than MAC for the total suspended matter in urban area, TSM, 85 μgm⁻³)

Table 1: The O_3 and SO_2 , NO_x and PM_{10} electro kinetic potentials, monitoring results and its average values and relative variation, ρ , %

	Timisoara I June, July	Pančevo August	Timisoara II November	Turn Severin November	Resita November	MAC μgm^{-3}
$\Delta E(PM_{10})$,	-0,0095	-0,0057	-0,0134	-0,013	-0,0247	100-150
$\Delta E(O_3)$, V	-0,0087	-0,012	0,011	0,027	0,0114	
$\Delta E(SO_2)$, V	0,0061	0,0114	-0,0075	-0,0296	0,0127	70 - 120
PM_{10} , μgm^{-3} Average v.	39-50, 44,5 $\rho=12\%$	37,3-46 41,6 $\rho=11\%$	39-69 54 $\rho=27\%$	38-51 44,5 $\rho=13\%$	48,4 - 98,77 73,6 $\rho=34\%$	TSM, 70 - 85
NO_x , μgm^{-3} Average v.	35,45-40,69 38; $\rho=6,2\%$	15,87-28,8 20; $\rho=21\%$	42,2-58,2 49,3; $\rho=14\%$	33,2-73 55,5; $\rho=31\%$	46,6 -71,9 59; $\rho=22\%$	70-120
O_3 , μgm^{-3}	16,1-22,36	27-53	14-33	12-16,4	34,5-48	65-85
SO_2 , μgm^{-3}	4,6-5,4	6,3-8,5	19,3-23,7	9-15,6	5,2-13,3	100-150

The negative electro-kinetic potential of the PM_{10} were found of the spontaneous polarized particles in reversible processes between adsorbed components: the lowest in Pančevo, $\Delta E(PM_{10}) = -0,057$ V in august and increased in summer in Timisoara 1 $\Delta E(PM_{10}) = (-0,009$ V) and in November (Timisoara 2 and Turn Severin) $\Delta E(PM_{10}) = -0,0134$ V and $-0,013$ V and maximal thermal value in Resita $\Delta E(PM_{10}) = -0,0247$ V.

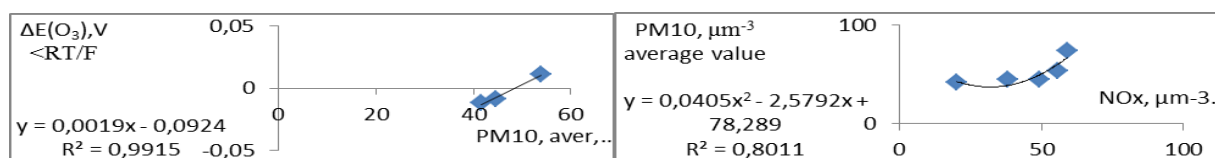


Figure 2. The functionally dependence of the ground-ozone level polarization on the PM_{10} average content; The functionally dependence of PM_{10} average content on the NO_x average content

The slowest concentration polarization of the PM_{10} average content favor the slow ozone build up in reversible process $\Delta E(O_3) < RT/F$ in the summer months (Timisoara I, Pančevo) and opposite direction in November (Timisoara II, Turn Severin). According to the functionally dependences PM_{10} on NO_x average content the depolarization processes in presence of up to NO_x $40 \mu\text{gm}^{-3}$ prevent PM_{10} average content increasing (Figure 2).

In November, in Resita, PM_{10} contents achieving the MAC of the TSM for urban areas, favor the parallel, forced decay of the O_3 and SO_2 .

CONCLUSION

Based on the obtained results it can be concluded:

1. The seasonal influence is found on the electro chemical gasification processes electric polarizations
2. In summer (Timisoara I, Pančevo), the PM_{10} spontaneous polarizations ($\Delta E < 0$), proportional to build up transport kinretik are lower than thermal energies of gas particles in air of examined urban area, $\eta(PM_{10}) < RT/F$, where gas ground-ozone build up during spontaneous polarization are equal or twice greater compared to PM_{10} build up and spontaneous polarization kinetic.
3. In November (Timisoara II, Turn Severin), the PM_{10} spontaneous polarization and build-up, lower than thermal values of electro-kinetic potential of gas molecules of urban area, $\eta(PM_{10}) < RT/F$ are found where the gas sulfur-dioxide build-up during spontaneous polarization is about twice less compared to PM_{10} (Timisoara II), or twice greater, balanced with thermal energy of the forced depolarizaatin ozone decay (Turn Severin).

4. In November, in Resita, where PM 10 content achieve MAC defined for the TSM for urban areas, spontaneous thermal polarization and build up of PM 10 is achieved, η (PM 10) = RT/F in equilibrium with the sum of the depolarization potentials of the ozone and of sulphur dioxide decay.

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POST-COMBUSTION CO₂ CAPTURE TECHNOLOGIES FOR COAL-FIRED POWER PLANTS

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ABSTRACT

Increased concentration of the emissions of greenhouse gases to the atmosphere, mainly CO₂, is considered the main cause of climate change. One option to reduce these emissions is to capture CO₂ from fossil fuel-fired power plants, especially from those based on coal combustion. There are three main pathways for CO₂ capture, namely post-combustion capture, pre-combustion capture and oxy-fuel combustion. This paper is focused on post-combustion capture technologies that can be applied to existing coal-fired power plants. Amine-, carbonate- and ammonia-based CO₂ capture processes have been analyzed and compared. Also, a process design using membranes has been described.

Key words: CO₂ capture, post-combustion, coal, power plant.

INTRODUCTION

Coal-fired power plants are the largest source of anthropogenic carbon dioxide emissions (CO₂), emitting over 8 GtCO₂/y to the atmosphere (IEA, 2010a). According to the International Energy Agency (IEA, 2010b), the electricity production from coal will increase by 35%, by 2035, which will inevitably lead to more CO₂.

The emissions of CO₂ from coal-fired power plants can be reduced by increasing the efficiency of these plants and/or by capturing CO₂ and storing it in geological formations. CO₂ capture and storage is considered the only technology that can capture at least 90% of the CO₂ emitted by existing fossil fuel power plants (ZEP, 2011). However, applying current CO₂ capture technologies may substantially reduce the net efficiency of a plant (up to 14% points) (Notz et al., 2011).

The CO₂ can be captured either from flue gas or from process streams before combustion (Global CCS Institute, 2011; Notz et al., 2011; ZEP, 2011). The removal of CO₂ from the flue gas is best known as post-combustion capture. The CO₂ concentration in power station flue gas, for coal-fired boilers is about 15% by volume, while for natural gas combined cycle power plants is 4% and for natural gas-fired boilers is around 8%. The concentration of CO₂ in the flue gas can be increased by using pure oxygen instead of air for combustion, resulting in a flue gas that has a CO₂ concentration higher than 80%. This is known as oxy-combustion. Also, carbon dioxide can be removed from the power cycle before combustion applying a pre-combustion CO₂ capture concept. The concentration of CO₂ in the CO₂/H₂ mixture would be 40-60% (by volume) for coal gasification, and around 20% for natural gas partial oxidation.

The major advantage of a post-combustion CO₂ capture system over oxy- and pre-combustion is that it can be applied to existing power plants with little modifications to the power station itself, or easily integrated into new ones.

In this paper post-combustion CO₂ capture technologies, namely, based on amine, carbonate and ammonia that can be applied to existing coal-fired power plants are analyzed and compared. Additionally, a membrane-based CO₂ capture process is discussed.

POST-COMBUSTION CONCEPT

Capture of CO₂ from flue gases produced by combustion of fossil fuels (e.g., coal) in air is referred to as post-combustion capture. A block diagram of a coal-fired plant with post-combustion CO₂ capture is illustrated in Figure 1.

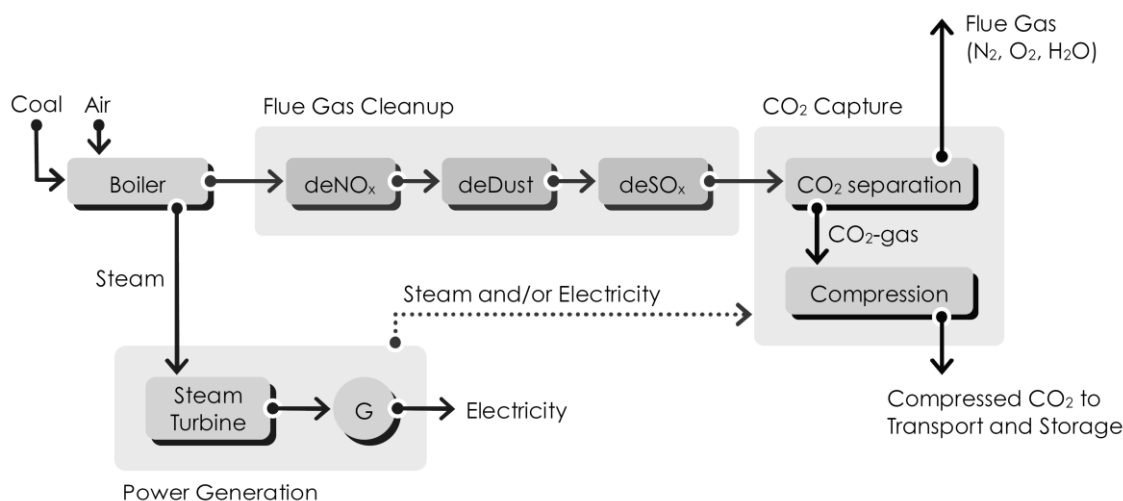


Figure 1. Power plant with post-combustion CO₂ capture

As it can be seen, the CO₂ capture unit is integrated in the power plant as a flue gas post-treatment unit after the removal of pollutants (e.g., nitrogen and sulfur oxides, particulates) in order to prevent plugging and fouling, and to minimize degradation of the CO₂ capture solvent.

Before discharging to the atmosphere, the flue gas, with low pollutant emissions content, flows through a cooling unit and then enters the bottom of the absorber where it comes into contact, counter-currently, with a chemical solvent (e.g., aqueous monoethanolamine (MEA)), which absorbs much of the CO₂. Then, the CO₂-rich solvent is sent to the top of the regeneration column (desorber or stripper), via a lean/rich heat exchanger. In the desorber, the CO₂ is released due to the heat provided by low pressure steam in the reboiler. The captured CO₂ is then compressed and further collected in a storage reservoir. Remaining compounds of flue gases, such as nitrogen, oxygen and water vapors are discharged directly to the atmosphere.

One of the disadvantages of this method is that the CO₂ partial pressure is very low due to the low CO₂ concentration in the flue gas (typically up to 15% by volume for coal-fired boilers) and hence large and expensive equipment is needed to extract the CO₂ (Davison, 2007). There have been proposed a variety of techniques for removing CO₂ from the flue gas (e.g., by chemical absorption or physical absorption, or membrane separation). Currently, absorption processes based on chemical solvents are the most preferred option for post-combustion systems, offering high capture efficiency and selectivity.

At present, there are a number of absorption solvents commercially available for CO₂ capture. Most of them are used for treating gas streams with low- to moderate-CO₂ partial pressure (Kohl and Nielsen, 1997). The typical chemical solvents are amines (e.g., monoethanolamine, diethanolamine (DEA)), which are commonly used in the form of aqueous solutions. Aqueous MEA solution is often regarded as the first chemical solvent to be used for CO₂ capture from coal-derived flue gases. Today, there are two MEA-based absorption processes commercialized, namely the Fluor's Econamine process and

Kerr McGee/ABB Lumus Crest's CO₂ capture process (Sander and Mariz, 1992; Chapel et al., 2001; Reddy et al., 2003; Reddy, 2008; Barchas and Davis, 1992).

The use of blended amines for CO₂ capture offers some advantages over the single amines, namely lower energy consumption and higher absorption capacity (Aroonwilas and Veawab, 2007). Most formulations of the blended amines are tertiary amine-based (e.g., methyldiethanolamine (MDEA)). The main disadvantage of MDEA is slow rates of CO₂ absorption. An addition of MEA or DEA into the MDEA solution helps enhance rate of capturing CO₂.

There are also a large number of solvents currently proposed and being investigated. The Kansai Electric Company and Mitsubishi Heavy Industry developed a family of KS energy efficient proprietary solvents (sterically hindered amines) (Mimura et al., 1999; Mimura et al., 2003; Suda et al., 1992; Yagi et al., 2004). Also, novel amine solvents developed by Toshiba, called TS-1 and TS-2, are being investigated at pilot scale (Ohashi et al., 2011). The performance of carbonates (potassium or sodium carbonate) has also been investigated (Oexmann et al., 2008; Knuutila et al., 2009). Aqueous ammonia has been proposed as an alternative to amine-based processes (Yeh and Bai, 1999; Resnik et al., 2004).

Recently, a post-combustion CO₂ capture process employing membranes with high CO₂ permeance has been investigated (Merkel et al., 2010).

POST-COMBUSTION TECHNOLOGIES

Amine-based processes

The most commonly used absorbent for CO₂ capture from low pressure flue gas is monoethanolamine. This amine was developed over 70 years ago as a general non-selective solvent to remove acid gases (e.g., CO₂, hydrogen sulfide) from natural gas streams (Kohl and Nielsen, 1997).

A conventional amine-based flue gas CO₂ capture process consists of two major sections, an absorption section where CO₂ in the flue gas is absorbed into a liquid solvent and a regeneration section where the absorbed CO₂ is stripped out by means of heat.

Prior to CO₂ removal, flue gases (usually at near atmospheric pressure and temperatures above 100°C) from power plant are cooled down to the temperature levels required for absorption, and treated for contaminants. After cooling, the flue gas is passed through an absorption vessel where it comes into contact with the chemical solvent, which absorbs much of the CO₂ by chemically reacting with it to form a loosely bound compound. Then, the CO₂-rich solvent from the bottom of the absorber is pumped to another column (desorber), via a heat exchanger. In the desorber, the CO₂-rich solution is heated (to about 100-140°C) to release almost pure CO₂. Water vapors are condensed in the condenser and fed back to the desorber, whereas the net CO₂ gas leaves the unit. The lean solvent, containing far less CO₂ is cooled down to 40-65°C, and recycled to the absorber.

Although amine processes can remove CO₂ at low concentrations, large amounts of energy are required for solvent regeneration (IEA GHG, 2007; Abu-Zahra, 2009). Approximately 50% of low pressure steam needs to be extracted for amine regeneration and CO₂ release (IEA GHG, 2007). Moreover, contaminants typically found in flue gases from coal-fired power plants (e.g., NO_x, SO₂, particulates) usually need to be removed prior to capture, as they can inhibit the ability of solvents to absorb CO₂ (Cebucean and Ionel, 2012). In order to avoid amine degradation, the following requirements to the flue gas composition are imposed by the amine-based capture system: SO₂~10-30 mg/Nm³, NO₂~40 mg/Nm³ and particulates less than 5 mg/Nm³ (at 6 vol% O₂) (IEA GHG, 2007).

At present, there are three amine-based processes commercially available for CO₂ capture in post-combustion systems: (i) the Kerr-McGee/ABB Lummus Crest process, which uses for CO₂ separation an aqueous 15-20 wt% MEA solution (Barchas and Davis, 1992); (ii) the Fluor Daniel Econamine

process (30 wt% MEA) (Sander and Mariz, 1992; Chapel et al., 2001; Reddy et al., 2003; Reddy, 2008); and (iii) the KEPCO/MHI process, which uses sterically-hindered amines (KS-1, KS-2 and KS-3) (Mimura et al., 1999; Mimura et al., 2003; Suda et al., 1992; Yagi et al., 2004).

The first two processes require large quantities of energy for solvent regeneration: 5-6.5 GJ/tCO₂ in the Kerr-McGee/ABB Lummus Crest CO₂ capture process (Barchas and Davis, 1992) and about 4.2 GJ/tCO₂ in the Fluor Econamine FG process (Chapel et al., 2001). The improved Fluor's process (Econamine FG Plus), which uses a 35 wt% MEA solution with inhibitors, needs much less thermal energy for solvent regeneration of about 3.24 GJ/tCO₂ (Reddy et al., 2003; Reddy, 2008). The KS-1 process requires approximately the same amount of energy (3.2 GJ/tCO₂) (Mimura et al., 1999). This process has been improved by the KEPCO/MHI researchers achieving a value of 2.6 GJ/tCO₂ (Yagi et al., 2004).

A study conducted by the researchers from the National Energy Technology Laboratory has shown that the net power output of a subcritical pulverized coal-fired power plant with an amine-based post-combustion CO₂ capture technology would decrease by approximately 30% (NETL, 2007). The net thermal efficiency would be also reduced from about 35% to 24.5% (efficiency penalty of 10.5% points). These values were reported for the case study with 90% CO₂ capture using a 30 wt% MEA solution and the solvent regeneration energy of 3.6 GJ/tCO₂. The study also suggested that a decrease in energy requirement will lead to a lower energy penalty, for instance, if the energy used for solvent regeneration is reduced from 3.6 to about 2.8 GJ/tCO₂, the energy penalty would be only 9.3 percentage points.

The energy requirement can be significantly reduced by optimizing the MEA-based process (Abu-Zahra, 2009). It was found that at a lean MEA loading of 0.32 and 0.3, using a MEA solution of 30 and 40 wt%, respectively, and a stripper operating pressure of 210 kPa, the thermal energy requirement is 3.29 and 3.0 GJ/tCO₂, respectively.

Although the energy consumption can be reduced by increasing the concentration of MEA, it will lead to higher corrosion. In addition, increased operating pressure/temperature of the stripper will cause higher solvent degradation rates.

The use of blended amines instead of MEA offers some advantages, namely lower energy consumption and higher absorption capacity (Aroonwilas and Veawab, 2007). For instance, by applying a MEA/MDEA-based CO₂ capture process to a supercritical coal-fired power plant, with a capacity of 500 MW, the energy penalty is about 2.6 percentage points drop, using 1.2 GJ/tCO₂ for solvent regeneration, and 4.8 points drop for the case with higher energy consumption of 2.4 GJ/tCO₂. Unfortunately, compared to MEA, the blended MEA/MDEA solution has lower CO₂ absorption rates. As a result, the MEA/MDEA-based CO₂ capture unit would need a higher absorber column to remove the same amount of CO₂ as MEA.

Carbonate-based processes

Aqueous solutions of potassium (K₂CO₃) and sodium carbonate (Na₂CO₃) have been widely used in several industrial processes for the removal of carbon dioxide from gas streams (Kohl and Nielsen, 1997).

The use of an aqueous K₂CO₃ solution for CO₂ capture from coal-derived flue gas, however, might be inefficient (Oexmann et al., 2008). The performance of a K₂CO₃-based CO₂ capture process can be improved if the solvent is promoted with, for example, piperazine (PZ) (Cullinane and Rochelle, 2004). Piperazine is characterized by a high rate of CO₂ absorption, is thermally stable and degrades, in the presence of oxygen, much slower than MEA (Freeman et al., 2010). Compared to MEA, a 36.2 wt% K₂CO₃ solution promoted by 11.3 wt% PZ has a CO₂ absorption rate up to 30% faster than a 30 wt% MEA solution (Cullinane et al., 2004).

The use of K_2CO_3/PZ , with a concentration of 22.1/13.8 wt%, in post-combustion CO_2 capture may significantly reduce the required energy for solvent regeneration in comparison with MEA (Oexmann et al., 2008). The study has shown that the specific reboiler duty for this solvent decreases from 2.4 GJ/t CO_2 for 90% CO_2 recovery to around 2.1 GJ/t CO_2 at a CO_2 capture rate of 70% and 50%. However, the study has also revealed that increasing the concentration of K_2CO_3 in the blend leads to higher energy requirements.

The energy requirement of a post-combustion CO_2 capture system based on sodium carbonate is about 3.2 GJ/t CO_2 (Knuutila et al., 2009). This value has been reported for the case study that achieves 90% CO_2 capture with a 30 wt% Na_2CO_3 solution. As it was mentioned earlier, the energy consumption of a K_2CO_3/PZ -based CO_2 capture process is much lower, which seems to be a more advantageous option. Compared to MEA, the amount of thermal energy needed for solvent regeneration is almost the same (Abu-Zahra, 2009).

As in the case of K_2CO_3 , the Na_2CO_3 solutions have low rates of CO_2 absorption, too. In order to increase the absorption rate a number of additives can be used (e.g., primary and secondary amines) (Knuutila et al., 2009).

Applying one of the carbonate-based processes to a coal-fired power plant, the net efficiency would decrease by 9 and 9.5 percentage points, using a solution of Na_2CO_3 and K_2CO_3/PZ , respectively (Knuutila et al., 2009; Oexmann et al., 2008).

The researchers from the University of Illinois are investigating a hot carbonate-based absorption process for post-combustion CO_2 capture (NETL, 2011). The process would use one of the carbonate salts (potassium or sodium) for CO_2 removal from flue gas. It is expected that this process will use less energy than a conventional amine-based process. The capture occurs in a high temperature absorption column where the CO_2 and other acid gases are absorbed by the solvent. Afterwards, the CO_2 -rich solvent flows through a crystallization unit, which separates bicarbonates, and the resulting slurry is then sent to a high pressure stripping column where the CO_2 is removed and the solvent is recycled.

Aqueous ammonia processes

Aqueous ammonia (NH_3) has been proposed as an alternative to traditional amine-based processes for post-combustion CO_2 capture (Yeh and Bai, 1999).

In comparison with MEA, higher CO_2 loadings can be achieved with aqueous ammonia (Yeh and Bai, 1999). This is mainly due to the NH_3/CO_2 system favoring bicarbonate over carbamate, particularly as CO_2 loading increases. A CO_2 removal efficiency of 99% can be achieved by means of NH_3 solution and the CO_2 loading capacity can approach 1.2 kg CO_2 /kg NH_3 (compared to ~0.4 kg CO_2 /kgMEA). It was also reported that the CO_2 loading capacity of NH_3 solution, with a concentration of 28 wt%, decreased by 11% between reaction temperatures 10 and 40°C. Another study confirmed that as the temperature approached the ammonium carbonate/bicarbonate decomposition temperature (~60°C), the CO_2 absorption rate decreased (Resnik et al., 2004).

The NH_3 process has also been shown to require less thermal energy for solvent regeneration than a MEA-based process (Yeh et al., 2005). This is due to the smaller reaction enthalpy for CO_2 absorption and higher CO_2 partial pressure at elevated temperature compared to MEA. It was estimated that the energy requirement for an ammonia-based process would be around 1.2 GJ/t CO_2 (Bandyopadhyay, 2011), which is much lower than the energy used in the CO_2 capture processes analyzed earlier in this paper. It was also found that the net power output of a coal-fired power plant would be reduced by 16% after integration with the NH_3 -based CO_2 capture technology.

Using ammonia for CO_2 capture from flue gas offers several other advantages, namely, (i) it is resistant to oxidative degradation and (ii) in the presence of SO_2 and NO_x forms ammonium sulfate

and ammonium nitrate (Yeh and Bai, 1999; Bandyopadhyay, 2011). These ammonium salts can be then used as fertilizers.

In 2006, another ammonia-based process (called a chilled ammonia process), which operates at low temperatures ($<10^{\circ}\text{C}$) was proposed (Gal, 2006). This novel CO_2 capture technology is currently implemented by Alstom (Alstom Power, 2011). The process is very similar to amine-based capture technology. It includes three main parts: flue gas cooling, CO_2 absorption and high pressure regeneration.

First, the flue gas is cooled using chilled water and a series of direct contact coolers. After the cooling subsystem, the cold flue gas enters the absorber where most of the CO_2 is chemically absorbed in the lean solvent from the stripper. The absorber removes CO_2 from the flue gas mainly by the precipitation of ammonium bicarbonate. The CO_2 -rich solvent flows to a heat exchanger where its temperature increases, and then flows to the desorber. According to the patent (Gal, 2006), the desorber temperature should be in the range $50\text{-}200^{\circ}\text{C}$, while the pressure $2\text{-}136$ atmospheres. Under these conditions, the vaporization of ammonia and water implied by the high temperature is reduced. The conditions cause CO_2 to evaporate from the solution. It leaves the top of the desorber as a relatively clean and high-pressure stream.

An assessment study carried out by Versteeg and Rubin (2011) has shown that by applying the chilled ammonia process to a coal-fired power plant would result in the energy penalty of 28.6%, which is almost the same penalty as in the case of amine-based systems. Also, their results have indicated that the concentration of NH_3 in the lean solution and the ratio NH_3/CO_2 significantly affect the capture process, ammonia slip, and solids precipitation in the absorber.

Membrane separation

The use of membranes in post-combustion CO_2 capture applications was recently investigated by the researchers from Membrane Technology and Research, Inc. (Merkel et al., 2010). The study focused mainly on presenting a novel process design (based on membranes with high CO_2 permeance) that uses incoming combustion air as a sweep to generate driving force.

There were first analyzed two modes of membrane module operation, namely, cross-flow and counter-flow. The superiority of counter-flow operation was evident: (i) the CO_2 concentration on the permeate side increased up to 41% in comparison with only 29% of the cross-flow module; (ii) the membrane area needed was reduced by 38%; and (iii) the consumption of energy decreased by 18%. It was also found that the use of vacuum pump on the permeate side of membrane is more favorable than the compression of flue gas before entering the membrane unit.

A two-step counter-flow/sweep membrane process to capture 90% of the CO_2 in flue gas from a coal-fired power plant was then described. This process design uses incoming combustion air as a sweep in order to generate driving force for CO_2 separation.

The flue gas, with a low concentration of impurities, enters a conventional cross-flow membrane module, in which the CO_2 is partially removed from the flue gas, due to the driving force generated by a permeate side vacuum pump. The CO_2 -enriched permeate from this module is then dehydrated. After that, the dry gas is sent to a condenser that produces a high purity CO_2 liquid. Uncondensed CO_2 together with non-condensable gases from the condenser are sent to another cross-flow membrane module. The permeate, containing mostly CO_2 , is recycled to the front of the compressor in order to enrich the CO_2 stream, while the residue stream is recycled and blended with the inlet flue gas.

The residue gas from the first cross-flow membrane module is fed into a counter-flow/sweep membrane unit, in which the largest portion of CO_2 permeates through the membrane and is recycled back to the boiler together with the air used for combustion.

The study showed that this membrane process, applied to a conventional pulverized coal-fired plant, will use about 16% of the power plant output, when the CO₂ recovery is fixed at 90%.

In comparison, a two-step vacuum membrane process will use about 24% of electricity generated by the plant (Merkel et al., 2010). Additionally, this configuration will require higher membrane area (3×10^6 m²), for removing 90% CO₂, than in a counter-flow/sweep design. In consequence, the cost of CO₂ capture will rise up to 39 \$ per each tonne of CO₂ captured, which is approximately 1.7 times higher than in the previous case.

CONCLUSIONS

In this paper, post-combustion CO₂ capture technologies that can be applied to existing coal-fired power plants were analyzed and compared.

CO₂ capture from flue gas with an aqueous solution of monoethanolamine is the most developed post-combustion capture technology. The major disadvantage of an MEA-based process is that a large quantity of energy is required for solvent regeneration. It was estimated that 50% of low pressure steam needs to be extracted for amine regeneration and CO₂ release. Additionally, the flue gas from a coal-fired power plant contains impurities, which need to be removed prior to capture, as they can inhibit the ability of solvent to absorb CO₂.

It was noted that the efficiency of a coal-fired power plant after integration with CO₂ capture, using a 30 wt% MEA solution, will be reduced by 10.5 percentage points and the power output will decrease by 30%. It was also suggested that a decrease in energy requirement will lead to a lower energy penalty.

The use of blended amine solutions (e.g., MEA/MDEA), instead of MEA, can offer some advantages such as great absorption capacity, low energy requirements and low corrosivity. Lower rate of CO₂ absorption is the main drawback of MEA/MDEA solutions.

CO₂ capture from coal-derived flue gas with potassium or sodium carbonate solutions might be inefficient because of low CO₂ absorption rates and low selectivity. The CO₂ capture process can be improved if the solvent is promoted with an amine. It was found that the net efficiency of a coal-fired power plant decreases by 9% points after integration with a CO₂ capture unit based on carbonate solutions.

The use of aqueous ammonia for CO₂ capture has a number of advantages over amine solutions such as higher absorption capacity, lower energy requirement as well as resistance to both oxidative and thermal degradation. It was estimated that the net power plant output will be reduced by 16% when using an ammonia-based process.

CO₂ capture from flue gas using membrane-based processes is currently under development. First estimates indicate that a two-step counter-flow/sweep membrane process will use about 16% of energy generated by the plant and the CO₂ capture cost will amount to about 23 \$/tCO₂. It is further suggested that this membrane process can be improved if the permeance of membrane is increased or the membrane cost is reduced.

Other post-combustion capture technologies are being developed, such as CO₂ capture processes based on amino-acid salts, ionic liquids, and metal-organic frameworks.

The first Romanian CO₂ capture project will use a chilled ammonia process to capture CO₂ from flue gas (Alstom Power, 2011). This post-combustion capture technology will be integrated into an existing coal-fired power plant. The captured CO₂ will be transported, via an existing network of onshore natural gas pipelines, to storage sites (saline aquifers) located not far away from the power

plant. It is estimated that up to 1.5 million tonnes of CO₂ will be stored annually (Global CCS Institute, 2011).

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**DETERMINATION OF REACTION ORDER AND LIMITING STEP OF
REACTION RATE OF NAPHTHALENE OXIDATION IN PRESENCE
OF CR-DOPED TiO₂ PHOTOCATALYST OBTAINED BY CHEMICAL
VAPOR DEPOSITION (CVD)**

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ABSTRACT

In this study gas phase photocatalytic oxidation of naphthalene in presence of nanosized Cr-doped photocatalysts prepared on TiO₂ base with chemical vapor deposition (CVD) is examined. Degradation level of naphthalene is examined with FTIR spectroscopy and identification of obtained products is made via GC-MS measurements. The kinetics of the reaction of photooxidation of naphthalene in excess of oxygen was investigated and the order of the reaction and rate constants were determined by means of mathematical modeling. It was found that kinetics of naphthalene degradation reaction follows first order reaction kinetics and the rate limiting reaction step is model of external film and surface particle diffusion. The prepared catalyst has shown excellent efficiency for naphthalene degradation in oxygen presence, which means complete mineralization of naphthalene to CO₂ and vapor was achieved.

Key words: *chemical vapor deposition, TiO₂ photocatalysts, naphthalene, kinetics, modeling.*

INTRODUCTION

Naphthalene is a common polycyclic aromatic hydrocarbon (PAH) which can be found in many anthropogenic fluxes, such as combustion fumes, used oil, bilge water, etc. It has been considered as possible carcinogenic to humans and it has both acute and chronic effects on human and animal health (Choplin et al., 2011; Carp et al., 2004).

Removing traces of naphthalene is possible with many techniques, including biofiltration, bioreactors, membrane bioreactors, ozonolysis, pulse radiolysis, electron beam irradiation, electrolytic aeration and photocatalysis (Choplin et al., 2011; Carp et al., 2004).

Photocatalysis is based of a semiconductor surface (TiO₂), by UV irradiation below 380 nm, which release electrons from the semiconductor's valence band. Photo generated electrons and holes react then with the organic compound to form radicals, making a strongly oxidant environment (Choplin et al., 2011; Carp et al., 2004; Fabbri et al., 2008; Pramauro et al., 1997).

Naphthalene oxidation by photocatalysis has been investigated in aqueous phase (Lair et al., 2008; Garcia-Martinez et al., 2005; Shi et al., 2000; Apátiga et al., 2006), and the authors have shown that degradation yields in formation of various compounds such as naphthols, naphthoquinones and cinnamaldehydes, and that naphthalene is finally completely mineralized into CO₂ and H₂O. Mainly, authors used co-solvents (acetonitrile, ethanol) that help dissolving naphthalene, but change the rate and the selectivity of the reaction (Choplin et al., 2011; Carp et al., 2004). However, there is a lack of investigation of naphthalene photocatalytic oxidation in gas phase; although this dangerous aromatic compound, or some similar aromatics could be found as a main carcinogenic parts, existing in the

exhausted gases. In addition, the kinetics of the reaction of naphthalene photocatalytic degradation in simulated environmental condition has not been examined, yet.

In this paper, the degradation of naphthalene by photocatalytic oxidation in the presence of TiO₂ was studied, kinetic of the degradation process, as well as the direction pathways of the mineralization process of naphthalene were determined. The kinetic study allowed determination of the reaction order.

EXPERIMENTAL

Materials

Naphthalene is purchased from Merck and used as received. In this work, TiO₂ anatase prepared by CVD with chromium as doping material (Ti:Cr=9:1) was used.

Preparation of thin film catalyst on the glass substrate

The UV laser induced CVD technique was used for making the film on the substrate, using the precursor TiCl₄ and CrO₂Cl₂ with initial pressure ratio of Ti:Cr=9:1. The prepared deposited film was annealed at 450°C for 2 hours, in order to remove crystal defects. Morphology and structure of the prepared thin film of catalyst was characterized by Raman spectroscopy. The degradation level of naphthalene was examined by FTIR spectroscopy and the reaction order and rate limiting reaction step was simulated by MATLAB.

Photocatalytic experiments

The irradiation experiments were carried out in a 1132 ml Pyrex cylindrical reactor with 55 mm diameter. The ends of Pyrex reactor are finishing with KrS 5 (thallium bromide-thallium iodide) windows. At the bottom of cylindrical reactor the glass substrate with thin film of TiO₂ based photocatalyst is positioned.

In all experiments the initial amount of naphthalene was 30 Pa, and the photoreactor was fulfilled with the mixture of naphthalene and oxygen in ration of 1:1000, which means the oxidation, was provided in total excess of O₂.

The light source was middle pressure mercury lamp with a power of 100 W, emitting in the near-UV region (mainly around 365 nm). Using the mirror, the UV light was directed toward the reactor quartz window and to the surface of photocatalyst. The irradiation time in all experiments was 3h. For kinetics measurements, the irradiation was stopped in certain times and FTIR spectra were collected (0, 10, 20, 30, 60, 120 and 180 min), At the end of the irradiation, GC analyses of the gaseous mixtures were carried out.

Analysis

FTIR spectroscopy (Nicolet Impact 400) was used to follow the degradation of naphthalene induced by UV light on the catalysts surface, as well as for identification of gaseous products after 3h irradiation.

For more precise identification of gaseous products GCMS Real Time Analysis, Shimadzu GC-MS-QP5050 with 50 m DB5 column was utilized.

For quantitative analysis of gas mixture Shimadzu GC-14B with 50 m DB5 column was used. The rate of heating was 10°C/min up to 230°C linked by Shimadzu C-R8A chromatopac.

Mathematical modeling

Reaction rate of naphthalene oxidation

Generally, the naphthalene oxidation in a gas phase according to Fogler can be written as:

$$r_A = \frac{dP_A}{dt} = -\frac{k}{(R \cdot T)^{n+m-1}} \cdot P_A^n \cdot P_B^m \quad (1)$$

where A-naphthalene, B-oxygen. The sign (-) indicates to naphthalene decaying, r_A -rate of naphthalene decaying ($\text{Pa} \cdot \text{s}^{-1}$), k - rate constant of naphthalene decaying which has units depending on reaction order, R -universal gas constant, ($\text{J} \cdot (\text{mol K})^{-1}$), T -temperature (K), P_A and, P_B -partial pressures of naphthalene and oxygen (Pa), and n, m -constants for the reaction order.

Mass transfer mechanism

Naphthalene oxidation in a presence of TiO_2 photocatalyst is taking place with contact of gas phase (naphthalene and oxygen) and solid TiO_2 photocatalyst (heterogeneous photocatalysis in gas phase). The steps of reaction are: 1) transfer of gas reactants to photocatalyst surface; 2) adsorption or chemisorption of reactants at the photocatalysts surface; 3) heterogeneous surface reaction; 4) desorption of products and 5) transfer of reaction products from photocatalyst surface.

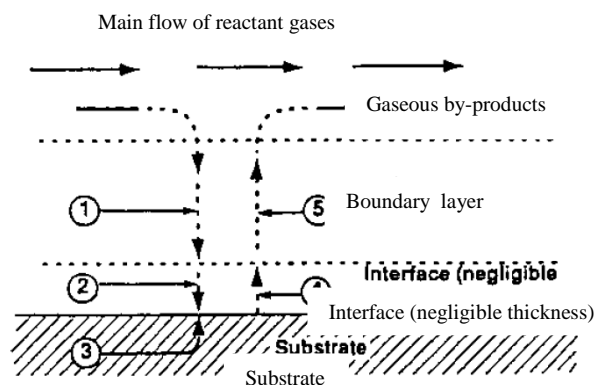


Figure 1. Reaction steps of naphthalene deposition

All these steps are goes subsequently and the slowest step will determine the overall reaction rate.

Usually, the gas reactants transfer to the photocatalyst surface and the gas products transfer from the photocatalysts surface are quick processes. So, the adsorption (chemisorptions), desorption and heterogeneous surface reaction are the steps which can determine the overall reaction rate.

Adsorption model in batch condition in existence of external film and diffusion on photocatalyst particles surface. If the diffusion into the photocatalyst particle is very quick, then the adsorption is taking place only on external surface whereby the overall rate will be controlled by diffusion in a laminar film of particle. Adsorption rate for a spherical photocatalyst particles is given as:

$$\frac{d\bar{q}}{dt} = \frac{3 \cdot k_f \cdot V}{R_p \cdot m} (C - C^*) \quad (2)$$

where \bar{q} - average adsorbed quantity (mg/g), C -concentration in a gas phase (md/dm^3), C^* -equilibrium concentration in a gas phase (md/dm^3), k_f -mass transfer coefficient through external film (m/s), t -time (s), R_p -radius of photocatalyst spherical particle (m), V -volume in liquid phase (m^3) i m -mass of photocatalyst (g).

If it is chosen linear equilibrium model (Freundlich isotherm):

$$q^* = K \cdot C^* \quad (3)$$

where q^* -equilibrium concentration of adsorbed phase (mg/g), K -equilibrium constant (dm^3/g).

In addition, by changing equation (3) into (2):

$$\frac{d\bar{q}}{dt} = \frac{3 \cdot k_f}{K \cdot R_p} (q^* - \bar{q}) \quad (4)$$

The initial condition for solving equation (4) is given by equation (5):

$$t = 0 \quad \bar{q} = 0 \quad (5)$$

If equation (5) write in pressure units:

$$\frac{d\bar{P}_A}{dt} = \frac{3 \cdot k_f}{K \cdot R_p} (\bar{P}_A - P_A^*) \quad (6)$$

where \bar{P}_A -average partial pressure (Pa), P_A^* -equilibrium pressure in a gas phase (Pa).

The initial condition for solving equation (6) is given by equation (7):

$$t = 0 \quad \bar{P}_A = P_{A0} \quad (7)$$

RESULTS AND DISCUSSIONS

TiO₂ photocatalyst prepared by cvd

Raman spectra for the system Ti/Cr is given on figure 2. Deposits are examined on Ta substrate with laser 473 nm, aperture 100 μm pinhole and a 100% laser energy.

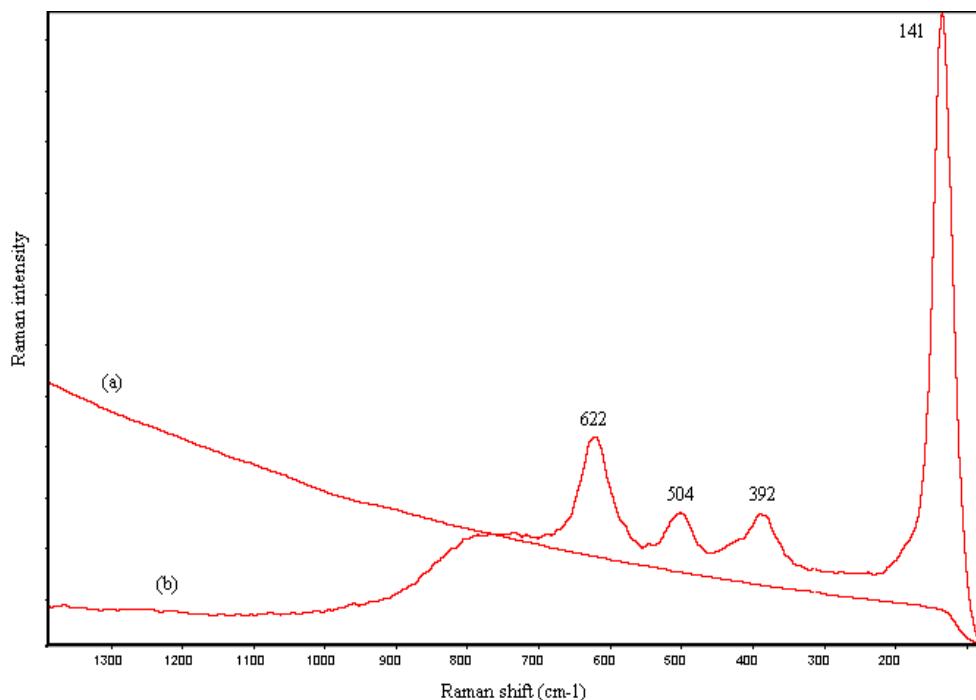


Figure 2. Raman spectra of TiO₂ deposits for systems Ti:Cr=9:1. (a) as prepared deposit; (b) annealed deposit at 400°C/2h

From figure 2 it can be seen that as prepared deposits has no peaks, fig.2(a), so the structure is amorphous. From figure 2(b) shows peaks at 622, 504, 392 and 141 cm^{-1} which are characteristic peaks for anatase structure (Rengaraj, et al., 2007).

Photocatalytic degradation of naphthalene

After the irradiation of naphthalene in excess of oxygen and with doped TiO_2 photocatalyst with chromium, with GC-MS analysis was obtained that main gaseous products after 180 minutes of irradiation are: CO_2 and water, although some traces of acetone and ethanol were also detected (less than 0.1 %). We consider that these compounds are absorbed on the reactor walls, after cleaning procedure, and because of that became identified between the reaction products. Therefore, complete mineralization of naphthalene in this system is achieved. The FTIR spectra after 180 min irradiation of naphthalene is shown on figure 3.

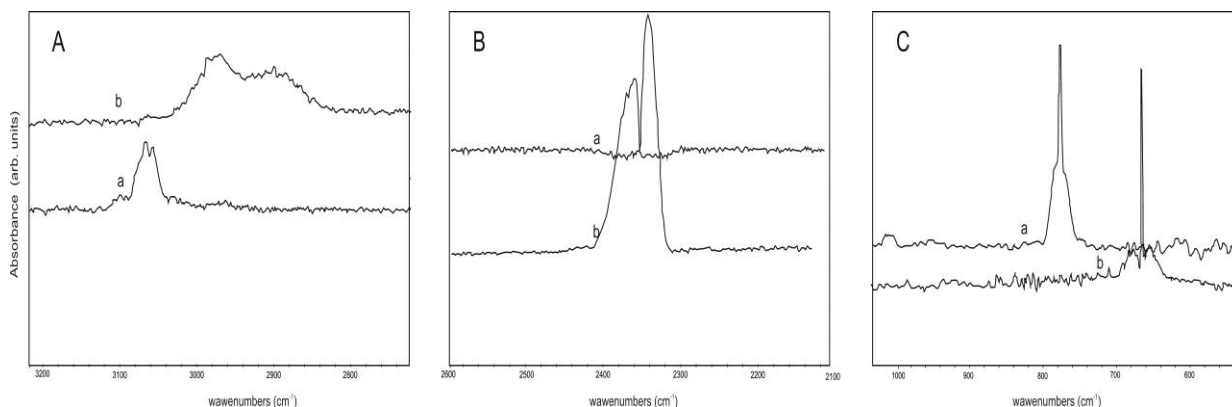


Figure 3. Areas from characteristic peaks for naphthalene (A) from $3200\text{--}2700\text{ cm}^{-1}$; (B) from $2600\text{--}2100\text{ cm}^{-1}$; (C) from $1000\text{--}500\text{ cm}^{-1}$. (a) before irradiation; (b) after 180 min irradiation

From figure 3A-a and 3A-c it can be seen that naphthalene has characteristic peaks in a mixture naphthalene, oxygen and TiO_2 photocatalysts like: middle peak at 3066 cm^{-1} , and peak with a strong intensity at 781.8 cm^{-1} . After 180 min irradiation in excess of oxygen and presence of TiO_2 photocatalyst it was obtained FTIR spectra showed on figure 3A-C-b. The peak at 3066 cm^{-1} completely vanish which shows C-H bonds from aromatic ring. That means degradation of two aromatic rings, but in order of their degradation, it shows peaks at 2970 and 2900 cm^{-1} . The peaks at 2970 cm^{-1} and 2900 cm^{-1} are peaks from presence of C-H stretching and CH_3 from acetone and ethanol, respectively. In the water region from $1800\text{--}1380\text{ cm}^{-1}$ it shows forming of big amount of water. In the region from $1100\text{--}1020\text{ cm}^{-1}$ it shows a new peak with maximum at 1068 cm^{-1} which is from SiO_2 from the rubber from quartz window glued with a Pyrex photoreactor. After the irradiation the characteristic peak at 781.38 cm^{-1} is completely gone. The peak at 668 cm^{-1} is bigger which shows formation of CO_2 .

After the irradiation of gas mixture, the photoreactor is filling with helium till atmospheric pressure, and after that 3 ml from gas mixture is taken for GC-MS analysis. The GC-MS analysis are given on figure 4.

Identification of gas compounds from GC-MS analysis are given in table 1.

Table 1: GC-MS analysis of gas mixture for system naphthalene-oxygen- TiO_2 (Ti:Cr=9:1)

Compound	retention time, min
O_2	2.85
CO_2	3.96
H_2O	~15
ethanol	21.35
acetone	22.55

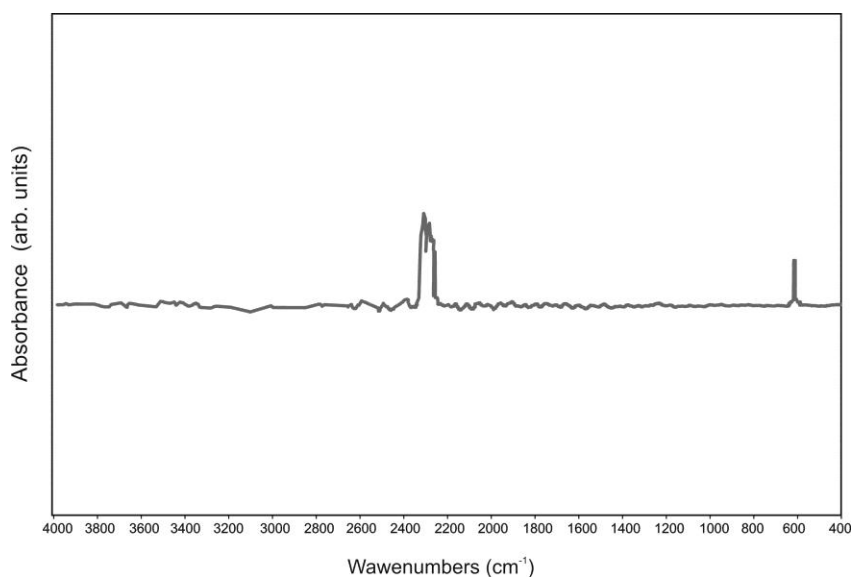


Figure 4. FTIR spectra of solid compounds after 180 min irradiation of naphthalene in presence of oxygen and TiO_2 photocatalyst (Ti:Cr=9:1)

After the 180 min irradiation, in a photoreactor are not present solid compounds, except a lot of amount of CO_2 peaks from $2385\text{--}2285\text{ cm}^{-1}$ which is surface CO_2 and peak at 667 cm^{-1} . There is no present of any aromatic compound. During the irradiation of naphthalene in excess of oxygen and TiO_2 (doped TiO_2 photocatalyst with chromium, Ti:Cr=9:1) photocatalyst it has been measured level of degradation with FTIR spectroscopy for 0, 10, 20, 30, 60, 120 and 180 min. The degradation level of naphthalene is after 180 min irradiation is shown on figure 5.

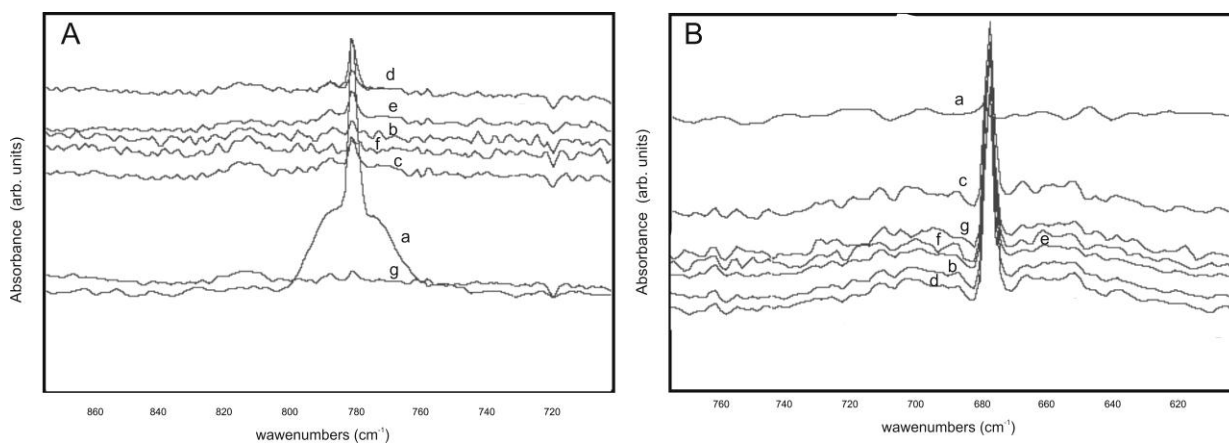
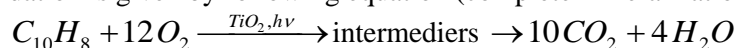


Figure 5. FTIR spectra of decaying naphthalene (A) and formation of CO_2 (B) for UV lamp irradiation of Cr-doped TiO_2 photocatalyst. (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 60 min; (f) 120 min; (g) 180 min

Kinetic reaction of naphthalene oxidation

Naphthalene oxidation is given by following equation (complete mineralization or degradation):



Fitting of experimental data for naphthalene and CO_2 pressure ratio as a function of irradiation time is done by Curve Fitting Toolbox, Matlab Software Package. The fitted data are shown in Figure 6.

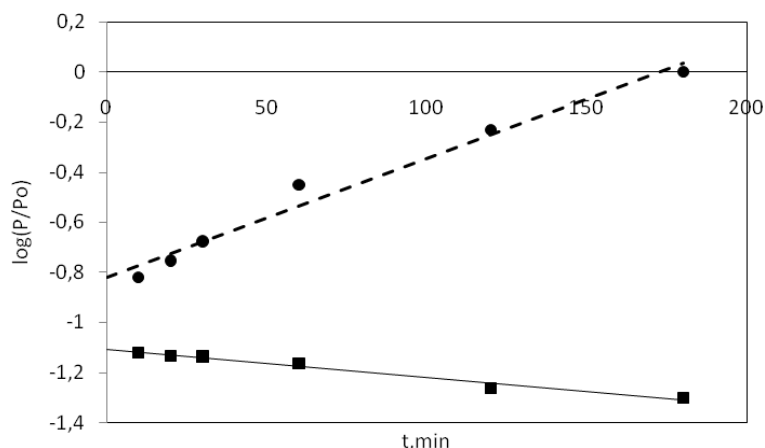


Figure 6. Logarithmic diagram for pressure ratio as a function of irradiation time
 ■ - experimental value for naphthalene decaying; ● - experimental value for CO₂ forming; ---- fitted values by first order reaction rate

By the fitting for naphthalene decaying reaction rate constant was determined to be $1,667 \cdot 10^{-5} \text{ s}^{-1}$ with correlation coefficient $R=0,977$, and for CO₂ forming reaction rate constant was determined to be $6,667 \cdot 10^{-5} \text{ s}^{-1}$ with correlation coefficient $R=0,979$, which are very good correlation. The naphthalene decaying (degradation) was done for the characteristic peak 781 cm^{-1} , and the fitting of CO₂ forming was done for characteristic peak for free CO₂ located at 667 cm^{-1} . The semilogarithmic shows that reaction rate follows first order kinetics of photodegradation of naphthalene in presence of Cr-doped TiO₂.

Determination of limiting step of naphthalene oxidation reaction rate

Beside reaction rate order, for degradation rate of naphthalene is important to determine limiting step which determines the overall reaction rate. Examination of kinetics in batch conditions is important because of equipment dimensioning and opportunity to obtain data which can furthermore using for continuous processes (Fabbri et al., 2008; Pramauro et al., 1997; Lair et al., 2008; Garcia-Martinez et al., 2005). If the diffusion inside the photocatalyst pellet is very fast than the adsorption taking place only on the surface of particle, from which the overall reaction rate will be controlled by diffusion in laminar film around the particle. Results of fitting the experimental data for naphthalene oxidation by photocatalyst are given on figure 7. Simulations were made by MATLAB.

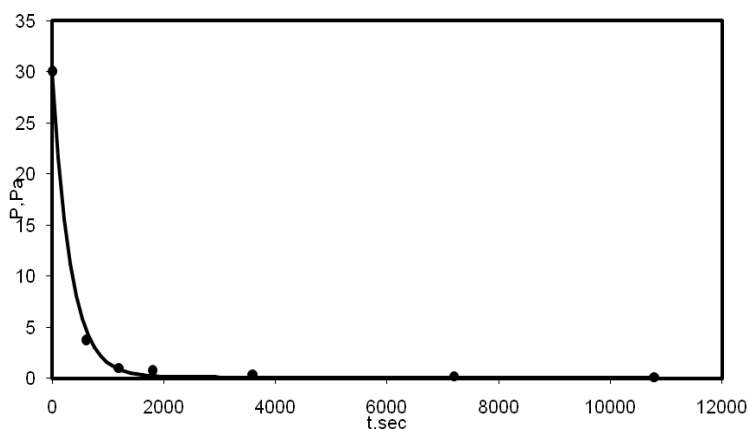


Figure 7. Dependence of partial pressure of naphthalene as a function of time for the first-order kinetic reaction

●- experimental data of Cr-doped TiO₂ photocatalyst obtained by CVD (Ti:Cr=9:1); — fitted data of Cr-doped TiO₂ photocatalyst obtained by CVD

Mass transfer coefficient through particle film of photocatalysts values for this type of TiO₂ photocatalyst is given in table 2.

Table 2: Mass transfer coefficient through particle film of photocatalysts values for Cr-doped TiO₂ photocatalyst

TiO ₂ photocatalysts	Mass transfer coefficient, k_f (m/s)
Ti:Cr=9:1	$2 \cdot 10^{-11}$

From table 2 it can be seen that the value for the mass transfer coefficient through particle film of photocatalyst is $2 \cdot 10^{-11}$ (m/s). Experimental data were fitted with other mass transfer models, but none of them weren't shown any good fit with experimental data.

So, naphthalene oxidation with TiO₂ photocatalyst prepared by CVD with ratio Ti:Cr=9:1 is limited by **adsorption in batch condition in existence of external film and diffusion on photocatalyst particles surface.**

CONCLUSIONS

Cr-doped TiO₂ photocatalyst by CVD was prepared. As prepared deposits are amorphous, and to obtain crystal structure, as prepared deposits were annealed at 400°C/2h. For preparation of TiO₂ photocatalyst TiCl₄ as a precursor, was used. The results from naphthalene degradation in a presence of TiO₂-photocatalyst are very powerfull for complete degradation of naphthalene, and it follows first order reaction kinetics. For the overall rate of complete naphthalene oxidation, reaction degradation rate will be controlled by model of of diffusion on particles photocatalyst surface.

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**THE DEVELOPMENT OF AMBIENT AIR QUALITY MONITORING
ON APV TERRITORY**

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ABSTRACT

The control of ambient air quality, from the beginning until now, went through different phases which included different scopes and levels of control. Generally, the control of ambient air quality system in the territory of APV was being developed at certain pace that was due to the capacity of institutions implementing it, concerning the human and technical resources, the budget for air quality control and primarily legal obligation that were not specified enough. Nowadays, the system for management and air quality control is still developing and adjusting to obligations defined by national and European laws, standards and recommendations but on its way to systematic arrangement of this area. This paper will demonstrate the development of legislation systems in the fields of ambient air quality control and protection, from the very beginning up to today when there are a contemporary air quality control networks which are on the way to fully adjust to national and European regulation requirements.

Key words: *air quality network, monitoring, national regulations.*

INTRODUCTION

Almost every country has its standards for the estimation of air pollution. European Union standards and directives for member states of EU, then NAAQS (National Ambient Air Quality Standards) in USA, or WHO-AQGs (World health organization Air Quality Guidelines) are effective in Europe. Regulations of national character have a binding force and are directly applicable and divided into two groups according to the bearer, legal significance and importance: legal regulations-LOWS, and subordinate legal regulation-BYLOWS.

THE DEVELOPMENT OF LEGISLATION SYSTEMS IN THE FIELD OF AMBIENT AIR QUALITY MONITORING IN THE REPUBLIC OF SERBIA

Environmental protection, as a general notion in national law regulation firstly appeared in Health Protection Laws (1987, 1990) where it was defined that medical care implies measures, activities and constitutions which preserve and improve health and environment. The primary goal of medical care is the preservation and improvement of citizens' healthcare and their work and physical and social environment. In the system of health service organization among medical institutions, Public Health Institutions are observing the influence of ecological factors on human health as a part of separate sectors: hygiene and environmental protection.

First Low on Environmental Protection was adopted in 1991, where the air protection was a separate section (article 18.-23.) A part of the Low related to the air quality consisted of a few sections where the ambient air quality and pollution control was defined through measurements i.e. observation of air quality and basic meteo parameters, records of immision and emission data and resources of air pollution, as well as systematic research of air pollutions affects on people's health, their environment and climate, on national and local level. Provisions of this part of the Low was specified with few acts, but the most important were:

1. Ordinance on Air Quality Control Programme which the Government approved for the two year period, in which the station network for the ambient air quality control was defined (basic meteo and urban station networks) i.e. exact number of measurement sites in urban areas and types of pollutants that are measured (basic and specific pollutants). First regulation of establishing the air quality control programme was adopted in 1993. These regulations also defined the obligation of observing the impact that the air pollution had on people's health in twelve cities and that was realized by the examination of people's biological reaction to air pollutants, physiological and pathophysiological changes, morbidity and mortality and the register of diseases which were mostly related to respiratory organs.

Observation of the impact that air pollution had on the environment was conducted by systematic pollutants deposition control (pH, ammonium ion, sulphates, chlorides, nitrates, lead, cadmium, manganese, zinc) in five measurement sites, by intensity in forests growth (chlorosis, bioindicator species of lichen, fungi and insects on trees) and cumulation of heavy metals into biological matter in three sites. Observation of the impact that air pollution had on the climate was conducted by parallel analyses' results which were based on systematic measurement of immision and on weather parameters.

It seems that subordinate legal act was assuring legal rights for conduction of all essential activities related to observing the air pollution and its impact on national as well as international level. However, after 94/95 and 96/97 Ordinances, the following (2000/2001, 2002/2003, 2004/2005, 2006/2007) had less content. In fact, number of measurement sites remained approximate, but VORMON and EMPEP programme measurements in international network were abolished. Ordinance (2000/2001) imposed these notions: basic meteo station networks and basic urban weather station networks where observations of gases that contribute to the greenhouse effect (GHG) were defined. Also, this Regulation was practically without elements which define register of specific diseases by the age group, without the methodology for estimation of the impact of air pollution on people's health, which was probably the result of ineffectiveness of the same studies during the last period.

2. Bylaw on treshold values, measurment methods, criteria for establishing measurment cites and registration of data (1999) which defined that the systematic air quality measurement should be conducted on the measurement sites that is not directly exposed to the influence of pollutant resources on the distance of 1.5 to 10 meters from earth level. These measurments should be conducted during the period of at least a year or six months or even less than six months when the goal is obtaining air quality data on some measurement sites. Results of systematic air quality measurement were recorded, processed and analyzed as concentration mean, number of days when treshold value was exceeded, frequency of high concentration and median and the results have to be based on 75% of regulative data. The bylaw defines pollutants which have to be measured and divides them into following groups:

- a. inorganic materials: SO₂, soot, suspended particles, nitrogen dioxide, ground-level ozone, carbon monoxide, hydrogen chloride, chlorine, hydrogen fluoride, ammonia, hydrogen sulfide, depositional material from the air, heavy metals in suspended particles: Cd, Mn, Pb, Hg
 - b. organic materials: carbon disulfide, styrene, tetrachloroethylene, formalhyde, 1,2 dichloroethane, acrolein
 - c. carcinogenetic materials: acrylonitrile, arsenic, benzene, chlorine (6+),nickel, polycyclic aromatic hydrocarbon, vinyl chloride, asbestos, ethylene dichloride, dioxin (2,3,7,8 tetrachloro-dibenzodioxin).
- By this bylaw these materials are not supposed to be contained in ambient air.

The bylaw also defined definition and values od warning immision and episodic pollution which commence when treshold value is overreached for sulfur dioxide, soot, nitrogen dioxide, carbon monoxide and ground-level ozone.

Next, local self-government had to make plans on how to improve the air quality and recovery programmes. Depending on the air quality, the plan determines activities and measures that the authorities and pollutants should establish in the specific time period, then, it determines the way of

alerting citizens and other activities and measures for improvement of the air quality.

Recovery programmes are established for specific areas where air quality is at risk in the case of warning immision. Using the recovery programme, in order to protect the air from local sources of air pollutants, local self-government can prohibit driving through certain streets for all or some motor vehicles in specific time period or during the specific level of warning immision and also to establish other measures for air pollution protection that are caused by motor vehicles and other air pollutants.

CURRENT STATE OF AMBIENT AIR QUALITY CONTROL

Today, basic act concerning the environment in the Republic of Serbia is defined by Environmental Protection Low (2004). The low establishes integral system of environmental protection which ensures human rights for living and growing in a healthy environment and balanced relation of economic expansion and environment (sustainable development). Environmental Protection Act serves as a basis for establishing the first law that would regulate the air protection since the system of the environmental protection started functioning in these areas. Low on Ambient Air Protection (2009) was completely adjusted to European and world standards and it regulates the conduction of the air quality and establishes measures for the ways of organization and also the control of conducting the protection and improvement of ambient air quality. Besides that, the Low regulates the questions in a few groups which refer to air quality requirements (network and measurments), strategies, plans and programmes, and measures for air quality improvement, informing and reporting, financing, surveillance and sanctions.

Air quality requirements

The most important step towards improvement of ambient air protection system is reorganization of air quality monitoring network and the setting of state and local air quality measurement network. After three years (the last one was in 2007), Ordinance of establishing the air quality control programme on the national level was legislated (2011). It shows that the APV territory has ten measurement spots: eight measurement spots for measuring air quality in urban, industrial and suburban areas, one station and/or measurement spot for measuring air quality in protected nature areas and protected immovable cultural property environment and one measurement station and/or measurement spot for measuring air quality on fields that are exposed to specific pollutants, including movable sources (Table 1).

Table 1: a part of state measurement stations network for measuring ambient air quality on the territory of APV

Type of measurement station	Name of measurement station	
	AMS	MS
Measurement stations and/or measurement sites for measuring air quality in urban, industrial and suburban areas.	Kikinda	
	Novi Sad-Liman	
	Beočin-centar	
	Sremska Mitrovica	
	Pančevo- Sodara	
		Pančevo 1
		Pančevo 2
Measurement stations and/or measurement sites for measuring air quality in protected nature areas and protected immovable cultural property environment		Pančevo 3
		Palić
Measurement stations and/or measurement sites for measuring air quality on area that are exposed to specific pollutants, including movable sources	Novi Sad-Dnevnik	

Local network for ambient air quality control includes automatic station network as well as measurement sites network on which the concentration of pollutants is being measured using manual methods. Local automatic station network could be divided into two levels:

1. “Regional“ level which includes 7 stations all over the territory of APV that are now under jurisdiction of Provincial Secretariat for Urban Planning, Construction and Environmental Protection.
2. “Local“ level which consists mostly of measuring sites (around 112 on the territory of the APV) for measuring the concentration of pollutants in urban, suburban or industrial areas of certain cities, as well as the system of automatic stations in Pančevo (4 automatic stations) which are under jurisdiction of Secretariat for Environmental Protection, Urban Planning, Construction and Utilities and Housing Services (Jovovic et al 2011).

Characteristics of measurement stations for every urban area are given according to Manual for air quality data exchange, characteristics of measurement stations and measurement configuration established by European Topic Centre for Air Pollution and Climate Change Mitigation (Council Decision 1997, Guidance Report to the Annex to Decision 1997, EEA-EUROAIRNET programme, Directive 2002, EMEP Task Force on Measurement and Modeling (TFMM)).

Second, but not less important change is defined by the air quality requirements. This chapter of the Law also serves as a basis for enactment of Ordinance on monitoring and air quality requirements (2010) which in a more detailed way defines the threshold values of some pollutants in ambient air, tolerance threshold, high and low evaluation thresholds, target values and hazardous substance concentration and concentrations harmful to human health which are presented to the public, as well as referential methods for measuring the concentration of certain pollutants: sulfur dioxide, nitrogen dioxide and nitrogen oxide, suspended particles (PM₁₀, PM_{2.5}), lead, benzene, carbon monoxide, and ground level ozone. Aforementioned topics are divided into two parts: conditions for monitoring air quality and air quality requirements.

Beside the detailed definition of establishing measurement spots criteria, as well as requirements for minimal number of measurement spots, new Ordinance defines maksimal allowed concentrations inorganic gaseous compound, organic matter, cancerous matter, total matter sediment, total suspended particles and soot, as well as high and low tolerance threshold, pollutant target values and also deadlines for reaching target values.

As far as concrete, numerical threshold values are concerned, the criteria have been tightened for sulfur dioxide so the new value is 25µg/m³ lower on a daily basis than the old threshold value which means that the 24-hour threshold value is 125µg/m³ instead of 150µg/m³. As a logical consequence of this, the criteria for annual threshold value of sulfur dioxide for protection of vegetation are also tightened as compared to the old threshold value for uninhabited and recreational areas and it is now 30µg/m³ lower. Moreover, new annual threshold value for nitrogen oxide is 20µg/m³ lower than the old one.

As already stated, until the enactment of the Law and its bylaws that regulate and direct the air protection area, systematic immission measurement was administered in every measurement site as a part of the network for at least a year or less (Bylaw on threshold values, measurement methods, criteria for establishing measurement sites and registration of data 1999). The criteria for data coverage are tightened and more precisely defined with new subordinate acts so the minimal data availability for sulfur dioxide, nitrogen dioxide, nitrogen oxide, and carbon monoxide, suspended particles (PM_{10/2.5}) and lead, benzene, ground level ozone is 90% for fixed measurements, and for indicative measurements which are administered in order to identify pollutions in certain areas, minimal time coverage is 14%.

The Act also prescribes a mandatory definition of zones and agglomeration and air quality evaluation within these areas which will contribute to better control, state preservation and air quality improvement.

Zones are defined as parts of territory with borders, established in order to evaluate and manage air quality which in terms of control, preservation and/or air quality improvement constitutes a characteristic functional whole. Agglomeration is defined as an area with more than 250000 residents, but it can also be an area with less residents. If population density in that area is larger than prescribed than the need for evaluation and air quality management is justified. If the number of residents in the zone is less than 250000 than the population density for establishing agglomeration is prescribed by the Government.

Definition of zones and agglomeration regulation (2011) established specified zones and agglomerations in the territory of Serbia so the territory of Vojvodina has one agglomeration: Novi Sad.

Evaluation of air quality within zones and agglomeration is done on the basis of established upper and lower evaluation boundary once in every 5 years, or more often, if changes in activities that can influence the monitoring of pollutants concentration occur.

Given the level of pollution with prescribed threshold and tolerance values and on the basis of measurement results, there are three categories of air quality in areas and agglomeration established by the regulation:

- 1) first category: clean or slightly polluted air where the level of threshold values is not exceeded by any of the pollutants;
- 2) second category: moderately polluted air where the level of threshold values is exceeded by one or more pollutants but tolerance values are not exceeded;
- 3) third category: excessive polluted air where tolerance values are exceeded by one or more pollutants.

Second innovation concerns the methods used for measuring the concentration of pollutants. While the old Ordinance (1992) defined the methods that dealt with manual analysis of samples in laboratories, the newly defined methods mostly deal with requirements and conditions for automatic measuring of pollutants in ambient air in real time as well as a certain number of methods which deal with sampling and their analysis. The use of “non-referential methods” can be approved by Ministry under the condition that the equivalency test is done i.e. to modify the data so that they are equivalent to those data which would be collected using referential methods. Equivalency tests in the Republic of Serbia are done on the location of automatic station Zeleno Brdo in Belgrade, where parallel measuring and sampling were established, setting the mass concentration of suspended particles PM10 and PM2.5 using gravimetric and automatic methods. The results of the test are still not published (Report of ambient air quality on the territory of the Republic of Serbia in 2011).

Strategies, plans and programmes

Strategies, plans and programmes, instruments of politics and air protection planning, are: strategy of air protection, air quality plans and short-term action plans that are established in order to preserve and improve air quality and avoiding, preventing or reducing harmful consequences for people and the environment. There is also an obligation to prepare a National programme for gradual reduction of national emissions of pollutants (SO₂, NO_x, VOC, NH₃).

As far as area dealing with strategic documents, plans and programmes is concerned, it is defined in more detail by the new act through its subordinate acts (The content of air quality plans ordinance 2010, The content of short-term action plans ordinance 2010). This is the first time that the Strategy of air protection, as the basic document of air protection strategy, was defined by law and it serves as a basis for establishing other plans and programmes (plans for air quality, short-term action plans and programmes for emission reduction). This strategy provides conditions for establishing institutional system of measures for avoiding, preventing or reducing air pollution and harmful consequences for human health and the environment.

Action plans are documents with which the strategy goals are realized, while for areas and agglomeration the air quality plans are made which state that the air quality is of third category, that is, the areas are excessively polluted and tolerance value limit has been exceeded by one or more pollutants.

Short-term action plans are equalised with Sanitation plans of the old Law but defined in a more detailed way through content and conditions of their making. Namely, short-term action plans are made in these three cases (Content of short-term action plans ordinance 2010):

1. in case there is a risk that the levels of air pollutants exceed one or more concentrations hazardous to human health
2. there is a risk that the concentration of ground level ozone is exceeded which is dangerous to human health
3. for the sake of human health and environment protection, if needed, if there is a risk of exceeding one or more threshold or target values for certain pollutants.

Air quality improvement measures, informing and reporting, financing, surveillance and sanctions

Air quality improvement measures, aside from legal basis for definition of threshold values of emission from stationary and mobile sources, reduction of gas emission with the green house effect, gradual reduction of use of ozone layer damaging substances and other measures for preventing and reducing the pollution which, among other things, innovate issuing licenses for newly constructed or reconstructed stationary pollution sources for which there is no prescribed obligation for issuing integrated license, that is, making the evaluation study about the influence on the environment.

Informing and reporting determines how often, through which media and what is being informed within the authorities and the public. The information content and deadlines for informing are also determined by this. More detailed obligations about informing are defined in Regulation on ways of exchanging information about measurement spots in state and local network, and by measurement techniques as well as ways of data exchange obtained by monitoring the air quality in state and local networks (2010).

Moreover, the formation of information system, that is, content of information system is also defined here.

Financing which determines the source of the budget for finding solutions for protection and improving air quality.

Surveillance, that is, the rights, obligations and authorities of inspector and in a separate chapter there are penalty provisions where fines for economic offences are defined.

CONCLUSION

The control of ambient air quality, from the beginning until these days went through different phases which included different scopes and levels of control. Generally, the control of ambient air quality system in the territory of APV was being developed at certain pace that was due to the capacity of institutions implementing concerning the human and technical resources, the budget for air quality control and primarily legal obligation that were not specified enough. Nowadays, the system for management and air quality control is still developing and adjusting to obligations defined by national and European laws, standards and recommendations but on its way to systematic arrangement of this area.

During the last two decades measurement station networks for manual monitoring were developed on the territory of APV. Results obtained from these stations were than presented into annual reports. The making of legally defined Plans for taking action in order to improve the current state was not common practice and reduction and preventing air pollution measures were reduced to inspection.

Today, there is systematic monitoring of air quality in Vojvodina. Air quality is monitored in a certain area in real time and this provides the possibility to assess the air quality in certain spatial units (areas and agglomerations). However, major efforts must be made in order for the system to function and to fulfill stated legal obligations. Namely, at the beginning 10% of its total value must be invested in maintenance and service of one automatic station and in subsequent years this percentage increases due to deterioration of the analyzer and the increasing demands in terms of maintenance. In the system of automatic stations on the APV territory, which are under the jurisdiction of Provincial Secretariat for Urban Planning, Construction and Environmental Protection, this influences the reduction of available data from year to year so, sometimes it is impossible to make the necessary evaluation and assessment of air quality. A second problem that arises is unsolved legal status of automatic stations which are under the jurisdiction of Provincial Secretariat and the City of Pančevo. Namely, air protection act defines that the competent body of autonomous province is responsible for monitoring air quality in a local network by an authorized person or expert organization accredited as a research laboratory that meets the requirements and has the license for air monitoring and/or emission measurement issued by the Ministry. It can also authorize a person to monitor air quality, stations, to collect and analyze data from the local network. It is important to solve the legal status of aforementioned automatic stations because expert and accredited institutions and authorised institutions will provide valid and comparable data which will serve as a basis for evaluation of air quality and take action in order to protect human health and the environment.

Moreover, the measurement sites network for determining the concentration of pollutants in ambient air using manual methods on the territory of APV is enormous (it consists of around 112 measurement spots) and requires a systematic rationalization as well as adjustment of used methods with referential methods.

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MODELS OF AIR QUALITY

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ABSTRACT

In this paper, a review of relevant findings from the available literature, and models: Gaussian air pollution dispersion equation and equation of Briggs lifting gas. Dispersion models are used to estimate or predict concentrations of pollutants or toxic substances emitted from sources such as industrial plants, traffic, or accidental spills of chemicals. Air dispersion models used by the department of public safety, as well as employees in the department of emergency planning in case of chemical accidents. Models are used to determine the consequences of accidental release of hazardous or toxic materials. Atmospheric dispersion models are also known as models of atmospheric diffusion and air quality models and models of dispersion of air pollutants.

Keywords: *models, quality, air dispersion.*

INTRODUCTION

Atmospheric dispersion modeling is the mathematical simulation of how the pollutants in the air spread in the atmosphere. It is performed using computer programs that solve mathematical equations and algorithms which simulate the dispersion (dispersion) of pollutants. Atmospheric dispersion models are known as models of air dispersion, air quality models and models of dispersion of air pollutants. Dispersion models are used to estimate or predict concentrations of pollutants or toxic substances emitted from sources such as industrial plants Figure 1, traffic or accidental spills of chemicals.

Such models are important for the government agency tasked to protect and manage ambient air quality. Models are typically used to determine whether they are current or whether the new industrial facilities comply with national standards of ambient air quality (NAAQS) in the United States and other countries. Models also serve to create an effective control strategy for reducing emissions aeropolutanata (AQI; CAQI. 2006; AQI. 2005).

Air dispersion models used by the department of public safety, as well as employees in the department of emergency planning in case of chemical accidents. Models are used to determine the consequences of accidental release of hazardous or toxic materials. Accidental discharges may result in fire, explosion or spills of hazardous materials such as chemicals or radioactive substances. The results of dispersion model, using the worst possible conditions under which there has been flooding and weather conditions, can provide assessment of sites affected areas, ambient concentrations, and may set out safeguards that comply with the event when any leaks. Appropriate measures protect may include evacuation or referral people which are in the direction of wind in the shelter. Dispersion models vary depending on the mathematical calculation that is used for its development, but all require data entry that can contain, (AQI. 2003; RLVE. 2006; WHO. 1999):

- Weather conditions such as wind speed and direction, the amount of atmospheric turbulence (as is the descriptive name of "stability class"), ambient air temperature, height above the bottom point of the inversion layer, covering of clouds, solar radiation.
- The conditions of release (concentration and amount of toxins in the air and accidental discharges) and the temperature of discharged substances.

- Discharge or emission parameters such as location, height, types of sources (ie, fire, pool, or vent pipe) and the exit velocity, exit temperature and mass flow rate or quantity of discharge.
- The amount of terrain at the site sources of contamination and the receptor sites (receiver), such as houses, schools, offices, and hospitals.
- The location, height and width of any obstructions (such as buildings or other structures) that are on the path of propagation of the emitted gas, rough terrain, or use more generic parameters such as rural or urban terrain.



Figure 1. Industrial sources of air pollution

According to the literature (Gallagher et al., 2012) is given as follows: Numerical modeling of the passive control of air pollution in urban street canyons asymmetrical using refined mesh discretization schemes.

Many of the modern advanced dispersion modeling programs include preprocedural module for insertion of meteorological and other data, and many also contain postprocedural module for graphical display of output data and / or graphic representation of map areas affected by air pollution.

Graphical presentation may also contain curves showing the area of high concentration to a minimum and define areas of greatest risk to health. The curves are useful in determining the measures to protect the public and the needs of the department of public safety. Atmospheric dispersion models are also known as models of atmospheric diffusion and air quality models and models of dispersion of air pollutants.

Based on the research (Liu et al., 2012) is given as follows: Diagnosis of air quality through observation and modeling of volatile organic compounds (VOCs) as pollution tracers.

MATERIALS AND METHODS

The atmospheric layers

Discussion of the layers of Earth's atmosphere is also necessary, in order to understand what the pollutants disperses in the atmosphere. Layer, closest to the earth, is known as the troposphere. It covers an area of level sea to a height of about 18 km and contains approximately 80% of the total mass of the atmosphere. The stratosphere is the next layer, and it covers an area of 18 km to 50 km. The third layer is the mesosphere which extends the range of 50 km to 80 km. There are other layers above 80 km, but they are irrelevant to the modeling of atmospheric dispersion.

The lowest part of the troposphere is called the atmospheric boundary layer (ABL) or the planetary boundary layer and extends from the Earth's surface up to about (1.5 to 2) km in height. The temperature in the atmospheric boundary layer decreases with increasing height, until it reaches the layer called the inversion layer (temperature increases with height) located at the top of the atmospheric boundary layer. The upper part of the troposphere (the layer above the inversion) is called the free troposphere and extends to 18 km altitude.

As for emissions, transport and dispersion of emitted pollutants, the most important atmospheric boundary layer. Part of the atmospheric boundary layer between the Earth's surface and lower inversion layer, called the mixing layer. Almost all the pollutants that are emitted into the atmosphere are transported and released into the mixing layer. A certain amount of emitted pollutants and breaks through the inversion layer into the free troposphere above the atmospheric boundary layer.

Layers of the Earth's atmosphere, seen from the ground up are: the atmospheric boundary layer is composed of layers of mixing that connects the inversion layer, free troposphere, stratosphere, mesosphere, and others. Many models of atmospheric dispersion models are called the boundary layer, because they generally modeled atmospheric pollution dispersed within the boundary layer. To avoid confusion, the models are called mesoscale models have a dispersion modeling capabilities that extends horizontally and up to several hundred kilometers. This does not mean that they are modeled dispersion mesosphere.

Gaussian air pollution dispersion equation

Technical literature on air pollution dispersion is very extensive and goes back to the 1930s, and even earlier. Under the stimulus, which is secured by stringent environmental control regulations, is the increased use of budget dispersion of gaseous pollutants in the air between the late 1960s and today. A large number of computer programs for calculating the dispersion of air pollution have been developed during this period and were called "air dispersion models." The basis for most of these models was the complete equation for the Gaussian dispersion modeling of continuous dispersed smoke plume, shown by the following equation:

$$C = \frac{Q}{u} \cdot \frac{f}{\sigma_y \sqrt{2\pi}} \cdot \frac{g_1 + g_2 + g_3}{\sigma_z \sqrt{2\pi}}$$

Where:

f = parameter dispersion under the influence of side wind

$$= \exp \left[-y^2 / (2 \sigma_y^2) \right]$$

g = vertical dispersion parameter = $g_1 + g_2 + g_3$

g_1 = vertical dispersion with no reflections

$$= \exp \left[- (z - H)^2 / (2 \sigma_z^2) \right]$$

g_2 = vertical dispersion for reflection from the ground

$$= \exp \left[- (z + H)^2 / (2 \sigma_z^2) \right]$$

g_3 = vertical dispersion for reflection from the layer above the inversion

$$\sum_{m=1}^{\infty} \left\{ \exp \left[- (z - H - 2mL)^2 / (2 \sigma_z^2) \right] \right. \\ \left. + \exp \left[- (z + H + 2mL)^2 / (2 \sigma_z^2) \right] \right\}$$

$$+ \exp \left[- (z + H - 2mL)^2 / (2 \sigma_z^2) \right]$$

$$+ \exp \left[- (z - H + 2mL)^2 / (2 \sigma_z^2) \right]$$

C = concentration of emitted pollutants, g / m³ for each receptor located on
 x - meters downwind in relation to the emission source
 y - meters in the lateral direction of the wind in the axis of the smoke plume
 z - meters above ground level

Q = amount of emitted pollutants, in g / s

u = horizontal wind speed along the axis of the emitted pollutants, m / s

H = height of the axial line of propagation of pollutants above the ground level, m

σ_z = standard deviation of the vertical distribution of the emission, m

σ_y = standard deviation of the horizontal distribution of the emission, m

L = distance from the ground level to the bottom of the inversion layer, m

exp = exponential function

The above equation, not only includes the refusal from the ground up, but includes a refusal from the bottom down, any inversion layer, present above the atmosphere. The sum of four exponential terms in g3, approaching the end value very quickly. In most cases, the summation of the series $m=1, m=2, m=3$ will provide an adequate solution. σ_z and σ_y The functions of atmospheric stability class (ie, measurement of turbulence in the ambient atmosphere). The two most important variables that influence the level of emissions of pollutants are dispersed altitude point source emissions and the level of atmospheric turbulence. The greater the turbulence, the greater the degree of dispersion.

The resulting estimates of air pollution concentrations are often expressed through the concentration of air pollution contour maps, to display the spatial variation of pollution levels in a large space that is under control. In this way the contour lines (contour lines) can detect the location of sensitive receptors and demonstrate the spatial relationship of air pollution in the relevant areas.

Briggs equations raising gas

Gaussian air pollution dispersion equation (about her previously discussed), ask for the values of H , which represents the height of the axial line of ascent of a plume above the ground. H is the sum of H_s (the actual physical height of the emission source plume) plus Δh (plume rise due to its molecular weight), Figure 2.

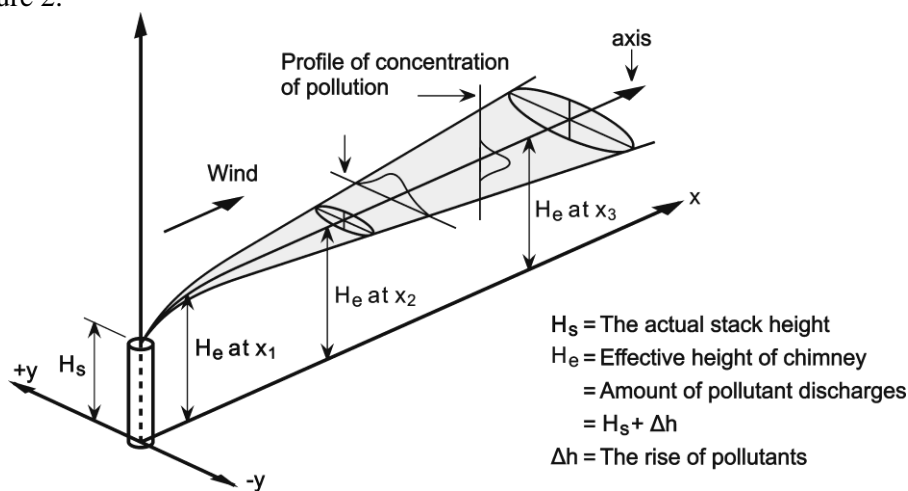


Figure 2. Showing Gaussian dispersion plume of smoke

To determine DH, almost all air dispersion models that are developed between the late 1960s and early 2000s were using Briggs's equations. Briggs is the first published observations and comparisons about raising plumes in 1965. year. 1968th at a symposium sponsored by CONCAWE (the organization from the Netherlands) and compared the rise of many flagship models that were available in the literature. That same year, Briggs wrote a section of the publication, by Slade (Slade) edited, and dealing with comparative analyzes of plume head model. 1969th years, this was followed by a critical review of the classical complete literature on the subject of raising the crest, where the proposed set of equations which later spread was known as Briggs equations. After that, 1971. and 1972. years, Briggs has improved his equation. Briggs divided air pollution plumes into these four categories:

- Cold plume, ejected under pressure from the calm conditions of ambient air,
- Cold plume, ejected under pressure from the windy ambient air conditions,
- Warm air from the plume easier in calm ambient air conditions,
- Warm air from the plume easier in windy ambient air conditions.

Briggs felt that the direction of propagation of the cold plume pressure depends on the initial rate pulse discharge, and that the direction of propagation of light from the plume of hot air depends on the time of their ascent, the pulse rate discharge is relatively unimportant. And if the Briggs equations for the proposed increase (propagation) smoke plume for each of these types of feathers, it is important to emphasize that "the Briggs equations", which began to be widely applied, one that he proposed to fold, scattered hot smoke plume.

In general, Briggs equation for folded, warm scattered smoke plumes, are based on observations and data of smoke plume from the usual sources of combustion, such as flue gases from the chimney of steam generators of large power plants, which are used to generate fossil fuels. Therefore, the output speed of the chimney were probably in the range (6 to 30) m / s, with output temperatures (120 to 260)°C.

Diagram for use Brigsovih equation, which is obtained by using the path of ascent folded smoke plume is shown in Figure 3.

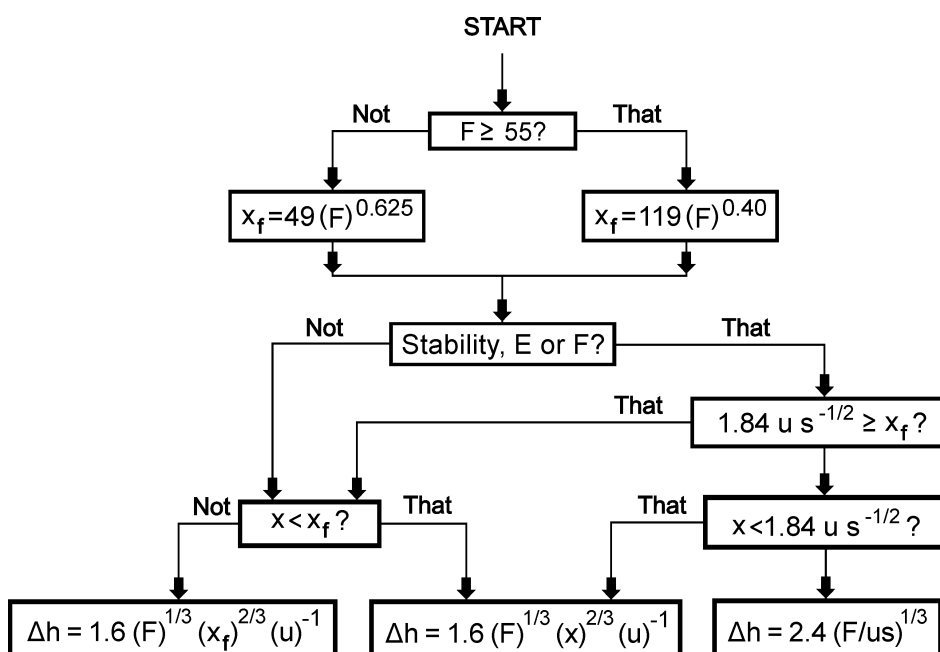


Figure 3. Diagram for the use of equations Brigsovih

Where:

- Δh = raising the smoke plume, the m
 F = factor in the rise, the m^4s^{-3}
 x = downstream distance from the source, in m
 x_f = downstream distance from the source to the point of maximum plume rise, of the m
 u = wind speed at the actual height of the chimney (emission sources), in m / s
 s = stability parameter, the s^{-2} .

CONCLUSION

Air pollution is a global problem of all mankind, and is particularly pronounced in industrialized countries and developing countries. Although the pollution and its effects are not easily distinguished spatially, but some differences appear at a certain area, depending on the concentration of industrial facilities and other sources of pollution, (Nikic et al., 2009). In addition to pollution from industrial facilities in urban areas, air quality and pollution affect the line sources, diffuse pollution, soil composition and configuration, construction: infrastructure, weather conditions and so on. (RAQM. 2008).

In this paper, given the mathematical model of dispersion of air pollution in the form of the Gauss equation and the mathematical model of gas in the form of raising Briggs equations. Dispersion models are used to estimate or predict concentrations of pollutants or toxic substances emitted from sources such as industrial plants, traffic, or accidental spills of chemicals.

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AIR POLLUTION IN ŽITOPRODUKT AD ZRENJANIN

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ABSTRACT

The most important preconditions for occurrence of industrial dust during reception and storage of cereals are the amount and composition of particles in grain mass brought from the fields and the efficiency of dust removal and air cleaning. There may be a lot of impurities in wheat mass coming to silos, although regarding the possibility of air pollution, particularly interesting are low-density particles which can pollute the air and hence the environment after sedimentation. The paper presents the results of air pollution that occurs during reception of wheat, its cleaning, drying and storage in Žitoprodukt silos.

Key words: *Air pollution, wheat, dust, Žitoprodukt.*

INTRODUCTION

Large-scale air pollution is seen as a permanent life threatening danger on Earth. The separation boundary between natural and anthropogenic air pollutant becomes indistinct (Kastori, 1997). Air is used directly, so poisonous gases, vapors or floating particles are dangerous if their concentration approaches critical level.

Air pollution can be easily transferred to long distances from its source. The space which may be polluted depends on the air pollution dispersion speed and pollutant sedimentation rate (Pavlović, 2004).

Wheat grains may become dispersers of considerable impurities due to their specific anatomic structure which enables concentration of pollutants of different origin on their surface (Žeželj, 1995). Žitoprodukt A.D.- Zrenjanin is a food processing company. Basic activities of the company are cereal storage, wheat grinding and flour storage for bakery products manufacturing. It belongs to a group of pollutants which pollute air with dust.

Every year in the harvest period during reception, cleaning, drying and grinding of the raw material, there is a big quantity of dust which spreads out.

Due to the said reasons, measuring of polluting substances has been performed in order to monitor the impact of Žitoprodukt operating on quality of ambient air.

Sources of ambient air pollution

There are two types of emission source (US EPA, Compilation of Air Pollutant Emission Factors: AP-42, Volume I, Chapter 9, Section 9.9.1.):

- Point source emission-polluting substances are released in the air through specially defined outlets. Point source emission comprises ventilation ducts of the machine house, cereal dryer

and wheat grain mill. The quantity of polluting substances emitted in the air depends on the raw material and the capacity of facilities.

- Diffusion source emission – polluting substances are emitted in the air due to raw material transportation.

MATERIAL AND METHODS

Polluting substances which are measured are total suspended particulate matter. They are found in atmosphere and have various chemical composition and size distribution so they could be transported to longer or shorter distances. Suspended particulate matter is present in the atmosphere for a specific time period which depends on their density, shape, size and current weather conditions.

Monitoring of the influence of the factory compound Žitoprodukt A.D. on ambient air quality in its influence zone was carried out on one measuring site – in Begejski red street No.23.

Sampling of total suspended particulate matter on the measuring site was carried out by means of High volume sampler-HVS. During sampling process the ambient air is separated by precisely defined speed, i.e. flow, which enables optimal filtering of suspended particles through filters of specific quality in specific time interval (24 h)(US EPA Method IO-2, IO-3.1).

Mass concentration of total suspended particulate matter is defined by gravimetric method based on the ratio of sampled mass of total suspended particles versus sampled air volume (US EPA Method IO-2, IO-3.1).

FACILITY OPERATING CONDITIONS

The emission sources of suspended particles operating during the measurement period were machine house, cereal dryer and wheat grain mill. The installed capacities of facilities is:

- machine house -100 t/h, capacity depends on raw material reception,
- cereal dryer - 40 t/h and
- wheat grain mill - 150 t/day

Table 1 shows data about capacities of specific facilities for measurement period.

Table 1: Facility operating conditions

Date	Machine house			Cereal dryer			Natural gas consumption		Wheat grain mill		
	t/h	%	h/day	t/h	%	h/day	m ³ /h	h/day	t/day	%	h/day
26.10.2011.	14.92	14.92	24	40	100	24	74	24	87.0	58.0	14.0
27.10.2011.	14.92	14.92	24	40	100	24	74	24	131.0	87.5	21.0
28.10.2011.	14.90	14.90	24	*	*	*	*	*	150.0	100.0	24.0
29.10.2011.	26.68	26.68	16	40	100	14	74	14	49.5	33.0	8.0
30.10.2011.	22.20	22.20	16	40	100	6	74	6	*	*	*
31.10.2011.	32.00	32.00	16	40	100	6	74	6	112.5	75.0	18.0
01.11.2011.	34.70	34.70	16	40	100	14	74	14	150.0	100.0	24.0
02.11.2011.	9.70	9.70	16	40	100	14	74	14	150.0	100.0	24.0

* Facility not in function

Weather conditions

Weather conditions have a great influence on degree of air pollution and its spreading during cleaning, drying and storing of wheat and other cereals in Žitoprodukt A.D. –Zrenjanin. Intensity of air currents, i.e. wind, is in direct connection with diameter of the circle in which dust and other mechanical impurities will be sedimented from the air.

Weather conditions taken from weather station Zrenjanin for the measurement period is given in Table 2.

Table 2: Average daily values of weather parameters in the measurement period

Date	Temp. °C	Air humidity %	Pressure mbar	Wind speed km/h	Prevailing wind direction	Description
26./27.10.2011.	11.3	67.6	1022.9	19.0	ESE	Mainly cloudy
27./28.10.2011.	10.0	56.3	1026.0	19.8	SE,SSE	Mainly cloudy
28./29.10.2011.	9.1	64.0	1028.9	9.0	ESE	Mainly cloudy
29./30.10.2011.	8.6	69.0	1028.1	9.0	SE,ESE	Mainly cloudy
30./31.10.2011.	9.0	65.1	1025.1	7.7	SSE,SE	Overcast and foggy
31.10./01.11.2011.	6.3	81.4	1023.8	3.6	SW	Overcast and foggy
01./02.11.2011.	6.1	82.5	1023.1	3.6	WNW	Foggy

RESULTS AND DISCUSSION

Results of analysis of total suspended particulate matter are shown in Table 3 and Figure 1. Total suspended particulate matter concentration is calculated in relation to the atmospheric conditions which comprise temperatures and atmospheric pressure on measurement day in accordance with the Decree on conditions for monitoring and air quality requirements (“Official Gazette of the RS” No. 11/2010 and 75/2010).

Table 3: Total suspended particulate matter content on the measurement site

Sampling date	Concentration $\mu\text{g}/\text{m}^3$	Measurement uncertainty $\mu\text{g}/\text{m}^3$
26./27.10.2011.	69.17	± 3.87
27./28.10.2011.	63.54	± 3.56
28./29.10.2011.	76.57	± 4.29
29./30.10.2011.	<40	-
30./31.10.2011.	80.53	± 4.51
31.10./01.11.2011.	107.49	± 6.02
01./02.11.2011.	101.06	± 5.66
Total number of samples		7
Mean value of quantified samples		$83.06 \mu\text{g}/\text{m}^3$
Allowed values		$120 \mu\text{g}/\text{m}^3$

Only one result was below the quantitation method limit (<40). Extended measurement uncertainty for total suspended particulate matter is 5.6%. Allowed value for total suspended particulate matter during daily measurement adopted according to the Decree on conditions for monitoring and air quality requirements (“Official Gazette of the RS” No. 11/2010 and 75/2010) is $120 \mu\text{g}/\text{m}^3$. According to the suspended particles concentration measurement it could be said that measured values were lower than the values prescribed in the Decree (2010).

The obtained results (fig.1) show that allowed value for total suspended particulate matter was not exceeded in any of the analyzed samples taken on the measurement site.

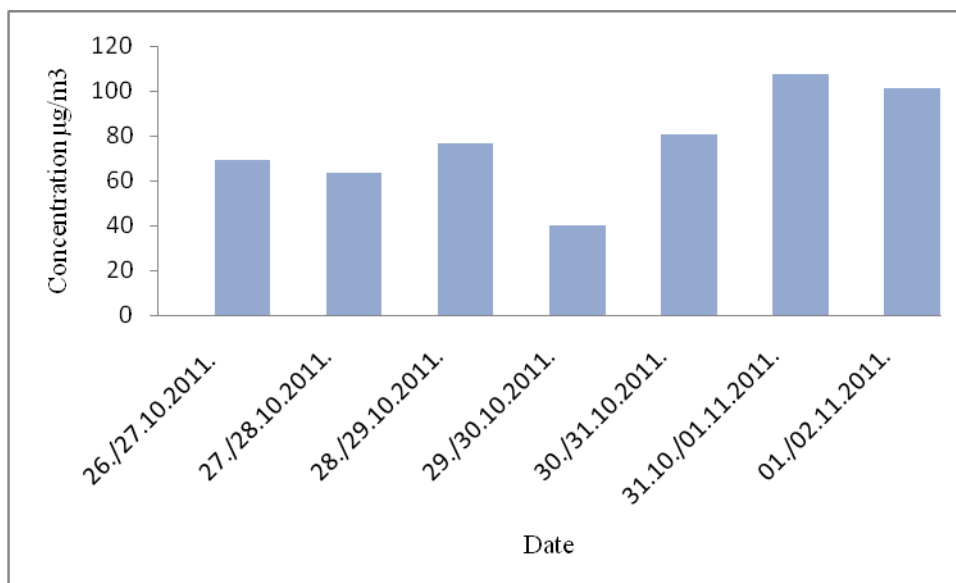


Figure 1. Total suspended particulate matter concentration in measurement period

CONCLUSION

Based on the results of performed measurement of total suspended particulate matter the following may be concluded:

- measured concentrations of total suspended particulate matter in the measurement period in all samples do not exceed the allowed value which is $120 \mu\text{g}/\text{m}^3$ and they are within limits prescribed in the Decree on conditions for monitoring and air quality requirements (“Official Gazette of the RS” No. 11/2010 and 75/2010).
- quality of air in the influence zone of Žitoprodukt A.D. Zrenjanin for the measurement period 26/10-02/11/2011 is satisfactory in relation to the level of total suspended particulate matter.
- regarding the air pollution during reception, drying and storing of wheat and other cereals, one of duties of Žitoprodukt A.D. Zrenjanin is to systematically monitor air pollution for the purpose of environmental protection.
- in order to protect the air from pollutants, it is necessary to use various solutions depending on the place of occurrence, type and nature of polluting substance, technical and financial conditions, legal regulations, etc.

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LINEAR EXPANSION OF AIR POLLUTION

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ABSTRACT

With the technological development the problem of air pollution emerged, especially in large cities. In this paper we analyze the case of air pollution originating from point source. Air pollution is considered in one dimension for the case when the diffusion processes, absorption and air flow occur. For adopted realistic parameters that characterize mentioned processes, partial differential equation that describe given processes is numerically solved.

Key words: air pollution, point source, Gauss model, Oylar model.

INTRODUCTION

Air pollution is the presence of compounds which are not commonly found in air or not in such concentrations typical for normal composition of air. Also, air pollution is defined as a state of atmosphere in which substances that harm environment are present in concentrations above normal values. Air pollution is a consequence of natural occurrences and human activity and therefore can be classified into [1] :

- Natural sources of pollution
- Anthropogenic sources of pollution

Natural sources of air pollution have always been present in biosphere and those are:

- Deflation – transfer of earth and sand (especially common in deserts and forest-steppe zones)
- Smoke of forest and steppe fires (contains CO, soot, pitch, tar, etc.)
- Volcanoes – during strong eruptions they emit huge amounts of dust, gasses, SO₂, CO₂, etc.
- Mineral and thermal springs – can emit CO₂, H₂S, methane, etc.
- Cosmic dust, for which is thought to be radioactive
- Ocean surfaces can be sources of CO₂, CO, H₂S, chlorides, etc.
- Elementary disasters can be followed by significant emission of pollutant substances in air
- Storms
- Earthquakes

Anthropogenic sources of pollution can be classified onto:

- Stationary or point sources
- Mobile sources

Mobile sources encompass motor vehicles with internal combustion engines (ICE). Sources of pollution from closed space encompass emissions from burning and heating, emissions from different materials or substances (vaporizing organic compounds, different synthetic chemicals, tobacco smoke, etc.)

Based on the quantity of sources and spatial distribution sources of pollution can be:

- Single
- Point (static or mobile)
- Group of sources (static or mobile)
- Line sources.

Based on the type of emission, pollution sources are classified on:

- Emitters of particles and
- Emitters of gasses.

Table 1: Pollution compounds and sources of pollution

Pollution compound	Main source of pollution
Sulfur dioxide SO₂	Combustion of coal, oil, massive and collared metallurgy
Hydrogen sulfide H₂S	Chemical processes, refineries
Carbon monoxide CO	Combustion, ICE
Nitrogen oxides NO_x	Combustion, ICE
C_n H_{n+2}	Vaporizing of liquid fuels, exhaust gasses
Soot	Combustion
Suspended particles	Technological processes, quarries, cement production
Vaporizing organic compounds	Chemical processes, Oil derivation, distribution of gasoline

By now several hundreds of different pollution compounds have been identified and possible creation of new, under the influence of sunlight and electric discharge should be noticed. Air quality is determined by concentration of polluting compound (pollutant) in air or their deposit on the surface during the certain amount of time. Concentration of pollutant is mass, volume or amount of substance located in certain volume or mass of air. Beside the concentration of polluting compounds from the polluting source, the quality of air in one area is also determined by meteorological element: the state of air pressure, direction and speed of wind, eddy currents, air humidity, the presence of fog, amount of rain, air temperature and temperature inversion. The highest concentration of polluting compounds is spread horizontally in the direction of wind. In periods of “silence” – the absence of air movement all polluting compounds remain in settled area. In lower levels of atmosphere air is warmer and is moved towards upper, cooler, layers allowing normal dispersion. However, under conditions of rapid cooling of earth temperature inversion occurs. Ground-level air is cooler than air in higher layers so the dispersion is not possible. Low air pressure, the absence of wind, high air humidity, fog and temperature inversion decrease the distribution of polluting compounds in height and distance, keep them in the ground level and concentrate near the pollution source. It is possible for smog to be formed along with compounds which are extremely toxic and dangerous for the human health. The level of polluting compounds is determined by measuring [1].

Air pollution can be transferred on great distances comparing with the place of source. Distance depends on the speed of distribution (diffusion) of polluted air masses and the speed of sedimentation (deposit) of polluting compounds. For the evaluation of air pollution it is necessary to know:

- The quality (physical and physic-chemical properties) of polluting compounds
- The quantity (amount), on which depends the action of each polluting compound individually

MATHEMATICAL MODELS FOR THE ANALYSIS OF AIR POLLUTION

The processes of spreading particles in the atmosphere are of great interest for many areas of human activity. Maturing awareness of the importance of these processes has made monitoring measurements and means of monitoring the same. Based on the measuring results empirical models of air pollution emerged. Latter, significant effort was made for the development of methods for the analysis of particle diffusion in the atmosphere. As a result of these efforts today, results of these researches are applied for the consequence forecast when emergency situation occurs due to the different accidents and similar spreading of dangerous compounds. Despite the great efforts made for these researches there exist no generally accepted models for the analysis of air pollution distribution. That is

objectively conditioned by the diversity and complexity of processes. Therefore, there exists great number of different type models. The main property by which models are classified is their empirical or theoretical character [2].

Classical empirical model is model of Pasquill-Gifford [3], while Berlands model can be given as an example of theoretical model of turbulent diffusion [2]. Today, there is the greatest interest for, conditionally stated, semi empirical models. According to these semi empirical models, empiric is supplemented by well-developed mathematical apparatus which allow analysis of very complicated situations and also allow synthesis of results of different experiments, for example meteorological and diffusional. Within these methods, timetable of winds and coefficient of diffusion according to heights is explicitly taken into account. Within empirical models, the physics of the process in atmosphere is almost completely not taken into account or is very roughly included.

Models also diverse according to applied mathematical apparatus. Empirical models use explicit forms, obtained after numerous measurements, which can be simply edited on microcomputers. Semi empirical methods are using procedures of numerical solving of partial differential equations. Theoretical models are using the most different procedures such as dimensional analysis, analytical solutions of partial differential equations, methods of simulations such as Monte Carlo method, etc. It should be appointed that when speaking of finding the analytical solutions, stationary processes are mainly analyzed, while for numerical analysis non stationary processes are analyzed too.

Current models can be classified according to spatial and time dimensions of their application to: local, regional and global. Local methods analyze air pollution in area up to ten kilometers for the time period from several minutes to several hours. Regional models analyze air pollution from several tenths to several hundreds of kilometers, while the time distance is taking from several hours to several days. Global models encompass the problem of air pollution in the area from several hundred to several thousands of kilometers while the time dimension takes several weeks [4].

In the sense of mathematical treatment of processes, models can be classified to: Gauss's, Oyler's and Lagrange's. Equations in these models are obtained by different solving of equations of turbulent diffusion. The simplest model for calculation of ground level concentration of particles/impurities is statistical Gauss model. In the basis of this model lies the assumption that particles expelled by continual point source create the cloud of smoke in which the distribution of particles is governed by normal Gauss distribution.

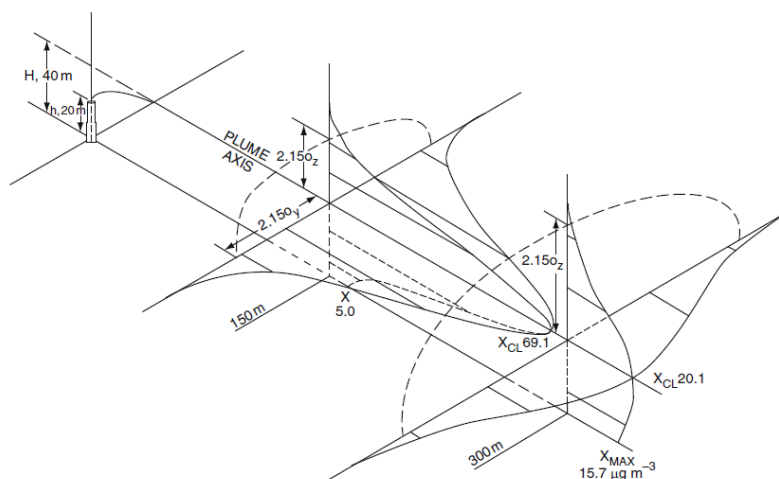


Figure 1. Gauss model of particle emission from point source [5]

In this model information concerning the wind speed is taken as a parameter from the closest meteorological station and is assumed that speed is maintained during the time needed for transfer of impurity particle to the distance of 20–30 km. Drawbacks of this model are:

1. In model is assumed that vertical and horizontal scattering of particles is mutually independent.

2. Components of wind speed are not taken into account therefore linear trajectory of particle is assumed
3. In model figures dispersion which describe scattering of particle cloud based on its distance from the source.
4. In the initial moment it is assumed that the concentration of particles in the source is infinitely high.
5. Using this model it is not possible to calculate particle concentrations for the low wind speed (less than 1 m/s).

Oyler model is based on the solving of semi empiric equation of turbulent diffusion [4]

$$\frac{\partial q}{\partial t} = -\vec{V} \cdot \nabla q + \frac{\partial}{\partial x} \left(k_x \frac{\partial q}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial q}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial q}{\partial z} \right) \quad (1)$$

Where $\vec{V} \cdot \nabla q$ - is adequate component of equation, k_x , k_y , k_z - are coefficients of turbulence of diffusion and q - is mean concentration of impurities.

Oyler model of impurity spreading takes into account fundamental characteristics of process of particle spreading: transfer of particles along the direction of convection/flow., turbulent diffusion, convection, spatial-time inhomogeneity of scattering parameters, interactions of particles with surface of earth, etc. This model allows calculation of particle concentration in the area of 50 km distant from point and other sources which continually radiate, under arbitrarily meteorological conditions, above surface of the arbitrarily relief. Also, it gives data concerning concentration of impurity particles in case of low speed winds, even in the case of steady weather. The model has to give results, for the concentration of impurity particles, consistent with the empiric models. Coefficients of turbulence depend on the speed of wind, state of the atmosphere, surface relief and distance cross by impurity particles from the observed point:

$$k_z = U_z \frac{\kappa^2 h_{SBL}}{\ln(z_r / z_0)} \left(\frac{x}{x_1} \right)^b; k_y = k_z P^{-1}; P = (k_z / k_y) \quad (2)$$

where U_z is wind speed measured on the altitude z_r within borders of ground level layer, z_0 is surface relief, κ is Karman's constant, h_{SBL} is altitude of near ground level layer of atmosphere, x is distance crossed by impurity particle from the source to the observed point, x_1 is standard distance equal to 1000 m, b - is exponent of power function while P -is coefficient of turbulence anisotropy.

In its general form, the task of mathematical forecast of air pollution can be defined as solving the appropriate equation of turbulent diffusion for adequate initial and border conditions.

Eq. (2) describes spatial distribution of middle concentrations as well as their change with time. In that sense it can be treated as forecast equation. Analytical approach for solving equations of atmospheric diffusion is very complex problem, possible if series of approximation is used. Difficulties during solving analytically mentioned equations occur even for simple cases, when the wind speed changes logarithmically with the altitude eliminating linear or power dependence of coefficients and thus making the job of finding analytical solution much easier. Research of atmospheric diffusion above the surface with complex relief assumes the change of many meteorological elements, which, each individually, complex the finding of analytical solution. Therefore, numerical approaches impose as a possible solution for integration of equations of turbulent diffusion. Regardless of possibilities of computer resources, for successful finding of air pollution distribution it is necessary to choose parameters of equation reasonably [6].

THE ONE DIMENSIONAL PROBLEM OF AIR POLLUTION DISTRIBUTION

This part is dedicated to the analysis of air pollution in the vicinity of point source. Case of distribution of point source of air pollution, when processes of diffusion, absorption and air flow occur, will be analyzed. We will limit ourselves on one-dimensional problem, since our goal is to evaluate spatial and time distribution of concentration of air pollution source according to given

dynamics of source. If it is certain idealization, by choosing one-dimensional problem, done then it is compensated by consideration of practically all possible physical mechanisms which act during the transfer of polluting compounds [7]. Also, we tried to model the function of source in analytical form which really emerges during the work of industrial facility. Equation of turbulent diffusion for this one-dimensional case is of following form [8]:

$$\frac{\partial q}{\partial t} + u \frac{\partial q}{\partial x} - b^2 \frac{\partial^2 q}{\partial x^2} + cq = A\phi(t)\delta(x) \quad (3)$$

where u is wind speed in the direction of x -axis; b^2 -is diffusion coefficient of impurity; $A\phi(t)$ -is amount of emitted impurity particles in unit of time; c -is coefficient which characterizes absorption of impurity particles (it can be obtained after chemical analysis of atmospheric processes leading to transformation of impurity particles and their absorption).

In order to make process, described by equation (3), more realistic, we will assume that $\phi(t)$ is periodic function given by following form [7]:

$$\phi(t) = \begin{cases} 0; & t \in (0, t_1) \\ 1; & t \in (t_1, t_2) \\ 0; & t \in (t_2, 2T) \end{cases} \quad (4)$$

where $0 < t_1, t_2 < 2T$, $t_2 > t_1$. Therefore, point source emits toxic compounds in the period of $t_2 - t_1$. Border and initial conditions for this case are: $q(\pm\infty, t) = 0$ and $q(x, \infty) = 0$.

It should be noted that equations describe mean values of concentrations. In equation (3) next values of parameters are taken:

$$u = 1 \text{ m}; u = 4 \text{ m}; 4b^2 = 1,39 \cdot 10^{-2} \text{ m}^2/\text{s}; c = 2 \cdot 10^{-3}; A = 10^{12}.$$

Adopted value for the diffusion coefficient is regarding to CO_2 . By numerical approach using *Mathematica* a solution is found and is shown on figure 2.

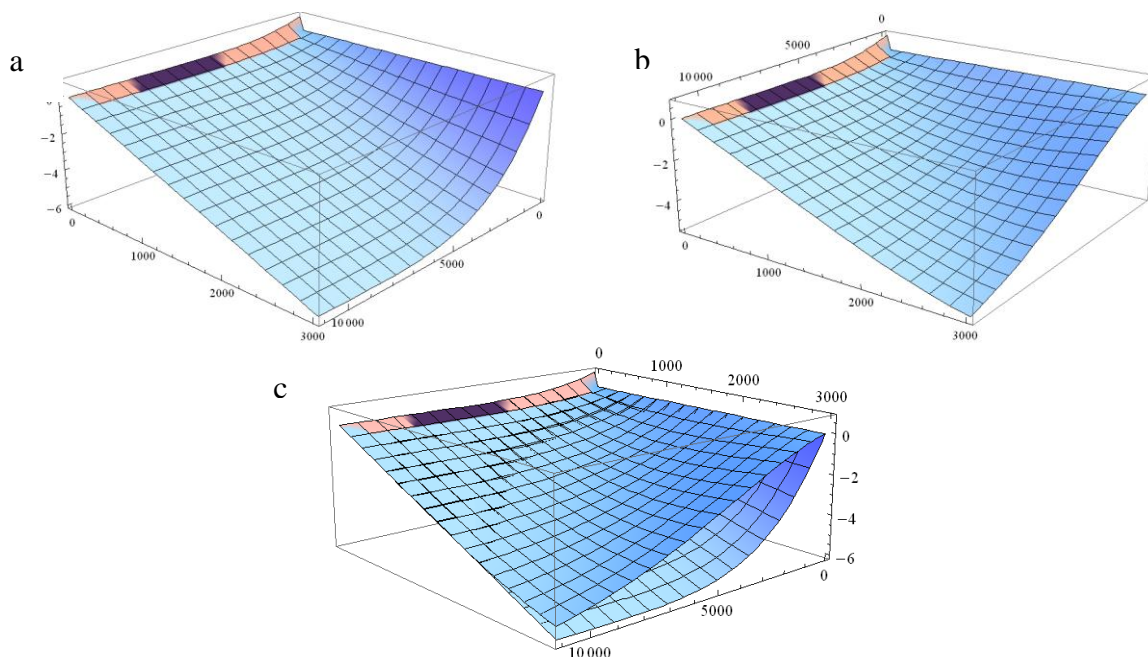


Figure 2. Spatial and time distribution of concentrations

On figure 2a, a spatial time distribution for the case when wind speed is 1 m/s is given, while on the figure 2b same distribution is given for the case when the wind speed is 4 m/s. On the figure 2c previous two cases are given together for easier comparison. It can be seen that concentration decreases with time, slower with higher values of wind speed. Also, concentration decreases with the distance from the source (in our example 5 mg/m^3 for the distance of 3 km). It should be noted that in work [7] analytical particular solution of equation (3) was found.

CONCLUSION

The problem of air pollution is closely related with the development of industry and transport. In all countries control of environmental state, mainly of atmosphere, is being introduced. Efficiency of control of environmental state is determined by two components: direct measurement of air quality using special instruments, which is consolidated in unique system of atmosphere monitoring, and indirectly by mathematical modeling of air pollution which allows determination of toxic compounds concentration in areas not covered by direct measurements. In such way mathematical modeling is being introduced as a part of monitoring of atmosphere pollution. Mathematical modeling is becoming more and more efficient instrument for research of atmosphere state influenced by improvement of mathematical methods for analysis of transfer processes and scattering of gaseous, liquid and solid components of air pollution. Determination of level of air pollution by application of mathematical model of distribution of air pollution allows simulation of spreading of toxic compounds for different assumed intensities of emission in known topological, urban and meteorological situation.

Connection between health state of population and state of environment is not direct, since there exist variety of other factors influencing health of population. However, environmental factor is important, beside heritage and individual characteristics, lifestyle and availability and efficiency of health service. It is considered that air quality in urban areas has greater influence on the health of population than other environmental factors, and that pollutants of ambient air represent one of the most significant causes of health problems generally. Numerous epidemiological studies unequivocally proved that air pollution in the form of respirable particles is related with the increase of morbidity and mortality from respiratory and cardiovascular diseases. Increase of some disease (cardiovascular diseases and hypertension, diseases of respiratory organs, malignant diseases, infective and parasitic diseases) might be result of modern lifestyle, but a consequence of air pollution as well. APHEA project “Air pollution and Health: a European Approach” is one of epidemiological studies in which short termed effects of air pollution towards some health parameters are tracked. Special attention was paid to the daily variability of lung function, frequency of hospital care and mortality. In Paris, risk of mortality due to the respiratory diseases increased to 17%, with 100 $\mu\text{g}/\text{m}^3$ of increment of hovering particles. Hovering particles, black smoke and sulfur dioxide (SO_2) are related with emergency hospitalization of respiratory patients. A study in Spain determined that oxides, especially nitrogen dioxide (NO_2) and ozone, are related with mortality from cardiovascular diseases, especially during summer. Carcinogenic influence of many toxic compounds is determined as well.

Using mathematical approach one can obtain realistic picture related with the dispersion of pollutants, which can serve as a basis for the evaluation of potential danger.

ACKNOWLEDGMENT

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THE INFLUENCE OF AIR POLLUTANTS ON HUMAN HEALTH

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ABSTRACT

Air quality is one of the biggest problems today in the whole World. Every day, an increasing number of patients suffering from respiratory diseases that are caused by pollution in the air. The paper will be presented impacts of air pollution on human health. Polluting components that will be analyzed are: Particulate matter (PM10 and PM2.5), ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide and VOCs. In addition to their direct impact on human health in the work will be analyzed and the polluting components, their formation and concentrations that adversely affect human health. Research and monitoring of air quality in urban and industrial areas is a first step toward the solution of the present problem of air pollution in order to protect human health and the environment.

Key words: *air quality, air pollutants, Particulate matter (PM2.5 and PM10), Ozone, Nitrogen Dioxid, Sulfur dioxide, volatile organic compounds.*

INTRODUCTION

There is an increasing understanding of how poor air quality poses a threat to human health. The troposphere across the whole of the populated world has some degree of pollution. Much of the research into pollution causation and effects has taken place in Europe or the northern America, but the conclusions are valid for every one of the planet's seven billion inhabitants. Air pollution affects all living things. It causes health problems in humans and animals, damages plants, kills fish, pollutes water, eats away at infrastructure and reduces visibility. It can also lead to acid rain, global warming and smog. The air quality in urban areas have an increasing impact on the health of the population than other environmental factors, and ambient air pollutants that are one of the most important causes of health problems in general. According to the World Health Organization, the world each year due to air pollution occurs over 2.7 million deaths.

Of the six pollutants identified by the EPA as being important in controlling emissions levels, four can be considered related to mobile emissions control, and two are not. Mobile emissions related pollutants is Ozone (O₃), Particulate matter, or PM, Carbon monoxide, or CO, Nitrogen dioxides (NO₂ and NO_x). Non-mobile (primarily stationary industrial) emissions related pollutants: Sulfur dioxide, or SO₂. In this paper will be handled another polluting element volatile organic compounds and the impact of these pollutants on human health

PARTICULATE MATTER (PM2.5 AND PM10)

Airborne particulate matter represents a complex mixture of organic and inorganic substances. Mass and composition in urban environments tend to be divided into two principal groups: coarse particles and fine particles. The barrier between these two fractions of particles usually lies between 1 µm and 2.5 µm. However, the limit between coarse and fine particles is sometimes fixed by convention at 2.5 µm in aerodynamic diameter (PM2.5) for measurement purposes. The smaller particles contain the

secondarily formed aerosols (gas-to-particle conversion), combustion particles and recompensed organic and metal vapors.

The larger particles usually contain earth crust materials and fugitive dust from roads and industries. The fine fraction contains most of the acidity (hydrogen ion) and mutagenic activity of particulate matter, although in fog some coarse acid droplets are also present. Whereas most of the mass is usually in the fine mode (particles between 100 nm and 2.5 μm), the largest number of particles is found in the very small sizes, less than 100 nm.

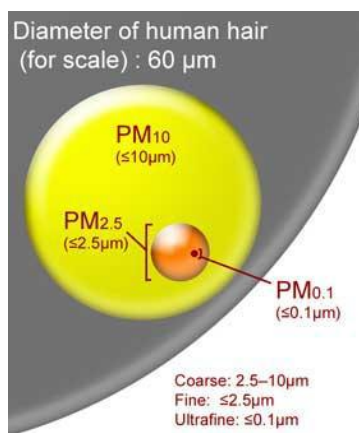


Figure 1. View the size of suspended particles

The size of suspended particles in the atmosphere varies over four orders of magnitude, from a few nanometers to tens of micrometers. The largest particles, called the coarse fraction (or mode), are mechanically produced by the break-up of larger solid particles. These particles can include wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations. Traffic produces road dust and air turbulence that can stir up road dust. Near coasts, evaporation of sea spray can produce large particles. Pollen grains, mould spores, and plant and insect parts are all in this larger size range. The amount of energy required to break these particles into smaller sizes increases as the size decreases, which effectively establishes a lower limit for the production of these coarse particles of approximately 1 μm . Smaller particles, called the fine fraction or mode, are largely formed from gases. (Figure 2.) The smallest particles, less than 0.1 μm , are formed by nucleation, that is, condensation of low vapor-pressure substances formed by high-temperature vaporization or by chemical reactions in the atmosphere to form new particles (nuclei).

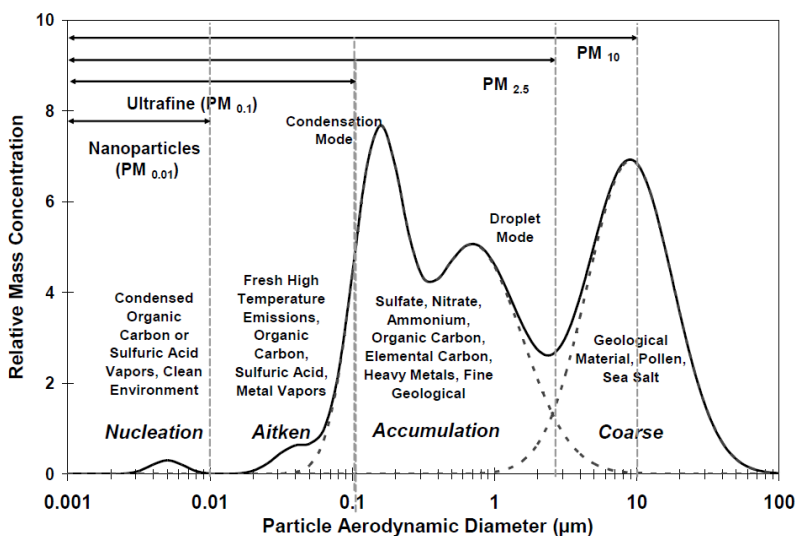


Figure 2. The relative ratio of the mass of particles in the air and the specific composition of individual bands

Respirable particles can be natural and anthropogenic origin, their size range is Relatively broad and very complex composition. Under natural sources include particles made of earth, dust, volcanic reactions, destruction of vegetation and rocks in the coastal area of salt particles, and the particles are formed by chemical reactions of various gas emissions (H_2S , NH_3 , NO_x and HC) to form sturdy product or chemically change the existing particles in the air. Combustion of fossil fuels such as coal, oil and petrol can produce coarse particles from the release of non-combustible materials, i.e. fly ash, fine particles from the condensation of materials vaporized during combustion, and secondary particles through the atmospheric reactions of sulfur oxides and nitrogen oxides initially released as gases (Report on a WHO 2003).

Sulfate and organic matter are the two main contributors to the annual average PM_{10} and $PM_{2.5}$ mass concentrations. On days when $PM_{10} > 50 \mu g/m^3$, nitrate becomes also a main contributors to PM_{10} and $PM_{2.5}$. Black carbon contributes 5–10% to $PM_{2.5}$ and somewhat less to PM_{10} at all sites, including the natural background sites. Its contribution increases to 15–20% at some of the kerbside sites (PUTAUD, J.P. ET AL. 2002).

99% of suspended particles in the air that is inhaled is immediately eliminated from the body during exhalation, which tend to remain in the upper parts of the respiratory tract. The remaining 1% of the particles are retained in the organisms, they come to the trachea and through to the lungs. Particles that are hazardous to human respiratory system are considered to be those that are less than 10 μm . Such small particles and tend to be deposited in the alveoli. What part of the inhaled particles will remain in the respiratory tract and depth that will arrive before the deposit depends on their size as the most important factor that determines the risk of inhalation of particles, as shown in Figure 3. If the particles reach the lungs slow exchange of oxygen and carbon dioxide, reducing breath. This leads to higher stress rate, which in terms of efforts to povedanog kompezovao reduced oxygen intake. Usually, people who are sensitive to these harsh conditions to suffer from respiratory diseases such as enfizem, bronchitis, asthma and heart problems. Particles and matter in the form of liquids and gases, which are brought together with the particles which are adsorbed, if inhaled, and are toxic, and can contribute to damage to internal organs, such as kidney and liver (ICRP, 1994)

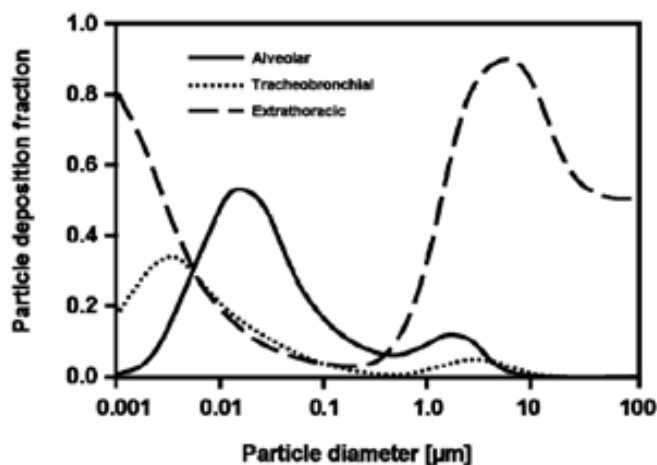


Figure 3. Probabilistic Model of particles depositing in certain parts of the total in the respiratory tract

Clear biological effects of PM exposure have been observed, and various path-physiological or mechanistic pathways have been explored. None of these pathways are definitively demonstrated to be the pathway that clearly and directly links exposure of ambient PM pollution to cardiopulmonary morbidity and mortality. In fact, it is unlikely that any single pathway is responsible. There are almost certainly multiple mechanistic pathways with complex interactions and interdependencies. Figure 4 provides a schema of some of the hypothetical mechanistic pathways linking PM with cardiopulmonary disease. Similar stylized attempts to illustrate these mechanistic pathways and their interactions have been presented elsewhere.

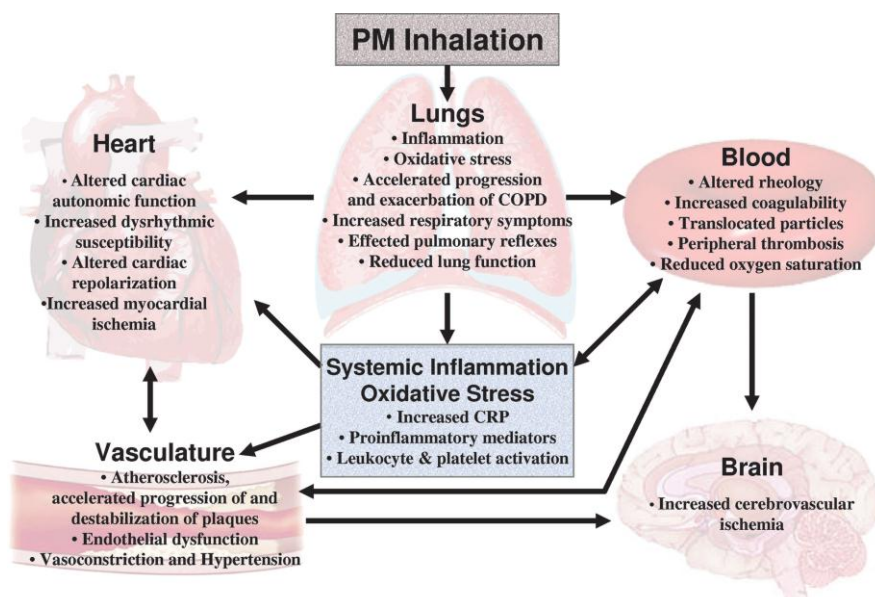


Figure 4. Potential general path physiological pathways linking PM exposure with cardiopulmonary morbidity and mortality (Pope C.A, Dockery D.W., 2006)

Ozone (O₃)

Ozone is the most important photochemical oxidant in the troposphere. It is formed by photochemical reactions in the presence of precursor pollutants such as NO_x and volatile organic compounds. In the vicinity of strong NO_x emission sources, where there is an abundance of NO, O₃ is “scavenged” and as a result its concentrations are often low in busy urban centers and higher in suburban and rural areas. On the other hand, O₃ is also subject to long-range atmospheric transport and is therefore considered as a trans-boundary problem. As a result of its photochemical origin, O₃ displays strong seasonal and diurnal patterns, with higher concentrations in summer and in the afternoon. The correlation of O₃ with other pollutants varies by season and location.

Ozone can make it more difficult to breathe deeply and vigorously, cause shortness of breath and pain when taking a deep breath, cause coughing and sore or scratchy throat, inflame and damage the airways, aggravate lung diseases such as asthma, emphysema, and chronic bronchitis, increase the frequency of asthma attacks, make the lungs more susceptible to infection, Continue to damage the lungs even when the symptoms have disappeared. Exposure to extremely low concentrations of ozone initially increases the reactivity of the airways to other inhaled substances (bronchial hyper responsiveness) and causes an inflammatory response in the respiratory tissue.

More severe symptoms have been seen following exposure to higher concentrations (greater than 1 ppm) and have included reduced lung function, extreme fatigue, dizziness, inability to sleep and to concentrate and a bluish discoloration of the skin (cyanosis). Intermittent exposure to 9 ppm for 3-14 days has produced inflammation of the bronchi and lungs. An acute occupational exposure to approximately 11 ppm for 15 minutes caused severe respiratory irritation and almost caused unconsciousness. A 30-minute exposure to 50 ppm is considered potentially lethal. Animal studies indicate that ozone can also cause a potentially fatal accumulation of fluid in the lungs (pulmonary edema). Symptoms of pulmonary edema, such as shortness of breath, may not appear for 24 hours after exposure and are aggravated by physical exertion (www.ccohs.ca/oshanswers/chemicals/chem_profiles/ozone/hazard_ozo.html)

Table 1: EPA Air Quality Index (<http://airnow.gov/index.cfm?action=pubs.aqiguideozone>)

8-hour average ozone Concentration(ppm)	Air Quality Index Values	Air Quality Descriptor	Health Effects
0.0 to 0.064	0 to 50	Good	No health effects are expected.
0.065 to 0.084	51 to 100	Moderate	Respiratory effects from prolonged outdoor exertion if you are unusually sensitive to ozone.
0.085 to 0.104	101 to 150	Unhealthy for Sensitive Groups	Respiratory symptoms (coughing, pains when taking a deep breath).
0.105 to 0.124	151 to 200	Unhealthy	Respiratory symptoms (aggravated cough or pain), and reduces lung function.
0.125 (8-hr) to 0.404 (1-hr)	201 to 300	Very Unhealthy	Severe respiratory symptoms and impaired breathing.

The effect of O₃ on daily mortality has been higher in persons older than 65 years (GOLDBERG, M. S. ET AL 2001)(GOUVEIA, N. ET AL 2000). There are very few time-series studies on mortality that have addressed effects in persons younger than 65 to allow confirmation of this finding. In the meta-analysis of time series studies on emergency admissions for respiratory causes, there was a pooled positive association with all respiratory admissions at all ages (mainly including old people) while there was no association for studies with asthma in children probably reflecting that the risk of O₃ effect increased with age (ANDERSON, H.R. ET AL.2002). By contrast, lung function decrements attributable to O₃ have been much greater in children and young adults than in older adults (Katsouyanni K, Touloumi G, Spix C, Schwartz J, Balducci F, Medina S, et al 1997)

NITROGEN OXIDES (NO_x)

The pollutant nitrogen oxides of concern are nitric oxide (NO) and nitrogen dioxide (NO₂). By far the major proportion of emitted NO_x (as the sum of the two compounds is known) is in the form of NO, although most of the atmospheric burden is usually in the form of NO₂. The major conversion mechanism is the very rapid reaction of NO with ambient ozone. An alternative third order reaction with molecular oxygen is relatively slow at ambient air concentrations.

As for PM and O₃, the evidence on NO₂ and health comes from different sources of information, including observational epidemiology, controlled human exposures to pollutants and animal toxicology. The observational data are derived from studies outdoors where NO₂ is one component of the complex mixture of different pollutants found in ambient air and from studies of NO₂ exposure indoors where its sources include unvented combustion appliances. Interpretation of evidence on NO₂ exposures outdoors is complicated by the fact that in most urban locations, the nitrogen oxides that yield NO₂ are emitted primarily by motor vehicles, making it a strong indicator of vehicle emissions (including other unmeasured pollutants emitted by these sources). NO₂ (and other nitrogen oxides) is also a precursor for a number of harmful secondary air pollutants, including nitric acid, the nitrate part of secondary inorganic aerosols and photo oxidants (including ozone). The situation is also complicated by the fact that photochemical reactions take some time (depending on the composition of the atmosphere and meteorological parameters) and air can travel some distance before secondary pollutants are generated.

These relationships are shown schematically in Figure 5.

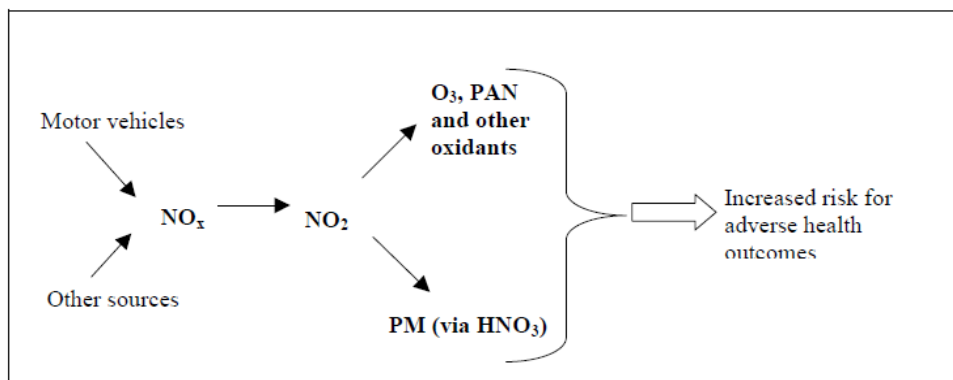


Figure 5. Simplified relationship of nitrogen oxides emissions with formation of NO_2 and other harmful reaction products including O_3 and PM

EPA first set standards for NO_2 in 1971, setting both a primary standard (to protect health) and a secondary standard (to protect the public welfare) at 0.053 parts per million (53 ppb), averaged annually. The Agency has reviewed the standards twice since that time, but chose not to revise the annual standards at the conclusion of each review. In January 2010, EPA established an additional primary standard at 100 ppb, averaged over one hour. Together the primary standards protect public health, including the health of sensitive populations - people with asthma, children, and the elderly. No area of the country has been found to be out of compliance with the current NO_2 standards.

Nitrogen dioxide among those gases which are very reactive and mainly responsible for the respiratory infection. One of the survey tell us the people working or living in the environment having higher concentration of nitrogen dioxide are at the greater risk of having the respiratory infection in lungs. Through some of the experiments have done of nasals reading the continuous exposure to the low concentration of nitrogen dioxide is leading one of the major diseases commonly known as emphysema and bronchitis in the lungs. Nitrogen dioxide gas mainly cause irritation in the mucus of the eyes, throat and nose. If someone experience extreme concentration of nitrogen dioxide for instance if there is a fire in the building it may result in pulmonary edema and causing diffuse lung injury. Low and continuous exposure of nitrogen dioxide may lead to problems like increasing in the bronchitis activities especially people suffering from respiratory problems like asthma, it may decrease the lung function for the people suffering from chronic pulmonary disease and the worst part of its exposure could be seen in children as they increase the chances of respiratory infection in them.

In healthy adults changes in lung function only at concentrations in excess of those normally encountered in ambient air. However, asthmatic people are characterized by having airways that are hyper-responsive to a wide variety of inhalation stimuli and, as a consequence, might be expected to exhibit a greater airways response to NO_2 than in normal subjects. Small scale human exposure studies in adult asthmatics with mild to moderate disease have failed to demonstrate consistent effects of NO_2 on either baseline airway caliber or on direct (e.g., methacholine) or indirect (e.g., SO_2 , cold air) airway hyper-reactivity even at concentrations higher than those typically achieved in outside air (JORRES. R, & MAGNUSSEN H.1991).

SULFUR DIOXIDE SO_2

Sulfur dioxide is a primary combustion product of fossil fuels that can be grouped together with acid aerosols and particles to form a complex group of distinct air pollutants associated with a wide array of adverse health effects, including short-term respiratory morbidity and mortality^[8] Chamber studies have determined that kerosene heaters are the major source of sulfate aerosols and indoor SO_2 . Some early controlled chamber studies have demonstrated that SO_2 can cause bronchi constriction in healthy adults and adults with asthma, but a more recent study found that SO_2 (200 ppb) and its reaction products (sulfuric acid 200 mg/m³ and ammonium bisulfate 2000 mg/m³) caused no significant

change in spirometry or symptoms in healthy subjects and subjects with asthma. However, a recently published report examining the effect of indoor heating sources on respiratory symptoms in nonsmoking women reported that a 10-ppb increase in SO₂ was associated with increased wheezing and chest tightness (ICRP, 1994). The gas will react with moisture on the skin and cause irritation. Liquid SO₂ may cause burns due to freezing. Symptoms of mild frostbite include numbness, prickling and itching in the affected area. The skin may become white or yellow. Blistering, necrosis (dead skin) and gangrene may develop in severe cases. Sulfur dioxide hurt and eyes, At 8-12 ppm, smarting of the eyes and lachrymator (tears) began. There is strong irritation at 50 ppm. In severe cases, (very high concentrations in confined spaces), SO₂ has caused temporary corneal burns. Liquid SO₂ can burn the eye and permanently affect vision. Injury from contact with liquid SO₂ may not be immediately noticed by the victim because SO₂ damages the nerves of the eye. Any eye contact should be treated as very serious.

Several epidemiological studies have examined the possibility that sulfur dioxide may cause cancers such as lung cancer, stomach cancer or brain tumors. In all of the studies, there were uncontrolled confounding factors, such as concurrent exposure to other chemicals. The International Agency for Cancer (IARC) has reviewed these studies and concluded there is inadequate evidence for carcinogenicity in humans. SO₂ may enter the body by the respiratory tract or following dilution in saliva. Most studies in both man and animals have indicated that 40-90% or more of inhaled SO₂ is absorbed in the moist upper respiratory tract. SO₂ is quickly converted to sulfurous acid upon contact with moist mucous membranes. Inhaled SO₂ is only slowly removed from the respiratory tract. After absorption in the blood stream, the sulfurous acid is widely distributed throughout the body, quickly converted to sulfite and bisulphate, which in turn is oxidized to sulfate and excreted in the urine.

CARBON MONOXIDE (CO)

Carbon monoxide is a tasteless, odorless, colorless, and nonirritating gas produced by incomplete combustion of organic material and is the leading cause of poisoning . The main sources of indoor CO are gas appliances, unvented kerosene heaters, and environmental tobacco smoke (ETS). The main health effect of CO is a result of its ability to impair the oxygen binding capacity of hemoglobin, which can cause headaches, nausea, dizziness, breathlessness, and fatigue, and with high exposures can lead to coma and death.

Table 2: Toxic symptoms for different concentrations and time of a pollution
(http://www.engineeringtoolbox.com/carbon-monoxide-d_893.html)

Concentration of CO in the air (ppm)	Inhalation Time	Toxic Symptoms
9	Short term exposure	ASHRAE recommended maximum allowable concentration in living area.
35	8 hours	The maximum exposure allowed by OSHA in the workplace over an eight hour period.
200	2-3 hours	Slight headache, tiredness, fatigue, nausea and dizziness
400	1-2 hours	Serious headache-other symptoms intensify. Life threatening after 3 hours.
800	45 minutes	Dizziness, nausea and convulsions. Unconscious within 2 hours. Death after 2-3 hours.
1600	20 minutes	Headache, dizziness and nausea. Death within 1 hour.
3200	5-10 minutes	Headache, dizziness, nausea. Death within 1 hour
6400	1-2 minutes	Headache, dizziness, nausea. Death within 25-30 minutes.
12800	1-3 minutes	Death within 1-3 minutes

The severity of CO poisoning is dependent on concentration, length of exposure, and the general underlying health status of the exposed individual. Because carboxyl-hemoglobin concentrations in blood are cumulative over time, prolonged exposure to low concentrations can result in considerable health effects. Carbon monoxide compared with the other major indoor gaseous pollutants, NO₂, SO₂, and O₃, was the strongest predictor of elderly patients being hospitalized for congestive heart failure.

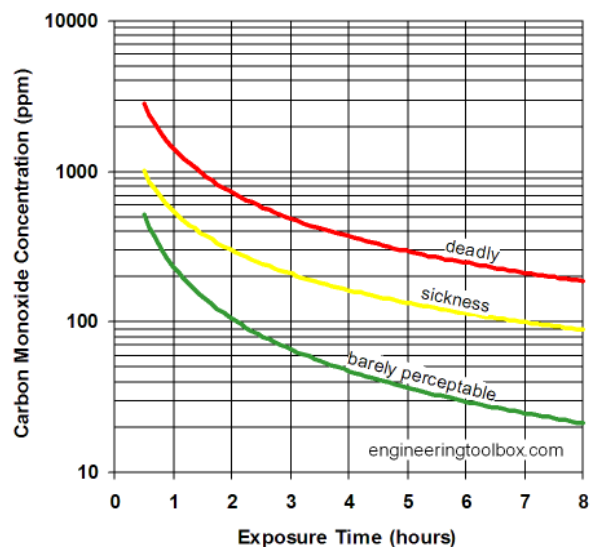


Figure 6. Health effects of various exposure time and concentration of carbon monoxide

VOLATILE ORGANIC COMPOUNDS (VOCs)

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands (Fatima H. Al-Shatti 2003.). Examples include: paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions.

Organic chemicals are widely used as ingredients in household products. Paints, varnishes, and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic, degreasing, and hobby products. Fuels are made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored.

Adverse health responses attributed but not proven to be caused by VOCs in nonindustrial indoor environments include: irritant effects resulting from mucous membrane irritation, systemic effects such as fatigue and difficulty concentrating and toxic effects such as carcinogenicity.

The strongest association has been with VOCs causing mucous membrane irritation. Formaldehyde is the VOC most familiar to the general public that has been associated with indoor air pollution. The major sources of formaldehyde are from indoor construction materials such as particleboard, fiberboard, and plywood. Formaldehyde concentrations are higher in residential buildings compared with office buildings because of the relatively large ratio of pressed wood products to air volume in homes.

A study at a London accident and emergency department found, that levels of benzene, propane and isoprene had a significant positive linear relationship with attendance so f very young children for

acute wheeze (Buchdahl R, Willems C D, Vander M, Babiker A, 2000). In a Norwegian study benzene was found to be more strongly associated with emergency hospital admissions for respiratory disease than particulates (Hajen J A, Nafstad P, Skrondal A, Bjorkly S, Magnus P, 2000). In the Bristol study the correlation coefficients for TVOC were very similar to those for particulates, suggesting a similar magnitude of effect (Rivett, A, Shallcross, D and Wood R 2003) .There is little information on some substances, but the relationship between benzene and toluene serves to show how complicated can be the problem. Exposure to benzene in concentrations in excess of 25 ppm over long periods, as occurs in printing or shoemaking industries, is associated with the development of a plastic anemia. Toluene is a competitive inhibitor of benzene metabolism and prevents the production of toxic metabolites of benzene, so the 70 antagonism could be used to reduce toxicity, however, the two chemicals act together additively to produce central nervous system depression.

The major effect of VOCs on human health is caused by their interference in the natural dissociation and recombination cycle between atmospheric oxygen and oxides of nitrogen. This interference leads to a production of peroxyacetyl nitrate (PAN) and the defense of the ozone, both of which have serious effects on the health of humans, animals and plants. Ozone is a strong pulmonary irritant that causes significant discomfort, clinical symptoms of respiratory illness, reduced pulmonary function (in sensitive individuals) and probably bronchitis, bronchopneumonia and lung tumors. The characteristics of volatile organic compounds differ greatly among each other. Some VOCs are very reactive at the troposphere level under the presence of sunlight while others are quite stable and remain in the atmosphere for a long time, like the CFCs, which tend to group in the atmosphere and react with the stratosphere zone. Volatile hydrocarbons, such as CFCs and CH₄ are capable of absorbing infrared light, and therefore act as greenhouse gases (Miller, G. T. 1997).

CONCLUSIONS

Information we obtained during research and information of a large number of studies have shown that air pollution has a great impact on human health. The most common diseases that occur during the long and short exposure to pollution are respiratory diseases, enfizem, bronchitis, asthma, heart problems, chronic bronchitis ... The big problem with air pollution is a complex activity and toxic component. Polluting component does not act individually, but the synergy with other polluted so that it can not single out just one element that affects the health impact of this is already more elements. A particular problem is that respiratory exposure to toxic component has an impact on other organs in man and the diseases that occur as the action of air pollution are becoming very quickly turn into chronic health problems for humans.

In the future, we should all make every effort to reduce pollution from the air. Constant monitoring of air quality, both in the world and in Serbia is an essential activity that can affect the improvement of air quality and thus human health. This must be fully supported by the authorities, who would be pollution when registering certain steps and sanctioning of pollutants (such as small and large) and improve the quality of air.

ACKNOWLEDGEMENTS

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**II International Conference
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AIR QUALITY

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ABSTRACT

Today, the pollution of the environment constitutes a major threat to our health. The pollution of the air we are breathing every day is continuously increasing. There is serious concern that the threat to human health from air pollution in towns is greater than the danger from smoking. It is estimated that air pollution is the cause of 24.000 premature deaths in the United Kingdom every year. One in every 10 deaths from lung cancer is attributed to air pollution. In my work I will present the most air pollutants and their health effects, air pollution in Serbia and smart systems in Serbia.

Key words: *Air pollutants, health effects, Air quality in Serbia, smart systems in Serbia.*

DEFINITION OF AIR QUALITY

The air pollution (smoke, dust, smog) has disappeared from many cities due to local, national and European initiatives. Air quality is defined as a measure of the condition of air relative to the requirements of one or more biotic species or to any human need or purpose. Air quality indices (AQI) are numbers used by government agencies to characterize the quality of the air at a given location. As the AQI increases, an increasingly large percentage of the population is likely to experience increasingly severe adverse health effects.

AIR POLLUTANTS AND HEALTH EFFECTS

Most air pollutants are: Particulate matter, nitrogen oxides, ozone, hydrocarbons (HC) and volatile organic compounds, sulphur dioxide, carbon monoxide...

Airborne particulate matter varies widely in its physical and chemical composition, source and particle size. PM10 particles (the fraction of particulates in air of very small size and PM2.5 particles are of major current concern, as they are small enough to penetrate deep into the lungs and so potentially pose significant health risks. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as of lung cancer. In developing countries, exposure to pollutants from indoor combustion of solid fuels on open fires or traditional stoves increases the risk of acute lower respiratory infections and associated mortality among young children; indoor air pollution from solid fuel use is also a major risk factor for chronic obstructive pulmonary disease and lung cancer among adults.

Nitrogen oxides (NO_x) - NO_x is a term used to describe a mixture of nitric oxide (NO) and nitrogen dioxide (NO₂). NO is produced in much greater quantities than NO₂, but oxidises to NO₂ in the atmosphere. NO₂ causes detrimental effects to the bronchial system. Epidemiological studies have shown that symptoms of bronchitis in asthmatic children increase in association with long-term exposure to NO₂.

Ozone (O₃) – O₃ unlike other pollutants mentioned, is not emitted directly into the atmosphere, but is a secondary pollutant produced by reaction between nitrogen dioxide (NO₂), hydrocarbons and sunlight. Ozone levels are not as high in urban areas (where high levels of NO are emitted from vehicles) as in rural areas. Sunlight provides the energy to initiate ozone formation; consequently, high

levels of ozone are generally observed during hot, still sunny, summertime weather. Excessive ozone in the air can have a marked effect on human health. It can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases. In Europe it is currently one of the air pollutants of most concern.

Hydrocarbons (HC) and volatile organic compounds (VOC) - HC are compounds of hydrogen and carbon only, while VOC may contain other elements. They are produced by incomplete combustion of hydrocarbon fuels, and also by their evaporation. Because there are many hundreds of different compounds, HC and VOC display a wide range of properties. Some, such as benzene, are carcinogenic; some are toxic and others harmless to health.

Sulphur dioxide (SO₂) - Fossil fuels contain traces of sulphur compounds, and SO₂ is produced when they are burnt. Exposure to SO₂ can damage health by its action on the bronchial system. Sulphuric acid generated from atmospheric reactions of SO₂ is the main constituent of acid rain, and ammonium sulphate particles are the most abundant secondary particles found in air. SO₂ can affect the respiratory system and the functions of the lungs, and causes irritation of the eyes. Inflammation of the respiratory tract causes coughing, mucus secretion, aggravation of asthma and chronic bronchitis and makes people more prone to infections of the respiratory tract.

Carbon monoxide (CO) - CO is an odourless, tasteless and colourless gas produced by the incomplete burning of materials which contain carbon, including most transport fuels. CO is toxic, acting by reaction with haemoglobin and reducing its capacity for oxygen transport in the blood.

AIR QUALITY IN SERBIA

Table 1: The air quality level in the districts

District	Area [km ²]	Number of inhabitants	Sulphur dioxide (SO ₂)	Black smoke (sooth)	Suspended particles PM ₁₀	Benzene (C ₆ H ₆)	Carbon monoxide (CO)	Nitrogen dioxide (NO ₂)	Nitrogen oxides (NO _x)	Lead (Pb)	Arsenic (As)	Cadmium (Cd)	Nickel (Ni)	Benzo(a)pyrene (BaP)
BORSKI	3 517 330	146 551	5	5	0	0	0	1	0	0	0	0	0	0
BRANICEVSKI	3 867 798	200 503	3	5	0	0	0	1	0	0	0	0	0	0
GRAD BEOGRAD	3 237 135	1 576 120	5	5	5	3	4	5	4	5	5	2	3	5
JABLANICKI	2 768 262	240 923	1	5	0	0	0	1	1	0	0	0	0	0
JUŽNO -BACKI	4 024 484	593 666	1	5	0	1	0	5	0	0	0	0	0	0
JUŽNO-BANATSKI	4 242 542	313 937	3	5	0	5	0	4	0	1	0	1	1	5
KOLUBARSKI	2 474 633	192 204	3	5	0	0	0	1	1	0	0	0	0	0
KOSOVSKI	3 124 470	672 292	0	0	0	0	0	0	0	0	0	0	0	0
KOSOVSKO-MITROVACKI	2 054 300	275 904	0	0	0	0	0	0	0	0	0	0	0	0
KOSOVSKO-POMORAVSKI	1 429 295	217 726	0	0	0	0	0	0	0	0	0	0	0	0
MACVANSKI	3 268 081	329 625	5	5	0	0	0	4	0	0	0	0	0	0
MORAVICKI	3 024 945	224 772	1	5	0	0	0	4	0	0	0	0	0	0
NIŠAVSKI	2 734 588	381 757	3	5	0	0	0	1	4	0	0	0	0	0

PCINJSKI	3 512 149	227 690	2	5	0	0	0	4	0	0	0	0	0	0
PECKI	2 559 710	414 187	0	0	0	0	0	0	0	0	0	0	0	0
PIROTSKI	2 762 960	105 654	1	5	0	0	0	0	0	0	0	0	0	0
PODUNAVSKI	1 241 872	210 290	3	5	0	0	0	1	0	0	0	0	0	0
POMORAVSKI	2 598 052	227 435	3	5	0	0	0	1	0	0	0	0	0	0
PRIZRENSKI	1 748 894	376 085	0	0	0	0	0	0	0	0	0	0	0	0
RAŠKI	3 926 801	291 230	3	5	0	0	0	4	0	0	0	0	0	0
RASINSKI	2 665 375	259 441	3	5	0	0	0	4	0	0	0	0	0	0
SEVERNO-BACKI	1 781 483	200 140	2	5	0	0	0	4	0	0	0	0	0	0
SEVERNO-BANATSKI	2 330 362	165 881	5	5	4	1	0	1	0	0	0	0	0	0
SREDNJE-BANATSKI	3 262 864	208 456	3	5	5	0	0	2	4	0	0	0	0	0
SREMSKI	3 478 272	335 901	3	1	0	0	0	0	0	0	0	0	0	0
TOPLICKI	2 209 986	102 075	0	0	0	0	0	0	0	0	0	0	0	0
ZAJECARSKI	3 632 548	137 561	0	0	0	0	0	0	0	0	0	0	0	0
ZAPADNO-BACKI	2 484 558	214 011	1	5	4	1	0	1	0	0	0	0	0	0
ZLATIBORSKI	6 161 137	313 396	3	5	0	0	0	4	4	1	2	1	2	0
ŠUMADIJSKI	2 379 254	298 778	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	88 504 141	9 454 191												

(Source: <http://www.ekoplan.gov.rs/aqptwinning/Report/docs/Preliminary%20assessment%20of%20Air%20Quality%20in%20Serbia.pdf>)

Table 2: Legend

Air quality level	SO ₂ , PM ₁₀ , C ₆ H ₆ , NO ₂ , NO _x , Pb	BS, CO	As, Cd, Ni, BaP
0	no data available		
1	max <= LAT	max <= LV	max <= LAT
2	LAT < max <= UAT	n/a	LAT < max <= UAT
3	UAT < max <= LV	n/a	UAT < max <= LV
4	LV < max <= LV+MT		TV < max
5	max > LV+MT		n/a

(Source: <http://www.ekoplan.gov.rs/aqptwinning/Report/docs/Preliminary%20assessment%20of%20Air%20Quality%20in%20Serbia.pdf>)

Smart systems in Serbia

In my paper I will show two examples of smart systems in our country. The first is EcoBus project, and second is System48 project.

EcoBus project in Pančevo

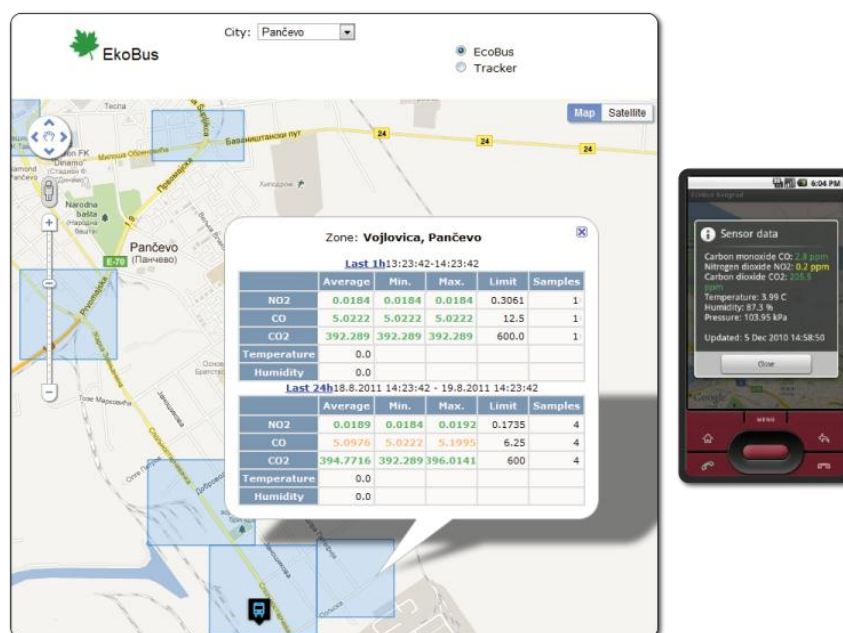
Pančevo is known as one of the most polluted cities, and it is one of the environmental “hot spots” of this country, identified as such by UNEP. It is generally accepted that the most urgent issue in Pančevo is the air pollution – an ongoing problem that lasts for more than three decades. Its main cause is the aforementioned industrial complex, local heating facilities (including the inefficient home heating systems) and traffic

The industrial complex presents the biggest challenge. It is located in close proximity to the residential area, and does not comply with the standard of a minimum distance from the built up areas.

Use of the obsolete technologies, worn out equipment, and insufficient investments in improvements and modernization of the production process, are further aggravating the air quality. Finally, the problem escalated during the 1999 NATO air strikes, that caused a release of hazardous substances with the long-lasting effects, such as organic chlorine compounds, and heavy metals whose harmful effects are well documented.

EcoBus is one of the projects being carried out over the last several years. In 2010, as a result of cooperation between Telekom Serbia, Ericsson, and City of Pančevo, the EcoBus Smart City Service was conceived and implemented in Pančevo. EcoBus project is framed within the SmartSantander project funded by European Union under its Future Internet Research and Experimentation Initiative (FIRE) program.

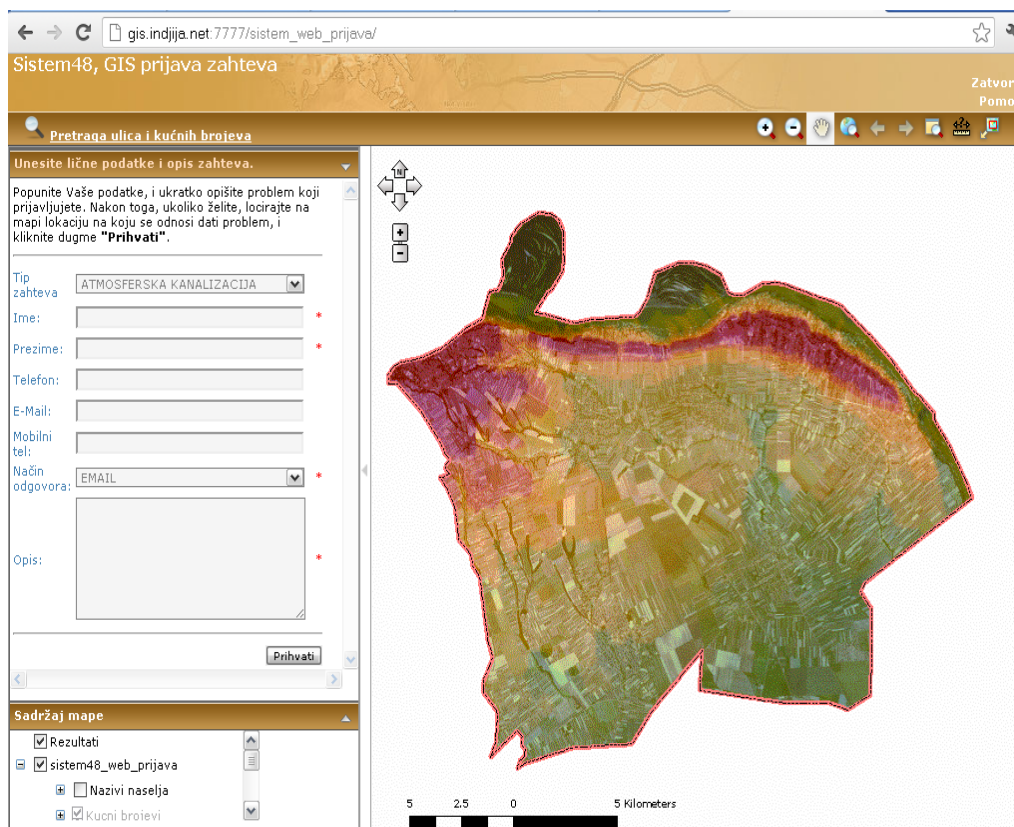
EcoBus uses instruments mounted onto the existing public transportation vehicles in order to monitor a set of environmental parameters over a broad city area. Sixty public transportation vehicles are equipped with these devices, which detect and measure six parameters: temperature, relative humidity, carbon monoxide, carbon dioxide, nitrogen dioxide, as well as a vehicle location. Constant readings of these parameters are performed whenever the vehicle is moving and, in this way, data are collected from various locations. These data are then delivered to the central server via the wireless network for further analysis and database storage.



Picture 1. Querying the environmental data from the interactive map using web and Android application

System48 project

Another example, named System48, comes from Indija. It is a municipal information system designed to improve cooperation between the local government, municipal departments, and public utility enterprises on one hand, and service recipients on the other. It allows citizens to easily report different issues, including those specifically relevant to environmental qualities: pollution incidents such as sewage leaks, improper disposal of waste, and similar. The inquiry can be sent online (using the text form, or pointing the location of the issue on the map), using SMS, phone or in person. In 48 hours, citizens are guaranteed to receive a proper response, followed by action of the respective department if needed. In this way, citizens are encouraged to actively take part in municipal affairs.



Picture 2. Reporting an issue and pinpointing its location on the web-based map
(Source: http://gis.indjija.net:7777/sistem_web_prijava/)

CONCLUSION

The health of the public, especially those who are the most vulnerable, such as children, the elderly and the sick, is at risk from air pollution. In many countries heart disease and lung cancer are the leading causes of death and even a small contribution from air pollution could mean a significant and important effect on public health. The first step to solving air pollution is assessment. Researchers have investigated outdoor air pollution and have developed standards for measuring the type and amount of some serious air pollutants. Prevention is another key to controlling air pollution. The regulatory agencies mentioned above play an essential role in reducing and preventing air pollution in the environment. Only through the efforts of scientists, business leaders, legislators, and individuals can we reduce the amount of air pollution on the planet.

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- <http://www.eea.europa.eu/soer/countries/rs/air-pollution-state-and-impacts-serbia>
- <http://www.sepa.gov.rs/>

**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

**IMPACT OF CHANGES IN CO₂ CONCENTRATION AND
TEMPERATURE ON GLOBAL WARMING**

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ABSTRACT

It has been known for a fact that the concentration of CO₂ has increased significantly over the last century, so it is almost certain that this is due to human activity. Therefore natural sources of CO₂ concentration changes exists, and among other volcanic eruptions. The Earth is a dynamic and not a static system. However, it is increasingly apparent that there is a strong correlation between CO₂ concentration and global average temperature. It was analyzed in terms of the global warming impact of changes in CO₂ concentration and temperature.

Key words: *atmosphere, pollution, global warming.*

The atmosphere created after the foundation of the earth as a planet, and that the release of gases from the Earth. First, the freed water vapor (H₂O) and carbon dioxide (CO₂) that formed the sea, oceans, and limestone in the earth's crust. Oxygen has emerged photo dissociation water vapor, with hydrogen as the light diffuse gas into space. The liberated oxygen and plants. From oxygen in the upper layers of Earth's atmosphere ozone is formed and became absorber of ultraviolet and cosmic radiation. The development of the plant world has led to the further release of oxygen that has reached the level it is today has an atmosphere. Nitrogen is liberated from the country and eventually became the primary gas atmosphere. It is believed that the current ratio of nitrogen and oxygen originated back ten million years. Changes in the atmosphere continue to occur, although very slowly and imperceptibly over time on the origin and formation of the Earth. Atmosphere is called an air layer around the Earth, reaching a height of about 970 km.

It has multiple functions and many important properties. This allows air depleting protecting life on Earth's surface from cosmic radiation and from another universe. On the other hand, the atmosphere provides the basic requirements for life: oxygen, carbon dioxide, solar radiation leaks stopping harmful high-energy radiation (UV rays) and others. Water, carbon dioxide and minerals from the soil and solar radiation are the main components that allow flow of photosynthesis in plants and thus formation of organic compounds, with the release of oxygen, which is essential to animal life and people on earth.

With the meteorological point of view, the atmosphere allows the transfer of solar energy, which leads to the movement of air layers with formation of wind to the evaporation of water from the soil and its circulation in nature, enriching oxygen and leads to the cycling of matter. Atmospheric and meteorological conditions have a significant impact on the local and global air pollution. They affect the distribution of contaminants after their shows, whether it be on their diffusion or transfer from one area to another and helping their dilution in the air. In this way, the distribution of pollutants in the air directly dependent on weather conditions. From the direction, intensity and duration of movement depends on wind direction and movement of pollutants and their distribution in the local and global scale. Also, their leaching from the atmosphere by rainfall, reduces their concentration in the atmosphere.

Air pollution, however, has a direct impact on the local and global atmospheric (weather) conditions. Particles in the air serve as nuclei for the formation of larger aggregates of water droplets (fog, rain), leading to changes in weather. Also, the particles absorb, scatter or bounce solar radiation, which has a significant impact on the weather conditions in an area.

Part of the reflected radiation from the sun is absorbed by the greenhouse gases (CO₂, N₂O, CH₄, HFCs, PFCs, SF₆). It is an important mechanism of maintaining the temperature of the atmosphere (no-gas temperature would be 30 degrees cooler). The earth is warmed by 0.5 °C during the last century. It is estimated that the global surface air temperature increased by about 1-3.5 °C by 2100. year. It is the fastest changing climate over the past 10,000 years. Warming of this magnitude will affect the change in temperature and rainfall distribution.

This will cause a rise in sea level and changes in the distribution of drinking water supply, which will cause significant migration of people from coastal areas to the interior. It will also affect the health and vitality of forests and other natural areas, and on agricultural production, food. Because more water in the atmosphere will be more rain and snow, causing flooding, soil erosion and massive damage. In other areas of the country will be drought. For the past 100 years, sea level has risen by 10-25cm. The melting of glaciers worldwide have contributed to an increase in sea level.

Warming and melting tundra (Siberia, Alaska) leads to the decomposition of organic matter and release carbon, creating an additional source of greenhouse gases.

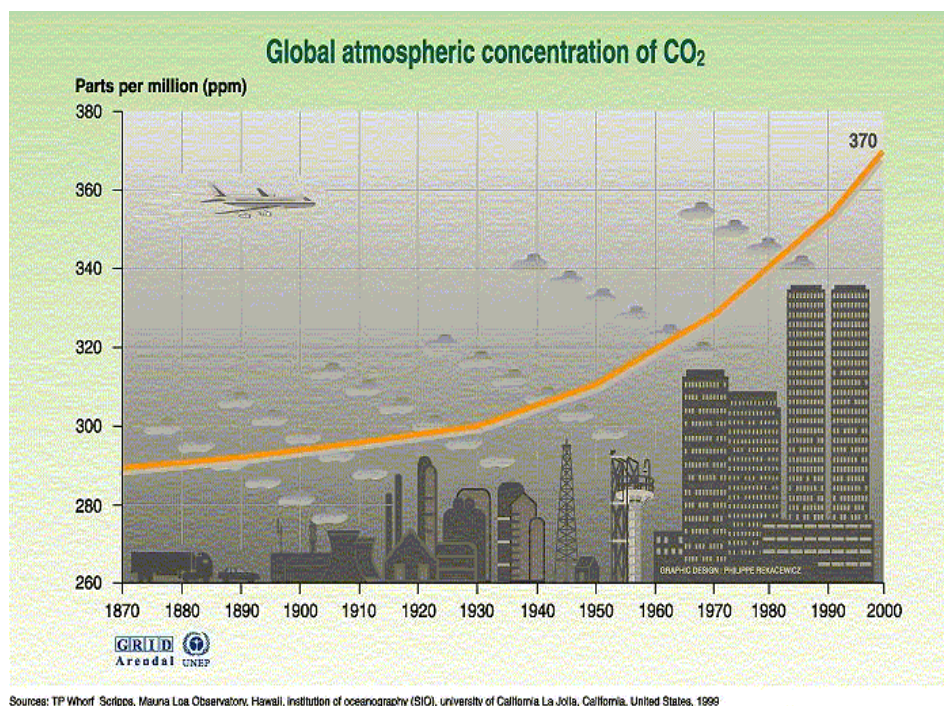


Figure 1. Changing the concentration of carbon dioxide (CO₂) measured in the atmosphere since 1870.

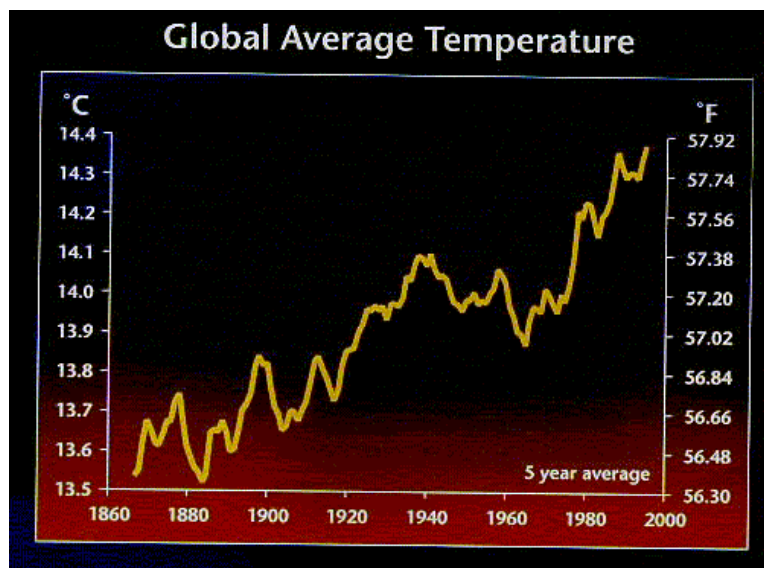


Figure 2. The average annual temperature changes from 1860. to 2000.

The phenomenon of global warming is based on almost imperceptibly rising temperatures on Earth, mostly due to human activities. The visible effects of this trend of increasing temperature are reflected in global climate change and the consequences of type droughts and water shortages and devastating floods, hurricanes and fires. All this is reflected in changes in the ecosystem in terms of changes in the composition and abundance of flora and fauna. It is estimated that the temperature in a period of 100 years (until 1990). Increased by about 0.5 °C. Except air pollution and greenhouse gases originating from industry and commerce, the destruction of tropical forest felling and burning increases the concentration of CO₂ and total albedo, ie. rebroadcasting of radiation from the Earth's surface. More actual environmental problem of global warming is so interpreted. greenhouse gases, as a phenomenon of state changes on the Earth's atmosphere. Natural balance that is maintained in the atmosphere is affected by human activity over the past 200 years. Intensive industrialization and all other forms of fossil fuels have increased the concentration of CO₂ and other so-called. greenhouse gases in the atmosphere from 265 ppm at the beginning of the 19th century at 380 ppm (data for 2000. whatever).

One of the causes of the increase in methane and carbon dioxide, intensive farming, particularly livestock farming. It is assumed that the amount of methane in the past 100 years has increased by at least 100%. Mention gases absorb infrared radiation (heat) radiated surface of the Earth into the atmosphere, which enables a favorable temperature for life on Earth and the rising heat of the atmosphere and the consequent climate change. As the climate gets warmer, some parts of the Earth ekosastava become dry season, which threatens cultural breeding species and favors the spread of resistant weeds.

The soil is contaminated with pollutants from water (~ 80%) and air (~ 13% of which are gases and aerosols in the vicinity of large cities, chemical, steel and power plants). Air pollution gases (CO₂, SO₂, N₂O) in the form of acid rain causes damage to soil and vegetation, is increasingly mentioned as a cause of death of the forests.

Applied Part interventions related to agricultural production is risky for the environment because: NH₃ emissions to the air, N₂, CH₄, SO₂ and CO₂ emissions to water NO₃⁻, NH₄⁺, K⁺, H₂PO₄⁻, SO₄. Having observed ozone depleting increasingly harmful effects of ultraviolet studies of UV-B radiation (290-320 nm) to the people and animals, and Photobiological effects on plants and their productivity.

The accumulation of heavy metals in the surface layer of soil contamination can be caused by human activity, and natural biogeological processes, such habitats or plant roots acquire a large amount from

the deeper layers and the transfer of these elements in the upper layers. Heavy metals via plants entering the food chain in the animal and human can have devastating consequences. Encouraging the consumption of unleaded gasoline has reduced the progression of lead pollution, although the concentration of previously deposited lead and other heavy metals in their bodies along roads and in urban areas of potential danger for growing food plants, especially root vegetables. Environmental pollution can have a local effect but also cause adverse changes in the global level.

Increase in world population has significantly increased the need for arable land. Intensive agriculture, grazing and intensive use of groundwater in irrigation systems has led to rapid soil degradation in many areas. Area of southern Spain is one of many examples of endangered land desertification. Changes in land use affect the climate parameters such as temperature and humidity of a given region, but on the other hand, this systematic regional changes have effects on the global climate.

Beginning of the industrial revolution global forest fund, which today is mainly distributed in the tropical rain belt, was replaced by another cultivated surfaces. Beside intensive agriculture, and other activities such as animal husbandry, which also requires large amounts of water, changing the environment. In addition to grazing that takes place in the wild animal kingdom, humans have changed significantly the incidence and prevalence of grazing cattle bred in farms and cattle households. Beside agricultural land use and has a remarkable effect of deforestation in order to provide firewood.

CONCLUSION

A 1,000-megawatt power plant for one year consumes about 2.5 million tons of coal and produce eight million tonnes of carbon dioxide, 40 million tons of sulfur dioxide, six million tons of dust and a half million tons of fly ash. Typical example, we find that even in our country is that every year on every acre in the radius of 100 kilometers around the power plant "Nikola Tesla" drop by 326 pounds of sulfuric acid. World Scientific experts believe that more than 30 pounds of sulfuric acid per hectare per year leading to an environmental catastrophe, and then within a radius of 100 kilometers around the TE Nikola Tesla eleven environmental disasters taking place simultaneously.

It is believed that the air is polluted, if the composition is changed, especially if it has reduced the percentage of oxygen. Usually the maximum permissible limit of 17% oxygen. Compounds the effect of pollutants on the respiratory system. CO binds with hemoglobin in the blood that carries oxygen. Since nitrogen compounds is the most common nitrogen peroxide (NO), which can easily exceed the nitrogen dioxide (NO₂).

Pollution of the atmosphere has already taken a few decades back momentum and shows no tendency to decrease or stagnation, just, unfortunately, constant progress. Cost of that pollution will pay and pay until all the inhabitants of the planet, regardless or not they have a stake in that. Industry, traffic, power plants, thermal power plants constitute irreparable harm. Proportionately, the growing number and natural disasters.

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MANAGEMENT OF SOLID URBAN WASTE

**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

**TRANSFORMATION OF URBAN WASTE INTO BUILDING
MATERIALS: PET LIQUID CONTAINERS**

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ABSTRACT

The building sector counts for more than 40% of the global energy consumption, out of which almost 10% only refers to the production of new building materials. Reusing urban waste as raw materials for building components pursues the goals of reducing new resource exploitations and embodied energy levels by offering an affordable and locally accessible source of building materials. This article presents a typology of constructive systems that reuse or recycle PET liquid containers (bottles) as composing elements for building envelopes (enclosures), as well as an analysis of the thermal efficiency of a PET container envelope model compared to more traditional building envelopes. The thermal parameters of the envelope lead, in certain conditions, to a better overall energetic behavior than the traditional building envelopes, proving the reliability of this particular approach to urban waste management.

Key words: PET bottles, building envelope, thermal transmittance, recycling, urban waste.

INTRODUCTION

Less than 1% of the materials embodied in the products people use are still in their possession six months after purchase. The rest becomes waste, whether from building, commerce, manufacturing or household (Cracknell, 2009). In spite of this, massive exploitations of new resources are continuously undergone. Since the Second World War only, mankind has consumed more fossil-fuel raw materials for energy production purpose than it has had its entire precedent history (Hegger et al., 2008a). Under these conditions, finding solutions to balance world’s energy consumption and waste production is compulsory in assuring a sustainable future.

The building sector represents the largest world energy consumer and is responsible for using more than 40% of the Earth’s total extracted resources, while producing 60% of the world waste. The use of new building materials can be reduced considerably, as a mean of reducing the energy consumption of buildings in terms of their embodied energy. It implies rational use of the materials and their integration in closed cycles. However, these solutions are only applied occasionally (Hegger et al., 2008a).

Every material should be used in closed life cycles (from cradle to cradle) as much as possible, so that waste resulting from some processes to become raw material for other processes. The successive use in cycling repetitions is critical for conserving new raw material exploitations meant to satisfy the needs of the building process by replacing it with processed ready-to-use materials. At the same time, the overall embodied energy of the material is diminished due to the replacement, in some cases, of the extraction process with the reshaping process (Cracknell, 2009).

There have been cases where reusing waste as building material stood at the base of prototype buildings. The transformation of wasted non-construction items, such as PET beverage containers, into building materials, through recycling or reuse, has a positive effect on the waste management strategies. It enriches PET bottles with a new use that extends their life-cycle by several times the normal life span of a PET beverage container, preventing it from becoming waste.

The present paper describes the strategies involved in transforming PET liquid building containers into building containers, some characteristics of the new constructive systems based on a few examples, as well as an analysis of the thermal performance of a PET container envelope model compared to more traditional building envelopes.

THEORY

Recycling vs. Reusing

Recent information show that in 2011 only, European post-sorting PET collection has reached 1,59 million tonnes, representing 51% of all PET bottles in the market (PETCORE, 2012). There are two main methods that allow PET containers to successfully be transformed into building materials: recycling and reusing. In each of the two cases, specific measures have to be taken in order for the used PET items to possibly become construction materials.

Recycling generally presumes a process of collecting waste and sorting it by type of material, which is, afterward, deconstructed and used as raw material. In the case of PET (Polyethylene terephthalate), it can then either be up-cycled by mixture with superior quality materials resulting in same quality products (other liquid containers), or it can be down-cycled by adding lower quality materials, thus obtaining lower quality products (carpets). Therefore, recycled PET can also be shaped as new building components and used in construction. This method drastically reduces the need of raw resource exploitations. The obtained constructive systems are composed of newly created modular elements that allow a controlled synergy resulting in high performance building elements. However, this approach requires additional energy and a certain level of technology necessary for the re-shaping process to occur.

In contradiction to that, reusing requires virtually no energy because the containers are integrated in constructive systems as they are. Reshaping processes or additional use of raw material is not necessary. Nevertheless, the various sizes and shapes of the bottles appeal to creative construction systems capable of integrating them in building components and calls for selectively disposal of the containers, without damaging their airtightness.

PET containers in building envelopes

Various projects reused wasted PET containers in the composition of the buildings' envelopes. Systems that simply reuse the bottles are realized by simple horizontal stacking of the bottles, in the case of a bottle-dome art installation of Jasmine Zimmerman (Linda, 2008). A temporary solar tent has been built during a workshop developed by the University of Technology in Berlin, where the reused bottles were screw-fixed using the cork to a plastic, airtight membrane (Burkhardt, 2000). The containers can sometimes be bonded with aggregates (mortar, earth) and tied by wires for increased compactness, as we can see in some areas in Nigeria (Disson, 2011). They can also be reused in composing other construction elements (floors, partition walls) that can determine up to 40% construction cost reduction, lending the system to low-cost buildings (Chávez, 2005). Systems that are based on recycling are more hi-tech and consist of reshaped modular PET bottles that are either bonded together independently or in larger, independent panels as shown by the Polli-Bricks[®] from the Eco-Ark[®] Pavilion at the 2012 International Flora Expo (Liggett, 2010). In the latter cases, a secondary supporting structure is needed, similar to a curtain wall (Table 1).

Table 1: Methods for transforming PET liquid containers into building materials

	Recycling	Reusing
Wasted PET bottles		
Condition of bottles	unimportant	undamaged
Collecting method	selective collection	remunerated submission
Transformation		
Process	deconstructing and reshaping	cleaning
Raw material use	mixed with recycled PET	none
Extra embodied energy	overall, less than new bottle production	minimum
The building bottle		
Construction item	adapted bottle to suit cohesion	normal bottle
Dimensions	identical; modulation	various
Constructive system	bonding, thermal bonding into panels	reinforced stacking
Building element		
Resulting element	self-baring wall, partition wall, floor	load-baring wall, floor
Technology level	high	low
Cost	medium cost	low cost

Transparency and thermal insulation

Transparent recycled PET containers can be integrated in glazed envelopes with significant contribution to the thermal balance of the building. Due to their airtightness, the air comprised inside the bottles acts as a buffer zone that prevents heat transfer from the interior to the exterior (Hegger et al., 2008b). At the same time, light passing through is diffused by multiple reflections from the faces of the bottles, resulting in a pleasant atmosphere (see Figure 1).



Figure 1. The diffuse light passing through a simple stacked wall made from reused PET bottles due to the multiple reflections generated by the honeycomb structure

METHODS

Description of experimental model

The theoretical model considered for this experimental part refers to a new PET container bottle that can be used as a building block at the end of its life as a container. Dealing with the world's waste problem should refer to the production of items that should last longer and become waste less quickly (Cracknell, 2009). The model offers an example of a bottle built through recycling old PET containers that is given a new usage, thus considerably prolonging its life. Having a 1 litre capacity, a prismatic shape and dimensions ($80 \times 80 \times 190 \text{ mm}^3$ wrapped around a 1 mm thick PET layer) for efficient storage in normal fridges, the bottle fulfills all the functions of a normal beverage container. Minor alterations have been imposed in order to allow it to be bonded with other bottles in a similar way to the LEGO® blocks, or to a masonry wall, after it has performed its role as a liquid container (Figure 2).

Bonding more bottles one into another results in a self-barring wall anchored through a series of cable thrusts and transversal bottles to prevent wind-caused movements. 150 bottles cover one square meter of a double-arranged, 164 mm thick wall. A silicone layer applied at all interior and exterior joints between the individual bottles assures proper airtightness (Figure 3). Even if recycling is necessary for the production of the proposed bottles, the design allows them to be reused as building components, if they are to replace the old bottles.

Thermal performance of the PET envelope model

The bottles are enclosed in a 1 mm PET skin ($\lambda_{\text{PET}} = 0.19 \text{ W/mK}$). In the case of the Eco-Ark® Pavilion, airtightness to wind and heat losses through ventilation has been assured by large superposed polyethylene sheets spread on the entire surface of the envelope and held in place by the screwed bottles, corks (Liggett, 2010). In the used model, airtightness is obtained by applying a 5 mm coat of silicone ($\lambda_{\text{silicone}} = 0.22 \text{ W/mK}$) over the joints between the bottles, both on the exterior and the interior.

We will determine the thermal transmittance of the theoretical model by using the calculation method described by the ISO 6946:1996 standard, appropriate for all building components excepting doors, windows and components through which air is designed to permeate. The principle of the calculation is to obtain the individual thermal resistances of each of the thermally homogenous parts of the component and to combine them so as to obtain the total thermal resistance of the component (ISO 6946, 1996). The value of the transmittance will be equivalent to the inverse of the resistance. In some cases, corrections can be applied to the obtained values.

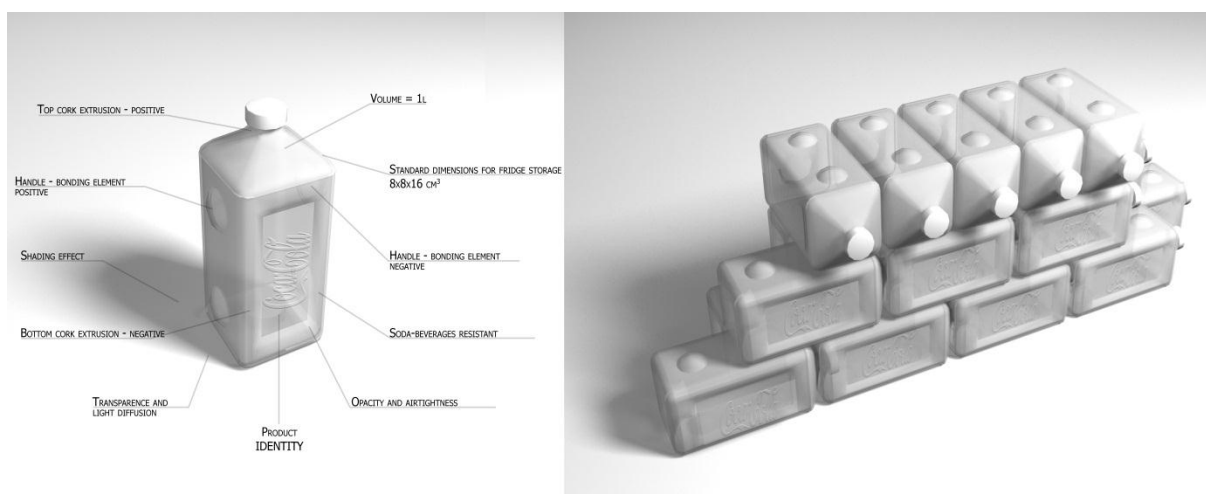


Figure 2. Both the handle and the cork offer the possibility for the bottles to be bonded in order to form a transparent building envelope. These are the only modifications made to the bottle that, otherwise, fulfills all the attributes of a normal container

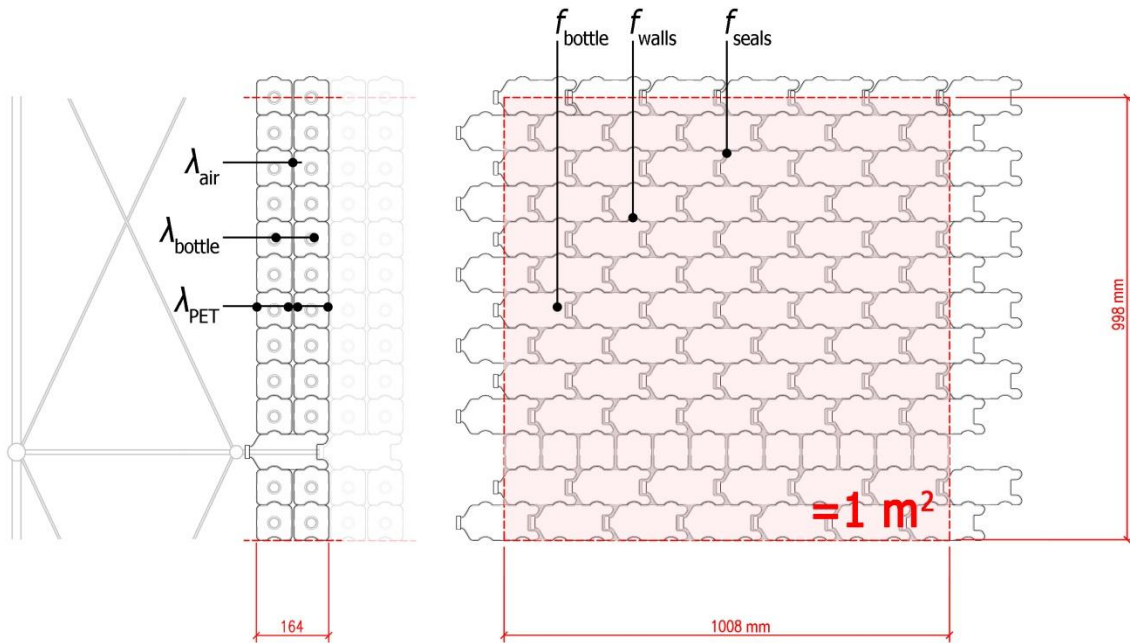


Figure 3. Section and view of the proposed PET bottle envelope

Given that the thermal resistance of a single layer is

$$R = \frac{d}{\lambda} \quad (1)$$

where d is the thickness of the layer and λ is the design thermal conductivity of the material, and that the total thermal resistance of a building component consisting of homogenous layers is

$$R_T = R_{si} + R_1 + R_2 + \dots + R_n + R_{se} \quad (2)$$

where R_{si} and R_{se} are the internal and external surface resistances respectively, and $R_{1...n}$ the designed thermal resistances of each layer, in case of a building component consisting of thermally homogenous and thermally inhomogenous layers parallel to the surface, the total resistance is

$$R_T = \frac{R'_T + R''_T}{2} \quad (3)$$

with R'_T being the upper limit of the thermal resistance and R''_T the lower limit of the thermal resistance.

The upper limit of the thermal resistance

The upper limit of the thermal resistance is calculated by assuming one-dimensional heat flow perpendicular to the surface of the component. It is given by the following expression:

$$\frac{1}{R'_T} = \frac{f_a}{R_{T_a}} + \frac{f_b}{R_{T_b}} + \dots + \frac{f_q}{R_{T_q}} \quad (4)$$

where $R_{T_{a...q}}$ are the thermal resistance from environment to environment and $f_{a...q}$ are the fractional areas of each section. For the proposed model, we can identify three sections as follows (Figure 3): a section for the interior of the bottles filled with air and the bottle walls enclosing the interior ($R_{T_{bottle}}$, $f_{bottle} = 85\%$), a section corresponding to the silicone airtighting seals ($R_{T_{seal}}$, $f_{seal} = 5\%$) and a last section defined by the adjacent frontal and horizontal walls of the bottles ($R_{T_{walls}}$, $f_{walls} = 10\%$).

Thermal resistance from environment to environment of each section will be calculated using (1) and (2). For the first section, we have:

$$R_{T_{bottle}} = R_{si} + 2R_{air a} + \frac{d_{PET}}{\lambda_{PET}} + R_{se} \quad (5)$$

We will consider $R_{si} = 0,125 \text{ m}^2\text{K/W}$, $R_{se} = 0,043 \text{ m}^2\text{K/W}$ and $R_{air a} = 0,17 \text{ m}^2\text{K/W}$ for a 14 mm unventilated layer of air subjected to a horizontal heat flow representing the interior of a single bottle (ISO 6946, 1996). If we count that there are 4 walls of 1 mm PET that enclose the two ranges of bottles, by replacing the above values in (5), we will get:

$$R_{T_{bottle}} = 0,529 \text{ m}^2\text{K/W} \quad (6)$$

For the section containing the silicone seals, we have:

$$R_{T_{seal}} = R_{si} + R_{air b} + \frac{d_{silicone}}{\lambda_{silicone}} + R_{se} \quad (7)$$

Silicone has been applied in a 5 mm layer, both on the interior and the exterior, also enclosing a 154 mm thick layer of unventilated air subjected to a horizontal heat flow, with a resistance of $R_{air b} = 0,18 \text{ m}^2\text{K/W}$. We thus obtain:

$$R_{T_{seal}} = 0,393 \text{ m}^2\text{K/W} \quad (8)$$

The last section represents the horizontal adjacent walls of the bottles, in a total thickness of 140 mm of PET. Its resistance is:

$$R_{T_{walls}} = R_{si} + \frac{d_{walls}}{\lambda_{PET}} + R_{se} \quad (9)$$

And by replacing the real values, we obtain:

$$R_{T_{walls}} = 0,904 \text{ m}^2\text{K/W} \quad (10)$$

From (4), (6), (8) and (10) it results that

$$\frac{1}{R'_T} = \frac{f_{bottle}}{R_{T_{bottle}}} + \frac{f_{seal}}{R_{T_{seal}}} + \frac{f_{walls}}{R_{T_{walls}}} = 1,844 \text{ W/m}^2\text{K} \quad (11)$$

and the upper limit of the thermal resistance is:

$$R'_T = 0,542 \text{ m}^2\text{K/W} \quad (12)$$

The lower limit of the thermal resistance

The lower limit is determined by considering that all planes parallel to the surface of the component are isothermal surfaces. Therefore, it should be calculated using (2). The proposed envelope presents four parallel layers as follows: two layers consisted of all the vertical faces of the bottles on the interior ($R_{PET int}$) and, combined with the silicone seals on the exterior ($R_{PET ext}$), an internal unventilated air layer ($R_{air c}$) and an inhomogeneous layer which comprises the interior of the bottles and their horizontal skin faces (R_{bottle}). The expression becomes:

$$R''_T = R_{si} + R_{PET ext} + R_{PET int} + R_{air c} + 2R_{bottle} + R_{se} \quad (13)$$

Since the first interior PET layer is homogenous and its thickness is 2 mm (2 walls of 1 mm each), the thermal resistance can be determined by (2). We get:

$$R_{PET\ int} = 0,010\ m^2K/W \quad (14)$$

We will consider the thermal resistance of the 4 mm thick unventilated layer of vertical air as being equal to (ISO 6946, 1996):

$$R_{air\ c} = 0,110\ m^2K/W \quad (15)$$

For the 152 mm thick inhomogenous layer, we will determine the equivalent thermal conductivity, using a similar relation to (4), which is applied only to this layer (ISO 6946, 1996):

$$\frac{1}{R_{bottle}} = \frac{f_{bottle}}{R_{air\ a}} + \frac{f_{seal}}{R_{air\ b}} + \frac{f_{walls}}{R_{walls}} \quad (16)$$

By using (1), we can say that:

$$\frac{1}{R_{bottle}} = \frac{f_{bottle}}{R_{air\ a}} + \frac{f_{seal}}{R_{air\ b}} + \frac{\lambda_{PET}f_{walls}}{d_{walls}} \quad (17)$$

We finally obtain:

$$R_{bottle} = 0,099\ m^2K/W \quad (18)$$

The same method applies to the exterior PET 2 mm thick layer due to its inhomogeneity because of the silicone seals. Analog to (17), we have:

$$\frac{1}{R_{PET\ ext}} = \frac{\lambda_{silicone}f_{seal}}{d_{silicone}} + \frac{\lambda_{PET}(f_{walls}+f_{bottles})}{d_{walls}} \quad (19)$$

After replacing the values, we get:

$$R_{PET\ ext} = 0,010\ m^2K/W \quad (20)$$

By replacing (14), (15), (18) and (19) in (13), we obtain the lower limit of the thermal resistance:

$$R''_T = 0,497\ m^2K/W \quad (21)$$

The thermal transmittance

From (3), (12) and (21), the value of the total thermal resistance of the PET bottle envelope results:

$$R_T = 0,519\ m^2K/W \quad (22)$$

with a maximum relative error of $e = 1,4\ \%$. Knowing that the thermal transmittance is the inverse of the thermal resistance, we obtain the following value:

$$U = 1,92\ W/m^2K \quad (23)$$

Considering the great number of bottles needed to compose an entire envelope, imperfections over the airtightness of the silicone seals have to be taken into account and, therefore, a correction has to be applied to the transmittance, using the expression (ISO 6946, 1996):

$$U_c = U + \Delta U \quad (24)$$

where U_c represents the corrected thermal transmittance and ΔU a correction term, equal in our case to the correction of air gaps for an envelope that allows air circulation on the warm side of the insulation and air gaps penetrating the insulation. Thus, $\Delta U = 0,04 \text{ W/m}^2\text{K}$. The final corrected thermal transmittance is:

$$U_1 = 1,96 \text{ W/m}^2\text{K} \quad (25)$$

RESULTS AND DISCUSSION

Interpretation and improvement solutions

The preliminary results show that the obtained value of the transmittance exceeds the maximum transmittance allowed by the building codes for glazed surfaces ($U_{max} = 1,30 \text{ W/m}^2\text{K}$). The calculations were realized for a 160 mm wall thickness (two widths of a bottle). The advantage of the designed PET recipient is that it allows various thickness walls to be built. Similar to a brick wall, we will add two other ranges of bottles, thus obtaining a 320 mm thick envelope (four widths of a bottle).

We will reiterate the calculus, bearing in mind some changes. In (5), the coefficient of the bottle resistance doubles ($R_{air\ a}$) and so does the thickness of the PET skin (d_{PET}), since there are 4 ranges of bottles, instead of just two. In (9), the thickness of the horizontal PET walls (d_{walls}) doubles also. In the end, we obtain the upper limit of the thermal resistance to be:

$$R'_T = 0,906 \text{ m}^2\text{K/W} \quad (26)$$

In (14), the resistance of the interior vertical walls of the bottles ($R_{PET\ int}$) has to correspond to 4 ranges (8 faces of 1 mm each except 2 exterior faces), and thus triples. Two new layers of vertical air will appear, meaning that their resistance will triple ($R_{air\ c}$), and the bottle resistance will double, thanks to the two newly added ranges (R_{bottle}). The lower limit of the thermal resistance becomes:

$$R''_T = 0,716 \text{ m}^2\text{K/W} \quad (27)$$

We finally get the thermal resistance of:

$$R_T = 0,811 \text{ m}^2\text{K/W} \quad (28)$$

with a maximum relative error of $e = 7,6 \%$. In the end, the thermal transmittance for the 4 bottle range envelope is:

$$U_2 = 1,23 \text{ W/m}^2\text{K} \quad (29)$$

Taking into account that the additional two ranges of bottles can improve the level of air permeability through the envelope, we can consider that no supplementary correction to the transmittance value is necessary.

Comparison to other types of glazed building envelopes

After adding another 2 ranges of PET bottles, the thermal performance of the envelope presented an improvement. Thus, the new value of the transmittance ($U_2 = 1,23 \text{ W/m}^2\text{K}$) is situated under the imposed limits of the building regulations in Romania ($U_{max} = 1,30 \text{ W/m}^2\text{K}$), in the case of doors,

windows or other glazed surfaces (Monitorul Oficial, 2010). Even with the thickening of the wall, the light passing through could still reach a satisfactory level of illumination (Figure 2). Moreover, the proposed envelope proved to be more efficient than other, more conventional types of transparent surfaces, such as traditional single-glazed windows ($U \sim 5 \text{ W/m}^2\text{K}$). The PET envelope presents a similar behavior to a high-performance double-glazed window (U between $1,2 \text{ W/m}^2\text{K}$ and $2,2 \text{ W/m}^2\text{K}$). Nevertheless, it does not assure a sufficient insulation such as a triple-glazed window (U between $0,6 \text{ W/m}^2\text{K}$ and $1,2 \text{ W/m}^2\text{K}$).

Passive solar system behavior

In the presence of solar radiation, the empty space inside the bottles can improve the thermal behavior of the envelope. The space can either remain hollow, in which case the air is heated because of the greenhouse effect and acts as a buffer zone preventing heat transfer from the interior to the exterior, or it can be filled with different materials (earth, clay, sand, water), in which case the entire wall becomes a passive solar system (Trombe-Michel, water wall) (Pucar, 2006). The 4 ranges of bottles can be detached into to groups of two, enclosing between them a layer of 200 mm thick unventilated air (Figure 3). This can either represent another buffer zone or it can be integrated in HVAC system while pre-heating the fresh air that enters the building. In this case, the thermal resistance will increase with the resistance of the new air layer, and the transmittance will reach:

$$U_3 = 1,00 \text{ W/m}^2\text{K} \quad (30)$$

close to a low performance triple-glazing.

The performed calculations indicate that the proposed PET bottle envelope performs at a comparable level to other medium-high glazed surfaces. Nevertheless, it would be recommended some experiments to be conducted in order to confront the theoretically obtained results with real-time collected data. Furthermore, studies should be carried out to determine the envelope's behavior to sun dilatation and which appropriate fire-proofing solutions can be applied.

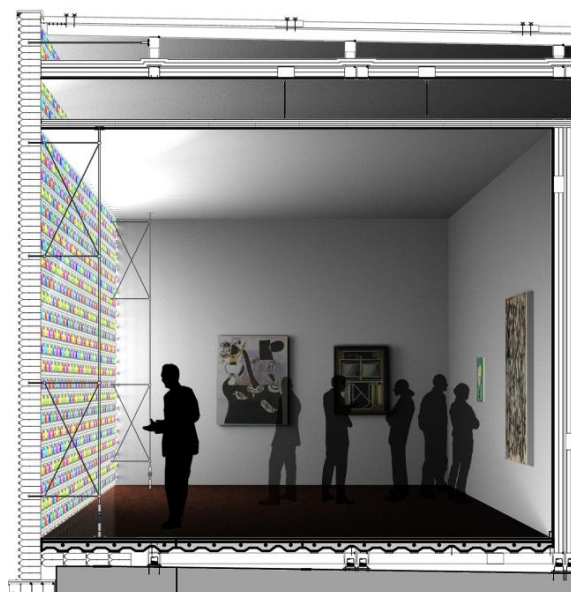


Figure 4. The bottle envelope enclosing an exhibition hall

CONCLUSIONS

The theoretical model analyzed in the current paper proposes a new approach to PET container production using a bottle model that can have a new life as a building component after its disposal as waste. If the described strategy were to be applied on long term, it would result in a sustainable

approach to low embodied energy material design. The PET bottles would be freely reused in erecting temporary constructions or emergency shelters and even more complex architectural programs (see Figure 4), by untrained supervised builders, with a significant reduction of costs.

Although the proposed system needs technical improvements, the resulting envelope proves high thermal performance for a low-cost transparent building component, comparable to the most efficient double-glazing windows. Furthermore, it has the potential to be transformed into a passive solar system due to the void of the bottles.

Recycling raw PET waste to produce the new bottles decreases the overall quantity of unprocessed waste. The embedding of the PET bottles into building envelopes depends on their condition when becoming waste. Collecting the new PET bottles undamaged could be realized in specialized centres (beverage producers or even construction companies) by means of a symbolic remuneration per each unbroken returned item. This could furthermore decrease the quantity of disposed waste in urban areas and improve the selective collecting process.

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**II International Conference
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**CHEMICAL ACTIVATION OF THE RED OPALITE AND IT'S
CHARACTERISTICS**

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ABSTRACT

The chemical activation of the red opalite is made in order to be extracted Fe - oxides and the residue to be used for synthesis of zeolites. Activation has been with 10 % HCl acid. Adsorptional properties of the obtained residue are tested with static gravimetric method. The results are shown graphically. For determination of the specific surface is used the equation of BET for multilayer adsorption. The test showed that the residue can be used as adsorptional agents. In order to be tested thermal transformations of the extracted residue of red opalite, are used DT and TG methods. The curves on Fig. 1 and Fig. 2 show that most expressed endothermic effect is the mineral kaolinite and then becomes its dehydratation. There also appear the effects of the mineral getite which is transformed into α -Fe₂O₃ and γ -Fe₂O₃. Since the red opalite is polymineral raw material the effects appear also on the other minerals. Calculated loss of mass on TG curve is 12,72% mass which coincides with the loss of chemical analysis.

Key words: red opalite, chemical activation, adsorption, specific surface, BET equation.

INTRODUCTION

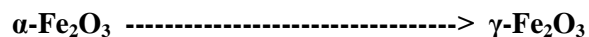
In the order to be tested if the residue can be used as an adsorption agent there have been tested its adsorption characteristics in relation to be the water steam at a temperature of 298 K. There has been applied a static gravimetric method. The material which has been taken to be tested is with particle size below 0,063 mm and above 0,063 mm. Determined specific surface clearly indicates that the residue can be used as an adsorption agent even beside the fact that by its structure it is a polymineral matter. Thermal analysis is particularly important for the minerals which are used for synthesis of zeolites. Having in mind that the red opalite represents a polymineral matter consisted of the minerals (kaolite, illite, cristobalite, tridimite, getite, quartz and amorphous matter) during the thermal treatment some minerals are transformed into other modification. The residue is obtained with chemical activation of the red opalite using 10 % HCl. Its chemical structure is given on Table 1. In order to be tested the thermal transformations of the extracted residue of red opalite, there have been used DT and TG methods. The curves which are shown on picture 1 and 2 show that the mostly expressed endothermic effect is appeared on the mineral kaolite when becomes its dehydration. There also have been appeared the effects of the mineral getite which is transformed into α -Fe₂O₃ and γ -Fe₂O₃. Since the red opalite is a polymineral raw material there have appeared effects also on the other material there have appeared effects also on the other materials. The calculated loss of mass of the TG curve is 12.72 % which coincides with the loss of the chemical analysis.

EXPERIMENTAL PART AND DISCUSSION ABOUT RESULTS

The testing have been made on the apparatus Netzeh in an airy oxidation environment with a heating velocity of 2.5 °/min. As a reference substance is used Al₂O₃ and the sensitivity is 1/1. The residue which is used for thermal testing is with pale pink color which is due to the small quantity of the present Fe₂O₃ oxide about 2.04 % mass (B. Cekova, MS. Thesis, Faculty of Technology and metallurgy, Skopje, 1983)[1].

The chemical structure of the residue is shown in Table 1.

Are the mineral ilite continues with separation of the water until 1173 K when its crystal grating is ruined at 1123 K. There becomes modification of getite as follows: α -getite which previously passed from:



The exothermic effect starts from 1183 K up to 1350 K where the new phase spines is formed and above temperature of 1223 K begins to appear glass mulite and crystobalite (Р. Грим, Минералогия и практическое исползование глин, Изд. “Мир”, Москва, 1967; М.А. Кашкаи, Алунитви их генезезис исползование, Том 1, Изд. “Недра”, Москва, 1970)[2,3].

TG curve gives the loss of mass as a result of the appeared endothermic effects. The great loss of mass is the range with expressed endothermic effect in which there is dehydroxylation of kaolinite, transformation of α - getite into α -Fe₂O₃ and discharge of water from the mineral ilite. The calculated loss of mass of the TG curve coincides with the result obrained from chemical analysis.

The adsorption capability of the residue is followed though the specific surface for whose determination is used adsorption isothermse on water steams. The adsorption isotherms are given on Fig. 3 (for the trials 1 and 4) and on the Fig. 4 is given their linear for in BET coordinates. The dependence between the specific surface and the monolayer capacity gives the equation: $S = am N Am 10^{-18} (m^2/kg)$.

Table 1: Chemical analysis of the residue with particle size below 0.063 mm

Components	Participation in (%)
SiO ₂	60,94
Al ₂ O ₃	23,33
Fe ₂ O ₃	2,04
MgO	/
CaO	0,72
K ₂ O	0,15
Na ₂ O	0,10
loss of mass	12,72
Total	100,00

DTA and TGA of the residue have been in the same conditions as of the initial raw material red opalite. The curves of the analysis are given on Fig. 1 and 2. The appeared first endothermic effect of DT curve starts from 660 K till 823 K and it ends to 923 K. At this endothermic effects α -getite releases the water at 660 K and it passes into α -Fe₂O₃. The mineral ilite discharges the water at 673 K and its diswatering compared with kaolinite goes slowly which depends on the particle size and time of heating (2). The mineral kaolinite discharges the water from 703 K to 923 K. The second endothermic effect is in the temperature interval from 1000 K till 1065 K.

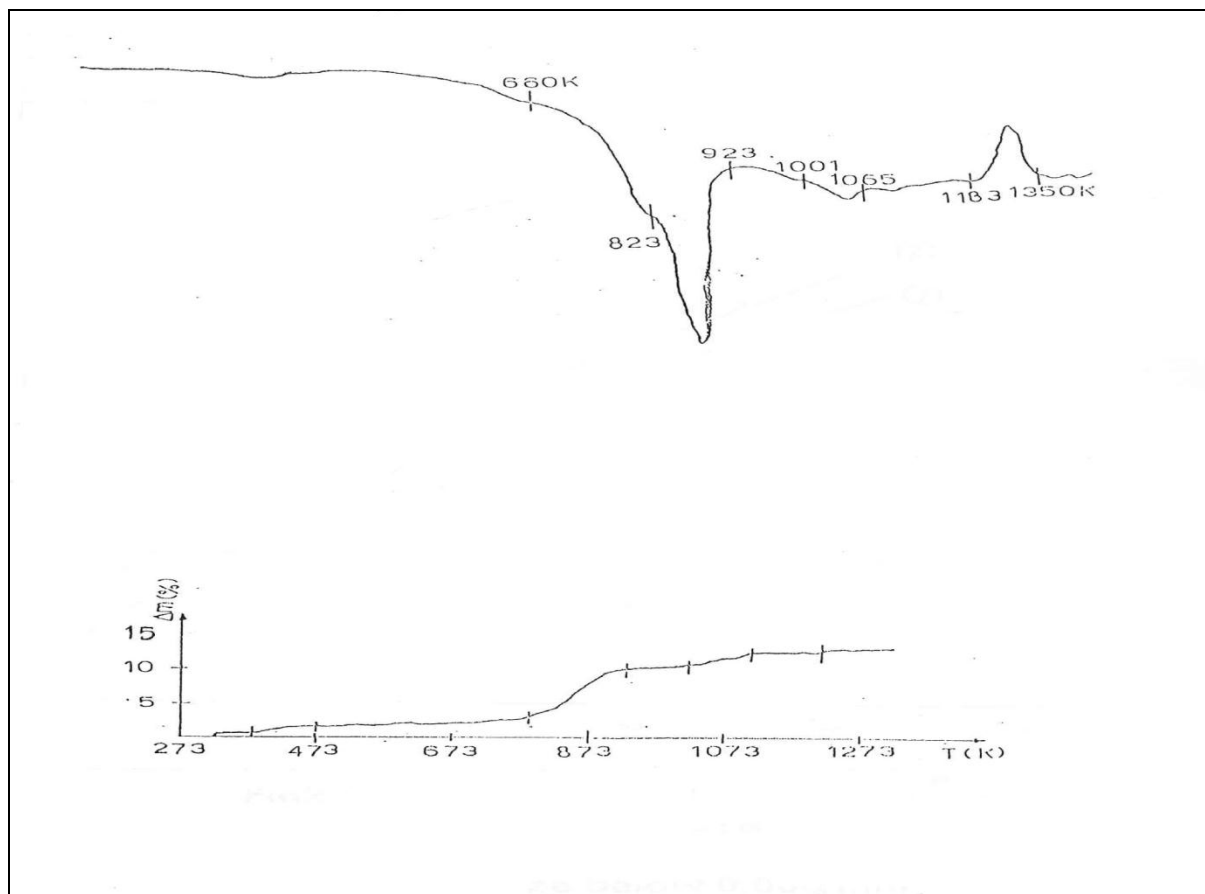


Figure 1. DT Curve of the residue

Figure 2. TG of the residue

Determined specific surface of the material with particle size above 0.063 mm is $39.92 \text{ m}^2/\text{kg } 10^3$, and for the material with particle size below 0.063 mm it is $37.01 \text{ m}^2/\text{kg } 10^3$.

Obtained values for the determined specific surface show that the residue by its adsorption characteristics is close to the red opalite although it has made chemical activation (B. Sekova, MS. Thesis, Faculty of Technology and metallurgy, Skopje ,1983; Б. Цекова, Адсорпциони особини на преципитатот SiO_2 исталожен од хидратизирани Na-силикати, Гласник на хемичари и технолози на Македонија,9,183-190, 1990).[1,4]

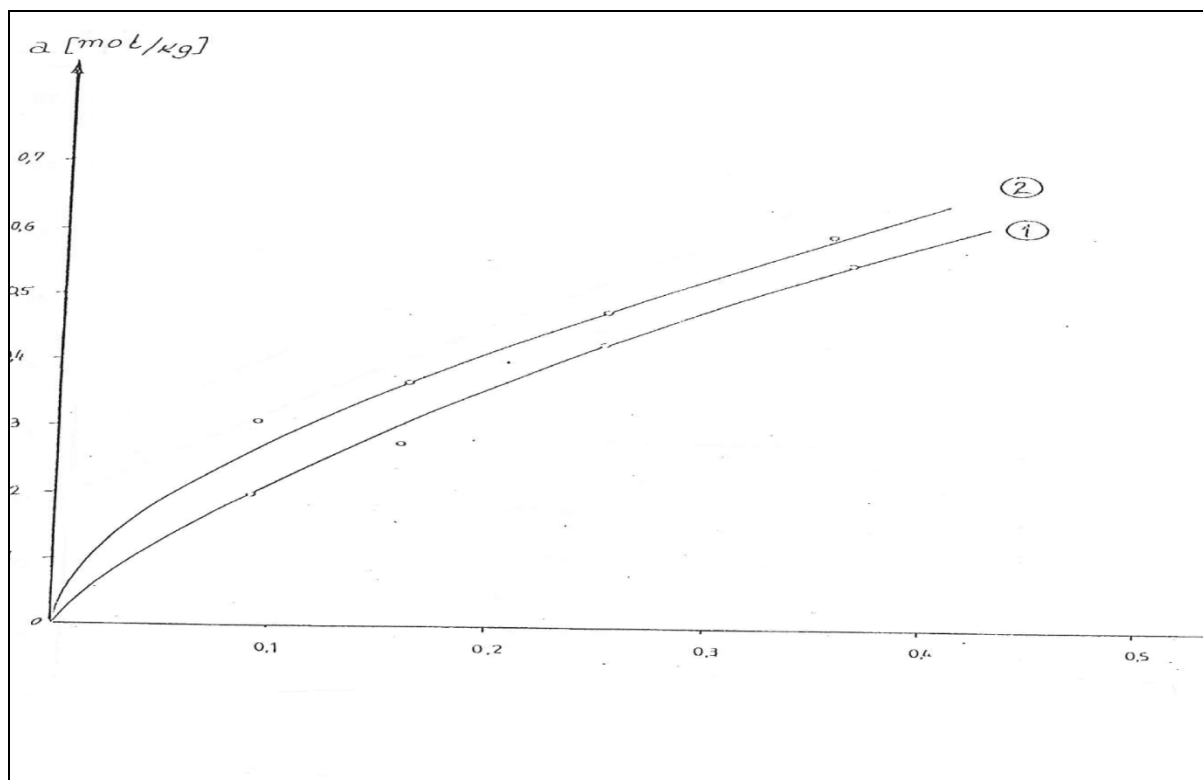


Figure 3. Adsorption isotherm of the water vapour on residue
1- Particle size above 0.063 mm
2- Particle size below 0.063 mm

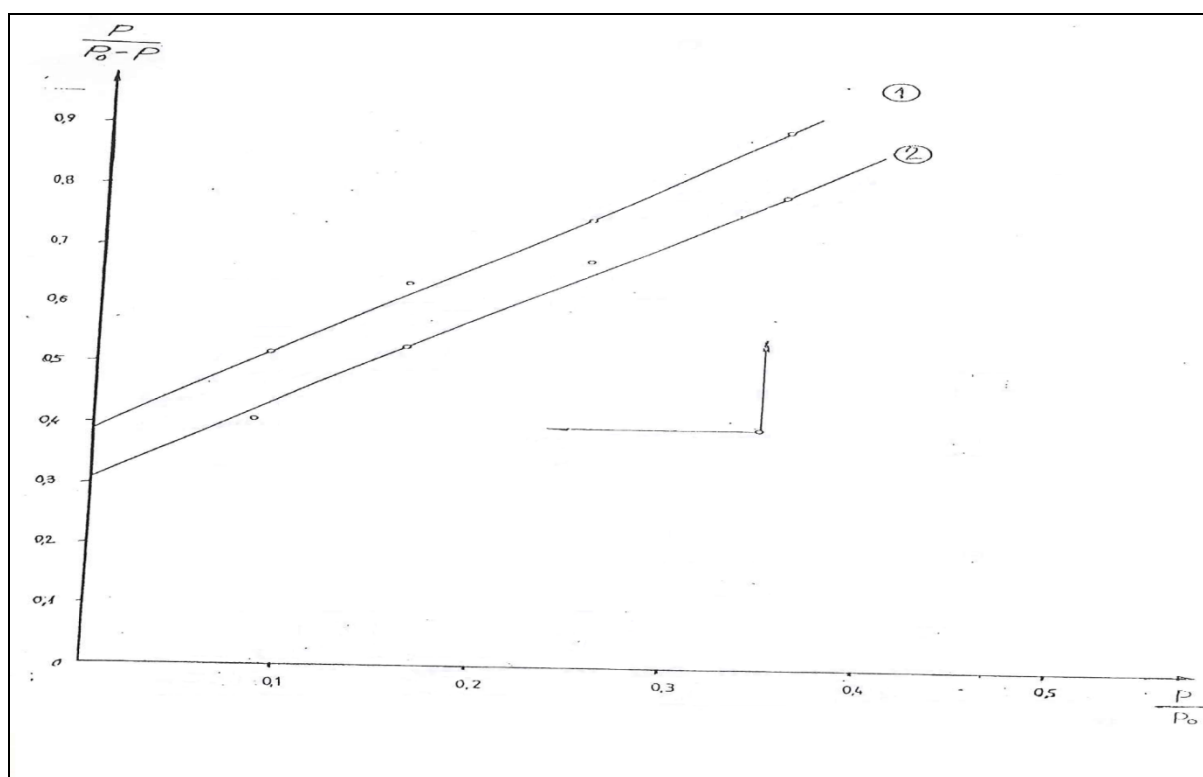


Figure 4. BET Adsorption isotherm (linear form) of the water vapour on residue
1- Particle size above 0.063 mm
2- Particle size below 0.063 mm

CONCLUSION

From the made testing and the obtained results represented with DT and TG curves it can be concluded that the biggest participation in the residue have the minerals kaolinite, getite and ilite.

Kaolinite and getite also suffer most transformations registered with appropriate effects. From the made testing and obtained results can be concluded that the residue beside its use for synthesis of zeolites can be also used as an adsorbent.

Theoretical testing on the adsorption phenomena have the purpose to explain the mechanism of the reciprocal effect adsorbate - adsorbent and adsorbate – adsorbate, but also to be obtained such laws allowing at minimal experimental data to be calculated thermodynamic and kinetic sizes necessary for projecting and optimization of the appliances and units for adsorption.

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**INTEGRATED IMPACT ASSESSMENT OF TECHNOGENIC AND
TOXIC SUBSTANCES ON ENVIRONMENTAL QUALITY IN THE
INDUSTRIAL COMPLEX ”ZELEZARA” SKOPJE**

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ABSTRACT

In this work, toxic waste from the metallurgical industrial complex “Zelezara” is analyzed, where major facilities in the metallurgical industry for ferroalloys and steel production are located. By application of modern methods for evaluation of toxic substances impact, identification of pollution is carried out and situation in the living and working environment is analyzed, in terms of quality of water, soil and air in the industrial capacity and its surroundings. The concentrations of manganese, MnO_2 and SiO_2 in the flue gas and dust in ferromanganese production and the amount and composition of toxic substances in flue gas and waste iron from steel production are analyzed. By applying the graph-analytical method intensity of technogenic and dispersion of toxic wastes in the industrial complex and its surroundings is defined. Based on overall analysis of produced waste, preventive measures and actions to reduce their impact on environmental quality can be given. Evaluation measures for the recycling of waste materials or the introduction of clean technologies in steel and ferromanganese production are presented.

Keywords: *technogenic, toxic substances, environment, ferroalloys, steel.*

INTRODUCTION

Republic of Macedonia has significant capacities for exploitation and enrichment of heavy and non-ferrous metals and smelters for iron, manganese and nickel base ferroalloys and non-ferrous metals: lead, zinc and copper. In ferroalloys metallurgy, as a result of the current favorable economic conditions in metallurgy (high stock exchange price of nickel, ferromanganese and silicomanganese) despite raw material from its own sources, imported raw materials with a high percentage of nickel and manganese are used (Stafilov T. et al, 2012). But with technological processes in the metallurgical facilities, technological waste which contributes to landfill waste materials appear more useful substances, some of which due to its toxic properties represent potential environmental contaminants. Environmental hazardous solid waste from metallurgical production, so called technogenic waste contains toxic components in their composition (manganese, zinc, lead). Sustainable management of industrial technogenic waste in Skopje region is interesting and important issue, which analyzes the impact of industrial waste degradation of the ecosystem and the ability to resolve abovementioned issue (Samsudin M., 1986). Industrial technogenic waste from metallurgical industry in the region of Skopje is concentrated in the industrial zone Zelezara, where the main facilities of the metallurgical industry for the production of steel and ferroalloys are located. In this context, based on scientific knowledge and data base on the status of the environmental aspects it is possible to analyze the main sources of pollution, the state of the environment and the measures and activities to be implemented to protect the environment or mitigate existing and prevent future pollution (Janke D., Slejter M., 2004). Smelter for ferromanganese and silicomanganese production processes about 80.000 tons manganese ore and produces about 40.000 tons ferromanganese slag, filter dust from flue gases and deposited solids from cooling systems. Solid waste has SiO_2 in its composition as technogenic waste as well as Mn in the form of MnO_2 as toxic waste (Trajkovski D., Milosevic D. 1992).

EXPERIMENTAL PART

Identification of pollution is carried out by analyzing the air in industrial capacity and its surroundings. Gas analysis was carried out with apparatus for flue gases for continuous direct probe measurement. Chemical analyses of the concentration of Mn, MnO₂, SiO₂ and Fe have been performed on atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Emissions and dust produced during FeMn and SiMn production process was carried out at two measuring points, the output of the electric oven and gas output from scrubbers (fig.1 and fig.2). Emission was monitored at different burdens of the oven (electricity consumption 15 - 28 MV), for specific stages of the process (charging, melting, molding).

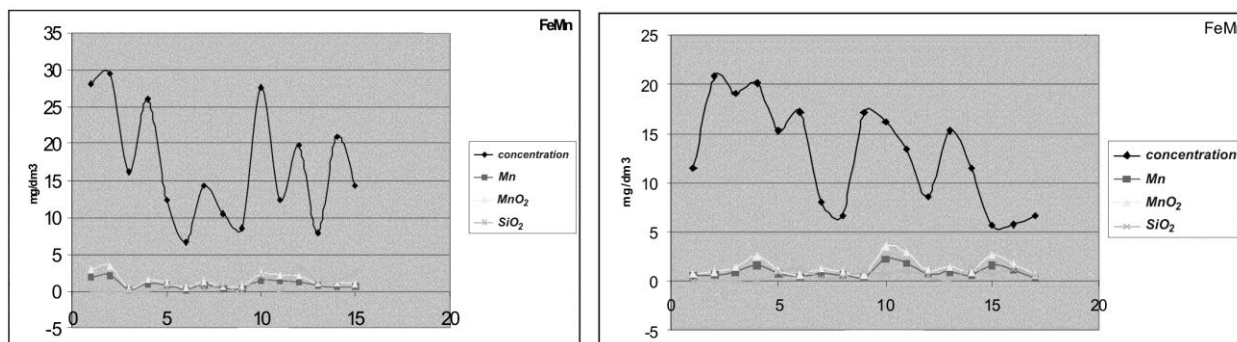


Figure 1. Concentration of technogenic waste (emission of flue gases and dust) during FeMn production (out of the chimney- Tajzen[1] and sintering zone[2])

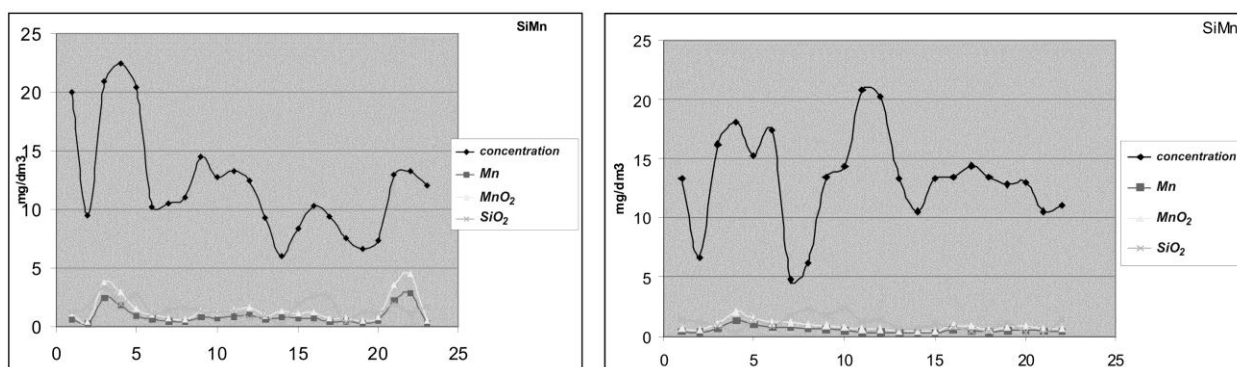


Figure 2. Concentration of technogenic waste (emission of flue gases and dust) during SiMn production (out of the chimney- Tajzen[1] and sintering zone[2])

From the measurements conducted on dust emission the concentration of manganese dust is established to vary in the range of 0.2 - 2.3 mg/dm³ and of manganese oxide between 0.35 - 3.5 mg/dm³. Amount of dust is in the range from 4.5 to 18 mg/dm³. Following concentrations are within the MAC (maximum allowed concentrations) for solid particles, and have the following values: from agglomeration section - 30 mg/dm³ and from electric oven - 20 mg/dm³ solid particles. The concentration of total SiO₂ is in the range 0.22 - 1.97 mg/dm³. Emission of dust from the hood ranges from 6 - 30 mg/dm³ which is higher than the concentration of manganese in the scrubbers, as a result of performance of this type of cleaner. The presence of SiO₂ in the electric furnace dust ranged from 4.5 to 9.5 %.

Emission of dust, i.e. the amount of manganese dust in the agglomeration plant is measured at the chimney for gases from sintering zone (*hot section*) and at the chimney of the cooling zone (*cold section*) which is linked to cyclones of rotational furnace, and eventually exhausted into the

atmosphere. Average value of the emission of dust from the sintering zone is 8.83 mg/dm^3 and from the zone of the cold part is 16.5 mg/dm^3 . The concentration of manganese is in the range of 0.6 to 1.02 mg/dm^3 . The amount of free SiO_2 dust from agglomeration is 3.4 %.

The analysis of the concentration of sediment dust in the close surrounding of the Steel Plant is monitored at six measuring points. Measurement of settling sediment are determined to indicate the real overview of the extent of air pollution in the immediate vicinity and at a distance 1-3 km in the surrounding neighborhoods. Manganese, MnO_2 and iron concentrations in sediment dust were analyzed. From the obtained results it can be concluded that the mean values for the concentration of manganese according to the measuring points is in the range from 0.21 mg/dm^3 to 5.40 mg/dm^3 (fig.3 and fig.4).

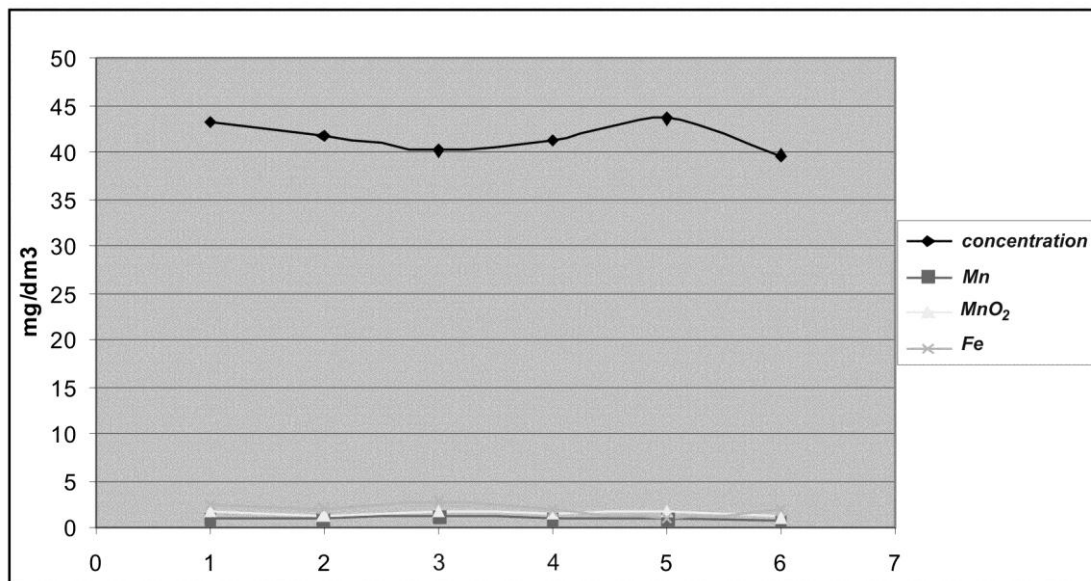


Figure 3. Concentration of sediment dust (hot section)

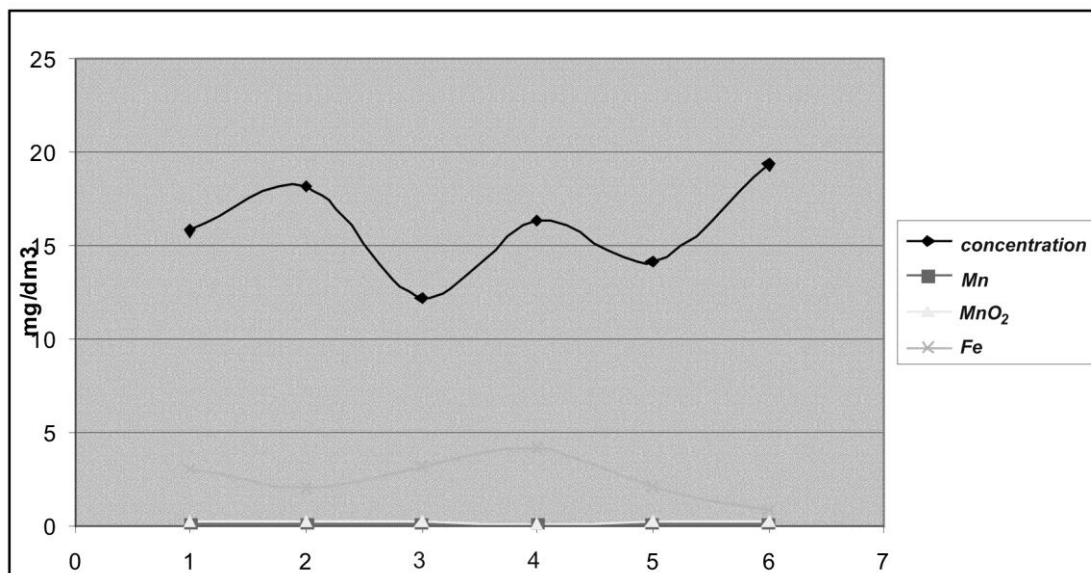


Figure 4. Concentration of sediment dust (cold section)

Emission of smoke from the flue gas in the ferroalloy smelting plant is monitored at four measuring points and the presented smoke values are within the maximum allowed concentrations (fig. 5).

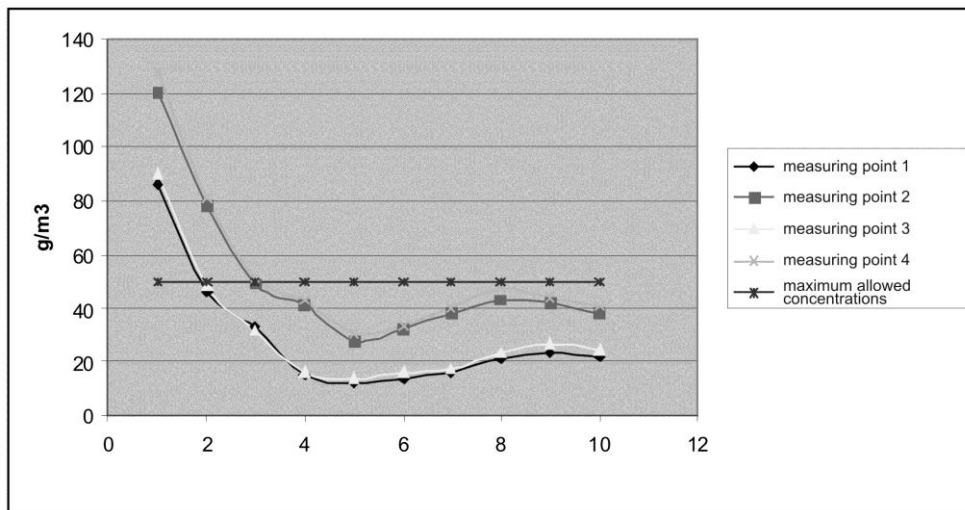


Figure 5. Concentration of smoke

The analysis of average daily concentrations of smoke from four measuring points show that the parameter values of smoke are within the limits of the maximum allowed concentrations.

By using graph-analytical method the intensity of pollution, certain way and timing of the movement of pollutants from hot spots in the vicinity of the investigated area are defined (fig. 6, fig.7, fig.8 and fig.9).

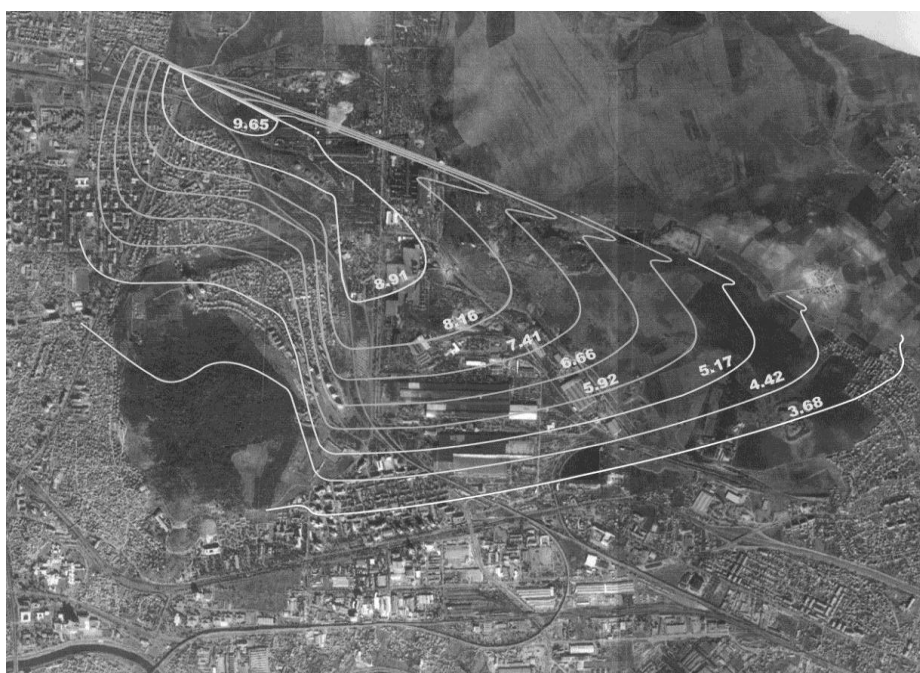


Figure 6. Image of technogenic dust and toxic substances dispersion in the atmosphere - Mn (mg/dm³)

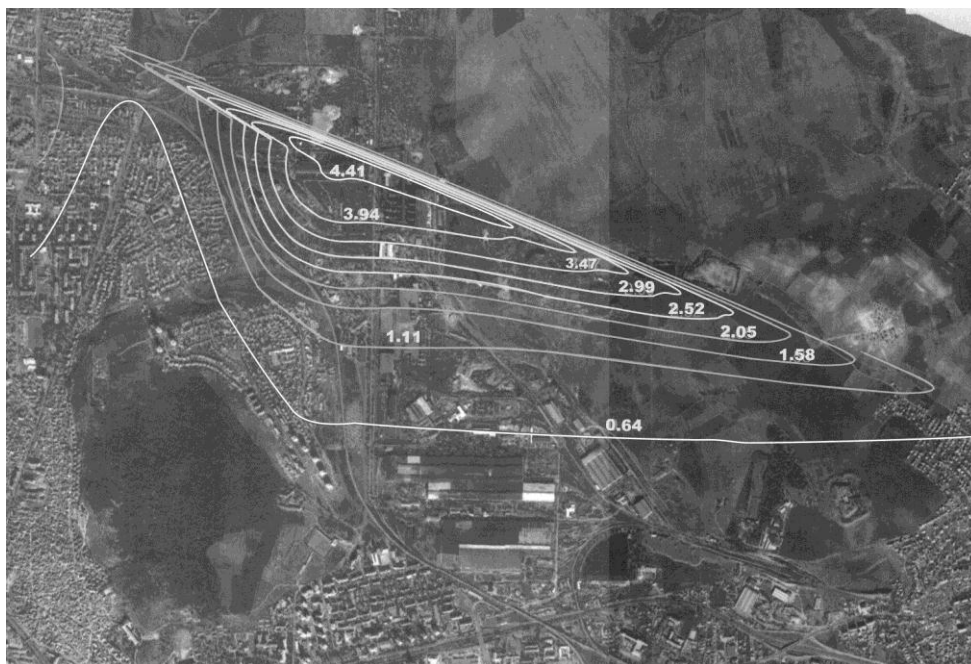


Figure 7. Image of technogenic dust and toxic substances dispersion in the atmosphere - Fe (mg/dm^3)



Figure 8. Image of technogenic dust and toxic substances dispersion in the atmosphere - MnO_2 (mg/dm^3)



Figure 9. Image of technogenic dust and toxic substances dispersion in the atmosphere - SiO_2 (mg/dm^3)

Images present the intensity of the concentration of the components in the composition of the dust in the given monitoring measurement points. From concentration intensity of components it can be concluded that the analyzed components are within the maximum allowed quantities. However, if we take into account the amount of flue gas up to $250,000 \text{ m}^3/\text{h}$ and concentrations of technogenic waste shown in mg/m^3 , annual accumulation of waste soil, overhead and underground water, there is a significant environmental footprint.

CONCLUSION

Emissions and dust produced during FeMn and SiMn production process for different electricity consumption of the oven are analyzed and the composition of the dust (Mn , MnO_2 and SiO_2) is defined related to concentrations in MAC limits. Concentrations of sediment dust for cold and hot section of the electric furnace are determined and it is shown that in the cold section of the concentration of toxic and technogenic wastes are lower. The analyses of average concentrations of smoke are within the limits of the maximum allowed concentrations. By applying the graph-analytical method the front of pollution intensity of technogenic and dispersion of toxic wastes in the industrial complex and its surroundings is defined.

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**ENVIRONMENTALLY CONSCIOUS VEHICLE RECYCLING: A
DISTRIBUTION OF THE CURRENT LITERATURE AND RESEARCH
OPPORTUNITIES**

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ABSTRACT

Waste management is an important topic among environmental issues today and at present, the vehicle sector generates about 5% of the world's industrial waste, whether from vehicles or the plants which produce them. This review paper is the second and final of two reviews by the author that consider the environmental engineering aspect of the end-of-life vehicle (ELV) recycling. In this paper, legislation oriented research papers are systematically addressed and analyzed. In addition, the author presented the major classification scheme and a distribution list of journal papers published in the period 1997-2012. It is concluded that the primary publication outlets for the considered research area are Resources, Conservation and Recycling; Journal of Cleaner Production; JOM; Journal of Industrial Ecology; Waste Management; Journal of Material Cycles and Waste Management; Waste Management & Research; and Minerals Engineering; jointly publishing about 55% of the total identified number of journal papers in the past 5 years.

Key words: review, end-of-life vehicle, legislation, ELV Directive, Japanese Law on recycling of ELVs.

INTRODUCTION

In the early 1990's ELVs have been identified by the EU as priority waste stream. Nowadays, ELVs are a major stream of waste in the EU (ECDGE, 2012). Recycling and reuse of ELV parts and components, and metal recovery is important to governments, manufacturers, suppliers, dismantlers and vehicle recycling factories. The shortening of vehicles average life to about 10-12 years in the EU (Fiore et al., 2012), produced in the last 15 years an impressive enhancement of ELVs number. Moreover, with the number of vehicles expected to increase to 1.85 billion by 2030 and the scrap generated from ELVs expected to be 3.71 billion tones (Paul, 2009), there is a strong motivation to properly process the flow of these materials.

This particular paper is the second and final of two reviews by the author that considers the environmental engineering issues of the ELV recycling. More detailed, legislation oriented research papers are addressed, analyzed and systematically classified in the present paper. On the other side, preceding paper named *Perspectives in vehicle recycling: A state-of-the-art survey*, published in the proceedings of the 2nd International Conference „Ecology of urban areas“ 2012 analyzed general discussion and modeling-oriented papers.

RESULT OF LITERATURE REVIEW

Legislation-oriented research

ELV recycling industries world-wide have been greatly affected by the implementation of various ELV-oriented legislative measures. Hence, in this sub-section the legislation-oriented research papers related to environmental engineering issues of the ELV recycling are classified into 4 categories: (1) *Comparative analysis of ELV-oriented legislations*; (2) *ELV Directive*; (3) *Japanese Law on recycling of ELVs*; (4) *Chinese legislations*.

Comparative analysis of ELV-oriented legislations

Kanari et al. (2003) described the ELV recycling practice in the EU and compared the Japanese Law on recycling of ELVs with the ELV Directive. Gesing (2004) reviewed issues and technologies in recycling with a focus on ELVs and compared the vehicle recycling regulations in the USA, EU and Japan. Sakai et al. (2007) compared the Japanese framework for the recycling of ELVs (the Law on recycling of end-of-life vehicles) with the ELV Directive. Zhao and Chen (2011) gave a brief overview of Japanese and Chinese legislations about ELVs, and also made a comparison of Japanese and Chinese vehicle recycling system. Che et al. (2011) made a comparative analysis of ELV recycling legislations between Japan, Korea and China and provided a several practical insights in an effort to promote international cooperation in these three countries.

ELV Directive

The emergence of vehicle abandonment, pollution, and waste in the EU has resulted in the creation of the 2000/53/EC Directive on ELVs. The ELV Directive has raised the profile of ELVs waste flow as an issue and led to the creation of recycling/recovery solutions that would not otherwise have existed (EC, 2005). It represents the first embodiment of extended producer responsibility in vehicle recycling (Xiang and Ming, 2011) and provides an example of a success framework for other industries to follow (Cherrington et al., 2012). Finally, positive outcomes already originated from the ELV Directive are increased rate of recycling, increased hazardous substance removal and improved information dissemination (Martinuzzi et al., 2011).

Abandoned vehicles represent one of the major problems for vehicle recycling industry. The causes of abandoned vehicles are: the substantial decline in the price of scrap metal, weaknesses in the vehicle licensing and registration system, growth in the pool of second-hand vehicles and significant motoring costs. Smith et al. (2004) examined how the abandoned vehicle problem is likely to develop with the implementation of ELV Directive. Mazzanti and Zoboli (2006) explored how the introduction of free take-back instrument can influence the behaviour of industrial actors towards different innovation paths considering the ELV Directive as a representative case. Muhamad Zamari and Zakuan (2006) explored the impact of the ELV Directive on vehicle design practice. They concluded that the investment in vehicle recycling infrastructure is essential to achieve the ELV Directive's ambitious recovery/recycling quotas for 2015. Gerrard and Kandlikar (2007) are identified that positive effects of implementing ELV Directive are changes in the material composition of new cars, increased design for disassembly, design for re-use and design for remanufacture, increased levels of recycling of ELV materials, and improved information provision. Smith and Crotty (2008) examined the impact of the ELV Directive on UK vehicle component manufacturers using questionnaire tool. Tavoularis et al. (2009) discussed the implementation of the ELV Directive into the Romania, and pointed out that illegal scrap yards and low capacity of the recycling market present major obstacles. Santini et al. (2011) reported on a campaign trial performed in Italy which involved 18 dismantlers, a vehicle shredding plant and 630 ELV representatives. They outlined that ELV Directive recovery rate quota has not been achieved due to the structural weakness of the Italian MSWIs framework. Blume and Walther (2012) discussed the legislative influence on the German vehicle industry and concluded that ELV Directive's future eco-efficiency quotas are the main driving force for material flow innovations. Nicolli et al. (2012) provided an econometric analysis of the effect of the ELV Directive in inducing innovation in ELV recycling area. They confirmed that it has played a pivotal role in inducing technological innovations.

Japanese Law on recycling of ELVs

In an attempt to reduce waste originating from ELVs, the Japanese Government introduced the Law on recycling of end-of-life vehicles (MEJ, 2002). It was enforced in January 2005 and automobile manufacturers and importers were required to collect and recover air bags, chlorofluorocarbons/hydrofluorocarbons and automobile shredder residue generated during the process of recycling ELVs. Hence, the Japanese Law is focused on the proper treatments of airbags,

air-conditioner coolants, and ASR (Nakamura et al., 2012). The purpose of the Law on recycling of ELVs is to create a new recycling system for the proper processing and disposal of this waste flow and their efficient use as resources (Zhao and Chen, 2011). Ogushi and Kandlikar (2005) studied the impact of the Japanese Law on recycling of ELVs from the perspective of product life cycle and discovered that it will have synergistic effects: the higher recovery rate (targeted at 95% by 2015) and the elimination of toxic substances from newly produced vehicles.

Chinese legislations

The vehicle number of China is on constant rise, so the treatment of the ELV becomes a serious environmental and social problem. However, present situation in Chinese vehicle recycling industry greatly differs from practices in the EU and Japan, as a direct consequence of the much cheaper labour cost. In that sense, most of the reusable parts and interior materials can be disassembled before hulk shredding operation (Zhou and Dai, 2012).

Chen (2006) gave a detailed overview of the Chinese Motor vehicle product recovery technology policy (SEPAC, 2006), and concluded that the challenges of implementing this policy are enormous.

Modelling approach

Material selection

Selection of materials for a vehicle application is affected by numerous factors including weight, composition, cost, recyclability, disassemblability and so on. In this part of the paper, the material selection related papers are divided on two categories:

- Design for X - Design for X (DFX) involves different design specialties such as design for recycling, design for disassembly, design for reuse, etc. In past 15 years, environmental factors have also been considered in vehicle material selection at a growing rate. In order to deal with the environmental criteria in vehicle design process, a number of tools and methodologies were presented by researchers. Sodhi and Knight (1998) proposed a product analysis procedure for combined disassembly and bulk recycling which could be used to evaluate the effects of material choices and assembly methods and to eventually facilitate the design of products for better recycling. Villalba et al. (2002) proposed the recyclability index and defined recyclability as the ability of a material to reacquire the valuable properties they originally had. Villalba et al. (2004) used the recyclability index proposed by Villalba et al. (2002) in order to incorporate it in the evaluation and optimization of disassembly and design for disassembly. Reuter and Van Schaik (2004) discussed the theory that relates vehicle design to recycling rates, while Van Schaik and Reuter (2005) presented a methodology how recycling rates should be assessed in practice. Ferrao i Amaral (2006b) proposed a new DfR tool based on the product's connection diagram to provide economically optimum recycling strategies, by combining dismantling, shredding, and post-shredding activities, for achieving specific recycling and reuse rates. Applicability of the developed tool is illustrated on a car seat case study. Santini et al. (2010) used a DfR software named ProdTect® to carry out a study on the impact that pre-shredder dismantling step could have in achieving 85% recyclability rate in 2015. However, they investigated only recyclability rate, while total and energy recovery rates has not been considered. Nazmi et al. (2011) developed artificial neural network (ANN) to predict the critical stress life of a vehicle door so that the optimal reusability can be identified. The optimization results showed that ANN application produced good reliability of the analyzed ELV part. Lu et al. (2011) proposed an easy to operate method that can be used to predict the residual strength and life of reused parts of ELVs.
- Recycling infrastructure - The vehicle recycling infrastructure is an independent business that collects, process and manages ELVs in an environmentally responsible manner and makes available vehicle parts for reuse and remanufacturing, facilitates the metal separation for recycling and allocates the disposal of waste. Isaacs and Gupta (1997) were the first researchers to model vehicle recycling infrastructure using the Goal Programming (GP)

method. They analysed the profitability of dismantlers and recyclers in the following cases of processing PI vehicles: increase in the polymer's share of the vehicle's material composition, mandatory plastics dismantling and increase in the landfill disposal cost for plastics. Boon et al. (2001) used GP to model the vehicle recycling infrastructure and investigated material streams and process profitability for the following AI vehicle processing scenarios: price increase in isolated non-ferrous (NF) metals, more detailed dismantling being carried out, increase in processing costs and change in AI vehicle design. They emphasised that the existing infrastructure, in most cases, is able to process these vehicles while making profits. Boon et al. (2003) expanded mathematical formulation for the recycling infrastructure from Boon et al. (2001) to assess the materials streams and process profitability for several clean vehicles cases. A successful vehicle recycling infrastructure helps to divert materials from landfills and recycles metals from high volume consumer product. Johnson and Wang (2002) created two types of optimisation models: an American model, the only one that is focused on profit, and an EU model in which optimisation depends on the defined vehicle recovery rate. Consequently, the researchers were able to conclude that it was not possible to renew 95% of the average weight of ELVs with existing equipment. Simulation is one of the most commonly used techniques to study the effect of different factors on the ELV recycling performances. Van Schaik and Reuter (2004) critically reviewed the vehicle recycling rate used in the ELV Directive and proposed two novel definitions of the vehicle recycling rate based on the various distribution functions for the lifetime, car weight and composition. Moreover, they used simulation models to characterise fundamental physical recycling limits for vehicle recycling. Bandivadekar et al. (2004) created a simulation model for material flows and economic exchanges (MFEE) to examine the effects of changes in vehicle material composition on the USA automotive recycling infrastructure. They noticed that the Japanese ASR recycling quota of 70% and EU recycling/recovery quotas by 2015 are unachievable without fundamental changes. Amaral et al. (2006) developed a system dynamics model of the Portuguese ELV recycling infrastructure and concluded that mechanical separation technologies are less expensive than component/part removal by dismantlers. Kumar and Sutherland (2009) used simulation MFEE model from Bandivadekar et al. (2004). They found that with change in vehicle design the profit of shredding factories will increase over time, due to the additional revenue from the aluminium in AI hulks. Coates and Rahimifard (2009) developed a post-fragmentation separation model capable of simulating the value-added processing that a piece of automated separation equipment can have on a fragmented ELV waste stream. The model takes the input composition of the ELV waste stream and determines the most likely route of each material flow. Kibira and Jain (2011) used system dynamics simulation to study the impact of hybrid and electric vehicles on the profitability of the recycling infrastructure.

Miscellaneous models

Sakkas and Manios (2003) applied generalized cost modelling approach to obtain a momentary snapshot of the current vehicle recycling practice in Greece. Ladjouze and Rahimifard (2004) presented a cost breakdown structure with parametric cost drivers and proposed a decision support tool for the recovery of process costs. Dantec (2005) created a simple technical cost model of the dismantler and shredder operations to study the recycling cost sensitivity to regional practices. Ferrao et al. (2006) used data obtained from a full scale shredding experiment to develop a technical model and access the eco-efficiency performances of several vehicle recycling strategies. They concluded that ASR mechanical separation may enable more extensive recycling and allow the achievement of the valid recycling quota. Ferrao and Amaral (2006a) developed individual technical cost models of vehicle dismantlers and vehicle recycling facilities to assess the influence of the ELV Directive on the profitability of recycling infrastructure. They identified that the main parameters affecting vehicle recycling facility economics are associated with ferrous scrap, namely its separation efficiency, the international price and the ferrous content of vehicles. Coates and Rahimifard (2006) presented a holistic end-of-life cost model for the vehicle recovery sector and focused on the potential applications of this model to support both high- and low-level decisions. Giannouli et al. (2007) developed a methodology and model for the evaluation of waste produced from road vehicles, both at their end-of-

life and during vehicle operation. Fuse and Kashima (2008) developed an automobile recycling input-output analysis based evaluation method to examine the appropriateness of recycling system scheme for ELVs imported from Japan. Coates and Rahimifard (2008) integrated several techniques, such as Activity Based Costing, regression analysis and time studies, and proposed the ELV costing framework. They framework allows various recycling operators to assess the economic consequences of their investment and processing decisions. Mathieux and Brissaud (2010) proposed method to build an end-of-life product-specific material flow analysis and applied it to aluminium coming from end-of-life commercial vehicles in Europe. However, they pointed out that the implementation of the method requires a lot of field effort. Carcangiu et al. (2010) used Failure mode, effects and criticality analysis method to criticality analyse ELV dismantling procedure in Sardinia, Italy. Vidović et al. (2011) presented modelling approach that could be used to locate collection facilities for end-of-life vehicles. In order to minimise aggregation errors, they developed novel approach to partition service zones into sub zones and incorporated this modification into the traditional formulation of maximal covering location problem. The proposed approach was illustrated on Belgrade city area and obtained results confirmed that it can be used very efficiently to position ELVs' collection facilities. Harraz and Galal (2011) developed a mixed integer linear goal programming model for location-allocation of the ELV recovery facilities and examined the effect of the model parameters on the network design. Hedayati and Subic (2011) proposed a decision-making support framework for recovery of ELVs to provide the integrated sustainable treatment option. It consists of four main stages: benchmarking study, development of the primary set of options, evaluation of options, and systems modelling. A case study illustrating the application of the proposed framework in an Australian context is provided. Matsubae et al. (2011) assessed the effects of alternative ELV treatment processes on copper contamination and CO2 emission by using waste input-output analysis (WIO) analysis. They considered two scenarios: conventional (the copper content is restricted to levels below 0.3%) and recycle-oriented ELV treatment (by intensive manual dismantling the copper content is kept below 0.1%). The obtained results indicated that under the conventional ELV treatment, the amount of copper contamination in crude steel production was 2% higher than that obtained under the recycle-oriented scenario. Modaresi and Müller (2012) developed a dynamic material flow model for the global vehicle system to assess the likelihood, timing, and extent of a potential aluminium scrap surplus and pointed out that rapid penetration of dramatically improved scrap sorting technologies for ELVs is immediately needed. Iranpour et al. (2012) discussed about the shortage of the Chinese vehicle recycling industry and illustrated three China-tailored value analyzing models: model of ELV to raw materials, model of intermediate scrap to product, and model of remanufacturing. Nakamura et al. (2012) used a hybrid input-output analysis approach to quantify the quality- and dilution losses associated with the recycling of ferrous materials from ELV due to the mixing of copper.

THE MAJOR CLASSIFICATION SCHEME AND DISTRIBUTION OF JOURNAL PAPERS

The details of the major classification scheme and the papers that come under each such classification are presented in Table 1.

Table 1: Summary of references related with environmental engineering issues of the ELV recycling¹

Classification and sub-classification	Literature	Total
<i>Review papers</i>	Go et al., 2011; Ilgin and Gupta, 2010; Kumar and Sutherland, 2008; Mayyas et al., 2012	4
<i>General discussion</i>		36
<i>Vehicle recycling practices world-wide</i>	Altay et al., 2011; Barakat and Urbanic, 2011; Bassam et al., 2011; Beck, 2009; Paul, 2009; Chen and Zhang, 2009; Chen et al., 2010; Chen, 2005; Cheng, 2012; Dalmijn and de Jong, 2007; Edward et al., 2006; Espartero et al., 2010; Forton et al., 2006; Joung et al., 2007; Kim et al., 2004; Muhamad Zameri and Blount, 2006; Nakajima and Vanderburg, 2005; Nwachukwu et al., 2011; Sakai et al., 2011; Serrona et al., 2010; Togawa,	22

¹ All reviewed papers (parts I and II of presented review paper) are included in the presented major classification scheme.

	2008; Wang and Chen, 2012	
<i>Extended producer responsibility</i>	Forslind, 2005; Manomaivibool, 2008; Wilts et al., 2011	3
<i>Remanufacturing</i>	Jaafar et al., 2009; Seitz, 2007	2
<i>ELV-generated materials recycling</i>	Bellmann and Khare, 1999; Brahmst, 2006; Hatayama et al., 2012; Ruhrberg, 2006	4
<i>Miscellaneous content</i>	Agbo, 2011; Amza et al., 2011; Bellmann and Khare, 2000; Marsh, 2005; Yu et al., 2011	5
Modelling approach		59
<i>Life Cycle Assessment</i>	Alves et al., 2010; Lazarevic et al., 2010; Gaidajis et al., 2011; Munoz et al., 2006;	4
<i>Sequencing planning</i>	Knight and Sodhi, 2000; Sodhi et al., 1999	2
<i>Production planning</i>		16
Deterministic models	Choi et al., 2005; Coates and Rahimifard, 2007; Gupta and Isaacs, 1997; Li et al., 2011; Miemczyk, 2008; Qu and Williams, 2008; Simić and Dimitrijević, 2012a, 2012b; Williams et al., 2007	9
Stochastic models	Castro et al., 2005; Ignatenko et al., 2008; Pehlken and Müller, 2009; Reuter et al., 2006; Van Schaik et al., 2002; Van Schaik et al., 2003; Van Schaik et al., 2004	7
<i>Material selection</i>		19
Design for X	Ferrao and Amaral, 2006b; Lu et al., 2011; Nazmi et al., 2011; Reuter and Van Schaik, 2004; Santini et al., 2010; Sodhi and Knight, 1998; Van Schaik and Reuter, 2005; Villalba et al., 2002; Villalba et al., 2004	9
Recycling infrastructure	Amaral et al., 2006; Bandivadekar et al., 2004; Boon et al., 2001, 2003; Coates and Rahimifard, 2009; Isaacs and Gupta, 1997; Johnson and Wang, 2002; Kibira and Jain, 2011; Kumar and Sutherland, 2009; Van Schaik and Reuter, 2004	10
<i>Miscellaneous models</i>	Carcangiu et al., 2010; Coates and Rahimifard, 2006; Coates and Rahimifard, 2008; Dantec, 2005; Ferrao et al., 2006; Ferrao and Amaral, 2006a; Fuse and Kashima, 2008; Giannouli et al., 2007; Harraz and Galal, 2011; Hedayati and Subic, 2011; Iranpour et al., 2012; Ladjouze and Rahimifard, 2004; Mathieux and Brissaud, 2010; Matsubae et al., 2011; Modaresi and Müller, 2012; Nakamura et al., 2012; Sakkas and Manios, 2003; Vidović et al., 2011	18
Legislation-oriented research		16
<i>Comparative analysis</i>	Che et al., 2011; Gesing, 2004; Kanari et al., 2003; Sakai et al., 2007; Zhao and Chen, 2011	5
<i>ELV Directive</i>	Blume and Walther, 2012; Gerrard and Kandlikar, 2007; Mazzanti and Zoboli, 2009; Muhamad Zameri and Zakuan, 2006; Nicolli et al., 2012; Santini et al., 2011; Smith and Crotty, 2008; Smith et al., 2004; Tavoularis et al., 2009	9
<i>Japanese Law on recycling of ELVs</i>	Ogushi and Kandlikar, 2005	1
<i>Chinese legislations</i>	Chen, 2006	1

From Table 2, it can be seen that the primary publication outlets for the environmental engineering issues of the ELV recycling research are Resources, Conservation and Recycling; Journal of Cleaner Production; JOM Journal of Minerals, Metals and Materials Society; Journal of Industrial Ecology; Waste Management; Journal of Material Cycles and Waste Management; Waste Management & Research; and Minerals Engineering; jointly publishing about 54% of the total journal papers in the whole analysed time period. More detailed, those scientific journals published about 56.6% and 55.3% of the total identified number of journal papers in the past decade and in the past 5 years, respectively.

Table 2: Distribution of journal papers in the period 1997-2012²

Journal	Year of publication											Total
	Prior to 2003	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	
<i>Resources, Conservation and Recycling</i>	1		2		2	1		2	3	3	3	17
<i>Journal of Cleaner Production</i>				1		3	2		1	1	1	9
<i>JOM</i>		1	1	1	1	1		1				6
<i>Journal of Industrial Ecology</i>	2	1			1					1		5
<i>Waste Management</i>			1					1	1	1		4
<i>Journal of Material Cycles and Waste Management</i>						2	1			1		4
<i>Waste Management & Research</i>										1	2	3
<i>Minerals Engineering</i>	1		1		1							3
<i>Others (29 Journals)</i>	7	1	2	4	7	1	5	1	1	9	5	43
Total (37 Journals)	11	3	7	6	12	8	8	5	6	17	11	94

Note: Others (37 Journals): *Advanced Materials Research; Advanced Science Letters; Annals of the CIRP; Bulletin of Science, Technology & Society; Business Strategy and the Environment; Car Recycling; CIRP Annals - Manufacturing Technology; Computers & Industrial Engineering; Ecological Economics; Environmental Economics and Policy Studies; Environmental Monitoring and Assessment; Environmental Science & Technology; European Journal of Operational Research; International Journal of Automotive Technology; International Journal of Computer Integrated Manufacturing; International Journal of Life Cycle Assessment; International Journal of Mineral Processing; International Journal of Production Economics; International Journal of Production Research; International Journal of Sustainable Design; International Journal of Sustainable Manufacturing; International Journal of Sustainable Water and Environmental Systems; International Journal of Technology, Policy and Management; Journal of Applied Sciences; Journal of Engineering Design; Journal of Environmental Management; Journal of Environmental Sciences; Journal of Manufacturing Systems; Jurnal mekanikal; Nigerian Journal of Technology; Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture; Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering; Reinforced Plastics; Renewable & Sustainable Energy Reviews; Technological Forecasting and Social Change; Technovation.*

CONCLUSIONS AND DISCUSSION

This paper is the second and final of two reviews by the author that considers the environmental engineering issues of the ELV recycling. In this particular part we comprehensively analysed the contents of all identified research papers and classified them in the belonging categories. This resulted in collection of 115 papers published between 1997 and 2012. More detailed, in this research (parts I and II of presented review paper) 94 journal publications, 13 conference proceedings, 6 book chapters, 1 report and 1 MSc thesis have been reviewed. Previous figures clearly indicate the great relevance and tremendous importance of the analyzed topic in environmental engineering research.

From the distribution list of journal papers it can be concluded that the primary publication outlets for the considered research area are *Resources, Conservation and Recycling; Journal of Cleaner Production; JOM; Journal of Industrial Ecology; Waste Management; Journal of Material Cycles and Waste Management; Waste Management & Research; and Minerals Engineering*; jointly publishing about 56.6% and 55.3% of the total identified number of journal papers in the past decade and in the past 5 years, respectively.

On the basis of this review, the following recommendations are presented:

- One of the major weaknesses of previous research is that little has been done to document present industry practice in case studies or surveys.
- Material waste reduction, recyclability of materials and innovative forming processes able to recycle materials have to be considered in more details.

² All reviewed papers are included in the presented distribution list of journal papers.

- There is a lack of research of uncertainties in the vehicle recycling system, none of the previous studies analysed the linkage and trade-off's between decision risk and system performances, and no previous research was reported on interval-based programming for vehicle recycling problem.

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**PROCEDURES FOR METALLURGICAL PROCESSING OF COPPER
SECONDARY RAW MATERIALS**

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ABSTRACT

Copper is a widely applicable metal and therefore the different composition and form of copper waste is generated. The technological procedures for their processing include two basic stages: pretreatment of the copper waste and its further metallurgical processing. All operations of pretreatment are influencing the quality of metallurgical processing. For metallurgical processing of raw materials prepared for the purpose of obtaining copper and copper alloys the shaft, flaming and short-drum furnaces, converters and electric furnaces (electric resistant, electric arc and induction furnaces) are used.

Key words: *copper, secondary raw materials, metallurgical processing, smelting.*

INTRODUCTION

Importance of use of non-ferrous secondary raw materials is reflected in the economic effects, through the preservation of primary resources, energy saving and prevention of environmental pollution (Muchova, L., et al., 2011, Jacobi, 1980, Shamsuddin, 1986). Copper is a widely applicable metal and therefore the different composition and form of copper waste is generated (Ilić et al., 2000). The most important waste material generated in production and processing of copper is scrap metal of copper and its alloys, scrap of copper cables and wires as well as slag, chips and dust from the production and processing of cathode copper and copper alloys, first of all brass (Ilić et al., 2010). In terms of pretreatment and processing technology, there are different applied procedures depending on the type of raw material.

Under the preparation of copper and copper alloys scrap it is considering to bringing them into a state which will provide efficient metallurgical processing. That means bringing waste to the standard gauges and size, separation of ferrous and non-metallic parts from the basic mass of metal, degreasing, removal of moisture and others. Conscientious and properly preparation of non-ferrous metal scrap contributes to an minimal losses of metals in metallurgical processing, reduction of fuel, energy and flux consumption, more efficient use of metallurgical and transportation equipment, and it will improve aggregate productivity and quality of the obtained metals and alloys (Friedrich, B. et al., 2006).

Preparation of copper and copper alloys scrap include sorting, electromagnetic and mechanical separation, degreasing and drying, packing into briquettes, electrostatic separation and other procedures are used depending on the type of secondary raw materials (Ilić et al., 2010, Kuprjakov and Radzihovski, 1988).

Copper cables and wires scrap preparation includes cutting, crushing, air separation and sieving; with the aim of separating the copper from the electrical insulation. The brass slag is grinded, followed by separation metal from oxide components (Matković et al., 1995). The process of chips preparing is more complex and consists of sorting, sieving, degreasing, magnetic separation, and briquetting.

Prepared copper and copper alloys scrap presents a valuable raw material for further metallurgical processing. All preparation operations directly affects on the quality of metallurgical processing, i.e. melting process, and therefore the quality of the obtained product.

METALLURGICAL PROCESSING OF COOPER SECONDARY RAW MATERIALS

Secondary row material generated in foundries from processing of liquid metal presents a great share of all cooper total waste which is recycled. The advantages of using these types of scrap material are as follows:

- the total quantity and dynamics of generation is known, so its use can be predicted in advance, which has a positive impact on the cost price,
- chemical composition of material is well known, which make him applicable for high-quality products production,

This return material is mostly consists of:

- gating of moulds and other materials obtained from the cleaning of moulds,
- bad products, abandoned in the manufacturing processes due to various defects,
- chips from cutting and mechanical processing,
- dross generated in the melting process of cooper and his alloys.

Beside basic raw material, during the melting process, the additional materials must be used in order to obtain high-quality castings. Additional materials should ensure protection of the basic material from oxidation and absorption of gases and to remove impurities and gases in the melt. In addition, it should allow obtaining of a better structure, by modifying material in the liquid state. As modifier, hardly soluble metals (Ti, V, Mo, W etc.) are used during the production of cooper alloys.

In order to provide appropriate purity, protection of molten metal during the melting process must be undertaken. Molten metal absorbs the gases forming oxides. Charcoal is the simplest means to protect the copper. Its application on the surface of the melt creates a reducing atmosphere and prevents the formation of copper oxide, regardless of its high affinity to oxygen. For alloys with high melting temperature (Cu-Sn, Cu-Al brass and similar), to protect the melt from oxidation a combination of potash, borax, and broken glass are used. For deoxidation of copper and its alloys phosphorus-copper alloy (Cu₃P) is used, which is characterized by a lower melting temperature than the melting temperature of a given material.

One of the most efficient methods of removing gases from the molten material is inert gas blowing, and nitrogen is the most common gas used for this purpose. Nitrogen is not only used for degassing, but also serves for the purification of materials by non-metallic inclusions and metal oxides present in the molten metal. By mixing materials, nonmetallic inclusions and oxides of metals are rising to the prominence of liquid bath. In addition to inert gas, for degassing salts based on chlorine are used.

One part of copper scraps is sufficiently pure so it can be processed without further refining. This includes scrap wire, copper sheet and the like. In the mentioned wastes copper is mixed with the other elements (phosphorus, tin, silicon, zinc, etc.) in a small amount.

Basic rule that applies for remelting of scrap is to heat furnace sufficiently, before batching, in order to provide more rapidly formation of liquid bath as well as melting of small pieces avoiding excessive oxidation during the melting. Congenerous materials should be melted and cast into ingots, and only after analyzing exploit it for making copper alloys. If metal is used for making alloys, it should be completely deoxidised. For all other types of scrap of copper and its alloys, refining process is applied to remove impurities and bringing them to tolerable levels.

Production of copper alloys from secondary raw materials is associated with a series of difficulties which usually appears as a consequence of the fact that the alloy composition includes metals with different physical and chemical properties (melting and vapor temperature, vapor pressure, specific weight, oxygen affinity, etc.).

During the melting, the components present in the batch are in constant interaction with gases present in the furnace (oxygen, nitrogen, water vapor, carbon dioxide, carbon monoxide, etc.). These gases act as oxidants according to one group of the present elements, and according to the others as a reducer. During the heating of furnace up to the melting of metals reducing atmosphere in furnace is useful, while after the melting process slightly oxidizing atmosphere inside of furnace is preferred. Variety of aggregates, for melting of secondary raw materials in order to obtain copper alloys, has been applied, such as: shaft furnace, converter, reverberatory (pot and bath) furnace, and electric furnaces (electric arc, resistance, induction furnaces) (Muchova, L., et al., 2011).

Melting in shaft furnaces and converters

One of the oldest metallurgical processes for the smelting of copper secondary raw materials is smelting in shaft furnaces. It is reduction melting, by its character. These furnaces can be both rectangular and round cross-section forms with the surface area of nozzle 1-10 m². Efficiency of furnace is 30-40 t/m² on day and highly depends on the quality of the batch which also affects on the reducer consumption, and if content of zinc and tin is high, amount of reducer should be over 10% of batch weight.

Products from the shaft furnace melting process are: black copper (containing zinc, tin and lead as impurities), dust (containing zinc, tin, lead, copper and other) and slag. Exhaust of slag and metal is performed together in one unit, where separation and obtaining of slag with low metal content is accomplished. Thus obtained black copper is refined from undesirable impurities, and sometimes it is used to create alloys. Complex utilization of all components from dust is realized only in certain smelters.

The U.S. Company, "American Smelting and Refining Co" (ASARCO) during the seventies was developed a special construction shaft furnace for melting metals, as shown in Figure 1. The furnace is designed to dissolve big-piece clean copper fractures and copper cathodes and it heats with liquid or gaseous fuel. In the upper part of the shaft furnace large pieces of the batch are charged. Furnace capacity is very large (up to 80 t/h Cu) and can easily be regulated by the burner nozzle (Günter, J., et al., 1999).

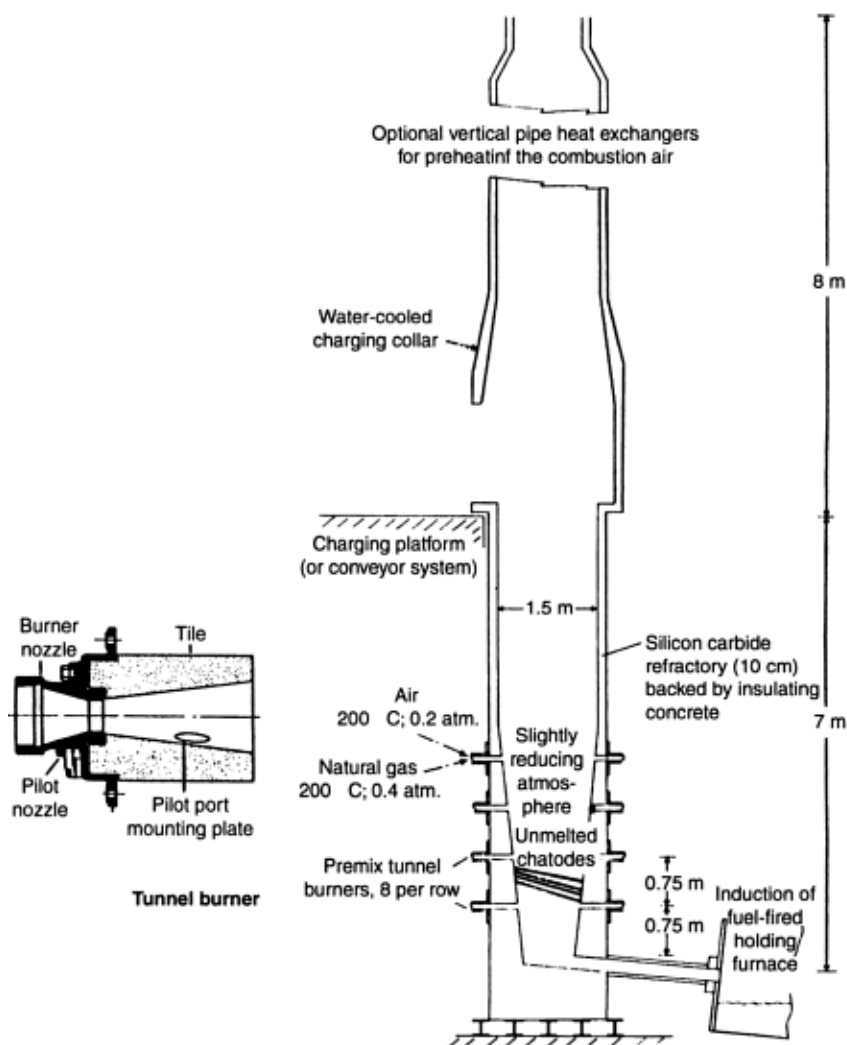


Figure 1. ASARCO shaft furnace for melting cathodes. The insert shows a premix tunnel burner in which combustion is complete before the gases enter the shaft

During of melting inside the shaft furnace until obtaining a black copper, copper recovery was 98% whereby in the slag goes 1.5 – 2.0% and in the dust 0.2 – 0.4 % from the charged copper. Share of zinc which goes in black copper is 12-15%, 45-55% vaporizes with gases and condenses into dust and 30% goes in slag. Share of lead, which goes in black copper, is about 60-65% and rest of it is disposed between dust and slag. And the share of Tin, which goes into black copper, is 65-75% Ti, 25-30% into the slag, and 2-4% goes with gas in dust.

Mixed copper fractures with poorly controlled composition frequently is processed in the converter, by melting batch with reducer and blowing air into melt, for removal of volatile impurities - zinc, tin and lead. Volume of converters for melting of fractures and wastes of copper and its alloys is so great that it can accommodate 8-20t of metals. The main disadvantage of fracture and waste processing in the converter compared to the melting of the shaft is dissemination of useful components in different products. These losses could be reduced by good preparation of scrap for melting. Converters generally works in conjunction with the shaft furnace, so the black copper generated in shaft furnace is further processed in the converter to remove impurities from the metal. Improving the process of converting the black copper is realized by improvement of the mechanical cleaning with nozzle and increasing of their dimensions, using oxygen-enriched air, pressurization etc. One of the promising ways of process intensification is use of natural gas to partially replace the coke. In addition evaporation of zinc is very intense and reaches 95-96%.

Melting in the flame and short-drum furnaces

When a small amount of molten metal is required pot furnaces (stable and tilt) are used. By burning of gaseous or liquid fuels, required amount of heat is obtained. Solid fuel is rarely used due to low utilization of heat. The largest application for melting of primary and secondary raw materials has the graphite pot manufactured from a mixture of fireclay, crushed coke, graphite etc.

Melting the primary and secondary copper-based raw materials in the smelting plant is performed in cases where larger quantities of metals, for melting large casts, are required. In the smelting plant metal is heated directly contacting with a flame and gases output as the heat radiation of combustion products and the fiery furnace walls. This provides a more complete utilization of heat in comparison with pot furnaces. Advantages of fiery furnace in relation to the pot furnace are the production of large quantities of homogeneous melt structure, control of chemical composition during the process, successful refining of the melt with flux material, due to the small depth and large surface of the metal bath, remelting of large pieces of waste etc. The main disadvantages are the direct contact of molten metal with a flame, furnace atmosphere control difficulty, possibility of saturation of molten metal with gases etc (Rentz, O. Et al., 1999).

Furnaces often work in conjunction with the mixer. Working of furnace in conjunction with the mixer reduces the period of metal spills and increases the capacity of the furnace up to 15-20%. Utilization of metal in the finished product is 93-95%, into a return material goes 3-4 % and in slag 1.5-2.5%. The amount of flux is 1.2 to 2.4% of the total weight of batch.

For melting brass and bronze in the form of blocks and castings, short drum furnaces are used. Furnace capacity is 7-10 t of batch and they are made along with casting tape. They have a length of about 3m and 2m in diameter. Prepared copper secondary raw materials and fresh raw materials are used for melting, and alloying is performed to obtain alloys of standard quality. The time of melting in these furnaces is about 8 hours. The temperature of metal in the furnace before casting is 1100-1150°C and combustion of zinc is 15-17%. Furnaces can be equipped with tubes (spears) for the oxidation of metals. The air is injected under the pressure through pipes immersed in the liquid metal and oxidation of impurities is carried out to achieve the required content of copper. After this, oxidation process is accomplished and alloying is performed after which alloy is cast into blocks.

Related furnaces, only larger in size (length of 6 m with 2.8 m diameter - external measures) are used to produce flame refined copper cathodes and wire-bars. These furnaces also have a pipe for insufflation of air and simultaneously, after the blowing of air, deoxidation is done. Charge in the furnaces is about 18-26 t and melting time of a batch is 10-12 hours. Furnaces have a greater dimension in order to perform melting, oxidizing refinement followed by reduction and deoxidation of metals. These operations and copper production are performed in the shaft furnaces, in the converter and the so-called anode furnaces, as to in two or more melting unit. The process of melting consists of the following phases: melting, oxidation of impurities, removing the slag and reduction of dissolved oxides. After this phase, the casting is performed at temperatures of 1170-1190°C. Consumption of fuel (oil or fuel oil) in these furnaces is about 5 kg / min, and with smaller consumption is about 2.5 kg/min (Rentz, O. Et al., 1999).

Melting of brass and bronze is made in small furnaces. Oxidation of impurities is possible by inserting a spear through the air is blown. The ratio of length to diameter is such that the length of the furnaces is slightly higher than its diameter. Furnaces for copper melting, after a flame refinery process, are significantly longer and greater number of metallurgical processes is performed in them. In these furnaces, after the merging in oxidizing environment, copper oxidation is performed after the batch melting and slag removal by immersion tube (coated with a refractory insulating material) and blowing compressed air (1-4 bar) in molten copper. Thereby the copper oxide is produced which subsequently oxidizes impurities (Zn, S, Fe, Pb, Sn, As, Ni, Bi and Ag). Formed oxides are removed through the slag with SiO₂ or evaporate and condense through dust. After removing the slag molten metal contains up to 11% copper (I) oxide. The reduction is achieved by introducing carbon from the

raw beech logs in the melt. The atmosphere in the furnace becomes reducing and metal surface is covered with wooden charcoal. This reduction process is performed in two phases. Immediately after deoxidation which is reduction phase to the density, afterwards charcoal is added and inflamed which is reduction to the forgeability. For the oxidation of copper, phosphorus-copper alloys can also be used. After deoxidation casting of metal is carried out on the casting machine.

Melting in the induction furnaces

Melting in induction furnaces is simpler compared to the previously described procedures of melting, in the light of process aspect, although technically these furnaces are much more complex and more expensive units. They are mainly used for melting brass, Copper and others. They are mainly used for melting brass, copper and others. Secondary copper and copper alloys may occur in the form of clump and in the form of chips. It is known that the chips are characterized by large surface area and their remelting is much more difficult.

Induction furnaces can be channel and pot. In channel furnaces liquid metal in the channel is always preheated, and with electromagnetic forces runs through the channel and the bottom of the furnaces giving off heat to material required for melting. In a pot induction furnace melting heat is produced in the material himself. Through coils magnetic field is established through the charging material where it induces a current producing heat of fusion. Rapidly immersion of chips material in the molten metal is essential to reduce the oxidation loss. This is especially important for melting brass due to the presence of zinc. For pot induction furnaces running in the bath is intense so mechanical mixing is not required. In addition, the movement causes the insinuation of chips which are melted in the absence of air.

Induction furnaces are mainly used for brass remelting. Described characteristics of the induction furnaces indicate that the motion of molten mass is determining factor for the economic remelting brass chips, as cheaper charge. Remelting of chips in the pot induction furnace must be conducted in the shallow and wider pot than with clump scrap remelting. These constructive changes have been obtained from following reasons:

- in the upper part of the pot should be a intensively running of material mass,
- in the waste must be induced a large electric power concurrently with the intensively running of material,

Channel furnaces for brass and copper have a number of advantages over the pot furnaces:

- a higher level of electric utility,
- lower electric power for the same melting capacity,
- slightly lower investment costs,
- lower power consumption,
- lower costs for ceramic walling etc.

However, when considering oxidation loss of metal in melting process of chips, reversed economic effects are obtained. For example, the pot furnaces capacity of 7.5 t/h, with charge composed of 80% of scrap and 20% of clump scrap oxidation loss of metal is about 3% or 225kg. With proper channel furnaces with charge of 30% of chips scrap oxidation loss of metal is about 4.5% or 340kg.

Comparing the costs of melting, they are 12% lower in the pot furnaces for annual production of 36 000 t, even for charge of 60% of chips, 20% of brass, 12% of cathode copper and 8% of zinc in block. With annual production of 15 000 t, with the same charge composition melting costs are 11.4% lower in the pot furnaces. These facts indicate that use pot furnace is economical when sufficient quantities of chips are processed. If the share of chips in the charge is less than 20% pot furnace is not recommended due to the lower cost.

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**PERSPECTIVES IN VEHICLE RECYCLING: A STATE-OF-THE-ART
SURVEY**

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ABSTRACT

End-of-life vehicle (ELV) is a specified vehicle which is discarded or is to be discarded by its registered owner as waste. ELV waste flow is an important environmental concern, because of its rapidly increasing amount and special composition of hazardous substances. Therefore ELV recycling is a matter of country's attitude towards supporting the environment preservation and it is emerged as a novel area of scientific research. In this paper, the environmental engineering issues of the ELV recycling are reviewed, while general discussion, mathematical modelling and legislation oriented research papers are addressed.

Key words: *review, end-of-life vehicle, general discussion, environmental engineering, mathematical modelling.*

INTRODUCTION

The transportation sector is one of the most complex and important direction of world economy development which is strongly correlated with new trends in science and innovation in technologies, and it has proven to be particularly difficult territory for the advancement of sustainable development oriented policies (Janicka et al., 2011). Additionally, it should be noted that the EU is the largest producer of motor vehicles in the world (Martinuzzi et al., 2011).

End-of-life vehicle (ELV) is a specified vehicle which is discarded or is to be discarded by its registered owner as waste. It is composed of many different materials that have a large impact on the environment such as mercury, cadmium, hexavalent chromium, anti-freeze, brake fluid and oils (Nicolli et al., 2012). ELVs are estimated to reach a volume of 14 million tonnes by 2015 just in Europe alone as the number and average weight of vehicles increases; this can be expected to further increase beyond 2015 (Cherrington et al., 2012). Therefore, the growing numbers of cars worldwide offer an extensive waste flow of valuable and/or toxic materials to be analyzed (Gaidajis et al., 2011).

From a waste management point of view, the concerns related to ELVs are twofold: on the one hand, about 25% of this waste flow has to be considered hazardous, and on the other hand about 75% of this waste flow (mainly steel and aluminum) can be easily recycled (Nicolli et al., 2012). In that sense, modern ELV recycling not only is supposed to help protect the environment and natural resources, but is also expected to work economically (Amza et al., 2011). However, the management of ELV recycling process is complex and requires a multi-faceted approach in order to recover, re-use, and recycle the materials (Stagner et al., 2012).

Due to the extensive numbers of vehicles that are in use and their bad environmental impact, there are numerous papers focusing on waste management of ELVs. In this paper, the environmental engineering issues of the ELV recycling are closely analyzed, while general discussion, mathematical modelling and legislation oriented research papers are addressed. However, this paper is only the first of two reviews by the author that consider the environmental engineering aspect of the ELV recycling, and due to enacted limit in paper's length, only general discussion papers and the first part of modelling-oriented research are systematically analyzed. Subsequent paper named *Environmentally conscious vehicle recycling: A distribution of the current literature and research opportunities*, to be

published in the proceedings of the 2nd International Conference „Ecology of urban areas“ 2012 will analyze and systematically classify a plethora of legislation-oriented research and the second part of modelling-oriented papers.

RESULT OF LITERATURE REVIEW

Due to the increasing importance of the subject of ELV recycling, a considerable number of research papers have been published in the past 15 years. Therefore, the purpose of this review paper is to give a comprehensive overview of the recent literature related to the environmental engineering issues in the area of ELV recycling.

Recently, several review papers have been published. Kumar and Sutherland (2008) provided an overview of studies on the vehicle recovery infrastructure and identified the following limitations in the available mathematical models: inadequate description of the complex material flows and economic transactions within the infrastructure, minimal consideration of market factors (such as scrap-metal prices), lack of consideration for government policies and limited variety of examined future scenarios. Ilgin and Gupta (2010) gave an excellent overview of the literature on environmentally conscious manufacturing and product recovery and concluded that more studies are needed to better control the effects of uncertainties. Go et al. (2011) presented a review on ELVs, recycling, disassemblability methods and the related fields. Mayyas et al. (2012) investigated the sustainability research within the vehicle industry, through a review of the different studies in vehicles' life cycle, disposal and end-of-life analyses, and the different sustainability metrics and models used to quantify the environmental impact.

As can be seen from contents analysis of published review papers, the scope of every previous review is limited to a specific area in the ELV recycling area. In this paper, we present a holistic view of the environmental engineering issues of the ELV recycling by covering a wide range of previously published papers. The literature is organized into three main sub-areas; namely, general discussion, mathematical modelling and legislation oriented research papers. In each main sub-area, papers are classified into appropriate sub-categories. However, one should keep in mind that this article only reviews general discussion and modelling-oriented papers, due to previously mentioned limit in paper's length.

General discussion

In this sub-section of the paper, the general discussion papers related to environmental engineering issues of the ELV recycling are classified into 5 categories: (1) *Vehicle recycling practices world-wide*; (2) *Extended producer responsibility*; (3) *Remanufacturing*; (4) *ELV-generated materials recycling*; (5) *Miscellaneous content*.

Vehicle recycling practices world-wide

Kim et al. (2004) surveyed using some questionnaires the ELVs recycling and recovery rates, and management status in Korea to aid the establishment of policies for the management of ELVs. Chen (2005) reviewed the Chinese ELV legislation, the ELV dismantling industry, the challenges and opportunities of ELV recycling and the state-of-the-art of remanufacturing of ELVs in China. Nakajima and Vanderburg (2005) described and analyzed the German ELV take-back system in terms of its impact on the environment and the vehicle producers involved, and found that it is not one that maximizes the value recovered from ELVs. Forton et al. (2006) discussed issues and drivers at play on ELV management in the UK, and outlined their actual effects on vehicle recycling practice. Edwards et al. (2006) described the recovery infrastructure and practices in the UK's vehicle recycling sector and concluded that the achievement of the ELV Directive quotas is dependent on accessibility of post-shredder separation technology. Muhamad Zamari and Blount (2006) provided a brief snapshot of vehicle recycling practices in EU, USA, Japan and Australia. Dalmijn and De Jong (2007) outlined the development of ELV recycling in Europe and concluded that exporting ELVs to China is more

economical than processing in the EU. Joung et al. (2007) analysed status of recycling ELVs in Korea and concluded that installation of advanced sorting equipment in a vehicle shredding facility could maximize its separation efficiency and increase the attained vehicle recycling rate. Togawa (2008) introduced the features and circumstances of Japanese vehicle recycling system and the ELV recycling law, respectively and also drawn attention to the significant increase in the exports of second-hand vehicles from Japan after 2005, when ELV recycling law was fully enforced. Paul (2009) explored ELV management practice in North America and revealed that dismantlers are very proficient at parts removal and resale and the infrastructure is very efficient at recycling high value and high volume materials. Beck (2009) outlined recycling conception of the ARN, company which play a major role in ELV recycling in the Netherlands. Chen and Zhang (2009) provided insight into thinking within China about ELV recycling problem and reported on the progress of process-related activities. Espartero et al. (2010) analysed the status of ELVs recycling in Spain and concluded that several EU member countries are high the Spanish recycling/recovery rates. Serrona et al. (2010) discussed the state of ELV recycling in China, Mongolia and the Philippines with reference to the experience of Japan and Korea. Chen et al. (2010) thoroughly described the principles and characteristics of the ELV recycling system in Taiwan and concluded that improving and optimising the process of tactical and operational planning is necessary to make recycled materials more competitive. Bassam et al. (2011) discussed opportunities and challenges facing the USA vehicle recycling industries in the future and concluded that new tools and technologies are needed to maximize the recycling of the ELVs. Barakat and Urbanic (2011) described the vehicle recycling system in Ontario, Canada and closely defined all the actors involved. Sakai et al. (2011) compared the current situation, historical background and effectiveness of 3R policies within EU, Japan, USA, Korea, China and Vietnam. In addition, the characteristics and effectiveness of 3R policies are examined, and the future directions of developments for a material cycles society are discussed. Altay et al. (2011) discussed the current situation of vehicle recycling in Turkey and revealed that adoption of specific regulation may create a new employment area. ELV treatment in developing countries is threatening to be one of the most difficult environmental issues of this century. Nwachukwu et al. (2011) studied the concept of environmentally friendly mechanical villages (i.e. large capacity buildings for vehicle works) in Nigeria. The obtained results indicated that the poor management of ELVs in mechanical villages is a cause of soil and water pollution with negative consequences to ecology, public health, and the overall quality of the environment. Cheng et al. (2012) examined the operational characteristics of recycling and treatment industry for ELVs in Taiwan and its relationship to recycling performance by using production capacity, power efficiency, and recycling rate as indicators. It is suggested that essential players in the ELV recycling business, i.e. vehicle shredding facilities, need to optimize their operation schedule to enhance recycling rate of ELVs. Wang and Chen (2012) explored development strategies for the used automotive electronic control components recycling industry in China. They analysed its strengths, weaknesses, opportunities and challenges using the strengths, weaknesses, opportunities and threats method. They pointed out that this ELV recycling industry responded well to all the factors and proposed new development strategies.

Extended producer responsibility issue

In the EU, ELVs are a prioritised waste stream and are managed on the basis of economic extended producer responsibility (EPR). Forslind (2005) examined how the existing Sweden's vehicle recyclers, aimed at creating economic incentives and financing end-of-life management, are affected by EPR. Manomaivibool (2008) explored the impacts of network management on the environmental effectiveness of the programmes for the management of ELV in the UK and in Sweden from an EPR perspective. Wilts et al. (2011) noticed that existing product-orientated EPR approaches with mass-based recycling quotas, such as ELV Directive, do not create adequate incentives to supply waste materials containing precious metals (like platinum group metals) to a high-quality recycling. They analysed incentive effects on EPR for the ELVs and precious metals, and developed a proposal for an international covenant on metal recycling as a policy instrument. The same authors concluded that covenants need to be signed as private law contracts between all groups involved in the European ELV reverse logistics network, and should define standards that are specific to groups of materials.

Remanufacturing

The automotive sector has a well-known history of parts remanufacturing. Vehicle part remanufacturing is transformation of an end-of-life part into a part with an “as good as new” condition. However, this operation is extensive and includes its disassembly, cleaning, recovery and re-assembly. Seitz (2007) reviewed the driving forces and motivations behind passenger car engine remanufacturing including: ethical and moral responsibility, legislation, profitability, aftermarket reasons, market share and brand protection, and customer orientation. Jaafar et al. (2009) explored the effectiveness of the institutional framework of the commercial vehicle remanufacturing industry in Malaysia using interviews as research tool, and identified that unavailability of effective communication mechanisms among the relevant government authorities presents the main weaknesses.

ELV-generated materials recycling

Bellmann and Khare (1999) thoroughly discussed the issue of recycling of plastics in the automobile industry and took a brief look at its economic, political and legal aspects. Brahmst (2006) studied the state of knowledge and efficiency in removing copper components from ELVs in the USA. Ruhrberg (2006) proposed the copper flow model to assess the recycling efficiency rate of copper from several end-of-life products, including ELVs. Hatayama et al. (2012) discussed on how the recycling of aluminum will change till 2050, focusing on the introduction of next-generation vehicles (HEVs and EVs) and modern scrap sorting technology. They demonstrated the limitations of the traditional, profit-oriented recycling systems and confirmed the validity of introducing modern scrap sorting systems. Moreover, the case study results indicated the effectiveness of scrap sorting in the future: if scrap sorting is carried out for ELVs, it reduces the primary aluminium requirement by 15-25%.

Miscellaneous content

Bellmann and Khare (2000) conducted a comprehensive study on ELV recycling systems. Numerous economic issues involved in developing markets for recycled parts were thoroughly analysed, and the concept of “critical mass” of returns for profitable recycling was suggested. Marsh (2005) analysed potentials for fibre reinforced plastic recovery from ELVs and proclaimed the foundation of the European Composites Recycling Services Company (ECRC). ECRC will promote the development of a European network of composites recycling centres, together with the associated logistics, to operate in parallel with European vehicle recycling industry. Amza et al. (2011) gave an overview of basic recycling techniques and compared modern shredding facilities with traditional hammer mills. Agbo (2011) quantified the raw materials potential of used vehicles imported in Nigeria, which is important destination for European used vehicles. Closing the loop of rare earth metal utilization is a necessary attribute of sustainable consumption and production, and urban mining (i.e. the recovery of rare earth metals from ELV and Waste Electrical and Electronic Equipment) is driving ELV recycling into sustainable waste management. Owing to previous, Yu et al. (2011) discussed the experiences of Japan and China in the field of urban mining.

Modelling approach

In this sub-section, papers in which authors used various methodological approaches to model different aspects of very complex system for ELV recycling are presented and thoroughly analyzed. The following categories are created: (1) *Life Cycle Assessment*; (2) *Sequencing planning*; (3) *Production planning*; (4) *Material selection*; (5) *Miscellaneous models*. However, due to enacted limit in paper's length, only categories (1)-(3) are systematically analyzed in this paper. Categories named Material selection and Miscellaneous models will be reviewed in the Subsequent paper named *Environmentally conscious vehicle recycling: A distribution of the current literature and research opportunities*.

Life Cycle Assessment

Although Life Cycle Assessment (LCA) has been established as the most broadly used methodology to assess the environmental sustainability of a products, applying LCA to support vehicle parts/components design decision making remains a significant issue of future research. For instance, Munoz et al. (2006) used LCA to compare a plastic door panel with a prototype panel, based on compatible polyolefins. The following scenarios are analyzed: land-filling, energy recovery in a municipal solid waste incinerator (MSWI), energy recovery in a cement kiln, and mechanical recycling. Recently, Lazarevic et al. (2010) reviewed plastic waste management in the context of a European recycling society and concluded that uncertainty analysis was disregarded in available LCA-based studies. Alves et al. (2010) used the LCA to demonstrate the possibility to use jute fibers to produce a structural frontal bonnet of an off-road vehicle. They results pointed out the advantages of applying natural composites in vehicle enclosures. Gaidajis et al. (2011) used LCA method to analyze three waste management scenarios of used oil filters (UOFs) deriving from ELVs in Greece, namely maximum recycling, simple infiltration without special facilities and landfill. LCA results have showed that recycling is preferable for every impact assessment method used.

Sequencing planning

Sorting sequencing deals with the problem of determining the best order of operations in the separation of a vehicle hulk into its constituent materials. Sodhi et al. (1999) investigated cases examining the sequencing problem for sorting individual and all target material(s), and they presented a solution based on dynamic programming. Knight and Sodhi (2000) developed two mathematical models which allow the evaluation of products for bulk recycling and could be used as design-for-recycling (DfR) tools in the early vehicle component design phase.

Production planning

In general, production planning models can be classified into two categories:

- **Deterministic models** - The literature provides a significant number of different deterministic mathematical models. Gupta and Isaac (1997) solved the ELV recovery planning problem using GP. Individual models were created for plastic-intensive (PI) and aluminium-intensive (AI) vehicles. They reached the conclusion that a polymer share increase in the vehicle material composition would not jeopardise the existence of the ELV processing industry but would deteriorate its business results. Choi et al. (2005) proposed a mixed integer programming model for tactical process planning in the case of traditional USA vehicle shredding facilities. Williams et al. (2007) expanded mathematical formulation from Choi et al. (2005) in order to make short-term tactical decisions regarding to what extent to process and reprocess materials through multiple passes in eddy current sorter. In addition, their mixed integer programming model determines whether to combine materials for shipment. Coates and Rahimifard (2007) pointed out that accurate methods are required to economically assess and optimize the ELV processing activities. Qu and Williams (2008) formulated the vehicle reverse production planning and pricing problem in a nonlinear programming model, developed an approximate supply function for hulks ordering when adjacent shredders price independently, and compared market with an optimised pricing strategy in three trends for ferrous metal and hulk costs: constant, increasing and decreasing. Miemczyk (2008) suggested that research within production and operations management is particularly needed to consider the effects of institutional environment policies on the choice of production strategy and product recovery. Li et al. (2011) presented a coupled upgrading and production mathematical programming model to identify economically efficient sorting strategies and their impact on scrap usage in the case of an individual recycling firm. The model is applied to a cast/wrought alloy sorting for typical EU secondary aluminium production from four scrap types: AI vehicles, shredded extrusion, old rolled, and commingled. Simic and Dimitrijevic (2012a) presented a tactical production planning problem for vehicle recycling facilities in the EU legislative and global business environments. They analyzed influence of the ELV Directive

(2000/53/EC) (EU, 2000) on the vehicle recycling facilities business and concluded that future eco-efficiency quotas will not endanger their profitability. In addition, they recommended that the control of the recycling system efficiency should be done at the system level because it will in no way jeopardise the ELV Directive objectives. Simic and Dimitrijevic (2012a) expanded linear programming modelling framework proposed by Simic and Dimitrijevic (2012a) in order to incorporate vehicle hulk selection problem and to answer to the following questions: Can modernly equipped vehicle recycling facility conduct profitable business? Are ELV Directive's eco-efficiency quotas actually attainable? How will the commenced change in vehicle design influence vehicle recycling facilities? To do so, they provided a production planning model of a modernly equipped vehicle recycling facility and tested it extensively using real data. They came to the conclusion that vehicle recycling facility transformation, from traditional (so-called shredding facilities) to modernly equipped, is not only necessary but completely justified and that the final success of the ELV Directive is realistic.

- Stochastic models - In a vehicle recycling system, it is difficult to express or obtain the overall modelling data in deterministic form. Moreover, a large number of factors in real world processes are influenced by uncertainties (Wu et al., 2010). Uncertainty is the key factor influencing vehicle recycling planning. For instance, in a vehicle recycling system, sorting and transportation costs are uncertain in reality, because they can vary temporally and spatially. In addition, the costs of land-filling, MSWI and advanced thermal treatment (ATT), i.e. gate fees, which vary among EU member states and their amounts are subject to continuous change. Van Schaik et al. (2002) proposed a dynamic optimisation model based on size classes for the recycling of aluminium from passenger vehicles which determines the recovery rate and covers in detail the processing of the ELV, starting from dismantling, shredding and metal production. Van Schaik et al. (2003) modified a dynamic optimisation model proposed by Van Schaik et al. (2002) in order to describe liberation classes. Van Schaik et al. (2004) combined a dynamic optimisation models proposed by Van Schaik et al. (2002, 2003) in order to describe the relationship between particle size reduction and liberation during shredding and recycling of ELVs. Through various simulations the authors illustrated the liberation behavior of vehicles and provided insight into the mutual compatibility of processes and material streams at various stages in the ELV recycling chain. Shredding mill represents the core element of every vehicle recycling factory. Castro et al. (2005) presented a simulation model that describes the relationships between vehicle design and the liberation level attained by shredding. The authors used a distribution functions for modelling the breakage and liberation (a function of the design parameters and shredding conditions) in the developed model. The obtained results showed that during product design the materials and joints among them can be chosen to obtain the best possible liberation and the lowest possible contamination, i.e. vehicle design has a large influence in the composition of the material streams produced by shredding. A detailed system model to optimise the performance of the ELV recycling system, in which quality, separation physics and thermodynamics are addressed simultaneously, is suggested by Reuter et al. (2006). The proposed model combines several dozens of processes (usually located on a single vehicle recycling plant) and flows to optimize the recycling of ELVs. The authors noted that simplistic LCA and similar environmental modelling approaches cannot provide the required depth to optimise, improve and understand the complete ELV recycling system. Ignatenko et al. (2008) extended optimisation model of the ELV recycling system proposed by [69] in order to add thermal treatment processes and energy recovery constraint enacted with ELV Directive. The obtained results showed that ELV Directive has the negative impact on the performance of the material and energy ELV processing system in its totality. More detailed, by imposing an energy recovery constraint, the required complexity of the recovery and processing routes increases and the energy and material recovery performance is negatively affected. Pehlken and Müller (2009) stated that modelling recycling processes and the uncertainty analysis needs to be simultaneously considered. They pointed out that more research concerning this matter has to be done.

CONCLUSION

As various resources are rapidly being depleted, recycling and recovery of ELVs are considered as one of the most important methods to promote sustainable development. Today, the sustainability of ELV recycling it is a well positioned and emergent research area. The main motive for this epilogue is the ever growing attention of world-wide governments and scientists toward ecological issues such as conservation of resources and global warming.

This paper is the first of two reviews by the author that consider the environmental engineering aspect of the ELV recycling. It presented a review of the state of the art literature on environmental engineering issues of the ELV recycling process published since the 1997. As a result, a broad literature review was conducted to review the environmental engineering issues of the ELV recycling from numerous journal publications, conference proceedings, book chapters, reports and thesis that could be seen as possible outlet for this research.

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**WATER QUALITY IN URBAN AREAS (GROUND
WATER, DRINKING WATER, WASTE WATER AND
FACILITIES)**

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**RADIATION INTENSITY DISTRIBUTION IN A RECTANGLE CROSS
SECTION UV REACTOR**

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ABSTRACT

UV fluid radiation at 254 nm is physical treatment to achieve micro-organisms inactivation (i.e. disinfection-sterilization) in UV transparent fluid, or oxidants decomposition due to its elimination, or rapid oxidation unwanted water content, that is difficult to achieve otherwise. Advantage of this physical method for air or water disinfection-sterilization is that there is no over-dosage problem, and it does not change either organoleptic or physical-chemical fluid characteristics, as with chemical treatments. In this paper we analyze UV radiation intensity distribution in a rectangular prismatic multi-lamp reactor, with rectangle cross-section, whose walls partly reflect UV radiation. Fluid flowing through the reactor longitudinally or transversely could be air, wastewater, potable water or UV transparent aqueous solution. UV radiation intensity distribution is necessary to determine fluid radiation doze that flows through the reactor and the geometry reactor optimization in the final design phase for the defined fluid transparency scope in UV spectrum. Fluid transparency, UV sources radiation power and defined radiation dose that must be achieved in UV reactor, under the worst conditions, determine the maximum fluid flow.

Key words: *UV radiation, UV reactor, UV radiation intensity, intensity distributioin.*

INTRODUCTION

About UV Reactor Radiation Intensity Distribution Importance

UV radiation intensity distribution in UV reactor (further UVR), which is, for example, applied to fluid sterilization (such as: water, air, water solutions, serums, etc.) is very important factor in UVR design, aimed to define optimal number and UV lamps displacement in it. In cylindrical UVR this type of analysis is much easier, particularly with one lamp UVR, due to geometrical compatibility of lamp, having cylindrical shape too, and UVR [1], [2]. UVR design and analysis becomes more complicated with many UV lamps in a cylindrical UVR vessel [3] [4], and especially in plan-parallel (prismatic shape) UVR, opened or closed [5]. These types of reactors are used for potable or waste water treatment in huge capacity systems ($\geq 1 \text{ m}^3/\text{s}$). In this paper we will analyse closed type UVR with water having slight overpressure, prismatic plan-parallel shape and rectangle cross-section.

UV Reactor Types

UVR could be roughly divided into two main categories:

- (1) **Closed** - they work under pressure that is slightly (barely) higher than the ambient or higher one, and that have radiation sources (lamps) immersed in the fluid, but rarely over it, and
- (2) **Opened** - they work under ambient pressure, and lamps could be in the fluid, or over it.

Closed UVR vessels are usually cylinder in shape, but they could be plan-parallel too, while opened UVR are mostly of plan-parallel type, with square or perpendicular cross section, but sometimes they could be cylindrical. UVR cross section is orthogonal to axis of lamps in it, and their axes are parallel to the UVR axis. Various and the most frequently used types of UV reactors are given at Figures 1 to 6 [4], [6].



Figure 1. Cylindrical UV reactor with one centrally positioned UV lamp, with negative radiation geometry [1,9]; longitudinal and perpendicular cross section

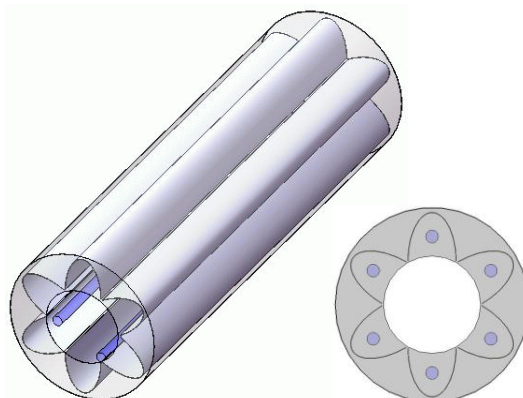


Figure 2. Multi-lamp cylindrical UV reactor with positive radiation geometry [1,10]; longitudinal and perpendicular cross section

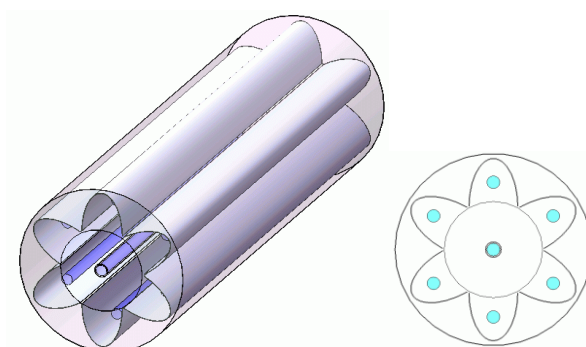


Figure 3. Multi-lamp cylindrical UV reactor with neutral radiation geometry [1,10]; longitudinal and perpendicular cross section



Figure 4. High capacity multi-lamp cylindrical UV reactor with neutral radiation geometry [1,10]; for capacities $\geq 1 \text{ m}^3/\text{s}$

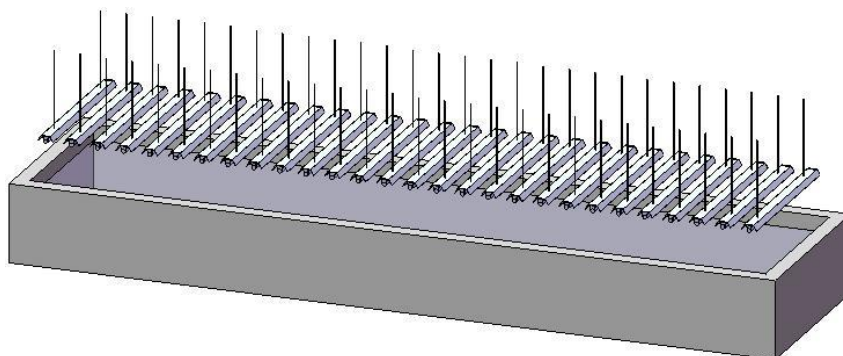


Figure 5. High capacity multi-lamp plan-parallel UV reactor with UV lamps over the fluid with negative or pseudo-neutral radiation geometry [1,10]

THEORY

Typical rectangle plan-parallel UVR is given at Fig. 6 and its cross section is given by Fig. 7. In this paper, when modeling described UVR, we started from the following assumptions:

A1 - We are assuming finite length lamps in the approximation of the infinite radiation source, as there are no ending effects. This is compatible with very important statement given in [7], where it is said: “For situations where the **average intensity within the reactor** is adequate to define kinetic rates, there is no practical reason to use the more complex finite-length lamp model instead of the infinite length lamp model. In many cases, especially for reactors with large length to lamp radius ratios and overall reactor radius to lamp radius ratios, the finite length model can predict higher average intensities than can the infinite length model.” This conclusion was of great importance in all UV reactor *a priori* analysis and modeling calculations.

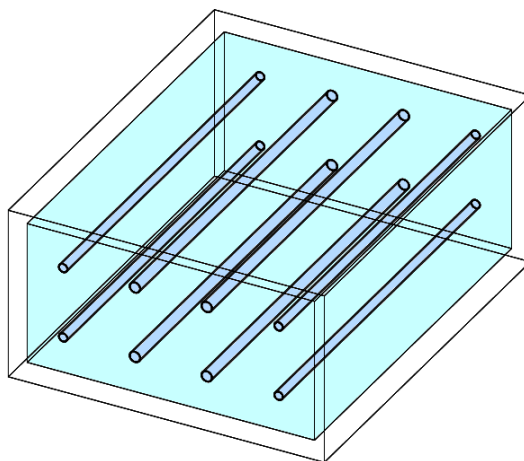


Figure 6. Plan-parallel rectangle cross-section UV reactor with lamps in fluid with negative radiation geometry [1,10]

A2 - We accepted laminar fluid flow through the UVR as the worst case in UV intensity analysis from the standpoint for further dose calculation. In this case there is no averaging effect to dose, characteristically for turbulence flow.

A3 - When taking into account the walls reflection, we will calculate only radiation intensity distribution in the fluid thin film (A2. laminar fluid flow) near reactor wall, for at it reaches the lowest UV radiation flux, due to fluid absorption. We assume a very rough approximation that the UV radiation intensity, in the thin film near UVR wall, will be sum of incident radiation and, reflected UV radiation from wall that is product of incident radiation and reflection coefficient.

A4 - We are not taking into account lamps shadowing effect that some lamps make to the others.

A5 - For the finite length lamps in the approximation of the infinite radiation source (where exists only radial component of radiation), radiation flux exists only through four reactor sides (walls) that are parallel to the lamps axis, which are parallel to the central reactor axis. Radiation flux does not exist through the walls that are perpendicular to the lamp axis.

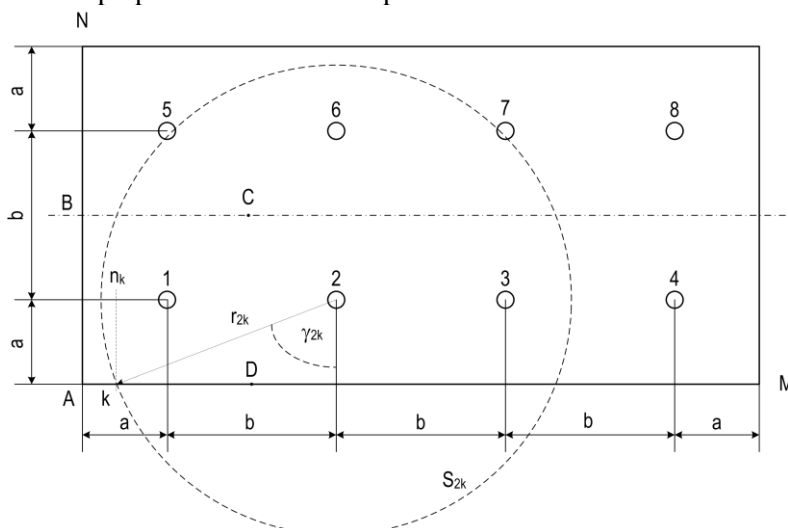


Figure 7. Plan-parallel rectangle cross-section UV reactor with 8 lamps immersed in fluid, denoted by numbers; k is arbitrary point (line) at one of reactor sides

Applying Modified Gauss-Ostrogradsky Theorem (Furthermore MGOT) to all reactor sides, according to [3], [4], we can formulate UV radiation intensity mathematical model for the whole UVR:

$$\oint_S \Phi \cdot d\vec{S} = \sum_i^N \bar{P}_{i,k} \quad (01)$$

Having in mind assumptions A1 - A5 and that the opposite (parallel) UVR sides are identical, according to radiation intensity and flux distribution, then the expressions for radiation flux and radiation intensity for horizontal or vertical walls will be the same:

$$\Phi_k = \sum_{i=1}^N \frac{P_{i,k} \cdot \cos \gamma_{i,k}}{S_{i,k}} = \frac{(1+\rho) \cdot \eta \cdot P_0}{2 \cdot \pi \cdot L_e} \cdot \sum_{i=1}^N \frac{T_{i,k}}{r_{i,k}} \cdot \cos \gamma_{i,k} = \Psi_k \cdot \cos \gamma_{i,k} \quad (02)$$

$$\Psi_k = \frac{(1+\rho) \cdot \eta \cdot P_0}{2 \cdot \pi \cdot L_e} \cdot \sum_{i=1}^N \frac{T_{i,k}}{r_{i,k}} \quad (03)$$

where $P_{i,k}$ is radiation power i -th lamp in place of k -th point (line) at vertical or horizontal side (see Fig. 7), Φ_k и Ψ_k are radiation flux and radiation intensity, respectively in point (at line) k . In this paper radiation flux is defined as power over unity surface and multiplied with cosine of incident angle, and radiation intensity as flux divided by cosine of angle of incidence. $S_{i,k} = 2 \cdot \pi \cdot L_e \cdot r_{i,k}$ is a part of a surface side of reactor at the place where virtual cylinder around i -th lamp cuts it in point (line) k . Virtual surface has effective length L_e , axis in i -th ($1 < i < N$) lamp axis, and radius $r_{i,k}$ measuring from i -th lamp axis to the line of k -th point. ρ is the macroscopic reflecting coefficient of reactor walls.

$$\bar{P}_{i,k} = \eta \cdot \bar{P}_0 \cdot T_{i,k}, \quad (04)$$

$$T_{i,k} = \exp(-a_w \cdot (r_{i,k} - r_Q)) \cdot \exp(-\alpha_Q \cdot d_Q), \quad (05)$$

Where P_0 is initial power of every UV lamp, $\bar{P}_{i,k}$ and $T_{i,k}$ are radiation power vector and transmission coefficient from i -th lamp axis to k -th point, respectively. a_w and α_Q are water and quartz glass (the quartz tubes are made of) absorption coefficients respectively, and r_Q is radius of quartz tube, in which is UV lamp protected from the fluid (water). Coefficient of losses η is given by the expression:

$$\eta = \eta_A \cdot \eta_T \cdot \eta_V \cdot T_F, \quad (06)$$

$$T_F = [1 - R_{FAQ}] \cdot [1 - R_{FQW}] \quad (07)$$

Where η_A , η_T , η_V , T_F , R_{FAQ} , R_{FQW} are: lamp aging factor according to lamps specification, power transmission factor to surrounding fluid according to [7], UV lamp voltage supply factor, Fresnel's transmission coefficient, Fresnel's reflection coefficients for air-quartz glass and for quartz glass-water interfaces [8], respectively.

According to expression (03) it is possible to define average intensity value and UV radiation dose distribution respectively that is transferred to the water during irradiation in UV chamber, in accordance with assumptions A2 to A4, as:

$$\bar{\Psi} = \frac{1}{K} \cdot \sum_k^K \Psi_k, \quad (08)$$

$$D_k = \Psi_k \cdot t_r = \Psi_k \cdot \frac{V_{re}}{Q_W} = \frac{S_e \cdot L_e}{Q_W}, \tag{09}$$

$$S_e = \left[(2 \cdot a + 3 \cdot b) \cdot (2 \cdot a + b) - N \cdot \pi \cdot r_Q^2 \right], \tag{10}$$

Where t_r , V_{re} , Q_W , $L_e=L_r$, a , b , are: fluid retention time in UVR, effective volume of the UVR, fluid flow rate, effective lamp length that is equal to the effective reactor length, lamp distance to the wall and distance between the lamps, respectively.

FINDINGS (RESULTS)

Results that are given in Figures 8., 9. and 10. are calculated for the following input parameters: a=50 mm, b=168 mm that influences rectangle width 2a+3b=604 mm and rectangle height 2a+b=268 mm, while effective reactor length is 111 cm, initial lamp power is 26 W, Frenel’s total transmission coefficient 0.955, quartz absorbance 0.005/cm, total losses coefficient (without Frenel’s transmission coefficient) 0.795.

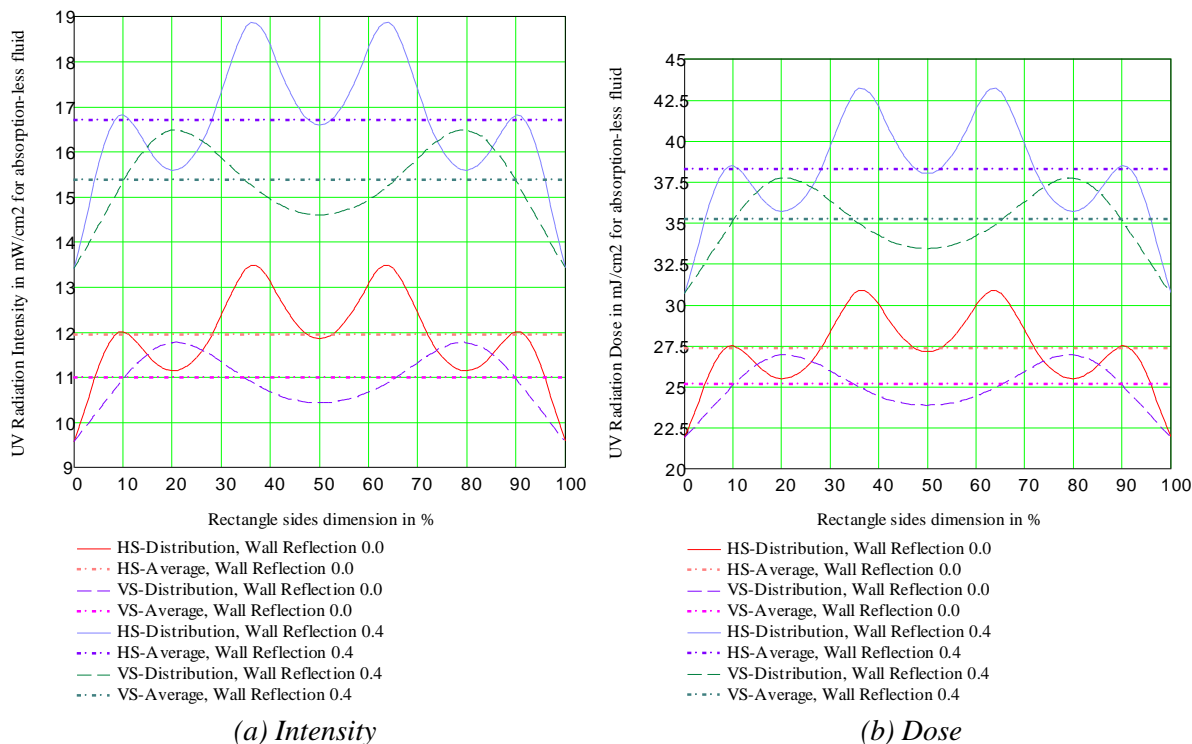


Figure 8. UV radiation distribution on horizontal and at vertical reactor side for various wall reflection coefficients (a) Intensity, (b) Dose (at the exit of the reactor) for air flow rate 75 l/s

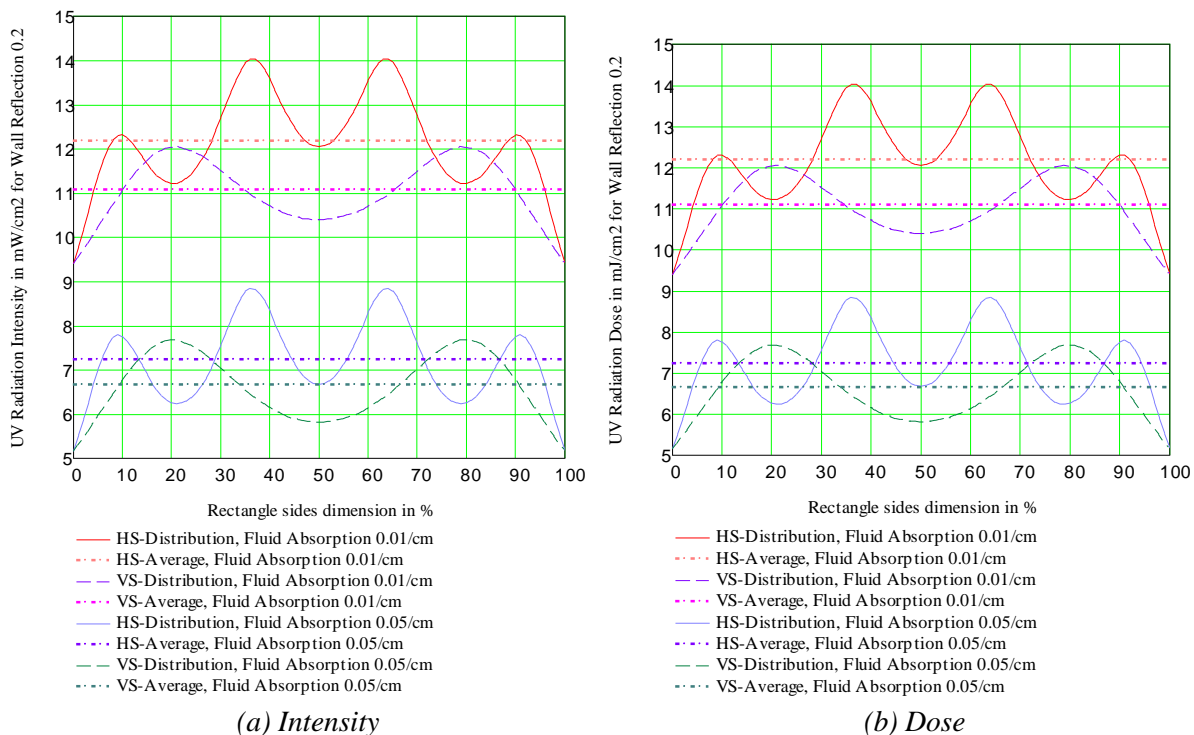


Figure 9. UV radiation distribution on horizontal and at vertical reactor side for various fluid absorption coefficients (a) Intensity, (b) Dose (at the exit of the reactor) for water flow rate 35 l/s

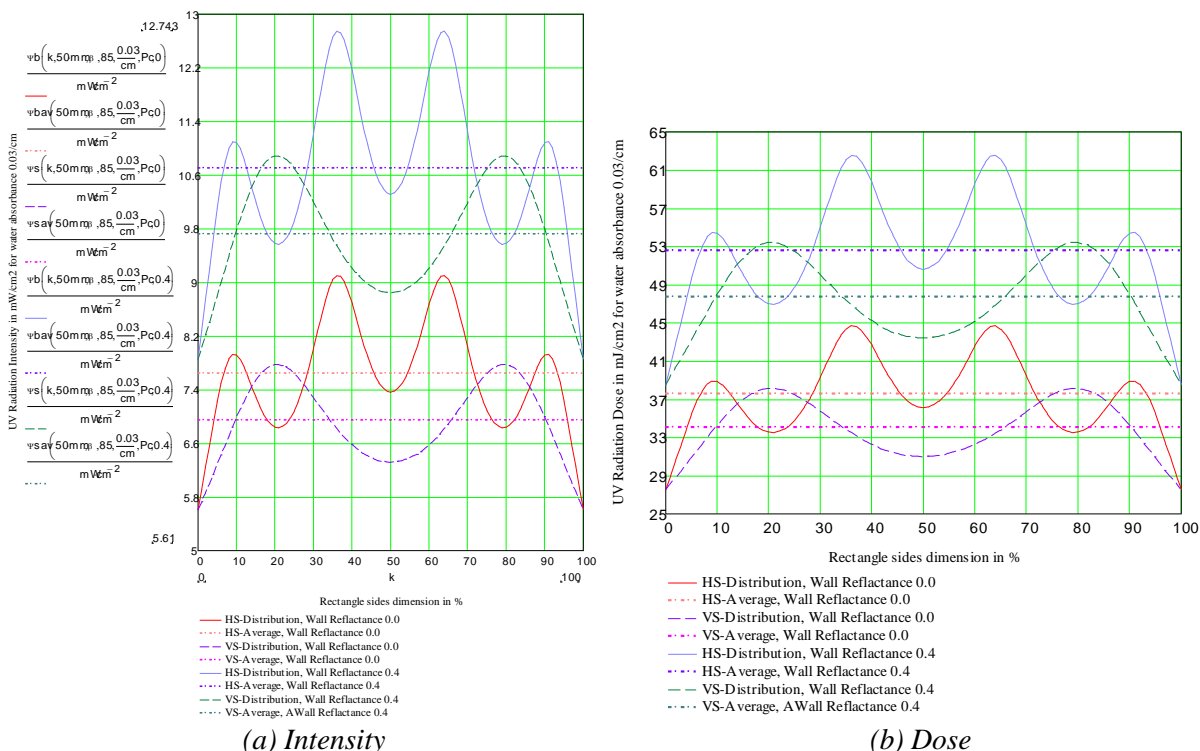


Figure 10. UV radiation distribution on horizontal and at vertical reactor side for various wall reflection coefficients (a) Intensity, (b) Dose (at the exit of the reactor) for water flow rate 35 l/s

CONCLUSIONS AND IMPLICATIONS

The most important contribution of this paper is selective formulation and Modified Gauss-Ostrogradsky Theorem application to rectangular cross section plan-parallel UV reactor, for a priori analyses, as well as for design of this type of UV reactors. This type of model enables UV reactor design for water disinfection, and disinfection-sterilization of other types of UV transparent fluids, taking into account UV reactor wall reflection in the thin film of fluid near the wall.

Next step is UV reactor final parameters design, such as: width and height of the rectangular cross section, UV lamps displacement, materials selection, due to reflection, which influences UV reactor dimensions. The most important part of mentioned design is optimal UV reactor dimensions and lamps displacement, according to defined flow rate of fluid, either longitudinal or transversal, but in both directions, for it is not the same as it will be for square cross section UV reactor [9].

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**ENVIRONMENTAL MANAGEMENT OF THE SEWAGE SLUDGE
RESULT FROM WASTEWATER TREATMENT PLANTS IN
ROMANIA AND THE EU. CASE STUDY – THE WASTEWATER
TREATMENT PLANT OF TIMISOARA**

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ABSTRACT

The developing of the infrastructure for wastewater collection and treatment in Romania, with respect to the Accession Treaty, is leading more and more to the production of huge quantities of sewage sludge, as a direct result of the wastewater treatment. The rapid and rational development of a national policy for the management of sewage sludge to establish a broad and short, medium and long term must be emerged and implemented, as a necessity. In EU, the ecological management problem of sewage sludge has existed since 1991, with the implementation of the EEC Directive 91/271, referring to the Urban Waste Water Treatment. After 2000 the solution for the optimized energy recovery technology by burning sewage sludge was tested and developed mainly in German,. These solutions can also be implemented in Romania. The present case study refers to a possible solution for energy recovery by direct combustion of the sludge resulted from the municipal wastewater treatment plant in Timisoara, within efficiently thermodynamic cycles. As a main conclusion one will support the idea that it is necessary to make a preliminary assessment of the thermodynamic energy content of the sewage sludge in order to depict and select the global vision of the process, assuring both the optimal energy development and environmental friendly treatment processes.

Key words: *wastewater, sewage sludge, energy recovery, combustion, thermodynamic cycles.*

INTRODUCTION

Sewage sludge resulting from municipal wastewater treatment, industrial or domestic is officially classified as waste, but the accepted policy is to use the sludge beneficially whenever it is feasible, either as organic fertilizer on land or as an energy source recovered by combustion. We must be aware that scattering sewage sludge on agricultural land can cause health risks by the infestation of soil and groundwater with heavy metals, pathogenic agents and viruses. These issues have generated particular interest to other disposal alternatives, one of which is the burning of sludge, thus removing potential pollutants from the food processing chain. The result of incineration is a small amount of suspended solids that can be removed easily. In addition, it is possible that the phosphorus within the ash be used as fertilizer in agriculture. Heavy metals can also be recovered and recycled. In case of energy recovery by burning sludge an optimized technological version should be chosen, which should be able to provide maximum energy efficiency, emissions and waste materials in small amounts and which are within the limits imposed for pollution.

THEORY

Wastewater treatment plant operators must identify the best environmental solutions and practices for the treatment, recovery / disposal of sludge, both sustainable and efficient in terms of costs. When choosing the sludge treatment process we must take into account the sludge management strategy (removal / recovery), the wastewater treatment plants (WWTP). We have the following options:

1. Using the waste in agriculture by spreading it over the agricultural terrain, followed by its immediate incorporation or by creating a bed compost together with other materials and use it as subsequent fertilization of agricultural land;
2. Energy recovery of sludge by co-fermentation or anaerobic digestion with biogas production and eventually fermented sludge incineration technologies, or incineration without fermentation, the facilities being functional in co-generation system, transforming the energy content of the sludge into usable heat and electric power, finally used for own purposes by the producer, in order to reduce its energy costs for the treatment processes of wastewater and sludge;
3. Co-combustion of sludge in solid waste incinerators under clean technologies and within high efficiency thermodynamic cycles;
4. Co-processing of sludge in the cement industry, if the humidity and calorific value of sludge meet the requirements of the production process.

Environmental management of the sewage sludge resulted from wastewater treatment plants in Romania and the EU

Using sludge in agriculture involves treating it, and the preferred method is anaerobic digestion. The result of this process is not only sludge stabilization and odour and pathogenic elements reduction, but also biogas production, which can be used as a source of heat and energy in wastewater treatment processes. Electricity from sewage sludge saves fossil fuels and reduces fossil originated CO₂ emissions.

If we choose energy recovery from the sewage sludge, we should take into account that more energy will be obtained from raw sludge (unfermented). In this case fermentation is no longer necessary. Combustion of the sludge to reduce its mass and to recover energy is an important alternative to using sludge on land.

Energy recovery from sludge for cogeneration of heat and power is achieved by using technologically advanced industrial and economically efficient plants, within advanced thermodynamic cycles. In addition to achieving maximum energy efficiency it is very important to analyze and treat emissions and waste materials resulting from thermal treatment processes to minimize any possible environmental impact.

The energy produced will be used in wastewater and sludge treatment and it will help reduce the specific consumption of materials and energy.

Status in Romania

The developing of the infrastructure for wastewater collection and treatment in Romania, with respect to the Accession Treaty, lead to an increasing need for a national short, medium and long term sludge management strategy, the last variant being elaborated in February 2012 (Mott Mac Donald et al., 2012).

As it is the most complex option, sludge agricultural use is regulated by Order. 344 of August 16th, 2004 for approving the Technical Norms regarding environmental protection, especially soil protection, and when to use sludge in agriculture (Order issued commonly by the Ministry of the Environment and Water Management, the Ministry of Agriculture, Forests and Rural Development, 2004).

If we choose energy recovery from waste sludge by incineration, we should keep in mind the following national regulations (The SOP Environment Management Authority, 2012):

- Government Decision 128/2002 regarding waste incineration (Official Gazette, Part I, no. 160, of 06.03.2002)”;

- Government Decision 268/2005 (Official Gazette 332 of 20.04.2005) which modifies and completes GD 128/2002 regarding waste incineration;
- Order of the Ministry of the Environment and Sustainable Development 756/2004 for the approval of the Technical Norm for waste incineration (Official Gazette 86 of 26.01.2005).

The current research on ecological recovery of sludge from municipal wastewater treatment plants in Romania is at an early stage because starting only with 2010 have there been put into operation high-performance wastewater treatment plants, and only in big cities, usually in county capitals. Sludge treatment stops for now at the preliminary treatment phases namely conditioning, thickening and dewatering to a dry solids (D.S.) content of min. 20%.

From the 114 wastewater treatment plants which process sludge, functional at the end of 2011, only 2 of them (1.75%) recover sludge by using it in agriculture, the other removing or storing it in various forms (Mott Mac Donald et al., 2012).

With increasing quantities of sludge resulting from putting new wastewater treatment plants into operation, from the total sludge production estimated at the end 2020, an amount of. 415,600 to.D.S / year, 50% will be used in agriculture, 20 % will be incinerated and the remaining 30% will be co-processed in cement plants. These figures are expected as a basic scenario, the use of sludge in agriculture being a priority.

Based on the evolution of energy consumption and reserves of conventional fuels an extreme scenario, "maximum EdD", was elaborated, which states that the total quantity of sludge produced in the year 2020, estimated at an amount of 415,600 to.D.S. / year, will be used for energy recovery by treating it in major regional treatment centres (Mott Mac Donald et al., 2012). The main operations are:

- partial stabilization by anaerobic digestion with biogas production;
- dewatering;
- composting;
- drying;
- incineration and co-incineration;
- co-processing in cement plants.

Using the total sludge quantity of 415,600 to.D.S./year, estimated at the end of 2020, one considers that energy will be recovered, in various ways, from the following quantities of sludge (Mott Mac Donald et al., 2012):

- 267,000 to. (64.25 %) - by mono-incineration or co-incineration of sludge, with other conventional fuels or biomass;
- 147,400 to (35.45 %) - by co-processing in cement plants;
- 1,200 to (0.3 %) - by composting.

Status in the EU

In the EU 15 environmental management of sewage sludge has become a priority for wastewater treatment plants operators with the implementation of Directives 86/278/EEC on using sludge in agriculture and 91/271/EEC concerning urban wastewater treatment.

Thus in the 15 European countries (EU 15) the amount of sludge used in agriculture increased from 3 million to D.S. / year in 1995 to 5.4 million in 2010 (an increase of 80%) with an estimated increase in 2020, to 6.1 million to. D.S./year (Milieu Ltd et al., 2008).

A greater emphasis was put on energy recovery from sludge incineration, so at the EU 15 level , the amount of sludge incinerated increased from 1.5 million to D.S./year in 1995 to 3.1 million in 2010 (an increase of 106.7%) with an estimated increase in 2020, to 3.6 million to D.S./year (Milieu Ltd et al., 2008).

Through the research-development activity and implementation of high technology in recovery renewable energy resources in Germany, energy recovery through incineration of sewage sludge increased significantly, from 9% in 1991 to 53.2% in 2010 (an increase of 491%) of the total sludge produced, with a humidity of 60% D.S. (Federal Institute of Ecology UBA 2011).

Sludge mono-incineration plants, in combined cycles, have been tested and developed in Germany beginning with 2005 at the Technical University of Braunschweig (Vockrodt, S., & Leithner, R., 2004), as well as in the "HUBER - sludge2energy" technology.

METHODS

The energy recovery option by burning sewage sludge can be discussed in the case of the WWTP Timisoara as well (Ionel, I. & Neamț I., 2012).

Because the WWTP Timisoara does not have sludge fermentation tanks for sludge stabilisation and biogas production, the excess sludge from the settlement tanks can be put into value from an energetic point of view by incineration in a thermodynamic cycle based on the HUBER concept.

The cycle will result in an electric efficiency of 32.3%. In case the heat from the air after-cooler and from the hot air at the turbine outlet may be used, the total efficiency of the CHP plant will be about 71.9%, of which thermal efficiency of 39.6% (Stevanovic, D., 2001).

For the Timisoara case study the basic start was accomplished in a composition analysis. The elementary analysis of the sludge, resulted in the following chemical composition (in percentage by mass of dry substance) for components: carbon C - 30.35 %, oxygen O - 27.85 %, nitrogen N - 3.05 %, hydrogen H - 4.73 %, phosphorus P - 1.48 %, sulphur - 0.74 % and 31.8 % inorganic residue.

After dewatering and drying, in view of incineration by monocombustion, the sludge will reach a humidity of 35%. In this case, the chemical composition is: carbon C - 19.74 %, oxygen O - 18.10 %, nitrogen N - 1.98 %, hydrogen H - 3.07 %, sulphur - 0.48 %, and 21.63 % phosphorous and the inorganic residue which are considered as constituents of the mineral substances.

The lower heat value can be determined with an approximation equation, based on the chemical elementary analysis of the fuel as follows:

$$Hu = 33.900 C + 120.120 (H - O/8) + 9.250 S - 2.510 H_2O \text{ [MJ/kg]} \text{ (Jădaneanț, M. 1990),} \quad (1)$$

$$Hu = 33.9 C + 121.4 (H - O/8) + 10.5 S - 2.24 H_2O \text{ [MJ/kg]} \text{ (Betitz, W., & Grote, K.H. 1997)} \quad (2)$$

$$Hu = 35 C + 94.3 H + 10.4 S + 6.3 N - 10.8 O - 2.44 H_2O \text{ [MJ/kg]} \text{ (Betitz, W., & Grote, K.H. 1997)} \quad (3)$$

After calculations, the following values result for lower heat value were obtained: $Hu (1) = 6.82773$ [MJ/kg]; $Hu (2) = 6.938565$ [MJ/kg]; $Hu (3) = 7.16987$ [MJ/kg].

In order to estimate the energetic balance of the burning installation, an average value $Hu = 7,00$ [MJ/kg] can be taken into consideration. For calculating the thermal energy available by the incineration of sludge it is necessary to know the sludge mass flow input of the biomass combustor.

The mechanical and thermal processes for the reduction of the humidity of thickened excess sludge for the WWTP Timisoara take place according to the technological flux presented in Fig. 1. The sludge mass flows per thermal treatment flux are presented in Tab. 1.

The energetic balance of the sludge burning installation

- Following results concerning the energetic balance of the sludge burning installation were achieved:
- Sludge mass flow input of the biomass combustor, $m_{\text{sludge}} = 665 \text{ kg/h} = 0,1847 \text{ kg/s}$;
- The lower heat value of the sludge (determined by calculation), $Hu = 7000 \text{ KJ/kg}$;
- The available energy of the biomass combustor, $Q_{\text{in}} = m_{\text{fuel}} \times Hu = 1293 \text{ KW}$;
- Total efficiency of the CHP, $\eta_{\text{CHP}} = 71.9\%$;

- Electrical efficiency of the cycle, $\eta_{el} = 32,3\%$;
- Thermal efficiency of the cycle, $\eta_{th} = \eta_{CHP} - \eta_{el} = 39,6 \%$;
- Power production of the plant layout (Power output) $P_{Ge} = Q_{in} \times \eta_{el} = 418 \text{ KW}$;
- Heat production of the plant layout $Q_H = Q_{in} \times \eta_{th} = 512 \text{ KW}$;
- Sludge mass flow input of the of the dryer, $m_{dryer} = 1200 \text{ kg/h}$;
- Water evaporation capacity, $m_{WVD} = 535 \text{ kg/h}$;
- The thermal energy factor of the dryer HUBER Belt Dryer BTplus = 0.85 kWh/kg WVD;
- Thermal energy consumption of the dryer, when drying 1200 kg/h of 36% DS to 65 % DS = 455 KW;
- The electric energy factor of the dryer HUBER Belt Dryer BTplus = 0.06 kWh/kg WVD;
- Electric energy consumption of the dryer, when drying 1200 kg/h of 36% DS to 65 % DS = 32 KW;
- Electric energy available to operate the sewage sludge treatment plant = 386 KW.

Table 1: Mass flow per flux of thermal treated sludge, possible to be executed at the Wastewater Treatment Plant Timisoara

Treatment installation	Average the sludge mass flow input [kg/h]	The sludge mass flow output [kg/h]	Index for the reduction of the sludge quantity after dewatering	OBSERVATIONS
Dewatering units using solar energy and heat pumps	2400	1200	2	- the input mass flow determined by weighing; - the output mass flow determined by calculus, taking into account the reduction of humidity of the sludge from 18%DS (measured after the chemical analyses of sludge) to 36%DS, according to the design data.
Band dryer having as heat agent hot air and hot water	1200	665	1.8	- the mass flow output determined by calculus, taking into account the reduction of humidity of the sludge from 36%DS to 65%DS, estimated according to the domain literature, in order to ensure mono-combustion.
High efficiency burning installation	665	137	4.85	- the mass flow output results from the mineral percentage (including the phosphorous resulted from the wastewater treatment process) of the DS, determined after the chemical analyses of the sludge. - it is considered that, by burning, the volatile components are totally eliminated
The technological flux for thermal treatment of the sludge	2400	137	17,5	- the reduction of the sludge volume from the input of the technological flux up to the output is of 17.5 times.

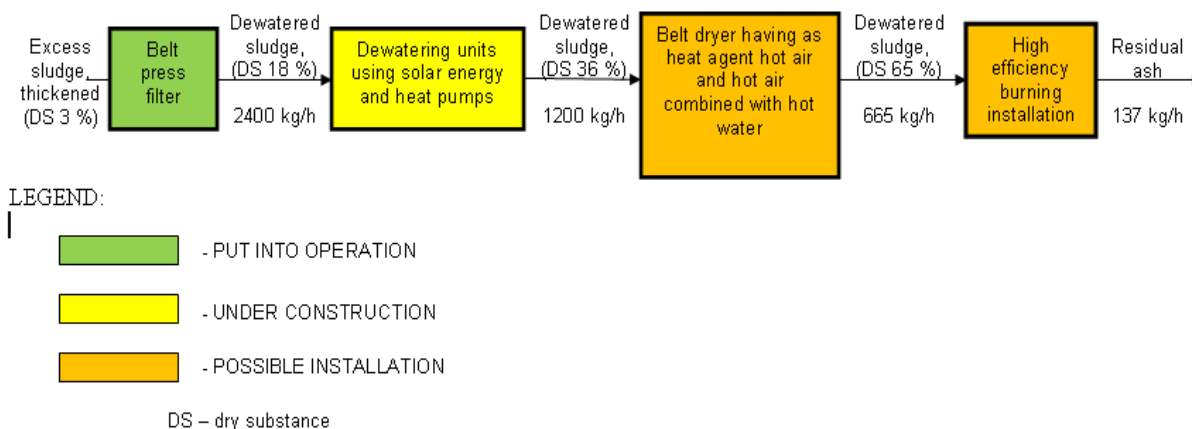


Figure 1. The possible technological flux for sludge dewatering at the Wastewater Treatment Plant Timisoara

RESULTS

After the energetic balance, the following observations can be made:

- The thermal and electrical energy obtained by cogeneration in sludge burning installations in thermodynamic cycles which are energetically efficient, based on the Pebble – Heater technology and hot air turbines fully cover the energetic consumptions of the burning and sludge dewatering processes;
- There results a supplementary gain of electrical energy of about 241 MWh, which represents approx. 25 % of the total electrical energy consumption of the WWTP Timișoara;
- Depending on the electrical energy consumption of the installations from the sludge dewatering flux, upstream from the dryer, the electrical energy gain obtained might cover the entire consumption of the sludge processing line; there may even be a surplus that can be used in the wastewater treatment process;
- The energy obtained by cogeneration within the sludge burning installation may increase with the increase of the calorific power, sludge biomass, which is possible by increasing the organic composition of the sludge;
- By implementing programmes for the calculation of the energetic balance one can optimise the components of the installation in view of increasing energetic efficiency.

CONCLUSIONS

The main advantages of the combustion or energy utilization of the sludge based thermodynamic cycles are:

- Electricity from sewage sludge saves fossil fuels and reduces fossil originated CO₂ emissions;
- One can make benefit of the green certificates offered by using sewage sludge as biomass, and finally selling them on the free market;
- The technology significantly reduces transport and storage costs for the owner of the water treatment plant;
- By implementing these thermodynamic cycles one can benefit by the full treatment sludge resulted from the water treatment process. Thus, bacteriological load with pathogen agents does not present any more risks for the use of residual ash in agriculture as dangerous bacteria and viruses are destroyed during the burning process;
- The amount of solid waste can be reduced by designing the ash to fit deposits, and/or recovery of incorporated phosphorus, thus being used as fertilizer for agriculture. Similarly one can store the heavy metals as well;
- The supplementary financial gains generated from electricity & heat selling – utilization for own purpose, as well the possibility to use the sludge as fertilizer for agriculture and bring

economies by reducing transport costs, covers most cases, the cost of drying and burning sludge.

ACKNOWLEDGEMENT

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II International Conference
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**BIOSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS
BY MICROBIAL BIOMASS**

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ABSTRACT

*The removal of heavy metals from wastewater is incorporated in the basis of the green chemistry' principles, that promote the application of alternative separation processes with minimal eco-footprint and maximal profitability. Common conventional separation processes are cost prohibitive, have inadequate efficiencies at low concentrations and may generate toxic sludge. The contemporary trends of environmental engineering regard the process of biosorption as a perspective bioseparation technique that is based on the metal binding capacities of various low cost biological materials. Practical application of biosorption of heavy metals from wastewater results from the ability of some types of biomass to accumulate heavy metals through metabolically mediated or physico-chemical pathways of uptake. Regarding practical experiences of the application of biosorption for heavy metal removal, it can be concluded that this non-conventional method has significant advantages over most of the conventional separation techniques. Research basis of this work directs to the utilization of microbial biomass (fungus *Aspergillus* sp.) for biosorption of heavy metals (Fe^{2+} , Ni^{2+}) from aqueous solutions. Biosorption dynamics was studied in batch conditions at various concentrations of Fe^{2+} and Ni^{2+} ions at different process parameters.*

Keywords: biosorption, microbial biomass, heavy metals removal, green chemistry.

INTRODUCTION

In recent years, the sustainable development of separation processes imposes the need of introduction of modern, nonconventional bioseparation techniques for elimination of toxic metals from wastewaters. This can be achieved through utilization of nonconventional low-cost sorbents. Biosorption is a contemporary eco-separation technique and its introduction to wastewater treatment is of essential interest to developing countries. Main advantages of biosorption are: low-cost sorbents, high efficiency, minimization of chemical and bio-contaminated residues, possibility of sorbent regeneration, and possibility of obtained metals' reuse (Yesim Sag and Tulin Kutsal, 2001; Azab M.S. and Peterson P.J., 1989).

Microbial biomass obtained as residue from fermentation processes can be efficiently used as a biosorbent for various heavy metals. Bacteria, algae and fungi can all be considered as efficient microbial biomass for removal of heavy metals, but they have different biosorption mechanisms and it is necessary to define the appropriate functional groups in the process (Amuda O.S. and Ibrahim A.O., 2006; Hussein H. et al., 2004).

Out of several microbial cultures cultivated in our department, *Aspergillus terreus* NRRL 265 which is generally used in itaconic acid production process can be considered as a low-cost biosorbent for elimination of heavy metals from their aqueous solutions (Preetha B. and Viruthagiri, T., 2005).

EXPERIMENTAL PART

Operating microorganism

Aspergillus terreus NRRL 265 was utilized as an operating microorganism obtained from lyophilized culture, product of National Research Resource Laboratory, Perioa II. This culture has been examined and raised by researchers from our department for a long period of time. The operating microorganism was activated on PDA (potato-dextrose-agar surface) at 28 °C.

Growth medium, inoculation and cultivation

Growth medium consists of 5% D-glucose, 0.33% (NH₄)₂SO₄, 0.08% MgSO₄·7H₂O, 0.05% itaconic acid, 0.0044% KH₂PO₄ and 0.0004% CuSO₄·5H₂O. Starting pH value after sterilization was set at 2.8 by addition of sulphuric acid. The inoculation of 100 cm³ from the growth medium was performed with 4.5 ml of spores' suspension, extracted from agar by sterile water. The cultivation was done on a laboratory shaker at a rate of 180 vib/min and a temperature of 36 °C for 36 h time.

Biosorption of Ni²⁺ and Fe²⁺ ions

After multistep washing procedure by demineralized water, obtained biomass was used for biosorption of Ni²⁺ and Fe²⁺ ions from their respective aqueous solutions. The biosorption process was conducted in a thermo-regulated batch reactor, placed on a laboratory shaker (168 vib/min) for 140 min of time. During the biosorption process, following operating parameters were altered:

- Starting concentration of aqueous solutions (separate and a mixture) – 0.25 g/dm³, 0.30 g/dm³, 0.35 g/dm³;
- Biosorption temperature - 30 °C, 33 °C, 36 °C;

RESULTS AND DISCUSSION

Morphological changes of the operating microorganism *Aspergillus terreus* NRRL 265 were monitored by a microscope during the cultivation period. During the initial 40 hours after being placed on the growth medium the microorganism forms pellets with an average diameter of 1 – 1.5 mm. This relatively long initial lag phase period results from the need of the microorganism to adapt on the growth medium as this culture has previously been used for biosynthesis of other useful metabolic products. During the exponential growth phase, already formed pellets grow branches forming voluminous micelle biomass.



Figure 1. Microscope photography of operating microorganism after 90 h cultivation (x200 zoom)

The branching of the micelle biomass significantly intensifies after 180 h cultivation period, during the stationary growth phase.

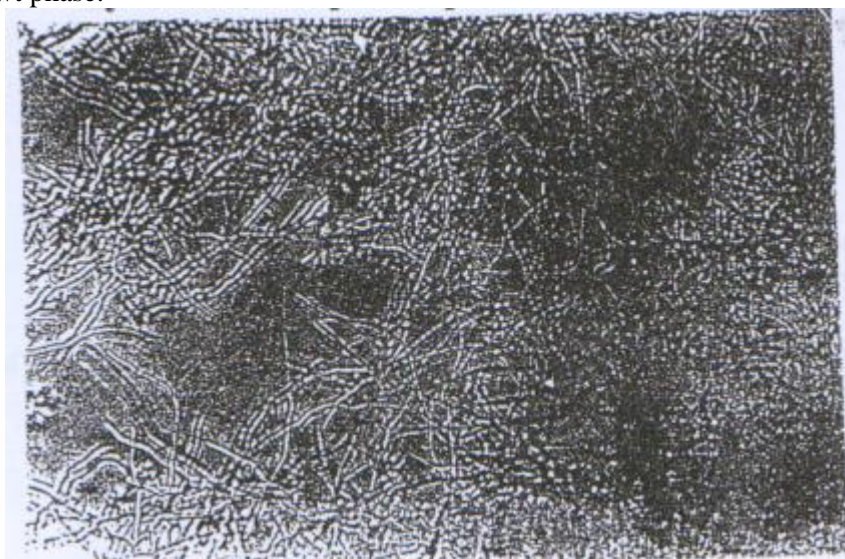


Figure 2. Microscope photograph of operating microorganism after 180 h cultivation (x200 zoom)

Monitored pH values of the system biomass-water indicate that the biomass carries negative charge which corresponds to consulted literature data.

Figures 3,4 and 5 as well as 6,7 and 8 represent the dynamics of the Ni^{2+} and Fe^{2+} ions biosorption process, respectively, from their aqueous solutions – NiSO_4 and FeSO_4 .

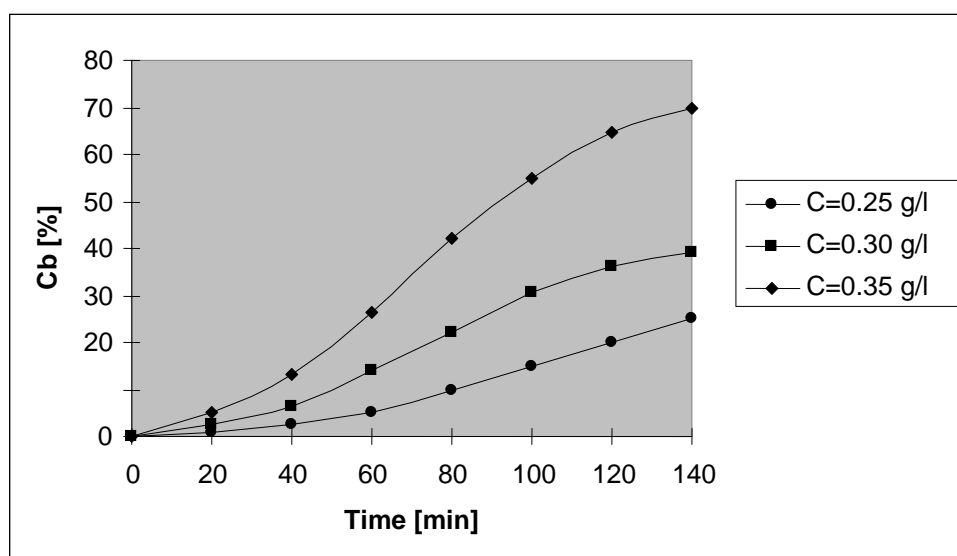


Figure 3. Dynamics of the process of biosorption of Ni^{2+} (%) – ($V = 40 \text{ cm}^3$, $t = 30 \text{ }^\circ\text{C}$, $q_{\text{biomass}} = 5 \text{ g}$)

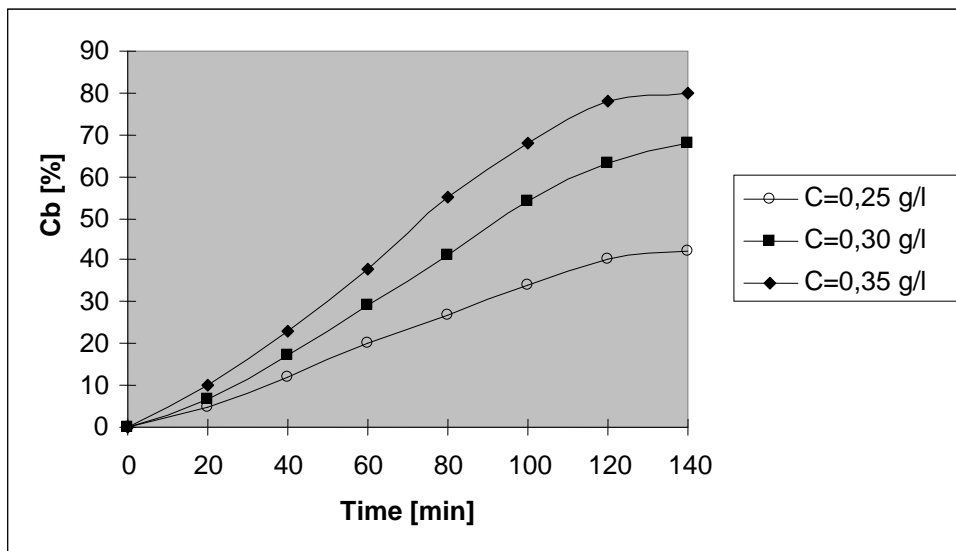


Figure 4. Dynamics of the process of biosorption of Ni^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 33\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

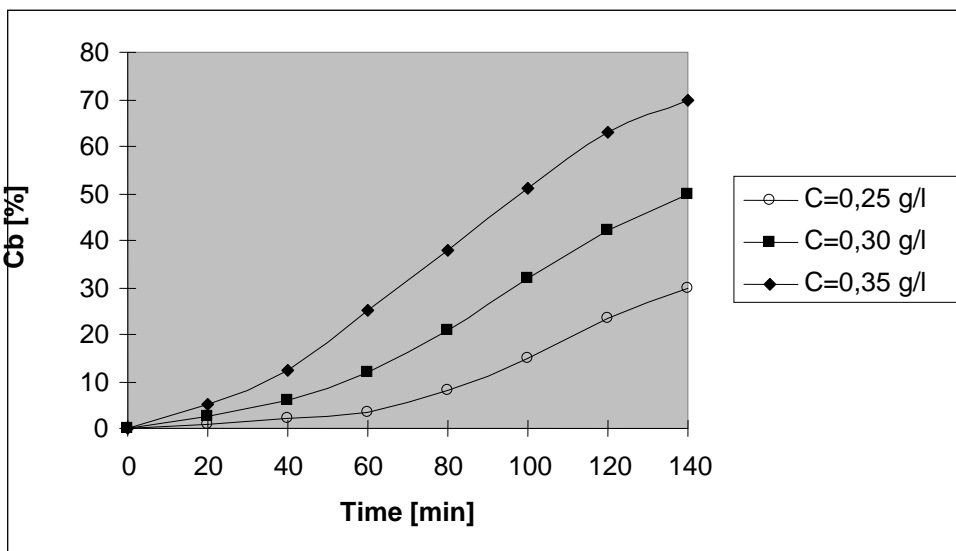


Figure 5. Dynamics of the process of biosorption of Ni^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 36\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

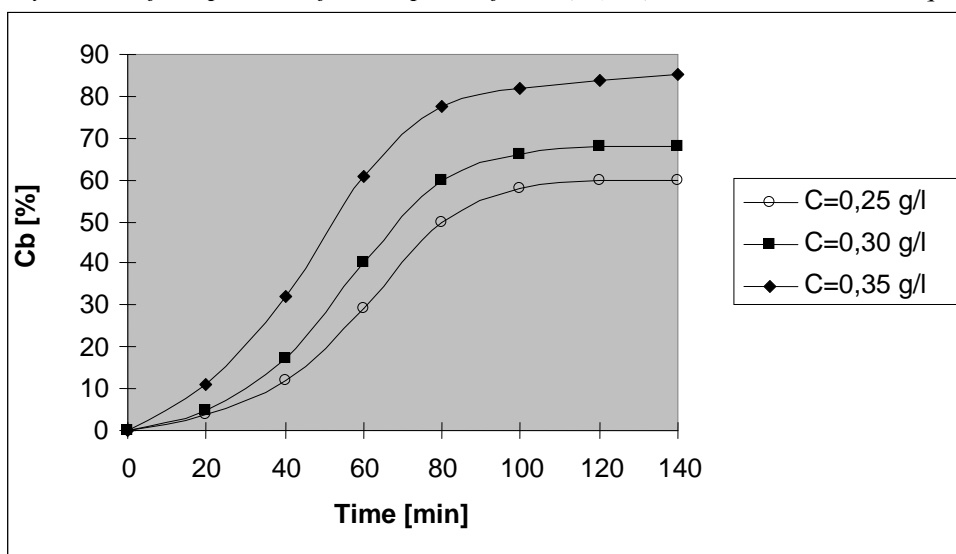


Figure 6. Dynamics of the process of biosorption of Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 30\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

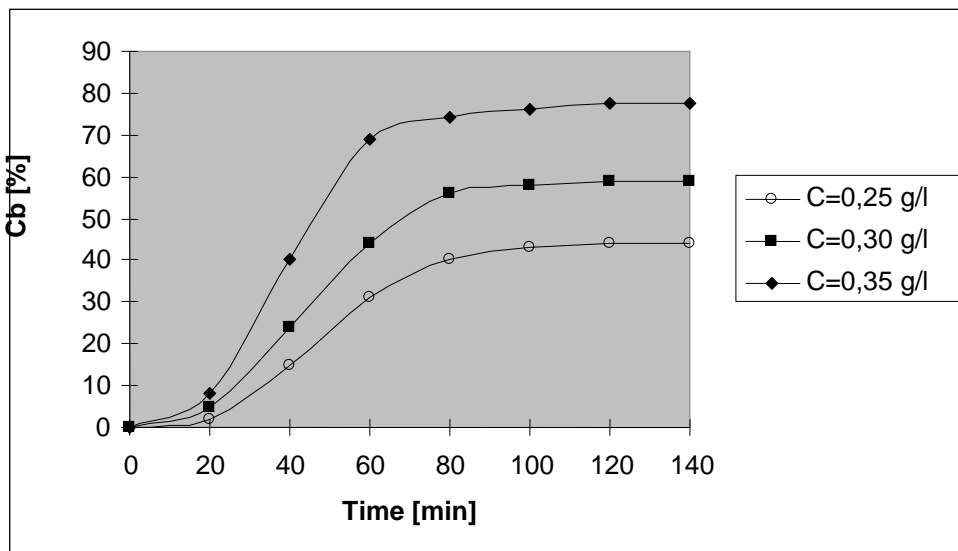


Figure 7. Dynamics of the process of biosorption of Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 33\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

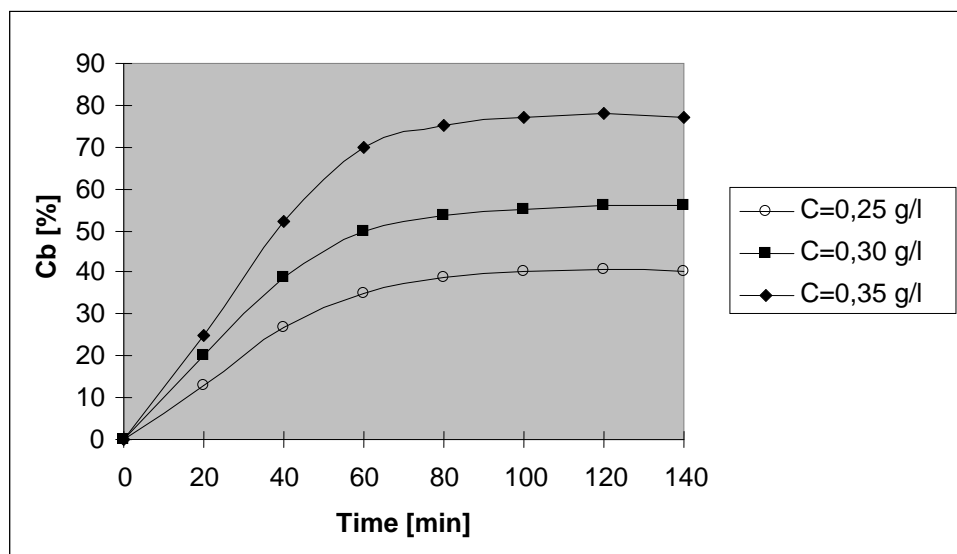


Figure 8. Dynamics of the process of biosorption of Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 36\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

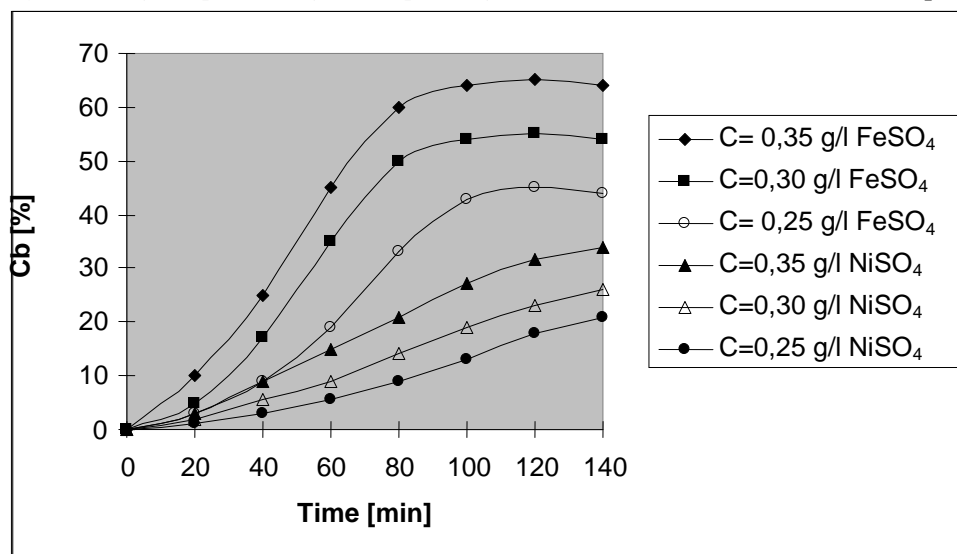


Figure 9. Comparative dynamics of the process of biosorption of Ni^{2+} and Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 30\text{ }^\circ\text{C}$, $q_{biomass} = 5\text{ g}$)

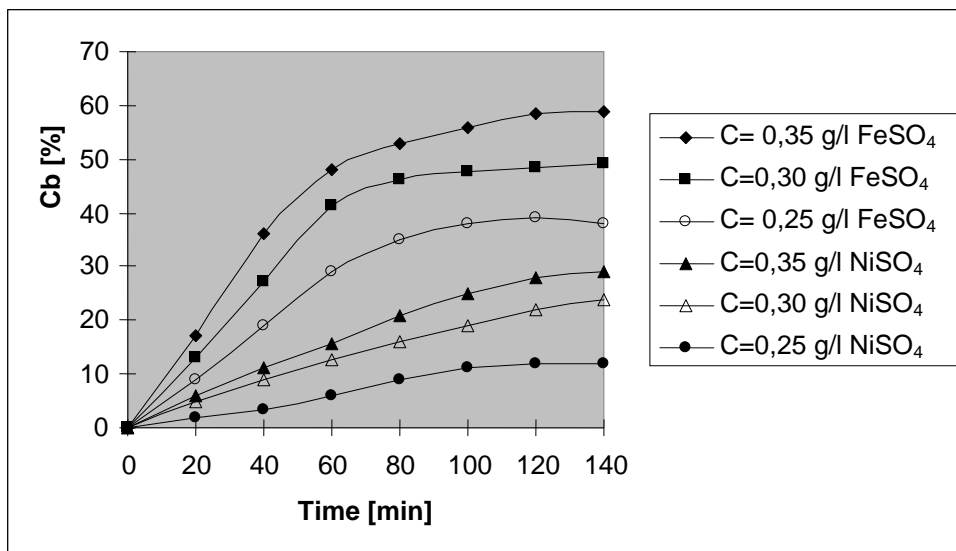


Figure 10. Comparative dynamics of the process of biosorption of Ni^{2+} and Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 33\text{ °C}$, $q_{biomass} = 5\text{ g}$)

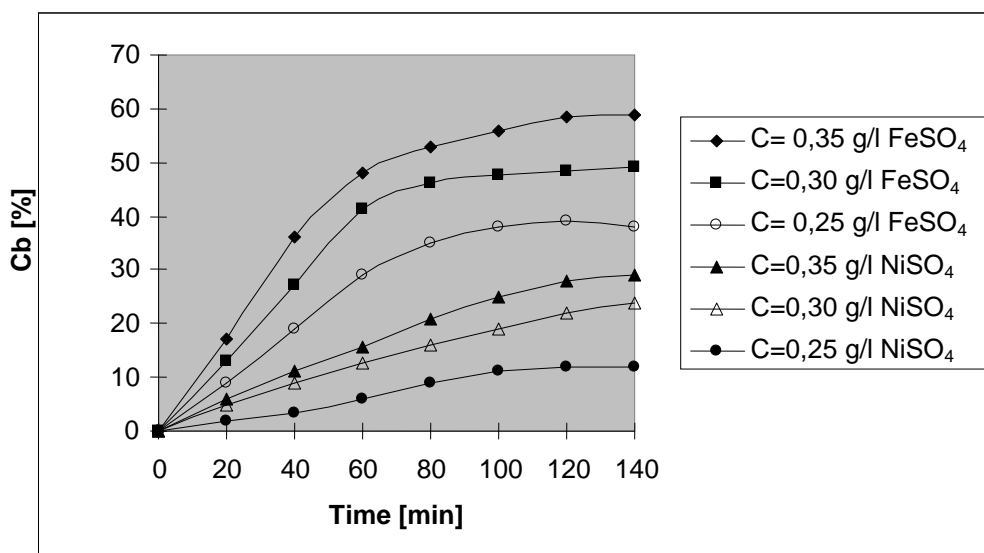


Figure 11. Comparative dynamics of the process of biosorption of Ni^{2+} and Fe^{2+} (%) – ($V = 40\text{ cm}^3$, $t = 36\text{ °C}$, $q_{biomass} = 5\text{ g}$)

CONCLUSION

Through analysis of separate biosorption dynamic curves (fig. 9,10 and 11) for Ni^{2+} and Fe^{2+} ions it can be concluded that the Fe^{2+} system enters the stationery state faster than the Ni^{2+} system. This comes from the fact that Fe^{2+} ions have less molecular mass than Ni^{2+} ions and therefore Fe^{2+} ions are more mobile. When operating with a binary system - Ni^{2+} and Fe^{2+} ions, the biosorbed quantity of Ni^{2+} ions decreases in favor of increased biosorbed quantity of Fe^{2+} ions. This results from the interaction between Ni^{2+} and Fe^{2+} ions with sorbent surface.

Generally, it can be concluded that some types of industrial fermentation biomass can be successfully used as a low cost and highly efficient biosorbent. In this case, studied fungal biomass from species *Aspergillus* represents a potential biosorbent for separation of heavy metals (Ni^{2+} and Fe^{2+} ions) from industrial wastewater.

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**II International Conference
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**IMPACT OF ECOLOGICAL FACTORS WITHIN FOREST
ECOSYSTEMS ON WATER FLOW AND RETENTION**

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ABSTRACT

This paper is to present analysis of ecological parameters' impact of forest ecosystems on water flow and retention. Data about forest and water ecosystems of Stara Planina in watershed of Trgoviski Timok were used for the analysis where the dominant plant is beech (Fagetum submontanum Jov. 1967.) having crucial influence with respect to formation of hydropedologic characteristics of forest soil. Natural conditions within which precipitation regime, characteristic for Stara Planina, transforms into water flow are presented by complex relations between habitat and biocenosis prevailing in the forest ecosystem.

Key words: *habitat, biocenosis, forest ecosystem, precipitations, water flow, forest of beech.*

INTRODUCTION

Eastern Serbia includes area with most forests, the highest quantity of rainfall and small population mainly being concentrated in lower regions, in settlements along river valleys and roads. Due to distribution of forest ecosystems, this mountainous area, as well as others in Serbia, is abundant of numerous ecological factors influencing retention and water flow which are critical in this century. How much water we may get from different basins in mountainous areas across our republic depends on different variables. Within each basin different ecological conditions are present influencing, more or less, water keeping, breeding or its runoff. Differences might be with respect to orographic, hydrogeological as well as pedological conditions, vegetation, climate etc. If we add to that way in which soil is used and other socio-economic factors, we have complete picture of complex conditions present in each basin. In order to precisely define yield of useful waters from some basins of mountainous areas, it is necessary to perceive, first and foremost, basic physical and geographical characteristics of the basin, as well as edaphic, then, vegetation, but also influence of anthropogenic factors on environmental conditions in the basin.

The subject of this paper is catchment area of Trgoviski Timok, right tributary of Beli Timok. This basin is interesting due to the fact that right tributaries of Trgoviski Timok drain south-western slopes of Stara Planina which is rather important and complex hydrological object.

OBJECT AND METODOLOGY

This paper's aim is catchment area of Trgoviski Timok which springs on Stara Planina and, together with Svrljiski Timok in Knjazevac, makes Beli Timok. The river's basin is elongated; it is narrow and steep on the left bank, while as broad and steep on the right, with numerous watercourses draining southwestern slopes of Stara Planina. The most important tributaries are Trgoviska, Zukovacka, Papratska, Gabrovnicka, Strma, Izvorska, Crnovrska, torrent Melo, Lesjanska etc. Length of the basin is 54,1 km, while as total area covered is 536,9 km. There used to be 35 villages and hamlets which have been left in the process of migration, or there is negligible number of elderly households. Being rather abrupt area, mainly forest vegetation is present in this basin counting for 50%. Dominating species is beech which is, with respect to hydrology, the most desirable vegetation concealer. Soils

where this vegetation is present are mainly acid-brown on limestone in the conditions of continental climate.

In order to obtain reliable estimates of contributions of some ecological parameters and their impact on water flow and retention in the forest ecosystem, analysis of achieved results as well as existing data have been done. On the basis of these results, bearing in mind the importance of catchment area's ecological factors in the conventional approach to the study of water flow and retention in forest ecosystems, essential elements are presented in the shortest possible extent.



Figure 1. Basin of Trgovski Timok

RESULTS OF THE SURVEY AND DISCUSSION

From the point of studying the role of retention in forest ecosystems on water flow, there is, among other things, rather important role of some types of forests, ecological conditions within them.

Analysis of hypsometric map ascertained that lower, hilly terrains within the basin count for 21,42% of its surface, low-mountainous (500-1000m ASL) 64,48%, while as middle and high-mountainous terrains (above 200m ALS) count for 14,10% of the basin. Medium altitude of the basin is 726,29m ALS.

Geological structure of the surveyed area is presented on the basis of BGM P=1:100000 (basic geological map). Terrain of Trgovski Timok consists of metamorphic, igneous and sedimentary rocks of different composition and geological age. The most common are metamorphic (crystalline schist, amphibolite, gneisses, phyllite, slade and quartzite), while as igneous are less widespread but there is a lot of variety (granite and granodiorite, and the appearance gabbro and dacite-andesite rocks). Following sedimentary rocks are present in this area: gravel, sand, sandstone, conglomerate, limestone, marl and tufa. In the area of Trgovski Timok association and association of formations are present whose age ranges from the upper Proterozoic to Quaternary (Nikic et al.,2008)

Using Pedological study of Timok's basin, Antonovic, G., (1974.), characteristics of soil in the catchment area have been determined (Picture 3). According to the data, following types of soil are present:

- Terrestrial-land: undeveloped land, active humus soil, cambio (acid-brown);
- Hydromorphic soil (fluvisols).

Among aforementioned types of soil rather important is cambio (acid-brown) being hydrologically the most favorable due to its structure (retention-accumulation characteristics), presence in the catchment and the type of vegetation. These soils are represented by distric cambisol that occur on different surfaces (micashist, phyllite, gneiss, granite, sandstone and andesite) being the most common type of this basin (72,15%) which vary with respect to aeration and water infiltration. Then, eutric cambisol, brown soil on gabro counting for 14,86% which has heavier texture than the previous ones with lower infiltration and retention characteristics and, at the end, kalkokambisols, brown, limestone soil of good structure and infiltration characteristics. Surveyed area, basin of Trgoviski Timok, surface where those soils have developed is mainly under high-quality beech forests.

Current condition of the vegetation is consequence of bare ground afforestation and erosion control in the basin that started in 1955, and those works included biological as well as technical measures. According to available data (Bilibajkic, S., 2009.), 45,99% of basin's surface is under the forest, 48,87% are agricultural land (41.57% meadows and pastures, 7.0% arable land, 1.3% of orchards and vineyards), road network and other unproductive areas account for 4.13%, Picture 2. Pure and mixed beech forests dominate within the basin, then oak, ash, hornbeam, turkish hazel as well as cultures of black pine and others. Beech forests, hydrologically the most important, are represented in in the belt between 400-1500m ASL. Within this area beech (*Fagetum montanum serbicum*) is located mainly in pure stands, with a negligible share of mountain maple, mountain elm, and, in some parts, there are mixed communities with hornbeam and oak. At higher altitudes, 1000-1200m ASL, communities of beech and fir (*Abieti - Fagetum serbicum Job.*) are present, while as above that height there are pure fir forests. Below 400m ASL, in the area of river valleys forest vegetation occurs in a narrow coastal belt with species conditioned by flood waters (willow, poplar, alder, ash etc.). Low-mountainous (500-1000m ASL) terrains dominate, 64,48%, which is the belt of the best beech forests on acid-brown soils having the most favorable retention-accumulation characteristic. Therefore, Basin of Trgoviski Timok has ecological parameters close to optimum for acceptance of maximum precipitation (Ducic et al., 2003), infiltration, and their light runoff. Condition of forest vegetation on the surveyed area was processed during 2011/2012, on the basis of General and Particular basics for forest management of forest-economic area of Timok, as well as available literature have been used.

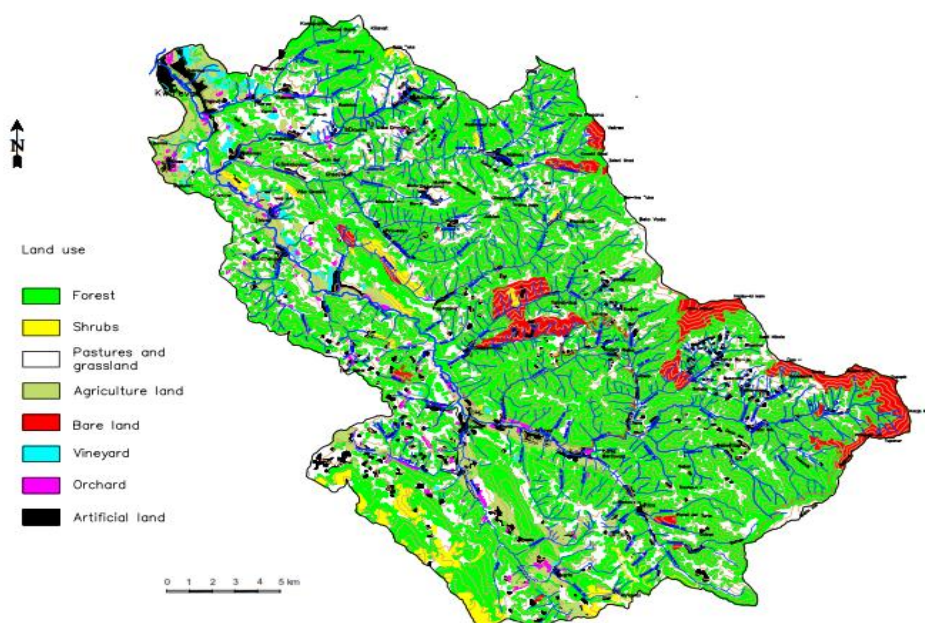


Figure 2. Ways of soil use in the basin of Trgoviski Timok

Rather diversified hydrographic network of rather asymmetric basin drains slopes of Stara Planina providing permanent flow to this water stream. Out of numerous tributaries, important ones are those on right side: Trgoviska, Zukovacka, Papratska, Gabrovnicka, Inovska, And Crnoviska, due to the fact that they drain slopes of Stara Planina providing Trgoviski Timok with permanent flow. Since there are no permanent flow measurement on watercourse, left one as well as on right one, data on discharges to their recipient, Trgoviski Timok, provided by RHMZ Serbia, have been analyzed.

Table 1: Typical flows in the surveyed catchment

River	Water gauge station	Area watershed (km ²)	Q _{sr} (m ³ /s)	Q _{min,95%} (m ³ /s)	Q _{max,1%} (m ³ /s)
Trgov. Timok	G.Kamenica	331	3,36	0,31	245
Beli Timok	Knjaževac	1,242	8,31	0,40	422
Beli Timok	Vratarnica	1771	10,46	0,45	383
Beli Timok	Zaječar	2,15	12,39		
Vel. Timok	Tamnić	4 191	28,64		
Aldinačka r.	Žukovac	77	0,80		
Crni Timok	Zaječar	1,199	12,51	0,58	410
Visočica	Visoč. Ržana	403	5,83		

Their span goes from 0,31 m³ s⁻¹ (Q_{min 95%}) to 245 m³ s⁻¹ (Q_{max1,0 %}), while as Q_{sr} =3,36 m s⁻¹ is average value (Table 1). Typical for this catchment is higher value of water flow than the average one in Serbia (q= 5,70 l/s/km²) counting for q= 10,10 l/s/km². These facts are rather important in terms of useful water return because with rainfall of 800-1000mm (in the zone of the central ridge 1100mm) Stara Planina has special significance for Serbia as a hydrographic and water management units being located between the two expressed precipitation depression (zajecarska on the North and nisavska on the South) where average annual rainfall counts for only 500-600mm which is lower value than the average of the Republic, 735mm.

Considering the conditions of the surveyed basin, and the state of ecological factors which enhance retention and (helpful) storm water runoff, the available data indicate the importance of presence and condition of forest ecosystems in the basin of Trgoviski Timok. Great presence of acid-brown soils, on whose hydrological characteristics beech forests have prevalent impact, dominate in the surveyed flow with continental pluviometric regime and the depopulation of areas indicating existence of positive developments in terms of environmental hydrology (Letic Lj.,2005).

CONCLUSIONS

According to available data analysis with respect to soil, the way it has been used, vegetation and climate, we may conclude following:

- Within surveyed basin of Trgoviski Timok, orographic-climatic conditions favor rapid, flood discharges. Rather hilly landscape with continental pluviometric regime (higher precipitation takes place during growing season) causes forming of harmful (torrential) runoff.
- Low-mountainous terrain domination favors the development of hydrological most productive community forest species, beech forests (belt *Fagetum moeziaeceae serbicum* Rud.). Ecosystem dominated by this community provides the highest retention capacity and maximum water yield being present at about 46% of the catchment area.
- Retention characteristics of this ecosystem are contained in the structure of acid-brown soils which are formed in the beech forests and occupy over 72% of the surveyed basin.
- In addition to factors previously mentioned with respect to climate and soil in the basin of Trgoviski Timok, there is a significant factor in depopulation, which contributes to the spread of vegetation, and thus to the change of its retention capacity.

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**SEASONAL ELECTRIC POLARIZATION OF THE CHEMISORBED
OXYGEN IN THE URBAN RIVER WATER**

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ABSTRACT

The seasonal influence on the electric spontaneous or forced oxygen polarization in coupled processes is examined based on the monitoring data on oxygen content, oxygen solubility degree and air and water temperature for urban river Begej on input and output from the town, Zrenjanin. Based on the months monitoring results in the 2010 year, based on the calculated chemisorbed oxygen electric polarization, the coupled relaxation processes electrochemical potential in the end point of the overall relaxation process as the sum of entropy and enthalpy driven relaxation processes are calculated depending on the sunlight energy and river water pollution, based on the best correlation coefficients with monitoring data with the, $R^2=0,7-0,9$. The calculated electric polarizations correspond to the decay kinetic of chemisorbed oxygen photolysis of irradiated urban river water saturated with oxygen depending on the season and location.

Key words: *Urban river, Input in urban area, Output from urban area, Oxygen solubility, Chemisorbed oxygen, Electric polarization, Seasonal influence, Pollution influence.*

INTRODUCTION

The data determining the polarization processes of the chemisorbed oxygen as natural phenomena, are calculated in this paper, depending on the season and urban river pollution. The thermodynamic analysis was carried out based on the examination in the literature (S. Sieniutycz, 2010). The results are used in the identifications of the chemisorption processes involved in the contact surface between the solution and air (Bard, ed., New York, Basel). The main objective in this study is to evaluate the effect of the river water location and season influence on chemisorbed oxygen electric polarization, based on:

- The Vant Hoff method, applied on the adiabatic achieved electrons chemical potential equilibrium with the specifically chemisorbed oxygen between the two phases (M. M. Ševaljević, S. N. Simić and P. V. Ševaljević, 2012)
- The Gibbs free energy depending on the equilibrium oxygen reaction constant determining with oxygen saturation degree, w_s depending on the oxygen enthalpy in the contact surface between liquid and gas phase.

The electric potential, $\Delta\phi$ defines oxygen desorption work from the active adsorption nucleuses determine the negative value of the adsorption work, of the sum of oxygen adiabatic work in adsorption layer, $\Delta_{ad}G^\theta$ and oxygen enthalpy in the diffusion layer $\Delta_{is}H^\theta$ in the end point of the coupled electrochemical relaxation processes:

$$\Delta\phi = -\frac{\Delta_{is}H + \Delta_{ad}G}{zF}$$

In the double layer of pollutants, active with polarized chemisorbed oxygen could be desorbed in presence of the oxygen reactions with equal electrochemical potential enabling oxygen depolarization and desorption in the gas phase.

EXPERIMENTAL RESULTS

Oxygen saturation, w_s , air and water temperatures are measured in Institute of the Public Health in Zrenjanin in 2010 each month, in the river water of Begej, before the input in the urban zone of Zrenjanin and after output. The modified Winkler method analogous to EN 25813 is used after oxygen oxidized manganese (II) to manganese (III) and in acidic solution form red complex with Titriplex for the photometrically determination with WTW photometer and oxygen cell test, WTW 14694.

The measured data and calculated results are analysed depending on:

- the season date

- and location of the samples for analysis

a) on the river Begej input in the urban zone, at the asphalt base

b) and on output from the urban zone, at the bridge in Ečka.

Oxygen contents and water temperatures are measured monthly in 2009 and 2010. in the river water of Begej, before the input in the town Zrenjanin and after output from the town, as the indicator of river water pollution.

Table 1: Monitoring data of the oxygen solubility, oxygen saturation degree, water and air temperatures

Input The dates	t_w °C	t_{air} °C	O_2 , mg/l	c/c^* %	Output The dates	t_w °C	t_{air} °C	O_2 mg/l	c/c^* %
13.1.2010	5,4	3,3	12,4	92	13.1.2010	5,5	1,7	12,7	92
3.2.2010	1,3	-0,5	11,1	78	3.2.2010	1	0,5	9,1	64
3.3.2010	8	6,9	11,8	100	3.3.2010	7,8	6,3	11,7	99
23.4.2009	9,5	9,6	7,1	62,4	23.4.2009	17,8	15,5	4,9	51,8
29.4.2010	16,8	19,5	9,2	95	29.4.2010	17,2	21,7	5,3	55
13.5.2009	19,5	16	9,9	109,3	13.5.2009	19,5	18,2	4,9	54
14.5.2010	18,5	19,3	7,8	82	14.5.2010	18,2	24,3	6,5	69
6.6.2010	24,4	29,6	5,7	68	6.6.2010	23,5	32,1	5,7	68
1.7.2010	24,6	29,7	4,2	51	1.7.2010	23,3	25,6	6,4	75
16.7.2009	26,9	25,3	5,7	70,9	16.7.2009	26,3	26	5,2	65,2
13.8.2010	25,1	26,3	5,7	69	13.8.2010	25,7	21,2	4,8	59,1
15.9.2010	19,6	18	6,8	75	15.9.2010	20	23	3,7	41
15.10.2009	13,1	6,7	8,7	71,7	15.10.2009	13,9	6,3	7,3	58,63
4.11.2009	8,2	3,6	9,2	70	4.11.2009	8	3,6	8,1	62
2.12.2009	8,7	6,3	10,1	81	2.12.2009	7,8	5,9	7,9	63

Table 2: The calculated seasonal electric polarizations of chemisorbed oxygen on input in the town

Input / Months	$\Delta_{ad} G^\theta = -T \cdot \Delta_{ad} S^\theta$ kJ/mol	$\Delta_{is} H^\theta$ kJ/mol	$\Delta\phi$ V	Identification of the oxygen polarization reaction
I-III	6,9	23,96	-0,32	$O_2 + e \rightarrow O_2^-$
IV-V	-89,196	69,554	0,2	$2O_2^- + H_2O \rightarrow O_3 + 2OH^-$
VI-VIII	-9,468	-6,915	0,17	$O_2^- / O_{2(G)} \rightarrow O_{2(L)}$
IX-XII	-26,536	-20,325	0,48	$2O_2^- + H_2O \rightarrow O_2 + HO_2^- + OH^-$

Table 3. The calculated seasonal electric polarization of chemisorbed oxygen on output from the town

Output / Months	$\Delta_{ad} G^{\theta} = -T_{ad} S^{\theta}$ kJ/mol	$\Delta_{is} H^{\theta}$ kJ/mol	$\Delta\phi$ V	Identification of the oxygen polarization reaction
I-III	27,016	42,534	-0,72	$HO_2 + e \rightarrow HO_2^-$
IV-V	-18,864	28,117	-0,09	$OH^- + hv \rightarrow OH + e_{aq}$
VI-VIII	-51,02	-18,52	0,72	$HO_2^- \rightarrow HO_2 + e$
IX-XII	-51,02	-19,787	0,73	$HO_2^- \rightarrow HO_2 + e$

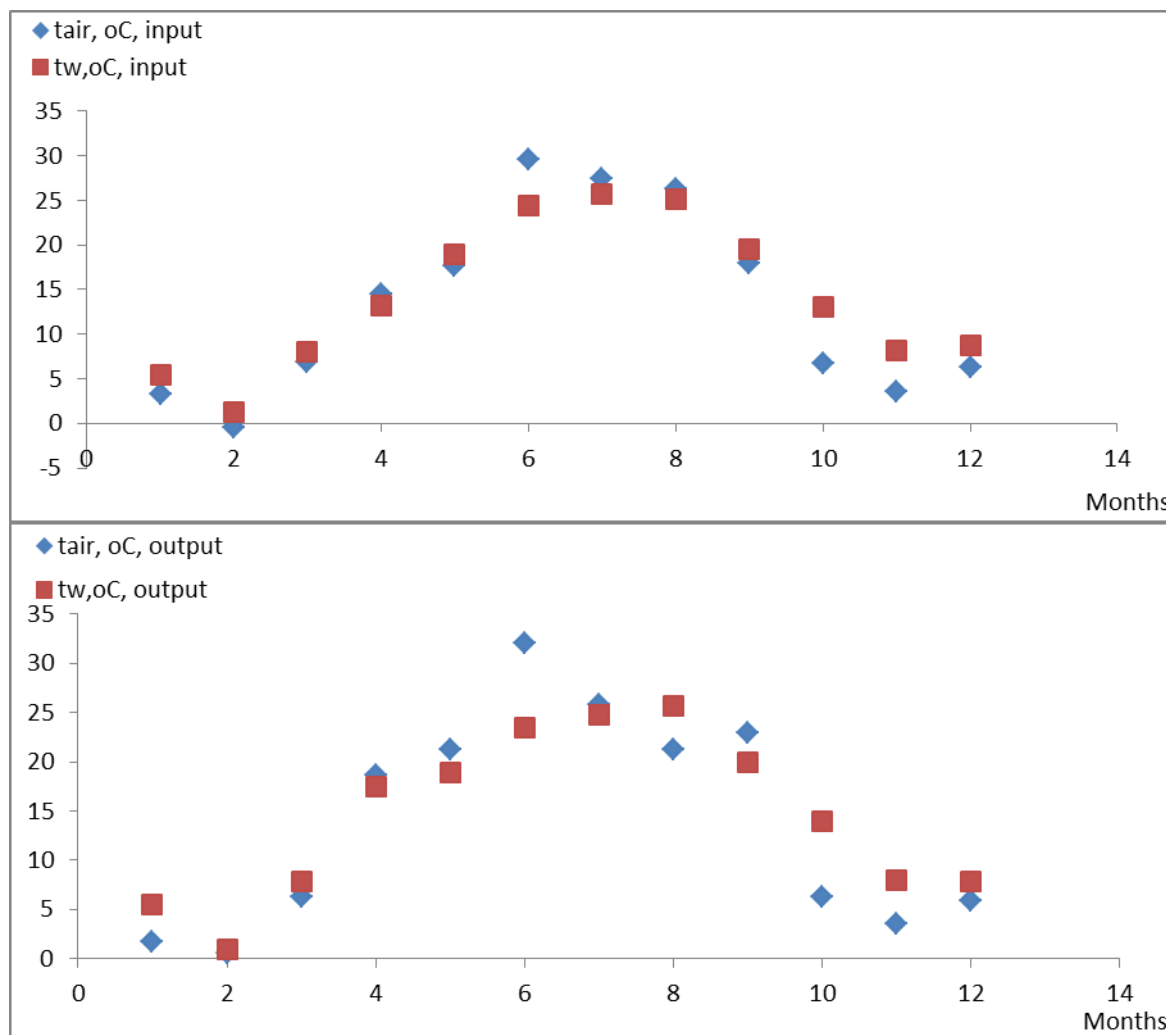


Figure 1. Seasonal temperatures of urban river water and air , on input and output from the town

The obtained results of the chemisorbed oxygen surface electric polarization, $\Delta\phi$ depending on the seasonal urban water irradiation are indicators of the end titration point of coupled processes (aggregation and electrochemical gasification) up to achieving of the stationary electric polarization of oxygen in the contact surface.

In the period in winter months, I-III on the both examined locations faster water than air heating determine the stationary oxygen polarization.

In the period IV-V, the air temperature jump above water temperature depending on water pollution favored:

- Ozone production on river input in the town
- Photochemical cathalytic reactions on river output from the town

In the period VI-VIII up to September, the stationary oxygen polarization favor air temperature increasing above water temperature is characteristic.

In the period IX-XII, in the November, minimal air temperature in comparison with the water temperatures determine the electrical oxygen polarization processes.

CONCLUSIONS

Based on the calculated data it can be concluded:

1. The chemisorbed oxygen electric polarization determines the sum of entropy and enthalpy driven relaxation processes, depending on the sunlight energy and river water pollution,
2. On the input of urban river in the industrial zone of the town the middle oxygen polarization in the range, $\Delta\phi_{\text{input}} = -0,32\text{V}$ to $0,48\text{V}$, favor the relaxation processes.
3. On output of urban river from industrial zone of the town, the twice increased oxygen polarization in the range, $\Delta\phi_{\text{output}} = -0,72\text{V}$ to $+0,72\text{V}$ are found.

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**II International Conference
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**UV WATER TRANSPARENCY IN HYDROGEN PEROXIDE
PRESENCE**

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ABSTRACT

Peroxides, hypochlorite compounds, ozone and other unstable oxidants have high absorption coefficient in UV spectrum. UV radiation energy absorption around 254 nm is strong enough to break weak covalent bonds in those molecules and high-reactive oxidants arise: OH radicals, and nascent oxygen. further on, they participate in combination and recombination processes with the newly obtained molecules and water content. Strong oxidants, generated in this way, quickly and effectively decompose harmful water content, for example stable organic macromolecules. In order to obtain better a priori UV reactor analysis and design parameters for unwanted water content oxidation, it is necessary to determine impact of non-stable oxidants to overall water absorption coefficient. In this paper, various concentration influence of hydrogen peroxide in water is analyzed in order to determine mathematical model defining absorption dependence from hydrogen peroxide concentration in water. Water absorption is very important parameter for overall water transparency, in UV reactors with high intensity UV radiation that decreases initial oxidant concentration. It has the direct impact to UV reactor parameters formulation (such as: water layer thickness, capacity of UV reactor, UV sources disposition), and therefore to UV reactor optimization, cylindrical as well as plan-parallel (opened and closed) for water treatment.

Key words: absorption, UV radiation, oxidants, transparency, UV reactor.

INTRODUCTION

Nowadays, hydrogen peroxide (H₂O₂) and especially OH radicals, obtained by UV decomposition of hydrogen peroxide, are frequently used as strong oxidant and/or disinfectant. Using hydrogen peroxide by itself, or in combination with some other components, can be very effective in water treatment processes. Having in mind that hydrogen peroxide is temperature unstable and decomposes by light irradiation during some period of time, it has to be measured periodically, for some investigations-processes, and especially when UV radiation is applied.

Spectrophotometer methods for H₂O₂ determination in water are described in article (Todd, Cerni et al, 2004), and applications of UV-H₂O₂ interactions are given in many articles aim to degradation of unwanted chemical compounds in aqueous solutions (Liao et al, 2001, Sarla et al, 2004, Forero, 2011).

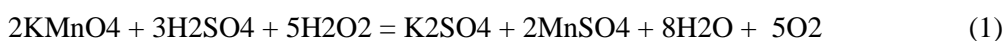
THEORY

Measuring the concentration of the hydrogen peroxide in water

Oxygen radical (O₂⁻) and: hydrogen peroxide, ozone (O₃), hypochlorite compounds, etc., in UV environment at 254 nm strongly absorb UV rays. Absorption of the ultraviolet light is in direct relationship with peroxide concentration.

As referent method for quantitative measurements of the peroxide concentration in the standard water samples, we used the classical method of measuring consumption of potassium-permanganate.

These analyses consist of the oxidation of organic and inorganic substances during cooking for ten minutes in the presence of sulfuric acid (Potable water, 1990). Beside oxidation of the organic substances, this chemical reaction oxidizes substances, such as ammonium ion, nitrites, sulfides, ferrous iron, manganese, etc. However, when dosed peroxide into the water, permanganate, in acid medium, reacts according to the following equation:



An important feature of this reaction is that permanganate with peroxide reacts as it is given in the following equation:



As a consequence of these facts, permanganate is used as a standard method for determining the concentration of peroxide in water. This allows us to quickly and easily control the dosage of peroxide in water.

It should be pointed out that natural water has its own content of many different substances, organic and inorganic, which directly influence the value of permanganate consumption. Once establishing the dependence between the concentration of peroxide, measured potassium permanganate consumption, and UV absorbance at 254 nm, then the concentration of peroxide dosage can be quickly and easily controlled by UV technique.

EXPERIMENT DESIGN

All experiments were conducted in the chemical laboratory within the Institute for the development of water resources »Jaroslav Cerni, a.d.«. Three different water samples (distilled, well water and river water from Sava) were selected. Samples were dosed with different concentrations of peroxide, and then determined by potassium permanganate consumption method - and simultaneously with UV technique at 254 nm. The volumes of 0.002 M potassium permanganate consumed for oxidation of several peroxide solutions are given in Table 1. Concentrations of hydrogen peroxide were calculated on the basis of permanganate consumption.

Table 1: Measured concentration values of H₂O₂, obtained from KMnO₄ consumption

Commercial sample		The samples prepared in the laboratory		
Declared concentration on the label		Values obtained by titration of 0.0002M KMnO ₄		
% H ₂ O ₂	mg/l H ₂ O ₂ ,	Distilled water, mg/l H ₂ O ₂	Well water, mg/l H ₂ O ₂	Water from River Sava, mg/l H ₂ O ₂
0.000075	0.75	0.9	/	0.7
0.00015	1.5	1.8	1.5	1.2
0.0003	3	3.4	2.8	2.8

Measurements have confirmed that there is a proper correlation between the concentration of peroxide and potassium - permanganate consumption in natural waters.

Second experimental step of the study was to determine the hydrogen peroxide solution concentration dependence and UV absorbance ($\lambda = 254 \text{ nm}$). UV absorption on 254 nm was determined by UV-VIS spectrophotometer Perkin - Elmer, $\lambda 2$. Commercial, 3 % hydrogen peroxide was used for preparing of the sequence solutions. Different types of water were used as solvents, such as distilled water, well water (Belgrade Source) and river Sava water at Belgrade profile. Test results interdependence concentration of hydrogen peroxide and UV absorbance are shown in the following Figures 1, 2 and 3.

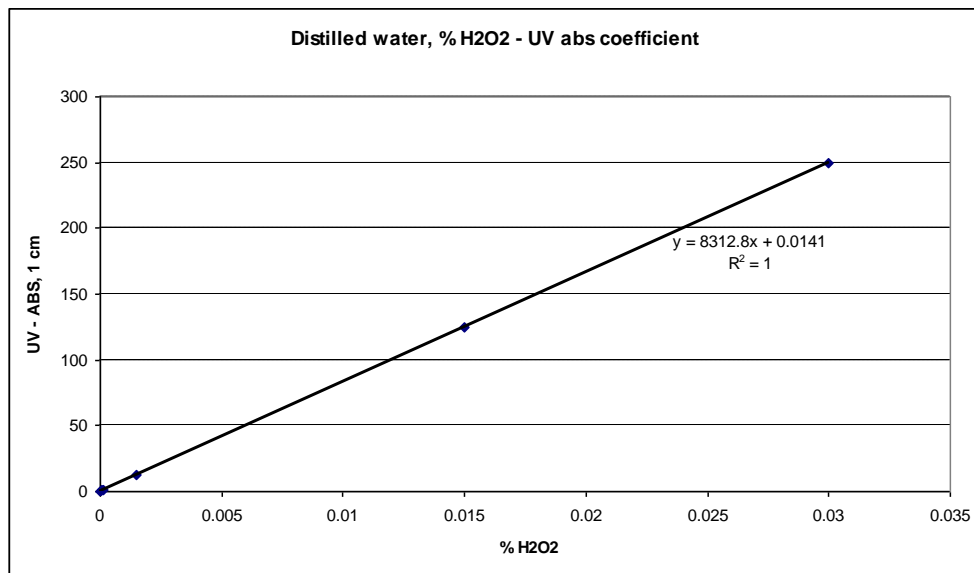


Figure 1.

For solution with distilled water a linear relationship was established with a correlation coefficient 1 (Figure 1). In cases where water from the well and river Sava were used, as a solvent for the preparation of the hydrogen peroxide solutions, the resulting correlation coefficients were 0.99 (Figures 2 and 3). UV correlation is examined in two ways. UV absorption of the natural water (well water and river water) was not taken into account (black line in the Fig 1 and 2) while in the second case, the total value of the UV absorbance was reduced for the value of the original UV water absorption (without peroxide). The resulting correlation is also shown in Figures 2 and 3 (black dashed line).

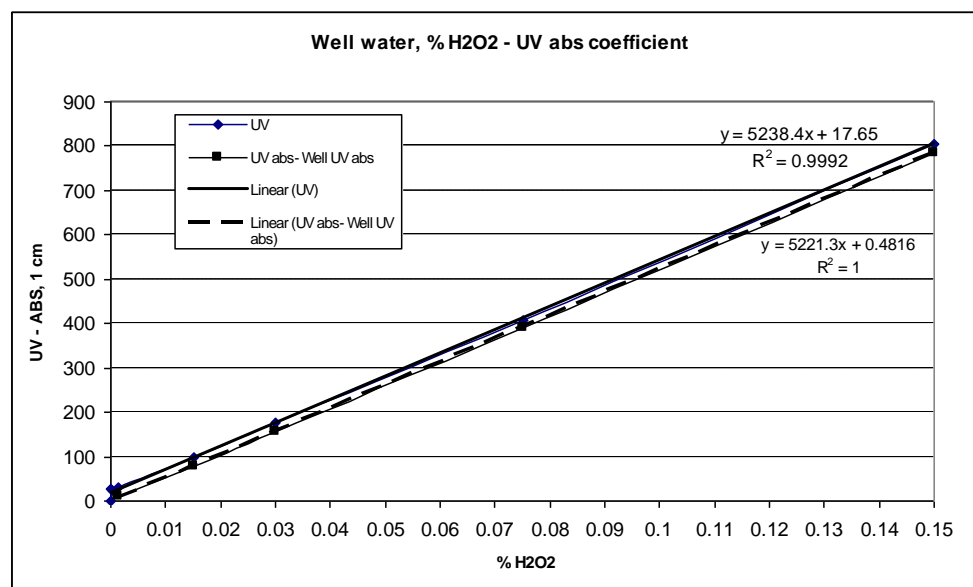


Figure 2.

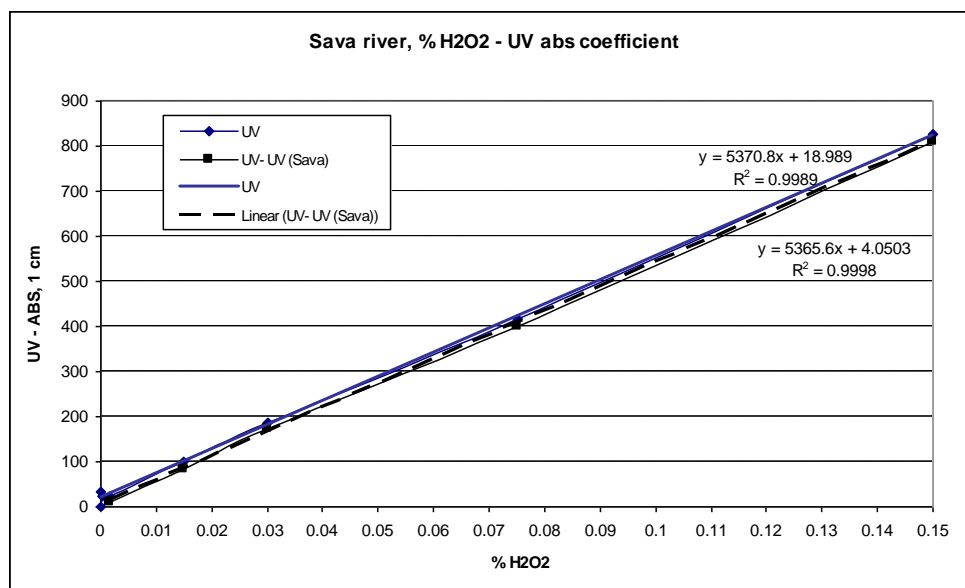


Figure 3.

CONCLUSION

Measurements have confirmed that there is a linear dependence of concentration of peroxide and potassium- permanganate consumption in natural waters. For distilled water solution, a linear relationship was established with a correlation coefficient 1. In cases, where water used for the preparation of the hydrogen peroxide solutions were from the well and river Sava, the resulting correlation coefficients were 0.99.

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**II International Conference
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**ASSESSMENT OF GROUNDWATER QUALITY IN ZRENJANIN
BASED ON FUZZY LOGIC**

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ABSTRACT

Uncertainties are one of the problems in the most commonly used methods for assessing the water quality. Fuzzy logic can successfully handle with these uncertainties in decision-making on drinking water quality. In this paper is shown the application of the fuzzy logic for the assessment of the physico-chemical quality of groundwater for drinking purposes in the City of Zrenjanin. Fuzzy rule based model offers a final water quality with the degree of certainty. Application of this fuzzy model is illustrated with samples from two wells that are located at depths of two aquifers from which water is taken to supply the population with drinking water. These samples were analyzed for 5 different physico-chemical water quality parameters. In this research arsenic concentration (As^{3+} , As^{5+}) is considered as the dominant parameter because of his suspecting carcinogenic effects on human health. The analysis showed that sample from well 1 provide an not acceptable quality of groundwater with certainty of 10, while sample from well 2 has acceptable quality of groundwater with the value of certainty 35.

Key words: groundwater quality, parameters, fuzzy logic, degree of certainty, arsenic.

INTRODUCTION

The availability and quality of groundwater as well as drinking water will be the main environmental and social issues in the future. The quality of groundwater is very important, especially when that water is used for drinking purpose. Water quality monitoring and quality decision-making based on the obtained data is complex and multidimensional task for decision makers. The main reason of such heavy work are uncertainties that occur in all steps, from sampling to analysis. The data set obtained from the field and their limits should not be considered as a classical sets but as a fuzzy sets.

Conventionally, the decision on the water quality is make by comparing the obtained parameters of the groundwater with their prescribed limits without involving any uncertainty. One of the most used methodology for assessing the quality of water is the water quality index (WQI). Sii et al. (1993) have discussed the uncertainties involved in water quality using fuzzy membership with values ranging from 0 to 1 to form an applicable fuzzy set instead of the conventional scale of 0 to 100 in WQI methodology. This methodology based on fuzzy set theory can be applied to real environmental problems. The essence of this methodology is to reduce the uncertainty of the criteria involved in decision-making.

Thanks to the flexibility of fuzzy set theory in decision-making through the environment assessment, it has been carried out the assessment of the quality of groundwater used as drinking water in the town of Zrenjanin.

THEORY AND METHODS

Zrenjanin is situated on the western edge of the Banat loess plateau, at the place where the canalized River Begej flows into the former water course of the River Tisza. The territory of the city is

pronouncedly Pannonian plain. The City of Zrenjanin is situated at a longitude of 20°23' east and a latitude of 45°23' north, in the center of the Serbian part of the Banat region, on the banks of the Rivers Begej and Tisza. The City is located at 80 meters above sea level in the range of 77-97 meters.

The territory of the City of Zrenjanin gravitates towards four navigable rivers and a dense canal network of the Water Utilization System "Danube – Tisza – Danube" and, therefore, it is ranked among the most dense river junctions in Europe. Zrenjanin has been formed and lies on the banks of the River Begej and, the River Tisza, the biggest tributary of the Danube on its entire course, flows only some ten kilometers away from the city. The actual confluence of the Tisza River and the Danube, some thirty kilometers away from Zrenjanin, represents the administrative border of the territory of the City. The fourth river in the town territory is the River Tamiš.

Population and much of the economy of the City of Zrenjanin is supplied with water from the shallower (30-75 m) and deeper (90-135 m) aquifers, which are characterized with high mineral, high iron, ammonia, manganese, sodium, organic matter, arsenic, disturbed organoleptic characteristics. The water are oxygen-poor and loaded with dissolved sulfur hydrogen and methane. Based on these facts we can say that the main groundwater aquifers in Zrenjanin have extremely adverse physical characteristics.

Water supply of the City of Zrenjanin is based on utilization of groundwater from the two main aquifer with the wells located northwest of the city with a total of 35-40 wells. 35 wells are grouped in the northwest, and another five wells are located at locations around the city (The Council for the strategic development of the Municipality of Zrenjanin, 2005). In Zrenjanin groundwater directly engages the pipeline system and it supplies the population as drinking water. The groundwater only passes through the microbiological treatment before enters the pipeline system. So, in this paper the parameters of the groundwater were analyzed as the parameters of drinking water.

The data of physico-chemical parameters of groundwater used in this paper are taken from the PUC "Waterworks and sewerage" Zrenjanin. Analysis is carried out on the two groundwater wells which are located in two aquifers from which drinking water is taken. One aquifer is on the depth of about 120 m and the other is on 60 m. There are selected five relevant parameters: ammonia, total iron, calcium, sodium and arsenic on which would be applied fuzzy logic approach. The aim of this study was assessment of the physico-chemical quality of groundwater for drinking purpose in the City of Zrenjanin.

Fuzzy set theory

Fuzzy set theory may be regarded as a generalization of classical set theory, since the elements membership to the fuzzy set may be characterized as a number from the interval [0,1]. Fuzzy sets are the basic elements that describe the uncertainty. This theory is applied to complex systems when the context of the problem is often unclear. It allows the integration of information from different parameters in the modeling and evaluation. A fuzzy set is defined in terms of a membership function which maps the domain of interest, e.g. concentrations, onto the interval [0,1]. The shape of the curves shows the membership function for each set. The membership functions represent the degree that the specified value belongs to the set. The membership function of the set A defined over a domain X takes the form (Kumar et al., 2009):

$$\mu_A: X \rightarrow [0,1] \tag{1}$$

The set A is defined in terms of its membership function by (Kumar et al., 2009):

$$A = \{(\mu_A(x)), x \in X, \mu_A(x) \in [0,1]\} \tag{2}$$

Or

$$\mu A : \left\{ \begin{array}{l} = 1, x \text{ is full member of } A \\ \in [0,1], x \text{ is partial member of } A \\ = 0, x \text{ is not member of } A \end{array} \right\} \quad (3).$$

When the membership function has a value of 1, it means that it is normalized and this is its highest value. Fuzzy membership functions are trapezoidal (Figure 1) for all 5 parameters on the basis of allowable limits under current legislation and according to studies of the World Health Organization - WHO (Table 1), and the perception of the author. They are described as “desirable”, “acceptable” and “not acceptable”.

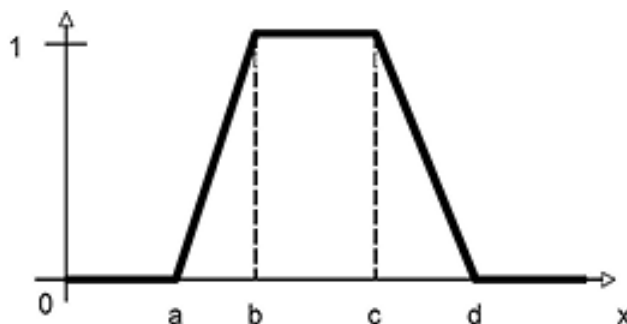


Figure 1. Trapezoidal membership function

Equation (4) describes the trapezoidal membership function by its specific parameters {a,b,c,d}:

$$\mu(x) = \left\{ \begin{array}{l} 0, x \leq a \\ \frac{x-a}{b-a}, a \leq x \leq b \\ 1, b \leq x \leq c \\ \frac{d-x}{d-c}, c \leq x \leq d \\ 0, d \leq x \end{array} \right\} \quad (4).$$

Table 1: The limits prescribed by current legislation and WHO

	Parameter	Units	Limits by current legislation	Limits by WHO
1.	Ammonia (NH ₄ ⁺ (aq))	mg/l	1	1,5
2.	Iron (Fe ²⁺ , Fe ³⁺)	mg/l	0,3	0,3-1
3.	Arsenic (As ³⁺ , As ⁵⁺)	mg/l	0,01	0,001-0,01
4.	Calcium (Ca ²⁺ (aq))	mg/l	200	75-200
5.	Sodium (Na ⁺ (aq))	mg/l	150	200

Fuzzy model of groundwater quality is created by dividing 5 selected parameters into three different categories i.e. groups according to predetermined quality criteria. The first group consists of iron and ammonia cations, the second group consists of ions of calcium and sodium and the third group is the parameter ionic arsenic. Arsenic is considered individually because he is one of the most important parameters of groundwater quality that characterize this region because it has a damaging effect on human health (carcinogenic).

The decision-making in fuzzy environments requires three steps:

- fuzzification of crisp variables;

- fuzzy decision using fuzzy operators;
- defuzzification back to crisp values (Kumar et al., 2009).

Following Zadeh’s definition, the “AND” operator is described by the intersection of the two fuzzy sets, which is given as the minimum of both of the membership functions (Kumar et al., 2009):

$$\mu_c(x) = \min(\mu_A(x), \mu_B(x)) \tag{5}$$

For the “OR” operator, the union of both the fuzzy sets defined as the maximum of both membership functions is taken (Kumar et al., 2009):

$$\mu_c(x) = \max(\mu_A(x), \mu_B(x)) \tag{6}$$

Fuzzy rule evaluation

Fuzzy rules appear no different to standard rule. They take the familiar form IF x is a, THEN y is b, where x and y are linguistic variables and where a i b are linguistic values. System based on fuzzy rules classifies water according to the obtained data on desirable, acceptable and unacceptable quality. Different parameters will be connected with the operator “AND”. For example: If ammonia is acceptable AND iron is acceptable THEN water quality is acceptable. This type of system is called Mamdani implication of max.min operator. Mamdani system assumes that the fuzzy set is output of the process of concluding (see Figure 2). This type of fuzzy set requires an aggregational process in the process of defuzzification.

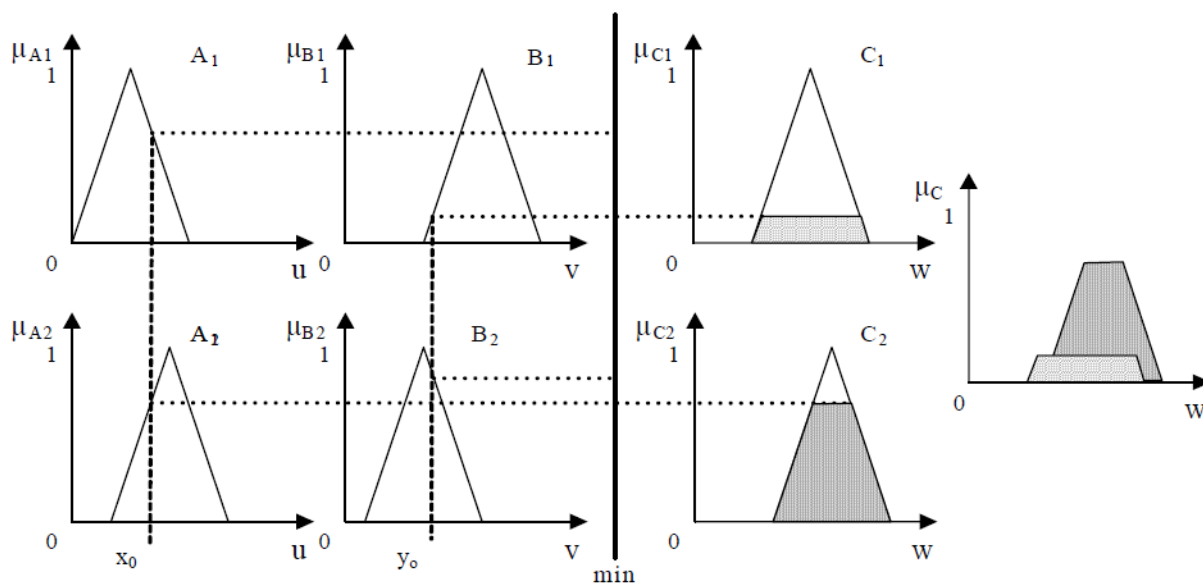


Figure 2. Mamdani implication of max.min operator

Defuzzification

Defuzzification is the transformation that replaces a fuzzy set by single numerical value representative of that set (Dahyia et al.,2007). Input of the process of defuzzification is fuzzy set and output is one and exact value from the fuzzy set. It was developed a set of methods for defuzzification. Mean of maxima (MOM) defuzzification method was used in this study. MOM form a single value from output variable as the average of local values where the membership function reaches the maximum value (see Figure 3). Defuzzification output is calculated as:

$$Z^* = \sum_{k=1}^j \frac{Z_j}{k} \tag{7}$$

where Z_j is the value whose membership functions reach the maximum value, and k is the number of such values.

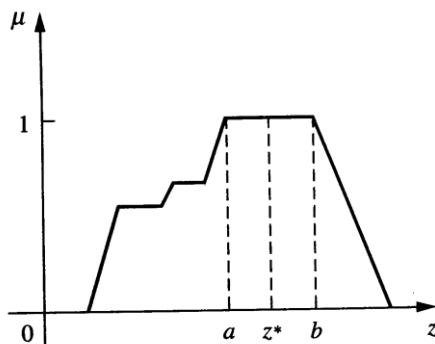


Figure 3. MOM defuzzification method

RESULT AND DISCUSSIONS

Physico-chemical characteristics of groundwater from Zrenjanin are shown in Table 2. There were taken two typical wells for the analysis in this study that are located at depths of two aquifers (120 m and 60 m) from which water is taken for drinking purpose.

Table 2: Physico-chemical parameters of groundwater from City of Zrenjanin

Sample	Ammonia (NH ₄ ⁺)	Iron (Fe ²⁺ , Fe ³⁺)	Calcium (Ca ²⁺)	Sodium (Na ⁺)	Arsenic (As ⁺³ , As ⁺⁵)
Well 1 July 2011	1,58	0,23	23,6	250	0,102
Well 2 July 2011	1,74	1,07	57,1	312,5	0,04

*all data concentrations in Table 2 are expressed in mg/l

Membership functions for the selected parameters are shown on the following figures 4-8.

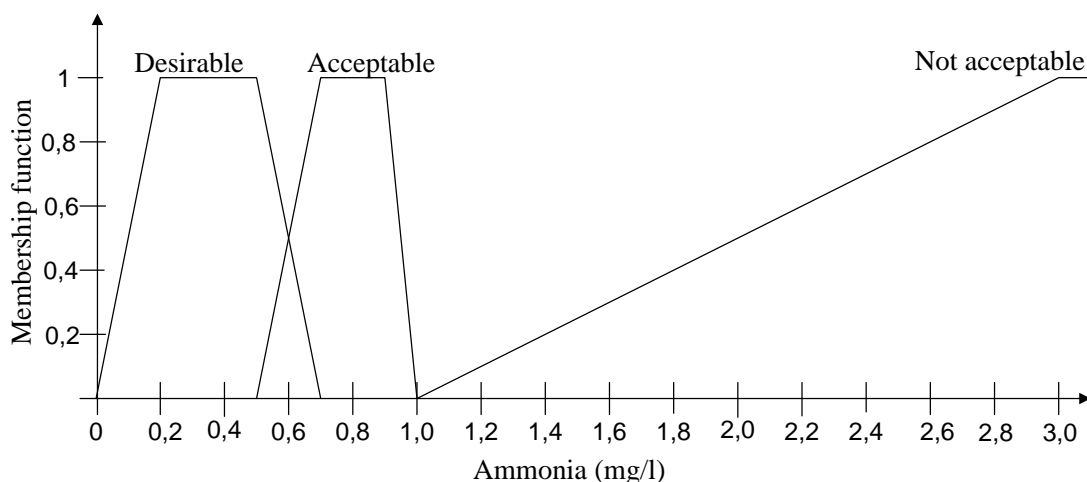


Figure 4. Membership function for the ammonia concentration

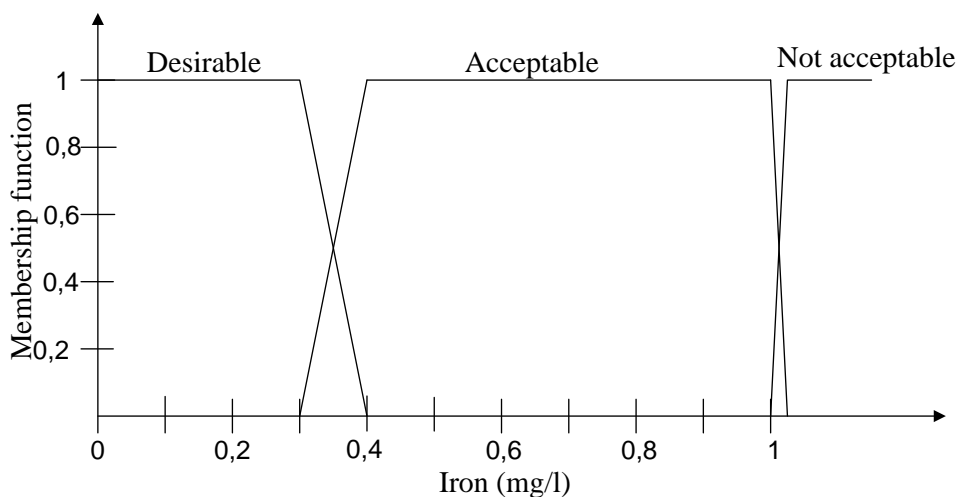


Figure 5. Membership function for the iron concentration

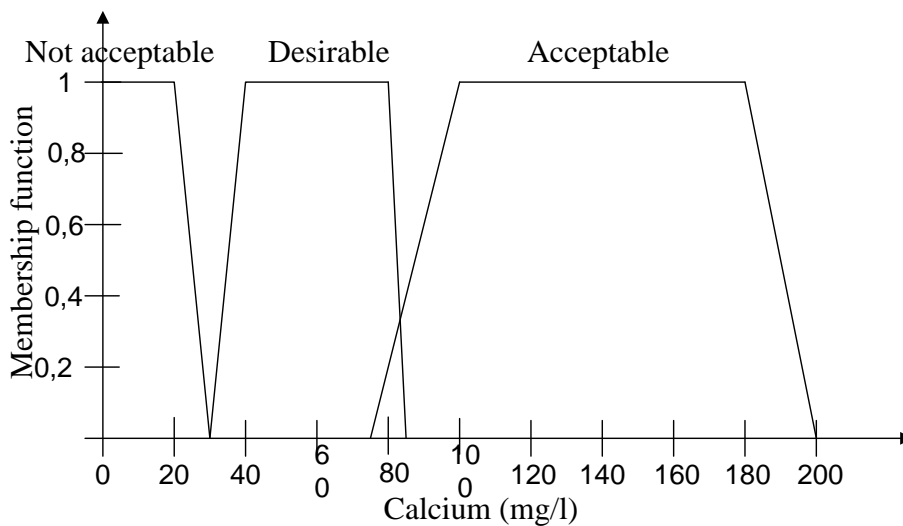


Figure 6. Membership function for the calcium concentration

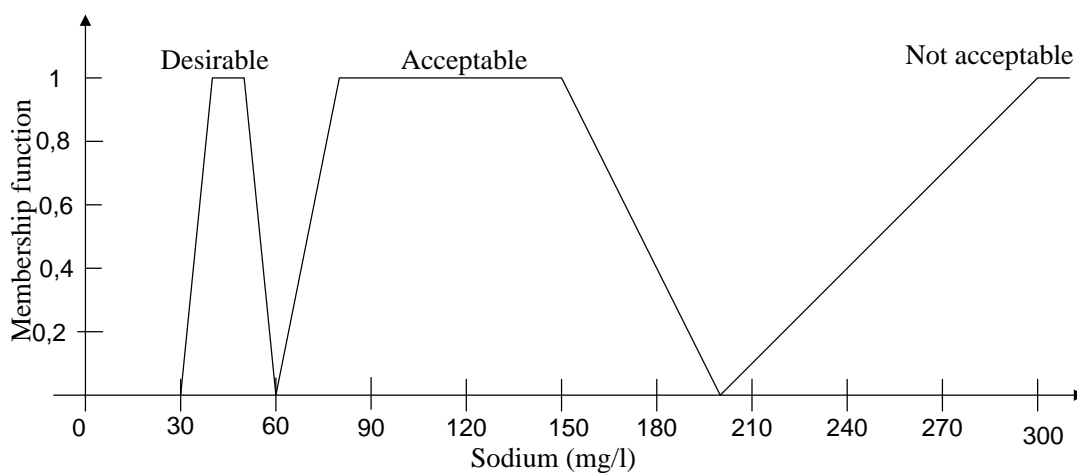


Figure 7. Membership function for the sodium concentration

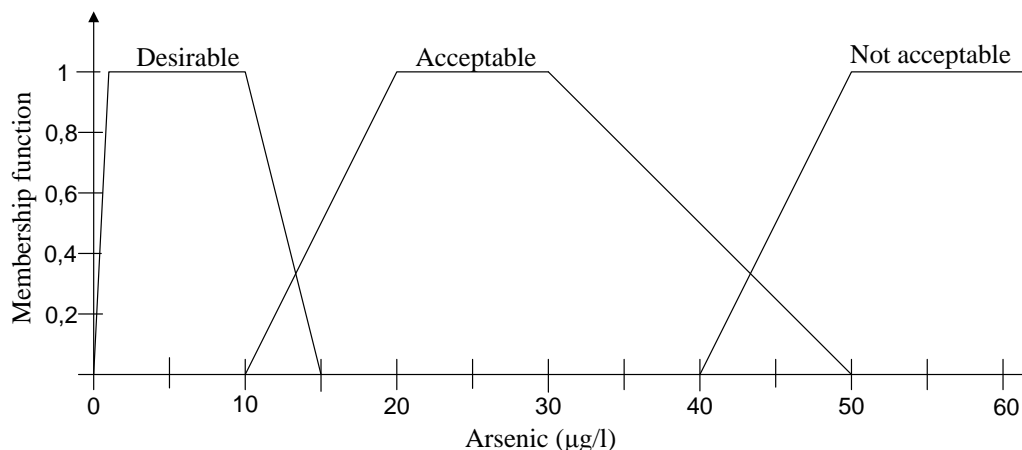


Figure 8. Membership function for the arsenic concentration

Membership function for the final quality of groundwater is shown in the following Figure 9, where it can be seen that it is divided into three groups: desirable, acceptable and not acceptable.

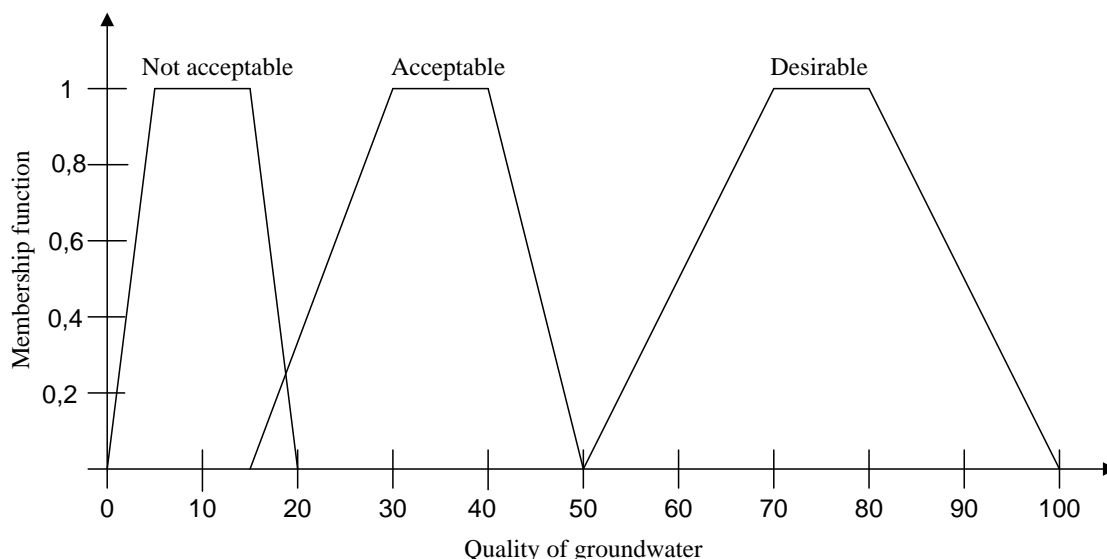


Figure 9. Membership function for the final quality of groundwater

Classification of groundwater quality is based on the phase rule. Each rule contains a set of statements that include the names of properties (ammonia, total iron, calcium, sodium and arsenic), their values and linguistic descriptions as desirable, acceptable and not acceptable. These linguistic descriptions contain some inaccuracies, because they are based on information about the health effects of each parameter individually, the integrated effect of all parameters of health is not covered. Fuzzy set theory has extensively been applied since it has been designed to supplement the interpretation of linguistic or measured uncertainties for the real world random phenomenon (Kumar et al.,2009). A well designed fuzzy groundwater quality model may be capable of covering the uncertainties existing in the sampling and analysis by comparing the analysis data of all the individual parameters by designing a suitable membership function and using the fuzzy operators (Liou and Lo,2004).

Fuzzy rules defined for the first group of parameters:

Rule 1: If ammonia is not acceptable AND iron is desirable THEN groundwater quality of group 1 is Acceptable.

Rule 2: If ammonia is not acceptable AND iron is acceptable THEN groundwater quality of group 1 is Not Acceptable.

Fuzzy rules defined for the second group of parameters:

Rule 3: If calcium is not acceptable AND sodium is not acceptable THEN groundwater quality of group 2 is Not Acceptable.

Rule 4: If calcium is not acceptable AND sodium is not acceptable THEN groundwater quality of group 2 is Acceptable.

Fuzzy rule defined for the third group of parameters: In this group there is only one parameter - arsenic. Results from the first two groups will be combined with a third group to obtain the final classification of the groundwater. For this group has created a special rule which says that if arsenic is unacceptable then the groundwater quality is Not Acceptable, regardless of the other two groups. If arsenic is acceptable then the final groundwater quality is Acceptable, but the degree of certainty is determined on the basis of all parameters.

Phase diagram of fuzzy concluding in this paper is shown by the following Figure 10.

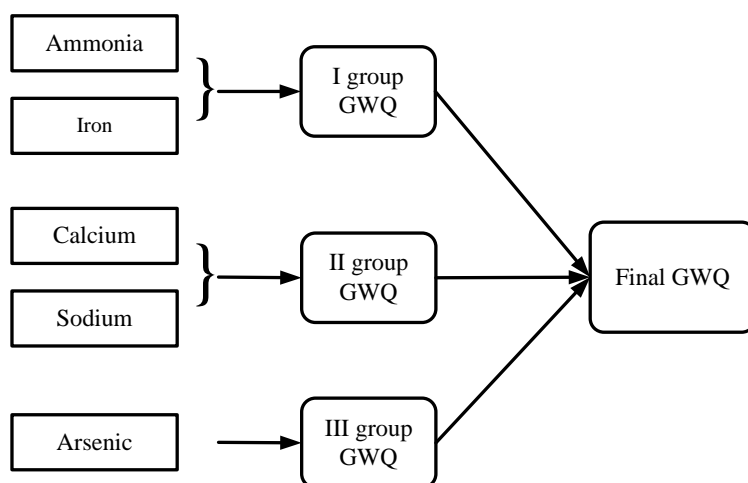


Figure 10. Phase diagram of fuzzy concluding

In the following Table 3 is shown the final classification of groundwater quality with its degree of certainty.

Table 3: Final results of groundwater quality

Sample	Groundwater quality with degree of certainty
Well 1 July 2011	GWQ Not Acceptable – 10
Well 2 July 2011	GWQ Acceptable – 35

CONCLUSIONS AND IMPLICATIONS

Classical methods for assessing the water quality show only if the examined date goes out of prescribed limits. So with them water quality is classified with acceptable and not acceptable. The main deficiency of such analyzes is that none of the tested parameter has assigned weighting factor. But in fuzzy model of groundwater quality each parameter was observed in terms of impact on human health and thus each parameter is assigned a specific weighting factor.

One of the main advantages of this approach is that the final water quality has assigned degree of certainty. So this method is much more convincing and more accessible to the people who deal with these matters and public which should be informed about the state of drinking water quality. Fuzzy model simply represent a clearer and better view of decision-making.

This analysis showed that sample from well 1 provide not acceptable quality of groundwater with certainty of 10, while sample from well 2 has acceptable quality of groundwater and the value of certainty is 35. These results showed that the quality of drinking water in Zrenjanin depends primarily on the geological structure. Sedimentary aquifers within the Pannonian Basin contain high concentrations of naturally occurring arsenic (Jovanović et al., 2011). The concentration of arsenic in drinking water is of natural origin, but such concentrations declassify this water and it is considered as not acceptable. According to the quality of groundwater used for drinking purpose, in 2004 provincial sanitary inspection banned drinking water for drinking and cooking due to increased concentrations of cancer-causing arsenic.

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**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

**METHODS USING PASSIVE SAMPLING TECHNIQUES IN
SEDIMENT**

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ABSTRACT

Sampling is the most important step of any analytical procedure. Errors committed at this stage cannot be corrected later during the analysis. There is a different specific methods, which depend on the nature of the analyte and their concentration levels. Solutions for this situation are methods of passive sampling and extraction of analytes, which involve measurement of the concentration of any analyte as a weighted average over the sampling and/or extraction time. The concentration of the analyte is integrated over the whole exposure time, making such a method immune to accidental, extreme variations of pollutant concentrations. Information obtained in this way is a suitable means of obtaining a long-term overview of pollutant levels in a environmental compartments. Techniques like Solid Phase Micro Extraction (SPME), Low Density Polyethylene- (LDPE), Silicon rubber- (PDMS) and POM- Solid Phase Extraction are applied to determine the pore water concentrations. TENAX extractions are used to estimate the available fraction, and In-vitro Passive Sampling (IVPS) gives an estimate of both pore water and available concentrations. Consequently, the partition coefficients of the compounds of interest for the available fraction in the sediment the are determined as well. The availability concept and how the different methods contribute to obtaining information on availability for uptake are discussed.

Key words: *passive sampling , sediment, SPME, TENAX, POM, PDMS, LDPE, IVPS.*

INTRODUCTION

Historically, environmental monitoring programs have tended to focus on organic chemicals, particularly those that are known to resist degradation, bioaccumulate in the fatty tissues of organisms, and have a known adverse toxicological effect.

Recently, it has been recognized that risks to aquatic and terrestrial organisms, including humans, are not limited to chemicals fitting the classical POP definition. An examination of the complex mixtures of chemicals present in natural water reveals the presence of organic chemicals covering a wide range of water solubilities and environmental half-lives. Many of these chemicals have been termed —emerging contaminants by the scientific community.

The first step in understanding the potential biological impact of ECs in the environment is to identify and quantify the types of ECs that are present. To do so, innovative sampling methodologies need to be coupled with analytical techniques which can confirm the identity of targeted and unknown chemicals at trace concentrations in complex environmental samples. (David A. Alvarez et.al. 2004)

The risk presented by hydrophobic ECs accumulated in sediment is not necessarily reflected by the concentration of the contaminants in the sediment, but rather by what can be released from the sediment to the water phase. The freely dissolved concentration in the water phase plays a key role in the uptake route for organisms, and exchange between the various compartments in the aqueous system (Foppe Smedes, 2007).

Partition coefficients can be applied to calculate freely dissolved concentrations from concentrations measured in sediment. Partition coefficients describe the ratio between the freely dissolved concentration in water phase and another environmental compartment (e.g. sediment) at equilibrium. For the sediment, the relevant constant is the sediment-water partition coefficient (K_{SED}).

For this purpose passive sampling has been introduced in several forms for the measuring of free dissolved concentrations (Mayer et al., 2003). In passive sampling, a reference phase (e.g. polyoxymethylene (POM) (Jonker and Koelmans 2001), polydimethylsiloxane (PDMS) (Mayer et al. 2000a and 2000b; Heringa and Hermens 2003) low density polyethylene (LDPE) (Müller et al., 2001; Booij et al. 2003) or TENAX (Cornelissen 1999, Ten Hulscher 2005) is introduced in a water/sediment suspension and shaken for an extended period of time. The sediment releases contaminants that are taken up by the reference phase. From the uptake, either the free dissolved concentration after equilibrium is estimated, or some measure of the releasable fraction is obtained (TENAX). These are both relevant for describing the risk of sediment contamination (Reichenberg and Mayer 2006). This paper describes the different passive sampling methods available for estimation of freely dissolved pore water concentrations of hydrophobic organic contaminants (Foppe Smedes, 2007).

SAMPLING METHODS

Development of a Sampling Plan

Obtaining a sample of the matrix of biotic and nonbiotic is an often-overlooked but vital component of any environmental monitoring program. Failure to properly collect a sample can invalidate any results subsequently obtained. The sample should be representative of the original environmental matrix (air, water, sediment, biota, etc.) and be free of any contamination arising during sample collection and transport to the analytical facility. The collection of a representative sample starts in the office or laboratory with the training of personnel and formulation of a sampling plan, moves to the field for the actual sampling, and ends with the shipment of the sample to the laboratory (David A. Alvarez at.al. 2008).

A successful sampling strategy must begin with a thorough plan and established protocols. Areas of questions which need to be addressed while planning the sampling trip include: 1) selection of the sampling method to obtain a representative sample, 2) determination of the sample quantity needed to meet the minimum quantitation limits of the analytical method, 3) identification of quality control (QC) measures to be taken to address any bias introduced by the sample collection, 4) identification of safety measures that need to be taken, and 5) determination of sampling objectives. The study plan must define the chemicals to be assayed in the sample and sample size requirements of the analytical methods. Different extraction and processing procedures may be needed to isolate targeted chemical classes from each other and potential interferences, resulting in larger sample size requirements.

The field log should include sample collection procedures, location of the sampling sites on maps, global positioning system (GPS) coordinates or other data to identify the site(s), date and time samples were collected, types of QC that were used, and names of the personnel involved in the sample collection. Additional information on weather conditions during sampling, visible point sources of contamination and surrounding land use can be useful during the final interpretation of the data. Photographs of the sampling sites are often helpful.

Regardless of the type of sample matrix method used, issues of sample preservation, storage conditions and time, and shipping methods must be resolved. Samples should be collected with equipment made of stainless steel, aluminum, glass, or fluorocarbon polymers. Materials made of polyethylene, rubber, Tygon®, or other plastics should be avoided due to the potential for these materials to absorb or desorb targeted chemicals from/into the collected sample. Since plasticizers and flame retardants are commonly targeted ECs, plastics should not be used as they may contain high levels of these chemicals from the manufacturing process. To prevent alteration, samples are shipped

chilled (<4-6 °C) via overnight carrier to the laboratory and if ECs are potentially sensitive to UV radiation, amber bottles are used to prevent photodegradation. (David A. Alvarez at.al. 2004)

Time-Integrated Sampling Techniques

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of a difference in chemical potentials. It can be used for the determination of both inorganic and organic compounds in a variety of matrices, including air, water and soil. The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane. Living organisms can also be used as passive samplers. In most cases, passive sampling vastly simplifies sampling and sample preparation, eliminates power requirements, and significantly reduces the costs of analysis. The technique is particularly suited to the determination of time-weighted average concentrations. (Tadeusz Górecki at.al., 2002)

Time-weighted average (TWA) concentrations of chemicals are commonly used to determine exposure, they are a fundamental part of an ecological risk assessment process for chemical stressors (Huckins et al., 2006). Since grab samples only represent the concentration of chemicals at the instant of sampling, TWA exposure is difficult to accurately estimate even with repetitive sampling. Episodic events are often missed with routine grab sampling schedules. In addition, the detection of trace concentrations of ECs can be problematic as standard methods are designed to handle small (<5 L) volumes of water. Passive sampling devices provide an alternative to grab sampling, overcoming many of the inherent limitations of those traditional techniques (David A. Alvarez at.al. 2004).

Integrative or equilibrium passive samplers can be used depending on their design, the exposure time in the field, and the properties of the targeted chemicals. Integrative samplers are characterized by having an infinite sink for the retention of sampled chemicals, providing a higher degree of assurance that episodic changes of chemical concentrations in the water will not be missed. The use of an integrative sampler is essential for the determination of TWA. (David A. Alvarez at.al. 2008).

PASSIVE SAMPLING METHODS

TENAX

About 1 g (dry weight) sediment is mixed with 50-100 ml water and shaken with the 1-1.5 g of pre-extracted TENAX for a selected time (Cornelissen et al., 2001). The pores of TENAX contain air which makes it float on water and can therefore be easily separated from the sediment suspension. Depending on the exposure time, different releasable fractions are extracted from the sediment; a rapidly desorbed fraction is considered to be extracted after 6 hours, a less available fraction after 24 hours, and a very slow fraction after 10-24 days (Noort et al., 2003). Since TENAX behaves as an infinite sink, i.e. the TENAX-water partition coefficients are infinitely large compared to the sediment-water coefficient, the results do not give information on the freely dissolved concentrations. By assuming that the rapidly desorbed amount ($C_{SED-RAP}$) represents the concentration bound to the regular organic matter (f_{OC}), this concentration can be combined with a generic value for K_{OC} for organic matter to calculate to a kind of estimate for the freely dissolve concentration (C_w) (1).

$$C_w = \frac{C_{SED-RAP}}{f_{OC} \cdot K_{OC}} \quad (1)$$

As the uncertainty of KOC is generally large, the values obtained for CW also will have large uncertainty (Foppe Smedes, 2007).

POM, PDMS and LDPE

The exposure procedure for reference phases other than TENAX is quite similar. A known mass of the reference phase is exposed to a sediment suspension while shaking. The shaking time is selected such

that equilibrium is obtained, typically 20-40 days. Using the reference phase-water partition coefficient (K_{SW}), an estimate of the freely dissolved concentration in the pore water is obtained (2).

$$C_w = \frac{C_s}{K_{SW}} \quad (2)$$

It should be noted that during the exposure period, the concentration in the sediment has decreased as a certain fraction of the contaminants accumulates in the reference phase. This fraction can be small, as in solid phase micro extraction (SPME) where only up to 1 μ l PDMS is used in combination with ~30g of sediment, or large as the solid phase extraction (SPE-POM) method described by Jonker and Koelmans (2001) where POM was exposed to almost equal amounts of sediment. In the latter situation, a considerable depletion of the contaminants in the sediment, compared to the initial conditions, may occur. Authors often correct for this by calculating a partition coefficient (K_{SED}) from the C_w obtained and the residual concentration in the sediment and use this, with the unaffected concentration in the sediment, to calculate the C_w in the unaffected situation. This extrapolation assumes a linear relationship between C_{SED} and C_w that passes through the origin, which is not necessarily an accurate reflection of the true situation (Foppe Smedes, 2007).

IVPS

In Vitro Passive Sampling (IVPS) uses PDMS and is in practical sense applied in a similar way as described above. However, the approach is different and may result in definition of a sorption isotherm, without assuming that the isotherm has any particular shape. In IVPS, the PDMS is coated on the wall of glass bottles and exposed to sediment suspensions in series of different ratios between Sediment and PDMS. A large amount of sediment with a small amount of PDMS will most closely reflect the original situation and lead to only a small decrease in C_{SED} and the estimate of C_w is almost unaffected by the experimental procedure.

Combination with data from exposures at intermediate ratios allows a sorption isotherm to be constructed. The remaining sediment concentration for each exposure ratio is calculated by subtracting the total amount in the exposed sediment by the amount that was accumulated in the PDMS. The isotherms obtained generally look like those depicted in Fig. 1. The x-axis represents the C_{SED} after exposure and the y-axis the C_w calculated from the concentration measure in the PDMS for each specific exposure ratio. Each point represents a different exposure ratio. Curve A shows a linear isotherm of a compound that follows ideal partitioning behavior. The inverse of the slope of the isotherm equals the partition coefficient. Line B shows a steep decrease in C_w for only a limited decrease in C_{SED} . The left part of curve B therefore represents a much higher partition coefficient than the right part.

Extrapolation of a straight line fitted through the points in case B intercepts the x-axis, and on the left side indicates the concentration that is limited or not available for exchange with the water phase. The portion of C_{SED} to the right from the intercept is probably held following the normal partitioning with regular organic matter (Foppe Smedes, 2007).

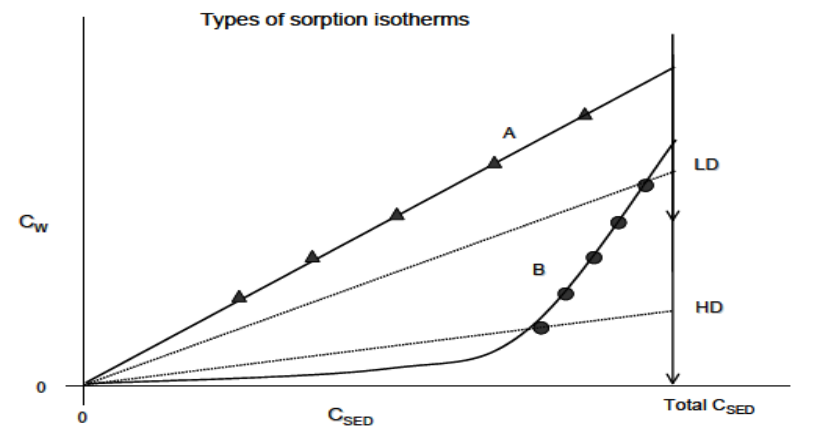


Figure 1. Sorption isotherms as observed by IVPS. On the x-axis, the concentration in the sediment (residual after exposure) is plotted (x axis) and on the y-axis the freely dissolved concentration calculated from the concentration in the PDMS. (A): linear isotherm and (B): non-linear isotherm. The line on the right side in the graph represents the total concentration in the sediment measured by a total extraction method, for example soxhlet extraction or accelerated solvent extraction (Foppe Smedes, 2007)

SUMMARY

Despite its relatively long history, passive sampling is still developing. It has many significant advantages, including simplicity, low cost, no need for expensive and sometimes complicated equipment, no power requirements, unattended operation, and the ability to produce accurate results. There are also some limitations that may sometimes be difficult to overcome, probably the most important of which is the possible effect of environmental conditions (such as temperature, air movement, and humidity) on the analyte uptake. Despite such concerns, many users find passive sampling an attractive alternative to more established sampling procedures.

Passive sampling methods like SPME, TENAX, POM, PDMS, LDPE, IVPS are used most often for the determination of concentrations, when the response time of the samplers is dictated by the length of the period studied. Once the measurement session is completed, however, passive sampling very often significantly simplifies further steps in the analytical procedure, as it generally combines sampling and sample preconcentration into a single step. Thus, with a few exceptions, passive sampling shortens the time between sample collection and analysis, improving the response time of the entire system.

Using passive sampling methods, the concentration of pharmaceuticals (caffeine) and pesticide (methomyl) have been monitored. The research is in the progress.

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**II International Conference
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**PRELIMINARY QUALITATIVE ANALYSIS OF PHTHALATES AS
INDUSTRIAL CHEMICALS IN SURFACE WATER AND
WASTEWATER IN THE VICINITY OF NOVI SAD**

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ABSTRACT

In the preliminary qualitative screening and analysis of surface and wastewater from the Danube River near Novi Sad, the presence of phthalates species, industrial chemicals that belong to the list of emerging substances have been registered. Compounds detected in both, wastewater and Danube surface water, 100 m downstream of the discharge were phthalates type 1.2 - benzenedicarboxylic, dibutyl ester and 1.2 - benzenedicarboxylic acid, mono (2 - ethylhexyl) ester. This type of research within the International Project has been conducted for the first time.

Key words: *Phthalates, surface water, wastewater, Danube.*

INTRODUCTION

Human population is obviously exposed to industrial chemicals through food, water, air, or from direct contact with a variety of consumer products. Many of these chemicals are toxic at some dose especially at the very low doses in the range of nano mole to the pico mole concentration level and under certain conditions of exposure. Phthalates represent a group of industrial compounds called “plasticizers” used in a wide range of consumer products, as solvents or to make plastics more flexible, to enhance transparency, durability and resiliency of plastic product.

Phthalates are ubiquitous in modern society, found in toys, food packaging, shower curtains, building materials, wall coverings, lubricants, adhesives, detergents, nail polish, hair spray, shampoo, etc (Schettler et al.) Reports in the scientific literature over the past 10 - 15 years have raised additional concerns.

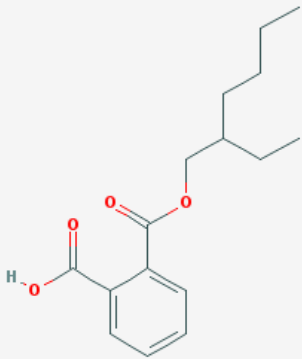
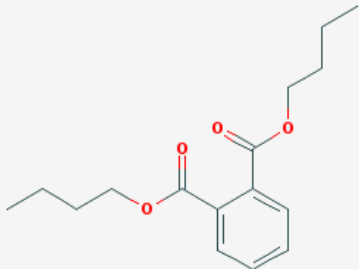
Developing organisms show vulnerability to phthalate exposures and in particular, the developing male reproductive tract appears to be the most sensitive organ. Phthalates are easily released into the environment because there is no strong covalent bond between the phthalates and plastics compound. Although few studies have proven the adverse health effects of phthalate exposure in humans, animal studies point to its known toxicities, carcinogenicity, and its potential to adversely affect normal hormone functioning. The physiochemical characteristics of phthalates vary with the chemical structure. Phthalates are generally lipophilic, which influences their leaching and environmental partitioning characteristics and are not chemically bound in the polymers. Therefore, migration or emission of phthalates from the products into the environment occur (Vojinović Miloradov et al.).

Basic properties of selected phthalates

Chemical 1.2 - benzenedicarboxylic, dibutyl ester is a colorless oily liquid, insoluble in water. It reacts with acids to liberate heat along with alcohols and acids. Strong oxidizing acids may cause a vigorous reaction that is sufficiently exothermic to ignite the reaction products.

Chemical 1.2 - benzenedicarboxylic acid, mono (2 - ethylhexyl) ester is clear colorless to cloudy white viscous liquid. It may react exothermically with strong oxidizing agents and also generate heat with caustic solutions. Next table shows basic physico-chemical properties of 1.2 - benzenedicarboxylic, dibutyl ester and 1.2 - benzenedicarboxylic acid, mono (2 - ethylhexyl) ester.

Table 1: Summary of physico-chemical properties, from EU RAR 2004

Chemical name	1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester	1.2 - benzenedicarboxylic, dibutyl ester
CAS Number	84-74-2	4376-20-9
Molecular Formula	C ₁₆ H ₂₂ O ₄	C ₁₆ H ₂₂ O ₄
Structural Formula		
Molecular weight:	278.35	278.35
Water solubility	11.2 mg/L at 25°C	1.49 mg/L at 25°C
Henry's Law Constant:	1.81·10 ⁻⁶ atm·m ³ /mole	5.08·10 ⁻⁶ atm·m ³ /mole
Log P (octanol-water)	4.73	4.50

Location description

Novi Sad is the second largest city in Serbia and administrative centre of the northern Serbian province of Vojvodina, with a population of 335,701. Deriving drinking water from the Danube River or from several groundwater reservoirs, the city of Novi Sad faces a specific problem. Two of three sources of drinking water in Novi Sad are located only a few hundred meters downstream of discharges of the Novi Sad two main sewers, GC1 and GC2.

Additionally, all of groundwater abstraction points are located under densely populated urban areas, and one of them is located in the proximity of the oil refinery and heating and power plant (Vojinović Miloradov et al.).

Research activities within the NATO project (<http://www.nato.int/cps/en/natolive/78209.htm>) started with a review of available data on organic and inorganic pollutants analyzed in the projects in order to collect reliable information on water quality and pollution for the part of the Danube River and its tributaries in Serbia.

For establishing the monitoring network of the surface Danube water in the vicinity of Novi Sad, selection of sampling points and defining of monitoring dynamic have been defined using knowledge and recommendations of the experts in close co-operation with Public Utility Company Waterworks and Sewage Novi Sad, as well as on experience of the research teams involved in the DriWaQ-NS project. The selected sampling points include raw water entering water treatment plant as well as wastewater from the collectors of sewage discharges and samples of surface water from the Danube River.

MATERIALS AND METHODS

Three sampling campaigns were conducted during the 2011. Sampling period and meteorological parameters are presented in table 1. One liter water samples were collected in amber glass bottles from all seven localities and were stored under appropriate temperature conditions, at 4°C.

Table 2: Samples of municipal and industrial wastewaters

	Survey I	Survey II	Survey III
Sampling period	June 2011	October 2011	December 2011
Mean temperature	20°C	13°C	8°C
Wind speed	8 km/h	30 km/h	10 km/h

Samples of municipal and industrial wastewater were taken directly from the sewage discharges collectors Cepelin, Ratno ostrvo, Beogradski kej and Rokov potok, while the samples of surface water from the Danube were collected at least 100 meters downstream of the each discharge (Figure 1).



Figure 1. Surface water sampling locations - preliminary qualitative analysis

Preliminary quality analyses were performed at Institute of Analytical Chemistry STU in Bratislava using optimized procedure developed during first half year of project duration. The GC-MS screening

analysis was performed using Agilent 6890 gas chromatograph coupled to Agilent 5973 mass spectrometric detector.

DISCUSSION

Phthalates, belong to the most frequently occurring compounds in the water samples as well as surface and waste water. Phthalates are commonly used as plasticisers, industrial and lubricating oils, defoaming agents, cosmetics and insect repellents.

Phthalates have high and hazardous pressure on humans, biosystem aquatic media, aquatic organisms and environment.

Dibutylphthalate which is already on the NORMAN list of emerging substances and di(2-ethylhexyl) phthalate, which is on the list of WFD priority substances, were detected in all samples which confirms statements on its ubiquitous presence.

Because of their properties, high production volumes, and widespread use, concentrations in various environmental compartments are measurable and expected to reflect a constant and diffuse release into the environment. Phthalates are becoming ubiquitous and pseudoresistant pollutants with high transport potential for most of the environmental media.

The ecotoxicity of dibutylphthalate shows that prenatal exposure of rats to dibutylphthalate resulted in teratogenic effects in offspring that included skeletal malformations, increased incidence of cleft palate, and decreased number of live fetuses at birth. Defects in male reproductive organ development following prenatal exposure to dibutylphthalate included increased incidence of undescended testicles, hypospadias, and other anatomical differences. Decreased testosterone, decreased pituitary hormones, and delayed puberty were associated with prenatal dibutylphthalate exposure. Exposure to dibutylphthalate during adulthood resulted in increased mortality in rats.

Several studies have examined the teratogenic potential of 1,2 - benzenedicarboxylic acid, mono (2 - ethylhexyl) ester and other phthalates. Teratogenicity is evident in some species, but only at very high doses. Testicular damage can be produced with several different chemical entities of the phthalates. Gonadal zinc deficiency is an observation consistent with phthalate-induced gonadal toxicity (Thomas et al).

The available information and results about pollution of water used for abstraction of drinking water in Novi Sad municipality are insufficient for eco-status of surface water in river Danube, risk management and for protection and improvement of human health and safety. Screening approaches are either not used at all or very scarcely and most of monitoring is limited just to the selected physical parameters and target compounds. Within the last 5 years, no detailed and no systematic monitoring programme for the screening of river pollutants and emerging substances in Novi Sad municipality was performed.

In the national scientific literature, there is little information available on the occurrence of emerging pollutants especially phthalates in wastewater and surface water of the Danube River and its tributaries.

CONCLUSIONS

Registered residual concentrations of phthalates in the Danube surface and waste water in vicinity of Novi Sad are showing serious contamination with these ubiquitous industrial chemicals. Due to their high toxicity potential teratogenicity and cancerogenicity quantitative analysis has been conducted. More detail research and quantification of emerging substances is in progress.

ACKNOWLEDGEMENTS

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**ARSENIC REMOVAL FROM WATER USING INDUSTRIAL BY-
PRODUCTS**

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ABSTRACT

Inorganic arsenic removal from water using waste materials as adsorbents is presented in this study. Selective removal of As(III) and As(V) from water was carried out with industrial by-products: waste filter sand (as a water treatment residual) and blast furnace slag from steel production, all inexpensive and locally available. In addition, the blast furnace slag was modified in order to minimise its deteriorating impact on the initial water quality. Kinetic and equilibrium studies were carried out using batch and fixed-bed column adsorption techniques under the conditions that are likely to occur in real water treatment systems. To evaluate the application for real groundwater treatment the capacities of the selected materials were further compared to those exhibited by commercial sorbents, which were examined under the same experimental conditions. Waste filter sand was found to be good and inexpensive sorbent for arsenic while blast furnace slag and modified slag showed the highest affinity towards arsenic. All examined waste materials exhibited better sorption performances for As(V). The highest maximum sorption capacity in batch reactor was obtained for blast furnace slag, 4040 µgAs(V)/g.

Key words: Arsenic removal, adsorption, industrial by-products, low cost sorbents.

INTRODUCTION

Arsenic presence is detected in groundwaters in South Eastern Europe (Milojević, 2004; Jovanović, 2011-1), Asia, North and South America (Wang et al., 2004) as a natural and anthropogenic contaminant. Arsenic occurs in natural waters in both inorganic and organic forms but inorganic species are predominant in natural waters. The valence and species of inorganic arsenic are dependent on the oxidation-reduction condition and pH of the water. Arsenite, the reduced trivalent form, exists in four forms in aqueous solution, depending on pH: H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-} . Arsenate, the oxidized pentavalent form, exists in four forms in aqueous solution, also depending on pH: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} (Issa et al., 2010). Most commonly As(III) is found in groundwaters (assuming anaerobic conditions) while As(V) is found in surface waters (assuming aerobic conditions). However, this rule does not always apply for groundwaters. Some groundwaters have been found to have only As(III), others with only As(V), and still others with the combination of both As(III) and As(V) (Wang et al., 2004). All arsenic compounds dissolved in water are toxic. Arsenic toxicity depends on its chemical formation. Inorganic arsenic compounds, most commonly present in natural waters, are the most toxic. In addition, inorganic As(III) is considered more toxic than inorganic As(V). Sea food (fish and shellfish) very often contains arsenic in significant amounts but it is mainly in organic forms which are approximately 1000 times less toxic comparing to inorganic forms (Vukašinović-Pešić et al., 2005; Issa et al., 2011).

Increased risks of arsenic related diseases have been reported to be associated with ingestion of drinking-water at concentrations of $<50 \mu\text{g/L}$ (WHO, 2008). However, considering the significant uncertainties surrounding the risk assessment for arsenic carcinogenicity and the practical difficulties in removing arsenic from drinking-water, a provisional guideline value for arsenic was set by WHO at

the limit of 10 µg/L in the 1993 Guidelines. In view of the scientific uncertainties, the guideline value is designated as provisional. A new maximum concentration limit of 10 µg/L for arsenic in drinking water was set by US EPA in 2001 (US EPA, 2001) and EU law in 2003 (2003/40/EC) requiring public water supply systems to reduce arsenic in drinking water not later than January 2006. In the Republic of Serbia the new arsenic concentration limit was set in 1998.

Available commercial arsenic removal technologies include adsorption, precipitation and membrane processes. Among them, sorption is considered to be relatively simple, efficient and low cost arsenic removal technique, especially convenient for application in rural areas (Jovanović et al. 2011-2). Wide range of sorbent materials for aqueous arsenic removal is available nowadays: biological materials, mineral oxides, different soils, activated carbons and polymer resins (Mohan et al. 2007). Nevertheless, finding cheap and effective arsenic sorbent is still highly desirable.

As reported in recent papers, certain agricultural and industrial by-products such as waste tea fungal biomass, rice husks, red mud, fly ash, etc. were found to be good and inexpensive arsenic sorbents (Vukašinović-Pešić et al., 2012; Jovanović et al., 2010). In addition, application of industrial wastes in water treatment follows the reuse-recycle concept. The aim of this paper is to investigate industrial by-products (blast furnace slag and waste filter sand), both inexpensive and locally available, as a potential sorbents for arsenic.

Blast furnace slag is a typical industrial by-product from steel production factories. It is a cheap material, widely available, containing relatively high amount of iron oxides which are efficient for arsenic removal. Disposed of after high temperature treatment during steel production, blast furnace slag is an environmentally safe material since the contained metals are tightly bound and can not be easily leached. In addition, the thermal treatment at high temperatures enhances the physical properties of the material which favor the sorption process (such as porosity and specific surface area). The reuse of steel waste slag in road construction, building materials and for ammonia and phosphorus uptake from aqueous solutions was investigated in recent studies (Jha et al. 2008). However, the arsenic removal performances of the material and the potential side effects in terms of its application in water treatment systems have not been widely and thoroughly investigated. Sand filter media, most commonly used in the treatment of iron and manganese contaminated water, is coated by flocks of metal oxides during the filtration operation and eventually the material requires replacement. While the metal oxide layer, built up over the years in the filter units, imposes negative features to the filter media, it has been assumed beneficial for aqueous arsenic removal purposes. Although the idea of the reuse of waste materials has already been promoted, its application in potable water treatment is far from widely spread, presumably due to the wide gap between the purity of the final product and the impurity of the applied waste material.

The physical properties and chemical composition of blast furnace slag and waste filter sand make them appropriate for arsenic removal from water. Moreover, both materials are inexpensive and locally available, which makes them suitable for application in rural areas of the developing world. With the aforementioned motivation, the evaluation of the arsenic removal performances of the cheap industrial by-products blast furnace slag and waste filter sand were investigated for arsenic removal. Both materials were obtained from local industrial facilities. Additionally, the slag material was modified to minimize its detrimental impact on raw water quality and, hence, ensure the safety of its use. Adsorption of both As(III) and As(V) was investigated under neutral conditions where the applied arsenic species are present in both molecular and ionic forms, which correspond to real groundwater conditions. The arsenic removal performances of the waste materials were further compared to those of commercial materials obtained under the same experimental conditions.

MATERIALS AND METHODS

Materials and characterization techniques

Blast furnace slag (BFS) and waste filter sand (WFS) were selected as the waste materials to be tested within the scope of presented investigations. Blast furnace slag was taken from the slag waste deposits in the steel mill US Steel Serbia (Smederevo, Serbia). The waste filter sand was obtained from the groundwater treatment plant WTP “Bežanija” in Belgrade, Serbia, just before replacement of the filter media after 7 years in use. The physical properties and chemical compositions of the waste materials are presented in the further text. The commercial materials: granular porous ferric hydroxide (GFH) and a hybrid polymeric anion exchange resin with nanoscale iron oxide particles (HIER) were examined under the same experimental conditions in order to compare their performances with those of the waste materials. The physicochemical properties of the commercial materials were obtained from the Manufacturer's technical data sheets: GFH (grain size: 2.0-4.0 mm, BET specific surface area 300 m²/g, iron (Fe³⁺) content: min 40 %, iron hydroxide content: min 70 %); HIER (mean bead size: 0.35 mm, bulk density: 0.765 kg/L, functional group FeO(OH)).

The microstructure of the analyzed HFO-coated material samples was examined by scanning electron microscopy (SEM) using a Jeol JSM 5800 instrument (Tokyo, Japan) (operated at 25 kV). The Brunauer-Emmett-Teller (BET) specific surface areas were determined by standard techniques of nitrogen adsorption using a Sorptomatic 1990 Thermo Finning (San Jose, California).

Reagents and analytical methods

An As(V) stock solution (100 mg/L) was prepared by dissolving 416.5 mg of sodium arsenate (Na₂HAsO₄·7H₂O, Analar analytical reagent) in 1 L of distilled water, which was preserved with 0.5 % HNO₃. An As(III) stock solution (3750 mg/L) was prepared by dissolving sodium arsenite (0.05 mol NaAsO₂, Riedel-de Haen (4.946 g As₂O₃ + 1.3 NaOH in 1 L)) in distilled water in a 1 L volumetric flask, which was preserved with 0.5 % HNO₃.

Arsenic was analyzed using the ICP-MS method (Standard methods, 1995.) using an Agilent 7500ce spectrometer equipped with Octopole Reaction System (ORS). Calibration was realized using external standards (2, 4, 20, 40, 80, 100 µg/L), which were prepared by appropriate dilution of a 1000 µg/L stock standard solution. Working standards, as well as blank solutions, were prepared with high purity HNO₃. The concentrations of the investigated samples were adjusted to the concentration range 5-100 µg/L. The experimental data measurements were accepted as reasonable data in cases of less than 5 % relative standard deviation (R.S.D.). In order to amplify the consistency of the results, the experiments were performed in triplicate and the mean values considered. The limit of detection was 0.1 µg/L. A laboratory pH meter (Metrohm 827) was used for pH measurements. The accuracy of the pH meter was ±0.01 pH units.

Sorption experiments

Batch experiments

Batch experiments were designed to investigate the efficiency of the waste materials in the removal of arsenic from water. The influence of contact time and initial arsenic concentration on the sorption by the selected waste materials were examined as the most crucial parameters which influence the sorption efficiency. The batch tests were performed under different As valence: As(III) and As(V). In order to meet the pH conditions in real groundwater sources, the pH of the model solutions was adjusted to pH 7 using HCl and NaOH prior to adsorption. Laboratory beakers containing 1 g of sorbent and 100 mL of model solution were placed on an orbital shaker (Rotamax 120, Heidolph Instruments) at room temperature. The beakers were shaken at 150 rpm. After agitation, each sorbent-solution suspension was left 1-2 min to settle. The supernatant water was carefully sampled and the samples were filtered using filter paper for extremely fine precipitates (Macherey-Nagel, grade MN

619-de; average retention capacity 1–2 μm) and the filtrates were analyzed for arsenic. The pH of the model solutions was measured prior to and at the end of each batch test. The amount of arsenic sorbed per unit of sorbent was calculated by $q = (C_0 - C_1)V/m$, where q (mg/g) is the amount of arsenic sorbed per unit mass of sorbent (sorption capacity), C_0 (mg/L) and C_1 (mg/L) are the initial and final concentration of arsenic in solution, respectively, V (L) is the solution volume and m (g) is the sorbent mass.

Kinetics and equilibrium experiments

Sorption kinetic experiments were performed using batch experiments at different time intervals: 15 min – 24 h, with an initial arsenic concentration $C_0 = 0.5$ mg/L and pH = 7. The initial arsenic concentration and pH value were adopted to match the conditions in real groundwater supply systems. During each set of conducted kinetic batch experiments it was observed that even 24h are not sufficient to reach absolute equilibrium. In each set of experiments $\tau = 6$ h was found to be the breakthrough point after which sorption rate is significantly lower and thus changes in sorption efficiency far less rapid. Moreover, rapid sorption rate range (0–6 h) was found the most interesting for detailed examination in terms of waste materials' potential application. Finally, the adsorption isotherm experiments were performed under different initial arsenic, As(III) and As(V) concentrations (0.5, 1.0, 5.0, 10.0, 50.0 and 100.0 mg/L) for a contact time $\tau = 6$ h, at pH = 7.

Column experiments

Column experiments were conducted in a fixed-bed downflow filtration unit as shown in Figure 1. The installation is designed so that it can examine the impact of different sorption-filtering parameters that affect the efficiency of sorption processes such as: contact time, surface hydraulic load, granulometric composition of the material, on various sorbent materials. The laboratory/field installation (pilot model) is consisted of a transparent (Plexiglas) column, inner diameter of $\varnothing 56$ mm, which is filled with an appropriate sorbent material. Column diameter is selected according to the recommended column diameter - grain diameter ratio, which should be at least 1:50 in order to minimise wall effect on the hydraulic performance of the filtration system. Overflow weir is installed in the upper part of the column to maintain constant pressure at the entrance of the downflow filtration unit. Sorbent material is placed at the bottom of the column, above 2 cm thick layer of coarse sand and gravel. Under the coarse sand-gravel layer an additional wire screen is installed to prevent penetration of fine particles further into the flow control unit. At the bottom of the column a pressure monitoring device (piezometer) is installed.

RESULTS AND DISCUSSION

Material characterisation

Table 1. summarizes physical properties and chemical composition of the investigated waste materials - industrial by-products. The dominant constituent of WFS was quartz (SiO_2) coated by metal oxide layers. The content of manganese (Mn) was 4 times higher than that of iron (Fe), also present in the metal oxide layer, which imparts a predominantly dark grey surface color to the material. The results of the chemical analyses show that the BFS was a complex heterogeneous material, mainly composed of silica, and iron and calcium oxides. During the first set of experiments, the pH measurements revealed that the BFS had a strong effect on the pH of the model solution. After addition of the BFS into the model solution, the pH drifted to 11.25. The explanation for the sudden pH increase was found in the presence of CaO in the original slag material, BFS, which dissolves in water forming $\text{Ca}(\text{OH})_2$ causing a rapid pH increase (7 to 11.25). In order to minimize its deteriorating effect on the quality of the model solution, the BFS was modified to neutralize the CaO effect on the pH. The raw BFS samples were treated with sulphuric acid and dried in oven at 70 °C for 24 h. After the modification, the pH was buffered (pH=7.90). The physical structure of the modified material (MBFS) was influenced by the formed gypsum giving it a “powder” appearance. As a result of the applied modification, the strong effect on the pH was avoided while the main components of the untreated

material, such as iron and iron oxides supposed to be beneficial for arsenic sorption, remained at nearly the equal content (Table 1). Therefore, this new, modified waste material was subjected to further detailed examination together with the other selected waste materials.

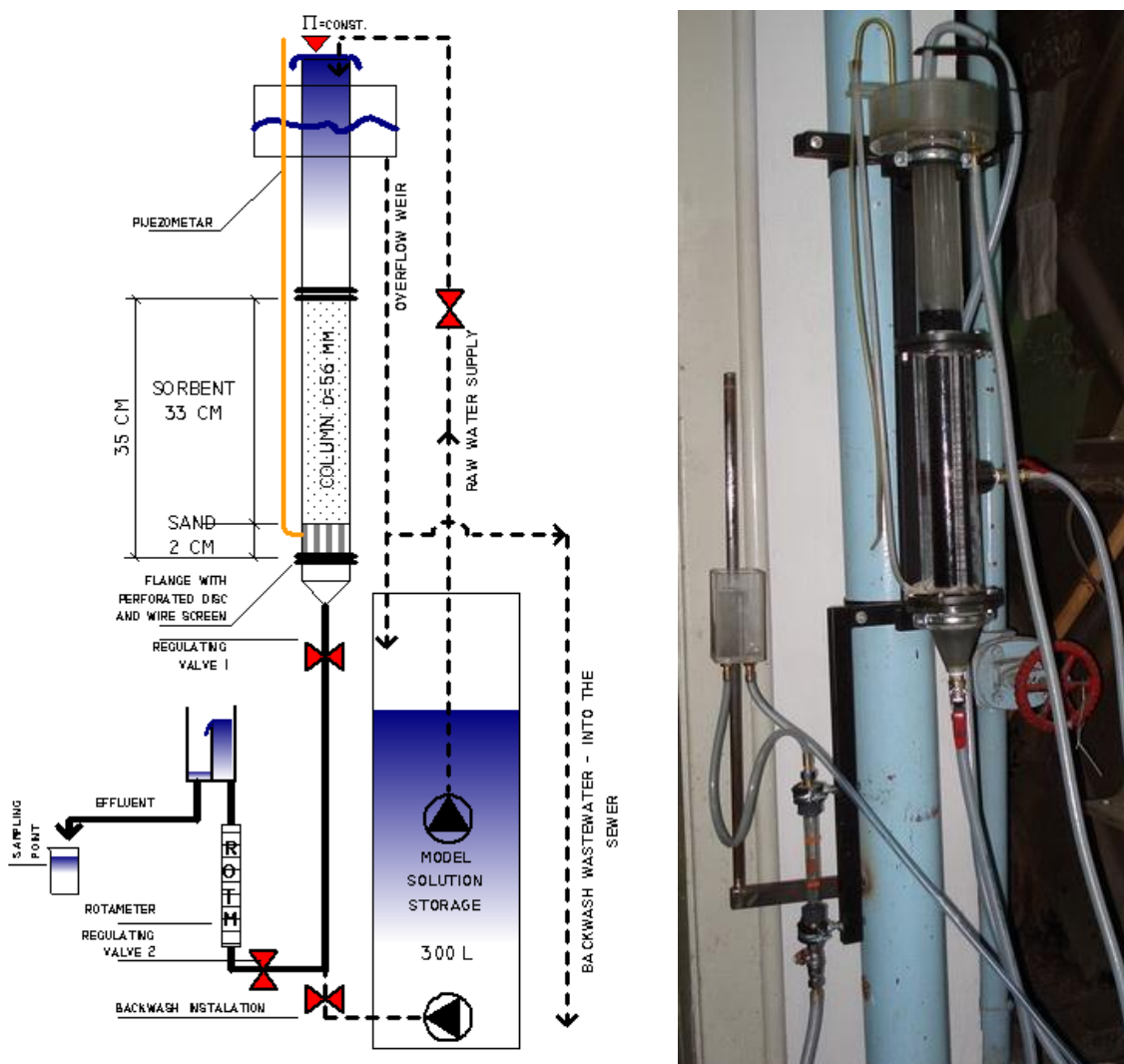


Figure 1. Experimental setup: pilot model of the sorption-filtration column for the arsenic removal from water

Table 1: Chemical composition and physical properties of the industrial by-products

Material	Chemical composition (%)								Physical properties	
	SiO ₂	Fe ₂ O ₃	FeO	Al ₂ O ₃	CaO	MgO	Fe	Mn	Grain size (mm)	BET specific surface area (m ² /g)
WFS	65.16	3.68	0.82	-	1.14	21.23	3.93	15.66	1.25	94.1
BFS	23.82	13.02	15.73	7.70	26.5	11.13	21.20	-	0.470	2.9
MBFS	21.45	15.94	14.50	-	24.53	8.67	22.42	-	0.340	17.167

The physical properties of the investigated industrial by-products are presented in Table 1. The porous microstructure with pores of different size and shape could be observed from both micrographs (Figure 2). Relatively high surface areas obtained for the waste filter sand is assigned to the iron and manganese oxides layer which coats the original grain of quartz sand. SEM microphotographs of the surface of the BFS revealed its highly porous structure (Figure 2b). The particles of BFS and MBFS

were much larger, up to 20 μm , and they occurred in rounded (BFS) to needle-sharp forms (MBFS). Modification of the BFS was not detrimental to the porosity of the original material, causing only a sharpening of the pore edges (Figure 2c). Additionally, modification increased the BET specific surface area of the new, modified material (17.167 m^2/g), which contributed to the efficiency of the sorption process.

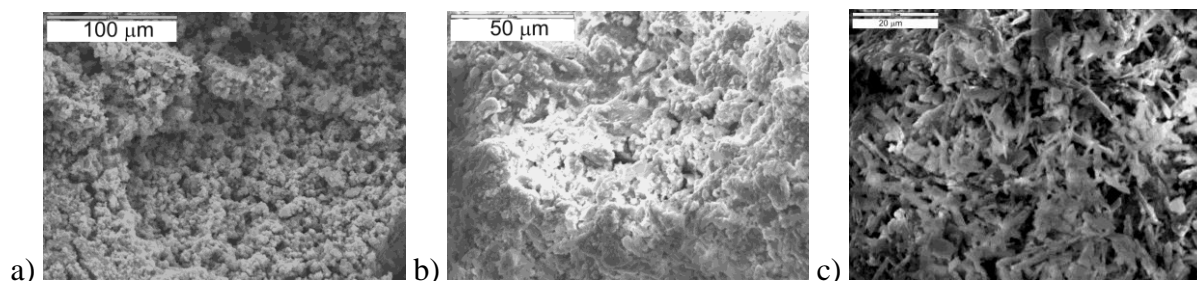


Figure 2. SEM microphotographs of a) waste filter sand, b) blast furnace slag and c) modified blast furnace slag

Batch kinetic and equilibrium studies

Several model equations have been established to describe sorption kinetics, among which Pseudo-second-order (PSO) model is the most frequently used. In addition, PSO model is found to be the most appropriate to describe the sorption process of a chemical nature - chemisorption. PSO model is described by the equation: $1/(q_e - q_t) = 1/q_e + k_2 t$ where q_t is sorption capacity at time t ($\mu\text{g}/\text{g}$), q_e the equilibrium sorption capacity ($\mu\text{g}/\text{g}$), k_2 the rate constant of sorption ($\text{g}/(\mu\text{g}\cdot\text{min})$). The experimental results are fitted to the pseudo-second-order model, applying non-linear regression analysis using MS Office 2000 Excel spreadsheets. The experimental and modeling results are presented in Figure 1. Values of the model parameters obtained from the regression analyses are presented in Table 2.

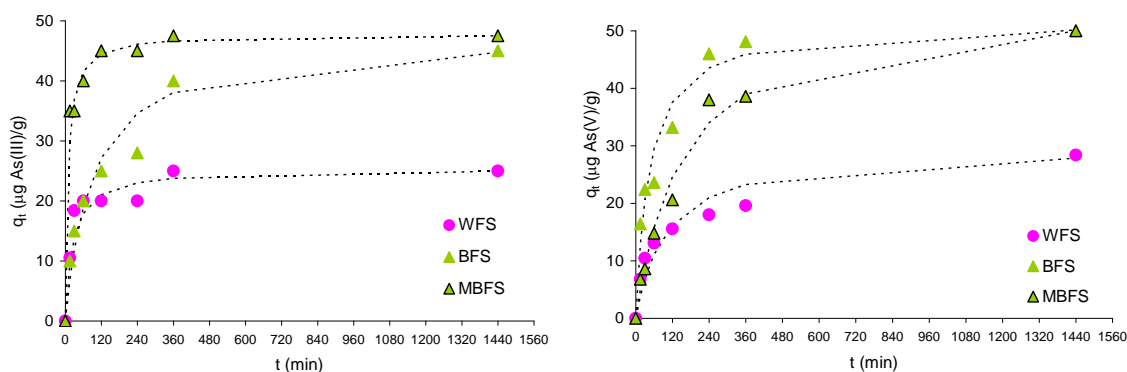


Figure 3. Sorption kinetics modeling of As(III) and As(V) on industrial by-products (Pseudo-second-order model)

Table 2: Pseudo-second-order kinetic model parameters for As(III) and As(V) sorption on industrial by-products

Materials	As(III)			As(V)		
	q_e ($\mu\text{g}/\text{g}$)	k_2 ($\text{g}/(\mu\text{g}\cdot\text{min})$)	R^2	q_e ($\mu\text{g}/\text{g}$)	k_2 ($\text{g}/(\mu\text{g}\cdot\text{min})$)	R^2
WFS	25.4	0.001572	0.999	29.8	0.000329	0.989
BFS	47.6	0.000233	0.994	51.7	0.000427	0.999
MBFS	47.8	0.002334	1.000	55.2	0.000121	0.996
HIER	45.1	0.000158	0.965	45.6	0.000167	0.982
GFH	49.0	0.000168	0.994	38.7	0.000169	0.987

The two times higher sorption capacities obtained with the BFS (47.6 $\mu\text{g/g}$) compared to WFS (25.4 $\mu\text{g/g}$) contribute to the assumption that chemisorption occurs, since slag material exhibit significantly lower BET specific surface area (Table 1) which is a crucial characteristic that enhances the sorption properties of a material. Further insight into the chemical composition of the examined materials (Table 1) revealed that the BFS exhibited higher sorption capacities due to the five times higher iron and iron oxides content compared to the WFS, despite their lower BET surface areas.

The contribution of manganese (15.66 %) in WFS to the sorption mechanism is probable since the low iron content in the metal-oxide-layer (3.93 %) hinders the WFS from being an efficient sorbent for arsenic. BFS exhibited specific arsenic removal efficiency of 220 $\mu\text{gAs/gFe}$. Applied to the WFS containing 39.3 mg/g of Fe, the contribution of iron to arsenic removal was expected to be 9 $\mu\text{gAs/gWFS}$. The obtained q_e values (25.4 and 29.8 $\mu\text{g/g}$, for As(III) and As(V), respectively) suggests that iron was not the only active component in the WFS. Although these results can not be directly correlated (due to the chemical and physical properties), the higher efficiency of WFS could be assigned to manganese activity. Assuming the difference between the contribution iron to the sorption and the total q_e values is the consequence of manganese activity only, the specific arsenic removal efficiency of manganese was estimated to be 115 $\mu\text{gAs/gMn}$.

In order to evaluate the applicability of the waste materials for the treatment of real arsenic-contaminated water treatment, these results were compared with those obtained for commercial materials. The same set of batch experiments was performed with commercial granular porous ferric hydroxide (GFH) and a hybrid ion exchange resin coated with nano-scale iron oxide particles (HIER). The obtained q_e values were 49.0 and 38.7 $\mu\text{g/g}$ for GFH and 45.1 and 45.6 $\mu\text{g/g}$ for HIER, for As(III) and As(V), respectively. The capacities exhibited by the waste slag materials (Table 2) attained the values realized with the commercial materials for As(III), while the results were even slightly exceeded for As(V). The lower performances of the WFS compared to the commercial materials were assigned to its low iron content. However, sand filter media from other groundwater treatment plants were reported with different contents of iron (ranging from 15-330 mg/g) and manganese (0.2–50 mg/g) (Sharma, 2001). Previous findings on specific arsenic removal efficiencies of active substances suggest that sand filter media containing a sufficient amount of iron (roughly estimated > 220 mg/g) can remove arsenic from aqueous solution equally efficiently as the examined commercial materials.

Adsorption isotherms are important for the description of how molecules of a sorbate interact with the sorbent surface and for the prediction of the extent of sorption. The Langmuir isotherm model ($q_e = q_{\max}K_L C_e / (1 + K_L C_e)$, where q_e is the amount of solute sorbed per gram of sorbent (mg/g), C_e the equilibrium concentration of solute (mg/L), K_L a constant related to the energy of sorption (L/mg) (Langmuir model), q_{\max} the maximum amount of solute sorbed per gram of sorbent (mg/g)) was derived under the assumption that the sorbate is sorbed in one molecule layer. The Freundlich isotherm model ($q_e = K_F C_e^{1/n}$, where K_F is the Freundlich constant (mg/g), n a constant related to the sorption intensity of the sorbent) is a consecutive layer model which does not predict any saturation of the sorbent by sorbate. Table 3 summarises Langmuir and Freundlich isotherm model parameters for the examined industrial by-products.

Table 3: Langmuir and Freundlich isotherm parameters for industrial by-products

Material	Langmuir						Freundlich					
	As(III)			As(V)			As(III)			As(V)		
	q_{\max} (mg/g)	K_L (L/mg)	R	q_{\max} (mg/g)	K_L (L/mg)	R	K_F (L/mg)	$1/n$ (L/g)	R	K_F (L/mg)	$1/n$ (L/g)	R
BFS	0.82	13.22	0.97	4.04	12.71	0.99	0.567	0.519	0.96	3.010	0.591	0.83
MBFS	0.70	6.20	0.95	2.79	18.63	0.99	0.369	0.587	0.94	1.779	0.526	0.75
WFS	0.55	0.37	0.79	0.77	1.18	0.97	0.110	0.843	0.96	0.157	0.727	0.92

The highest maximum sorption capacities were found for BFS: 0.82 mg/g and 4.04 mg/g for As(III) and As(V), respectively. The BFS and MBFS exhibited significantly higher q_{\max} values for As(V) compared to As(III), while the WFS attained nearly equal values for both. The differences in the q_{\max}

values for As(III) and As(V) might suggest that the arsenic species present under neutral conditions (As(III) in the molecular form while As(V) in the ionic form) influence the sorption efficiency of the waste slag materials. Although iron was found efficient for arsenic uptake, arsenic removal was found to be valence dependent (As(V) removal more effective than As(III)). The higher sorption capacities of the BFS and MBFS (5 and 4 times, respectively) for As(V) suggest that molecular arsenic was less efficiently bound to the slag materials than its ionic forms. While iron was the main active component in the slag materials, manganese was dominant in the WFS. The low content of iron in the WFS is presumed responsible for its lower As(V) sorption capacity.

Column studies

Hydraulic characteristics of the pilot model

Hydraulic and sorption-filtration characteristics of the pilot model are adopted to meet the operational range of similar reactors in real water treatment plants. Experimental investigations in batch system showed that the increase of contact time contributes to the increase in the efficiency of arsenic removal for all tested materials, including the commercial. However, the practical application of sorption processes substantially limits the value of applied contact time in real reactors since the contact time is directly related to the dimensions of the reactor: the higher contact time - the bigger reactor. For this reason, the real reactors are designed for the contact time from 2.5 to 5 min. In the presented column examinations adopted empty bed contact time (EBCT) is 4 min. For the applied surface hydraulic load of 5 m/h calculated height of the adsorption filter media is 33 cm. Hydraulic characteristics of the pilot model are summarised in Table 4. Arsenic sorption investigations in the continuous flow system were performed under the same experimental conditions as examinations of arsenic sorption kinetics in the batch reactor: $C_0 = 0.5$ mg/L, pH neutral and constant temperature of the solution.

Table 4: Characteristics of the pilot model

Hydraulic parameters			
Inner column diameter, D_k (mm)	56	Empty bed contact time, EBCT (min)	4
Mean grain diameter, d (mm)	1	Surface hydraulic load, v (m/h)	5
Height of the media, H_i (cm)	33	Hydraulic load, Q (L/h)	12,3
Height of the coarse gravel sand layer, h_n (cm)	2	Backwash surface hydraulic load, v_{pf} (m/h)	50
Operating column volume, V_R (dm ³)	0,81	Backwash hydraulic load, Q_{pf} (L/h)	123,2

Breakthrough curves for As(III) and As(V) sorption on blast furnace slag and waste filter sand are shown in Figure 4.

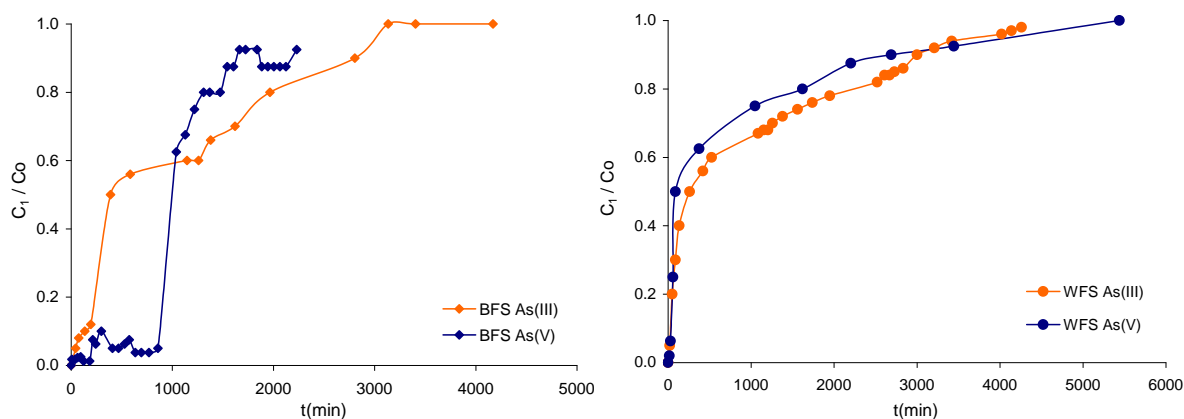


Figure 4. Breakthrough curves for As(III) and As(V) sorption on blast furnace slag and waste filter sand

The difference in the sorption kinetics of arsenite, As(III), and arsenate, As(V), on BFS in continuous flow system is apparent. In the first 860 min the effluent arsenate As(V) concentration is changing slowly in low range of arsenic concentrations (less than 50 mg/L). After this stage, the effluent arsenate concentration increases rapidly and media reaches 90% saturation in the next 13 h. In contrast, sorption of arsenite in the early stages of the experiment is less efficient. Arsenite concentration of 50 mg/L is exceeded after only 38 min. In the next 5.8 h effluent arsenite concentration is rapidly growing to 50% saturation after which it continues to increase slowly until the full saturation in the next 46 h. Unlike the slag material, breakthrough curves for As(III) and As(V) sorption on WFS are almost identical. This indicates that WFS exhibits the same performance in the sorption of both arsenic species in continuous flow system.

Arsenic sorption investigations in the continuous flow system were performed under the same experimental conditions as examinations of arsenic sorption kinetics in the batch reactor. In case of identical experimental conditions, equilibrium sorption capacity, q_e , obtained in batch experiments should correspond to the total sorbent capacity, K_E , obtained in continuous flow reactor. Table 5 summarises the equilibrium capacity data from the batch tests and the total capacity of waste materials. Values of equilibrium sorption capacity, q_e , are lower than total capacity, K_E , for all examined waste materials and both arsenic species. Hydraulic conditions in batch reactor are favourable only for the development of the sorption process. However, continuous flow through the sorption-filtering unit enables development of several contaminant removal processes such as: sorption, coagulation, flocculation, sedimentation, filtration. The joint effect of all these contaminant removal processes are assumed to increase the overall sorbent performance in the continuous flow reactor.

Table 5: Maximum sorbent capacity at $C_0=0.5$ mg/L in batch and continuous flow reactor

Maximum sorbent capacity ($\mu\text{gAs/g}$)	BFS		WFS	
	As(III)	As(V)	As(III)	As(V)
Equilibrium capacity in batch reactor, q_e ($\mu\text{gAs/g}$)	47.6	51.7	25.4	29.8
Total sorbent capacity, K_E ($\mu\text{gAs/g}$), continuous flow reactor	87.4	66.3	139.9	108.8

CONCLUSION

Industrial by-products: blast furnace slag, waste filter sand and modified blast furnace slag exhibited substantial affinity towards inorganic arsenic species. Kinetic studies revealed that the slag materials were the most efficient in arsenic removal, attaining equilibrium sorption capacities in the range of 47.6-55.2 $\mu\text{g/g}$ while waste filter sand exhibited sorption capacities in the range of 25.4-29.8 $\mu\text{g/g}$ for an initial arsenic concentration $C_0 = 0.5$ mg/L. Complex nature of the sorption process in industrial by-products, including both chemisorption and physical sorption, was revealed by the equilibrium studies. Sorption capacities for As(V) compared to As(III) were significantly higher for blast furnace slag while waste filter sand exhibited similar removal efficiencies for both arsenic species. Arsenic sorption process on the waste materials continued after monolayer saturation following Freundlich isotherm model. Blast furnace slag exhibited the highest equilibrium sorption efficiency of 0.05 mg/g under the conditions that occur in real water treatment systems while waste filter sand reached 0.02-0.03 mg/g. Comparing to the equilibrium sorption efficiency of 0.05 mg/g obtained for the granular ferric hydroxide, commercial arsenic sorbent, these results indicate that application of industrial by-products is feasible in real water treatment systems. Better sorption efficiencies are obtained in continuous flow reactor compared to batch reactor. The joint effect of sorption, coagulation, flocculation, sedimentation and filtration that are developed during continuous flow in a fixed bed reactor are assumed to benefit the efficiency of arsenic sorption in the continuous flow reactor.

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II International Conference
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SEASONAL TEMPERATURE AND POLUTION INFLUENCE ON
OXYGEN SATURATION IN THE URBAN RIVER WATER

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ABSTRACT

Based on the months monitoring data on input and output of urban river Begej from the town Zrenjanin 2010, the seasonal influence on the oxygen distribution efficiency from thermal gas in the chemisorbed energy states is examined on the two locations: - the river input in the urban zone; - the river output from the urban zone. Oxygen mass diffusion and thermal transport energy ratio with thermal gas energy are calculated based on the measured oxygen saturation values and compared with the entropy driven oxygen adsorption, enthalpy driven diffusion and electric polarization of chemisorbed oxygen in double layer depending on season and dominant pollution, suspended matter and organic matter content measured as chemical oxygen demand, COD.

Key words: Urban river, Input in urban area, Output from urban area, Oxygen thermal distribution efficiency, Seasonal influence, Pollution influence, Relaxation processes thermal energy efficiency.

INTRODUCTION

In order to obtain the data about the oxygen dissolution efficiency depending on the season as natural phenomena, and urban river pollutions, the respective thermodynamic analysis was carried out. In our previously paper, the results are used in the identifications of the electric polarization of chemisorbed oxygen double layer (Petar Ševaljević, Olivera Grozdanović, Mirjana Ševaljević 2012) determining the oxygen dissolution efficiency in comparison to distilled water. According to literature (Gilbert M. Masters, 1995), when impurities can activate the dissociative oxygen processes with the rate constant, k_{ch} the step response function describes in un-conservative aerated sistem:

$$(cV_L)_{iz} - (cV_L)_{ul} / d\tau + d(cV_L)_w / d\tau - k_{ch} V_L c_w = 0 \quad (1)$$

Oxygen saturation determine the distribution in the contact surface between the diffusion stationary mass transport rate constant and the saturation time ($\tau_s = 1/k_s$):

$$w_s = \frac{c_s}{c^*} = 1 - e^{-k_d/k_s}, \text{ where, } k_L = k_d = \frac{D}{\delta} \quad (2)$$

The stationary states determine the chemical or electrochemical reversible processes balanced with the diffusion mass transport through water film in liquid phase of the contact surface. The diffusion distribution, $\frac{k_d}{k_s} = \ln \frac{1}{1-w_s}$ defines the ratio, $(\frac{k_d}{k_s})_L = 1$ where is oxygen saturation, $w_s = 0,63$.

The oxygen saturation in liquid determine the oxygen desorption efficiency in gas phase $w_{s(G)} = 0,37$, $k_{d(G)} = 0,46 \cdot k_{s(G)}$.

To the Boltzmann distribution law oxygen equilibrium state in air, between the two energy state, equilibrium and stationary energy difference ΔE_B achieve the balanced state with the oxygen thermal energy $\frac{\Delta E_B}{RT} = 1$ where oxygen desorption efficiency $w_{s(G)} = 0,74$ can be achieved after much longer

saturation than diffusion oxygen transport time, $\frac{k_{des}}{k_s} = 0$, $\frac{c_s}{c^*(c_{iz})} = \frac{1}{1 + e^{-\Delta E / RT^*}}$.

The thermal transport energy, ΔE_B through condensed water film in gas phase, $\frac{\Delta E_B}{RT} = \ln \frac{w_s}{1 - w_s}$ at

equal diffusion and saturation rate constant has to be, $(\frac{\Delta E_B}{RT})_G = -0,53$ at the room temperature and

the transport polarization, electro-kinetic potential, $\Delta \chi_{(G)} = \frac{\Delta E_B}{F} = -0,013V$.

The oxygen thermal desorption efficiency, with the transport energy in the gas bubbles dissolved in liquid as well in the air in contact with condensed water vapor, according to (M. Ševaljević, 2009)

determine the Galvani potential of the chemisorbed oxygen. $F \cdot \Sigma \Delta \phi = 3RT$, $\frac{F \cdot \Sigma \Delta \phi}{RT} = 3$.

EXPERIMENTAL RESULTS

Oxygen saturation, w_s , air and water temperatures are measured in Institute of the Public health in Zrenjanin 2010 in the each month, in the river water of Begej, before the input in the urban zone of Zrenjanin and after output. The modified Winkler method analogous to EN 25813 is used after oxygen oxidized manganese (II) to manganese (III) and in acidic solution form red complex with Titriplex for the photometrically determination with WTW photometer and oxygen cell test, WTW 14694.

The measured data and calculated results are analysed depending on:

- the season date
- and location of the samples for analysis
- a) on the Begej input in the urban zone at the asphalt base
- b) and on the output from the urban zone, at the bridge in Ečka)

The monitoring data (table 1) and calculated data of ratio between oxygen mass diffusion transport and saturation rate constants in liquid, $(k_d/k_s)_{ws(L)}$ and oxygen thermal desorption efficiency, $(\Delta E^0/RT)_{ws(G)}$ based on the oxygen saturation values, w_s with the aim:

- to compare the thermal energy efficiency in the work of the oxygen chemisorption, $\Delta_{ad}G^0/3RT$, in the oxygen enthalpy work in diffusion layer $\Delta_{ad}H^0/3RT$, and in the electric polarization, $F\Delta\phi^0/3RT$
- to find the functional dependences between oxygen saturation, w_s and the dominant pollutants content (suspended matter and organic matter, measured as chemical oxygen demand, COD).

Table 1: Monitoring data of the water and air temperatures, the oxygen solubility and saturation degree, w_s

Input The dates	t_w °C	$t_{air} - t_w$ °C	O_2 , mg/l	w_s %	Output The dates	T_w °C	$t_{air} - t_w$ °C	O_2 mg/l	w_s %
13.1.2010	5,4	-2,1	12,4	92	13.1.2010	5,5	-3,8	12,7	92
3.2.2010	1,3	-1,8	11,1	78	3.2.2010	1	-0,5	9,1	64
3.3.2010	8	-1,1	11,8	100	3.3.2010	7,8	-1,5	11,7	99
29.4.2010	16,8	2,7	9,2	95	29.4.2010	17,2	4,5	5,3	55
14.5.2010	18,5	0,8	7,8	82	14.5.2010	18,2	6,1	6,5	69
6.6.2010	24,4	5,2	5,7	68	6.6.2010	23,5	8,6	5,7	68
1.7.2010	24,6	5,1	4,2	51	1.7.2010	23,3	2,3	6,4	75
13.8.2010	25,1	1,2	5,7	69	13.8.2010	25,7	-4,5	4,8	59,1
15.9.2010	19,6	-1,6	6,8	75	15.9.2010	20	-3	3,7	41
15.10.2009	13,1	-6,4	8,7	71,7	15.10.2009	13,9	-7,6	7,3	58,6
4.11.2009	8,2	-4,6	9,2	70	4.11.2009	8	-4,4	8,1	62
2.12.2009	8,7	-2,4	10,1	81	2.12.2009	7,8	-1,9	7,9	63

Table 2: The calculated data based on the monitoring on input in town, of ratio between oxygen diffusion and saturation rate constants in liquid, (k_d/k_s) , oxygen thermal desorption efficiency, $(\Delta E^0/RT)w_s(G)$ and efficiencies of thermal energy in oxygen adsorption, diffusion and polarization (The data for $\Delta_{ad}G^0$, Δ_dH^0 , $F\Delta\phi^0$ are calculated in the Ref ((Petar Ševaljević, Olivera Grozdanović, Mirjana Ševaljević 2012)

Input / Months	w_s , % (meas.)	$(k_d/k_s)_{ws(L)}$	$(\Delta E^0/RT)_{(G)}$	$\Delta_{ad}G^0/3RT$	$\Delta_dH^0/3RT$	$F\Delta\phi^0/3RT$
I-III	90 $\approx w_{st}$	2,3	-2,2	0,95	3,3	- 4,26
IV-V	95,4 $\approx w_{st}$	3	-3,2	-12,3	9,6	2,66
VI-VIII	64,7	1	-0,7	-1,3	-0,96	2,26
IX-XII	74,4	1,34	-1	-3,66	-2,8	6,4

Table 3: The calculated data based on monitoring on output from town, of ratio between oxygen diffusion and saturation rate constants in liquid, (k_d/k_s) , oxygen thermal desorption efficiency, $(\Delta E^0/RT)w_s(G)$ and efficiencies of thermal energy in oxygen adsorption, diffusion and polarization (The data for $\Delta_{ad}G^0$, Δ_dH^0 , $F\Delta\phi^0$ are calculated in the Ref ((Petar Ševaljević, Olivera Grozdanović, Mirjana Ševaljević 2012),

Output / Months	w_s , % (meas.)	$(k_d/k_s)_{ws}$	$(\Delta E^0/RT)_{(G)}$	$\Delta_{ad}G^0/3RT$	$\Delta H^0/3RT$	$F\Delta\phi^0/3RT$
I-III	85	1,9	-1,73	3,73	5,9	- 9,6
IV-V	57,4	0,85	-0,28	-2,6	3,9	- 1,2
VI-VIII	66,8	1	-0,66	-7,0	-2,6	9,8
IX-XII	56,1	0,82.	-0,24	-7	-2,7	9,7

In period of winter months , I-III and IX-XII and also in VIII on output of the river Begej from the town Zrenjanin, the negative values of the measured air and water temperature difference (table 1) in the comparison with the oxygen thermal desorption efficiency, $(\Delta E^0/RT)w_s(G)$ correlate with the 2-4 times greater thermal energy efficiency in oxygen processes (table 2.):

- in spontaneous electric polarization in period (I-III)
- and in forced electric polarization in period (IX-XII),

In period in the months IV-, V and VI-VIII and IV-VII on output from the town Zrenjanin, the positive values of the measured air and water temperature difference (table 1), approximately equal oxygen diffusion mass transport and saturation rate constant ratio, (table 2) with the thermal energy efficiency determine:

- the oxygen forced electric polarization, in period (IV-V) or spontaneous electric polarization on output from the town
- the oxygen spontaneous enthalpy driven diffusion, twice greater on the output then on the input in the town, in period (VI-VIII)

Based on the best correlation coefficients between the measured oxygen saturation, w_s (table 1) and urban river water pollution (Fig 1) the dominant pollutants influenced on the oxygen saturation are found depending on the season and location (suspended matter and COD).

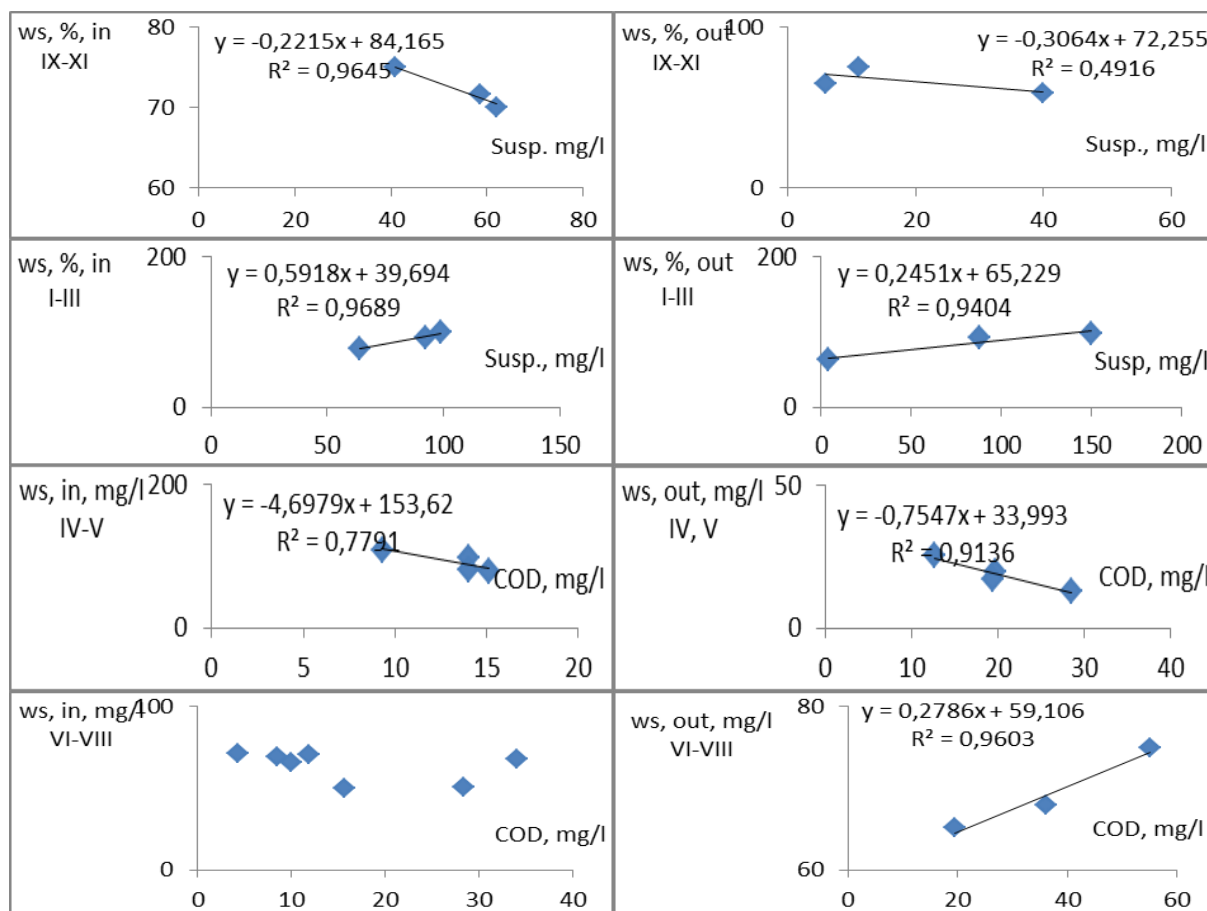


Figure 1. Pollutants influence on the oxygen saturation in the monitoring period:
 - the suspended matter content in period IX-XII and I-III
 - and organic matter content measured as chemical oxygen demand, (COD) in period IV, V ad VII-VIII

The increasing pollutants content (suspended matter and COD) decrease the oxygen saturation on the both location in the all season, except ;

- the suspended matter increased in the winter months (I-III) increased above 60 mg/l in the II and IV class of the water quality,
- and COD increased in summer period VI- VIII., above the 15-20 mg/l, in the III and IV class of water quality.

CONCLUSIONS

The results based on monitoring oxygen saturation degree and thermodynamic study indicate on the seasonal influence on the processes in the double layer of the two water films in the contact surface on the oxygen mass diffusion and thermal transport in liquid and air:

1. In winter the depolarization where is suspended matter above 60-100 mg/l and 100-150 mg/l, approximately equal thermal collisions and mass oxygen diffusion transport, on air input and output are twice times greater than chemical depolarization processes
2. In April May, the COD increasing from 10-15 mg/l on input of the river in the town activate three times faster depolarization diffusion and thermal collisions compared to chemical saturation rate constants, than on air output where COD are 10-30 mg/l.
3. In summer the increased COD up to 30 mg/l in the IV class of water quality on output decrease oxygen saturation at approximately equal diffusion, and saturation rate constants ration on water input and output from the town.
4. In the autumn in the aggregation and sedimentation of suspended matter less than 60 mg/l the mass diffusion transport and the thermal collisions determine the chemical relaxation processes rate constant on rinput of the river in the town and the slowest thermal relaxation on output.
5. The thermal energy efficiency in the oxygen electrical depolarization processes in the period IV-V correspond to the mass dissusion is the least on river water output from the town, -1,2 and on input about 2,5 also in VI-VIII. In the period of I-III and IX-XI increase 4-5 times on input and about 10 times on river water output from the town.

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ECO WASTE AS BIOSORBENT FOR LEAD

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ABSTRACT

*Removal of heavy metals from wastewaters is of great concern caused by the health risk they pose. It has been recognized that aquatic plants, both living and dead, are heavy metal accumulators so the use of aquatic plants for the removal of heavy metals from wastewater gained high interest. In this work sorption of Pb(II) ions by fresh tissues of *Myriophyllum spicatum* was investigated in batch experiments. Aquatic weed from Sava Lake which belongs to capital city of Serbia is mowed with mechanical underwater harvester 3 - 4 times per year reducing 35 m³ plant material per day. From one point of view, therefore, it can be considered as a waste product. Biosorbent was characterized by Scanning Electron Microscopy (SEM). The efficiency of aquatic weed in Pb(II) ion removal was examined varying pH value and contact time. On the basis of the obtained results, the experimental investigation was performed at pH 5.0. Metal sorption was fast and equilibrium was attained within 20 min. The kinetic study indicated that sorption process of lead ions on fresh tissues of *M. spicatum* followed pseudo second order. Data obtained from the batch adsorption studies have indicated that *M. spicatum* is efficient in lead removal from solution.*

Key words: *biosorption, Myriophyllum spicatum, lead.*

INTRODUCTION

The release of heavy metals into the environment by industrial activities presents a serious environmental threat. (Lesage et al, 2008). Almost all heavy metals are toxic even in trace amounts, non - biodegradable, non termodegradable and they can accumulate along the food chain causing a number of serious environmental and health problems (Sharma et al., 2007; Qaiser et al., 2009). Heavy metals can be removed from industrial wastewater by a range of physico-chemical remediation technologies such as precipitation, ion exchange, adsorption, electrochemical processes and membrane processes (Kurniawan et al., 2006). Furthermore, these technologies are expensive and energy-intensive, driving towards a search of cheaper alternatives in both developing and developed countries (Kivaisi, 2001).

Lead is introduced to water as spare product from industry of: mining, metal plating, paint production, fertilizer production, paper production etc. Lead is hazardous heavy metal because it interferes with a variety of body processes and it is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems (Zhu *et al.*, 2008).

Biosorption can be defined as the removal of selected ions or other molecules from solution by certain biomolecules (or types of biomass). The development and implementation of a cost-effective alternatives process such as biosorption for the removal and recovery of heavy metals is necessary because it improves the competitiveness of mining (and electroplating) industries and its eliminates toxic metals from effluents as required by environmental regulations (Volesky, 2007).

It has been well-known that aquatic plants, both living and dead are heavy metal accumulators, thus the application of aquatic plants for the removal of heavy metals from wastewaters has gained considerable interest (Kuyucak and Volesky, 1989; Keskinan *et al.*, 2004). Processes of metal

removal by aquatic plants include two steps: (1) an initial fast, reversible metal-binding step - biosorption relating to physico-chemical processes such as chelation, ion exchange, precipitation and adsorption and (2) a slow, irreversible ion-sequestration step - bioaccumulation consisting of biological processes like intracellular uptake, vacuolar deposition and translocation (Salt *et al.*, 1995) (Keskinan *et al.*, 2003).

Biosorption includes a combination of several processes: electrostatic attraction, complexation, ion exchange, covalent binding, Van der Waals' forces, adsorption and precipitation. Biosorption is a metabolically passive process, in which metallic ions remain at the cellular surface by different mechanisms. Bioaccumulation is an active metabolic process driven by energy from a living organism where contaminants – heavy metals are incorporated inside the living biomass.

Myriophyllum spicatum (Eurasian water milfoil) is a submerged aquatic plant, native to Europe, Asia, and north Africa and it was introduced into North America where is invasive species (Couch and Nelson 1985). *M. spicatum* reproduces primarily by vegetative fragmentation and it can quickly recolonize areas that have been cleared of the species because of the viability of even small fragments (Aiken *et al.*, 1979). The plant is tolerant to a wide range of water quality conditions and can be found in fresh and brackish water (APIRS, n.d.). From one point of view, thus, it can be thought of as a waste product (Keskinan *et al.*, 2003). The control methods for grow *M. spicatum* can be classified as physical (mechanical harvesters and chopping machines), chemical, and biological.

The aim of this work is to investigate adsorption of Pb(II) ions on fresh tissues of *M. spicatum*.

METHODS

Preparation of the plant biomass, compost and chemicals

M. spicatum is harvesting from artificial Sava Lake every year. Sava Lake belongs to the capital of Serbia, Belgrade. It covers the area of 0.8 km² and it is 4.2 km long, 4 to 6 m deep with dominant spices of aquatic weed *M. spicatum*. *M. spicatum* is mowed with mechanical underwater harvester 3 - 4 times for year. With mowing amount of unwounded aquatic weed is significantly reducing (around 35 m³ per day). Mechanical underwater harvester and *M.spicatum* are shown on figure 1.



Figure 1. Mowing of plant material *M. spicatum* from Sava Lake

Samples of fresh harvested tissues of *M. spicatum*, used for experiment, were taken from Sava Lake. Plant biomass was washed with diluted HCl solution (3%) and then with distilled water for three times before being used. Analytical grade $\text{Pb}(\text{NO}_3)_2$ was used as sources of lead and stock solutions of Pb(II) ions were prepared in deionized water.

Batch experiments

In order to investigate the effect of pH, contact time a batch sorption experiments were conducted at room temperature $22^\circ\text{C}\pm 1$ in flasks (250 ml) using shaker. 2 g wet weight of fresh tissues of *M. spicatum* and 100ml of solution was added to each flask. Using a precise pH meter (Consort C 830 P) the initial pH value was regulated to appropriate value with 0.1 M HNO_3 or 0.1M NaOH (analytical grade). Sorption kinetics study was investigated with initial Pb(II) concentration of 0,5 mmol/l at initial pH about 5.0. After specified contact time, the contents of flasks were filtrated to separate biomass from solution. Clear solutions were analyzed with atomic absorption spectrophotometer (Perkin Elmer AAnalyst 300) to determinate lead concentration. All sorption experiments were performed in duplicate.

FINDINGS AND DISCUSSION

Characterization

Scanning electro-micrographs (SEM) show the surface texture and morphology of the biosorbent (Figure 2). The surface is wavy with a large number of properly spaced square openings dimensions of $10\mu\text{m}$ - $5\mu\text{m}$. Therefore, *M.spicatum* has a large surface for interaction and the observation of the biosorbent section indicates that channels may exist in the external layers of the material that can make easier the diffusion of the solute to the center of the particles.

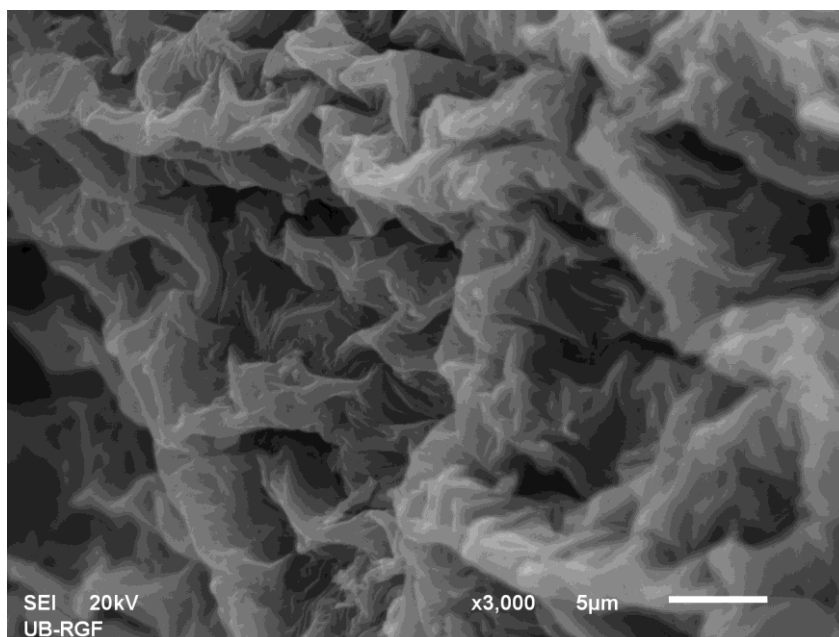


Figure 2. SEM micrographs of *Myriophyllum spicatum* powder surface: magnification 3000

Effect of pH

The effect of pH on sorption Pb(II) ions on compost was studied at pH range 2 - 6. The maximum of Pb(II) sorption was observed at pH 5.0, thus all sorption experiments were carried out at that pH value.

Effect of contact time

The effect of contact time *M. spicatum* was studied with initial Pb(II) concentration of 0.5 mmol/l, initial pH was around 5.0 and contact time ranged from 10 to 145 min (Figure 3). Sorption rate was very fast and contact time of 20 min was enough to reach equilibrium.

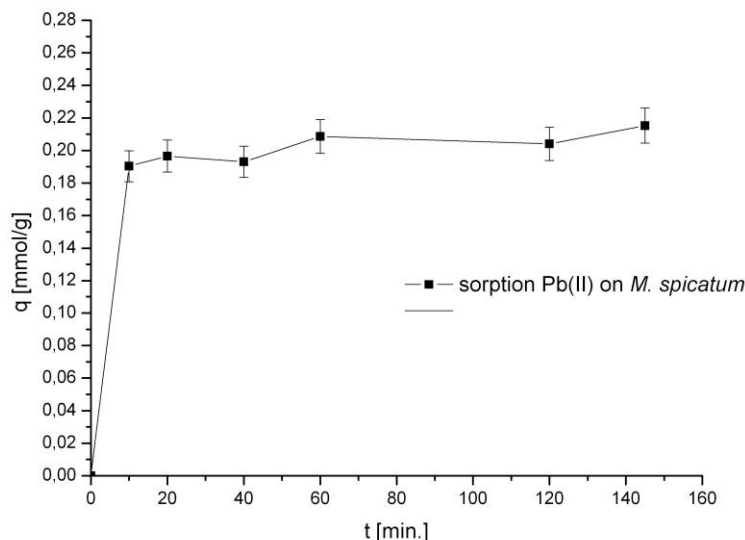


Figure 3. The effect of contact time Pb(II) onto fresh tissues of *M. spicatum* (Pb(II) initial conc. 0,5 mmol/l, dry weight of biomass 0.2 g, pH 5.0)

Table 1 shows a comparison of the maximum adsorption capacities for Pb(II) per g *M. spicatum* obtained in other studies.

Table 1: Comparison of maximum adsorption capacity q_{max} [mmol/l] for lead

biosorbent	Adsorption capacity mmol/l Pb(II)	Reference
<i>M. spicatum</i>	0,198552124	(Yan et al., 2010).
<i>M. spicatum</i>	0,217181467	(Keskinan et al., 2007).
<i>M. spicatum</i>	0,2253861	(Keskinan et al., 2003).
<i>M. spicatum</i>	0,268339768	(Wang et al., 1996)
<i>M. spicatum</i>	0,2153	This study

Biosorption kinetics

In this work three kinetic models were applied to the experimental data: Lagergren pseudo first order (Lagergren, 1898), Lagergren pseudo second order (Ho and McKay, 1999) and intraparticle diffusion (Weber and Morris, 1963) model. It was found that adsorption process was best described by the pseudo second order kinetic where lead binding capacity was proportional to the number of active sites occupied on the sorbent *M. spicatum*. Pseudo-second order model is obtained on the basis of the sorption capacity of the solid phase, expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

Where, k is the equilibrium rate constant of pseudo second order sorption kinetics [g/mg min], q_e the amount of metal ion adsorbed at equilibrium [mg/g], q_t the amount of sorbate on the surface of sorbent at any time t [mg/g]. Integration of this equation with boundary conditions $t = 0, q_t = 0; t = t$ and $q = q_t$ results in (linear form) (Febrianto *et al.*, 2009.)

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \tag{2}$$

On Figure 4 is shown a plot of t/q_t versus time. In table 2 are listed rate constants and correlation coefficients for pseudo second order reaction model.

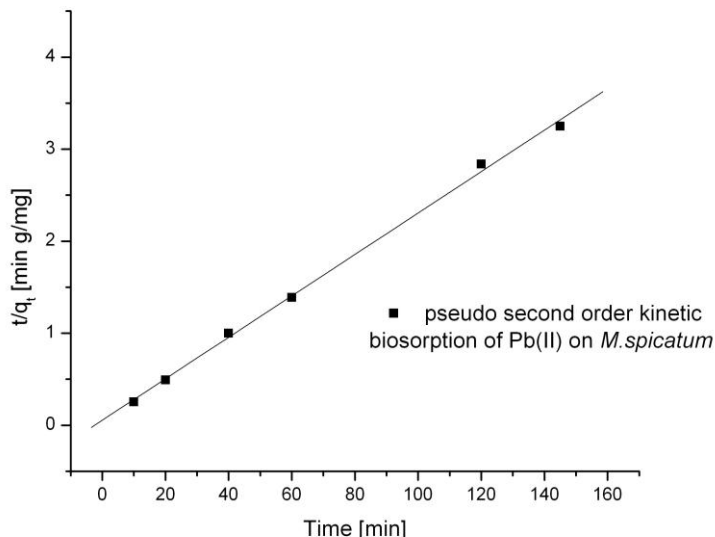


Figure 4. Pseudo second order kinetic of adsorption Pb(II) onto *M. spicatum* (Pb(II) initial conc. 0,5 mmol/l, dry weight of *M. spicatum* 0.2, pH 5.0)

Table 2: Pseudo second order rate constants for lead

biosorbent	Reaction rate constant k [g/mg min]	Correlation coefficient R ²
<i>M. spicatum</i>	0.009	0.99905

Obtained results for pseudo second order kinetic of adsorption Pb(II) onto *M. spicatum* comply with research of Yan *et al.*, 2010.

CONCLUSIONS

Data obtained from the batch adsorption studies have indicated that *M. spicatum* is efficient in lead removal from solution. Adsorption process was best described by pseudo second order kinetic. Although further investigation is necessary, on the basis of the obtained results, aquatic weed as eco waste can be recommended as sorbent of lead from wastewaters, especially for developing countries such as Serbia. The main advantage of this biosorbent is that it is low-cost, efficient and available.

ACKNOWLEDGMENT

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**QUALITY OF DIFFERENT DRINKING WATERS IN SETTLEMENTS
OF AUTONOMOUS PROVINCE OF VOJVODINA**

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ABSTRACT

Basic human need is to ensure sufficient quantities of health safe drinking water. Health safety of water means absence of pathogenic microorganisms, chemical and radiological contaminants that can affect human health. In this regard, drinking water has to meet the quality standards prescribed by the relevant Regulation. The humans can use drinking water from public distribution systems, artesian wells, spring, or as bottled water. Each water supply has its advantages and disadvantages. This paper considers the basic chemical quality of different drinking waters. Some samples were taken and analyzed from distributive systems of different settlements in Vojvodina: Novi Sad, Žitište, Zrenjanin and Bačko Gradište, and from some artesian wells. The results of analyses are discussed, compared with quality of some bottled waters and with parameters prescribed by the Regulation on hygienic quality of drinking water.

Key words: *drinking water, quality.*

INTRODUCTION

Water is life. It is necessary for functioning of the human body, and it is the only “foodstuff” used by entire population, regardless of geographical location, religion, race and socioeconomic status. People use water for drinking, food preparation, bathing, washing, recreation, fishing etc. Also, it is one of the most important industrial raw materials in many technological processes. Thus, water is one of the most important basic matters in the nature. Besides that, water is an important strategic resource because her global supplies are limited.

Supplying population with hygienic drinking water is one of the basic prerequisites for good health. More than 1.2 billion people do not have possibility to use hygienic safe drinking water, so they use water from different sources contaminated with microorganisms, toxins or organic matters which leads to various diseases and death. About 15 million people a year die worldwide from unsafe water.

Today, people in our country are supplied with drinking water mainly from water systems (tap water). This water has to meet quality standards prescribed by the Regulation on hygienic quality of drinking water (Regulation 42/1998). In some cases tap water does not meet prescribed quality, so people use bottled water, water from artesian wells and tap water that passed through a house purifier. However, the question is what is the quality and safety of these waters. Quality of drinking water in our country is controlled by different institutions; distributive systems also have laboratories that analyze water quality daily.

Also, there is the Regulation on quality and other requests for natural mineral water, spring water and table water (Regulation 53/2005). Both Regulations contain lists of substances and compounds that can be found in the water and their maximum allowable concentrations. These Regulations (42/1998, 53/2005) also prescribe other categories of water quality such as: pH, turbidity, color as well as microbiological indicators that are most important in terms of health. Besides that, Regulations prescribe frequency of analyzing for water samples and the parameters that are important in emergency cases (floods, wars). What can be seen in Regulation on hygienic quality of drinking water (Regulation 42/1998) is that some maximum allowable concentrations are more stringent than those

prescribed by European Regulation (Council Directive 98/83/EC). For example, water with high concentration of ammonia can be at the same time microbiologically contaminated, so maximum allowable concentration in Regulation (Regulation 42/1998) is lower than that prescribed by the EU Regulation (Council Directive 98/83/EC). Also, Regulation (Regulation 42/1998) is more stringent in terms of substances that are not harmful for human health, but they affect disinfection process. Presence of ammonia, iron and turbidity can affect disinfection process, so their maximum allowable concentrations are lower compared to EU Regulation. Just because of that many analyzed samples do not meet quality prescribed by the Regulation (Regulation 42/1998), which breaks general statistics of water quality. All of the above has resulted that drinking water in many settlements in Serbia does not meet prescribed quality. Therefore, people gain the impression that tap water is bad and they use bottled water or tap water that passed through a house purifier. People use mineral water to improve the health or as a low-calorie beverage. Although it is believed that bottled waters have a better quality than tap water, their use is not completely without risk. The main risk is that disinfection is forbidden for bottled waters. Also, mineral composition of these waters is not adequate for all categories of the population. Except that there are no limit and maximum allowable concentrations for most of the parameters in bottled waters. So, many mineral waters exceed maximum allowable concentrations for some parameters prescribed by the Regulation (Regulation 42/1998). Because of that public needs to be informed when and in what quantities they can safely drink some bottled waters (due to the fact that this information is not given on the declaration). If people must use bottled water instead of tap water they should use still water with low content of Na^+ , K^- , F^- , SO_4^- and NO_3^- .

Parameters in water purified by some kind of house purifiers are mostly lower than that in tap water and they meet the quality prescribed by the Regulation (Regulation 42/1998), but many studies showed that consumption of this kind of water is not recommended because of low content of mineral compounds. Also, content of organic matter in purified water can be higher than in tap water, which indicates membrane fouling and risk of formation of biofilm on the surface of membrane for house purifiers. So, if house systems are not maintained and serviced regularly they will give water with poorer quality than tap water.

In terms of physical and chemical parameters, 76% of tested samples of tap water in Serbia meet the quality prescribed by the Regulation (Regulation 42/1998), while 95% meet microbiological quality. From the controlled distributive systems in Serbia, 21% has both physic-chemical and microbiological contamination. In 2008, 15 patients with epidemic caused by contaminated water were registered (Shigella, Hepatitis A virus and meningitis) (HSYRS, 2008). Data for microbiological quality of drinking water in Vojvodina indicates that 93% of samples that are purified and chlorinated, 75% of untreated but chlorinated samples and 76% of samples that are not purified are microbiologically safe. Physical and chemical quality in these three categories has 89%, 21% and 30% of samples, respectively. Considering that the last two data shows values for untreated water it can be sad that parameters that make samples incorrect are turbidity and high content of iron (HSPAPV, 2007). Hence, it can be said that drinking water in Serbia is not ideal, especially in some regions, but things that are presented in media about our water systems are bad. Therefore more and more people use bottled waters.

The aim of this work is to examine the chemical quality of drinking water from distributive systems of different settlements in Vojvodina, and some artesian wells. The results of analyses are compared with quality of some bottled waters and with parameters prescribed by the Regulation of hygienic quality of drinking water (Regulation 42/1998).

MATERIALS AND METHODS

Material

Figure 1 represents settlements in Vojvodina from which distributive systems water samples were taken for analyses.

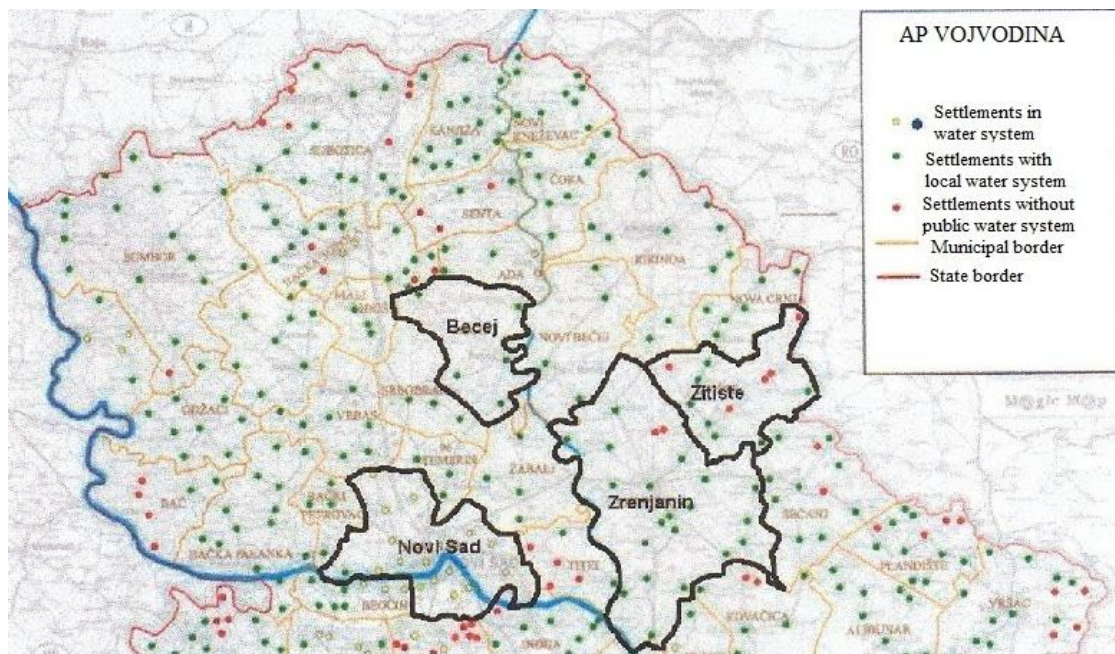


Figure 1. Settlements from whose distributive systems samples of drinking water were taken (Dalmacija 2009)

Average daily taking of water samples from distributive systems of Žitište, Zrenjanin, Novi Sad and Becej are: 11 L/s, 286 L/s, 1220 L/s and 115 L/s respectively (Dalmacija, 2009). That means that large, medium and small distributive systems were chosen for sampling. Samples from artesian wells were taken from two locations in Novi Sad and from public fountains in Bačko Gradište, Paragovo, Sremski Karlovci and Zmajevo.

Basic requirement of water sampling is that the sample must be representative, which means that its physical, chemical and biological characteristics have to be the same as in the medium from which sample was taken. The samples for chemical analyses were taken in clean plastic bottles of 2000 ml. Before sampling tap water was opened to flow 3 – 5 minutes and then sample was taken. During the experiment samples were stored at a temperature of 5 – 10°C.

Analytical methods

Dry matter, pH, turbidity, hardness, alkalinity, content of Ca^{2+} , Mg^{2+} , total Fe, NO_3^- , and Cl^- were determined according to the Standard Methods (APHA, 1989).

RESULTS AND DISCUSSION

Results of analyses for drinking water from distributive systems of Žitište, Zrenjanin, Novi Sad and Bačko Gradište

Results of analyses of tap water samples are presented in Table 1.

Table 1: Results of analyses for water samples taken from distributive systems of Žitište, Zrenjanin, Novi Sad and Bačko Gradište

Parameter	Water samples from distributive systems of:				Maximum allowable concentration (Regulation 42/1998)
	Žitište	Zrenjanin	Novi Sad	Bačko Gradište	
pH	8.02	7.89	7.26	8.21	6.8 – 8.5
Turbidity [NTU]	0.20	0.22	0.33	0.18	<1
Dry matter [mg/L]	718.7	701.7	413.6	1179.0	-
Total hardness [°N]	4.95	5.93	15.00	4.95	-
Mg ²⁺ [mg/L]	9.10	13.75	22.52	8.88	50.0
Ca ²⁺ [mg/L]	20.32	19.66	91.49	20.73	200.0
Total Fe [mg/L]	0.33 – 0.49	0.33 – 0.49	<0.33	<0.33	0.3
HCO ₃ ⁻ [mg/L]	403.2	439.2	170.0	686.2	-
NO ₃ ⁻ [mg/L]	<1	<1	4.25	<1	50.0
Cl ⁻ [mg/L]	n.d.*	4.25	23.74	17.0	200.0
Residual chlorine [mg/L]	n.d.	0.35	0.53	n.d.	<0.5
Organic matters [mgKMnO ₄ /L]	35.33	35.88	4.48	46.87	<8

* n.d.-not determined

According to presented results for water from Žitište, it can be said that all parameters except content of iron and organic matters meet the quality standard prescribed by the Regulation on hygienic quality of drinking water (Regulation 42/1998). As can be seen from Table 1, content of iron is slightly higher than maximum allowable concentration, while content of organic matters significantly deviates from the values prescribed by the Regulation (Regulation 42/1998). Also it was determined absence of residual chlorine. Based on results for hardness of water sample it can be concluded that drinking water from distributive system of Žitište is moderately hard water.

Similar results are obtained for water sample from distributive system of Zrenjanin (Table 1). Content of iron and organic matters does not meet the values prescribed by the Regulation (Regulation 42/1998). Also, it was determined presence of residual chlorine in the sample, which corresponds to requirements prescribed by the Regulation (Regulation 42/1998). In terms of hardness, drinking water from Zrenjanin is also moderately hard.

The settlements of Žitište and Zrenjanin are known for exceptionally high content of organic matters in drinking water, which is proven during the experimental tests that were conducted with the water samples taken from these regions.

According to results obtained for water sample from distributive system of Novi Sad (Table 1) it can be concluded that all parameters except content of residual chlorine meet the quality prescribed by the Regulation (Regulation 42/1998). As can be seen from Table 1, content of residual chlorine is slightly higher than maximum allowable concentration. Considering results for total hardness it can be concluded that drinking water from Novi Sad is hard.

Results of analyses of water sample from distributive system of Bačko Gradište are also presented in Table 1. As can be seen from presented results most of the parameters meet the quality prescribed by the Regulation (Regulation 42/1998). However, values for content of organic matters and dry matter are very high. Based on presented results for total hardness, drinking water from Bačko Gradište is moderately hard.

Results of analyses for waters from some house purifiers

Some parameters for water from distributive system of Novi Sad that were pass through different house purifiers (Zepter with reverse osmosis system and Aquaphor) were examine in this work. Obtained results are presented in Table 2.

Table 2: Results of analyses for waters purified with different house purifiers

Parameters	Tap water	Purified water from:	
		Zepter (with reverse osmosis system)	Aquaphor
pH	7.26	7.41	5.43
Total hardness [°N]	15.00	1.5	4.2
Cl⁻ [mg/L]	23.74	2.8	24.0
HCO₃⁻ [mg /L]	170.0	36.6	54.9

As can be seen from presented results total hardness in purified water is lower than in tap water, which means that purified waters have fewer minerals compared to tap water. Consumption of these waters in large quantities is not recommended because of low content of minerals, since they are essential for normal functioning of human body. Currently in our country there is no prescribed standards related on water purified by house purifiers, and they are not included in the Regulation (Regulation 42/1998).

Results of analyses for water from artesian wells

Waters from artesian wells that were examined in this work were taken from public fountains that people frequently use for drinking. Results of analyses of these waters are presented in Table 3.

Table 3: Results of analyses for water samples taken from different artesian wells

Parameter	Artesian waters from:						Maximum allowable concentration (Regulation 42/1998)
	Novi Sad 1	Novi Sad 2	Bačko Gradište	Paragovo	Sremski Karlovci	Zmajevu	
pH	7.22	7.04	7.84	6.85	7.31	7.72	6.5 – 8.5
Turbidity [NTU]	5.81	4.08	1.09	0.05	0.09	1	<1
Dry matter [mg/L]	537.0	530.4	556.7	683.3	471.0	n.d.*	-
Total hardness [°N]	20.05	20.8	16.1	27.7	26.25	2.9	-
Mg ²⁺ [mg/L]	44.3	55.0	33.6	12.6	19.5	7.20	50
Ca ²⁺ [mg/L]	70.3	57.8	59.6	177.1	155.4	8.90	200
Total Fe [mg/L]	0.75	1	<0.33	<0.33	<0.33	n.d.	0.3
HCO ₃ ⁻ [mg/L]	472.7	481.9	652.7	516.9	587.1	436.1	-
NO ₃ ⁻ [mg/L]	22	22	1.5	36	26	8	50
Cl ⁻ [mg/L]	1.5	1.5	61.24	95.86	44.24	17.5	200
Organic matters [mgKMnO ₄ /L]	3	3.95	8.48	3.15	3.34	98.75	<8

*n.d.-not determined

As can be seen from Table 3, content of iron for artesian water samples from Novi Sad is two to three times higher than maximum allowable concentration prescribed by the Regulation (Regulation 42/1998). Presence of iron in these concentrations is not harmful, but it affects physical quality of water, so it can be sad that these waters are not hazardous for human health. Also, turbidity for these two samples is higher. Very high concentration of organic matters in artesian water from Zmajevu can affect disinfection process, but since artesian waters are not disinfected these parameters are not problems. In this case, turbidity is probably caused by presence of particles of sand, soil, dissolved salts etc. Concentration of magnesium for artesian water (2) from Novi Sad and organic matters for water from artesian well of Bačko Gradište are slightly higher than maximum allowable concentrations prescribed by the Regulation (Regulation 42/1998). Considering presented results (Table 3) it can be concluded that most of the parameters for artesian water samples meet the quality standard prescribed by the Regulation on hygienic quality on drinking water (Regulation 42/1998). For one sample of artesian water (Novi Sad 1) content of some heavy metals (Pb, Cu and Cd) were analyzed by potentiometric stripping method. Based on the obtained results it was found that Pb and Cd are not present in the sample, while concentration of Cu meet quality prescribed by the Regulation (Regulation 42/1998).

Comparing the quality and composition of tap water and waters from artesian wells it can be sad that in some cases artesian waters are more mineralized, with different ratio of minerals. Content of organic matters for all examined tap waters, except water from distributive system of Novi Sad, significantly deviates from the values prescribed by the Regulation (Regulation 42/1998). Based on the presented results for hardness, artesian waters are very hard compared to tap waters. In terms of content of NO₃⁻ artesian waters and tap waters are significantly different. Although microbiological parameters are not determined, it can be assumed that artesian waters are safe because otherwise the wells should be sealed by the competent institutions. So, artesian waters can be used instead tap water, but question is how often these waters are controlled. According to the Regulation on hygienic quality of drinking water (Regulation 42/1998), waters from public fountains are controlled once a month,

while tap water in large distributive systems analyzes daily, taking samples from different points in the distributive system, public institutions and wells.

What characterizes bottled waters compared to tap water is their mineral composition with different ratios of minerals. Dry matter in some bottled waters produced in our country ranges from 58 mg/L (Vlasinska Rosa) to 3282.00 mg/L (Bivoda). Content of Ca^{2+} ranges from 2.2 mg/L (Prolom) to 242 (Duboka), Mg^{2+} from 0.03 mg/L (Prolom) to 96 mg/L (Karadjordje), Cl^- from 1.9 mg/L (Vujić Voda) to 308.00 mg/L (Minaqua) and HCO_3^- from 42.8 mg/L (Vlasinska Rosa) to 3233.00 mg/L (Bivoda) (Dalmacija et al, 2006). For mineral waters, specific mineral balance is much more important than their individual quantities. Considering that influence of minerals on human body is different, people need to know how to use bottled waters properly because large absorption of minerals in the body can affect human health. Some bottled waters have similar composition as tap water and can be used as its replacement. In 2005 in our country adopted a new Regulation of quality and other requests for natural mineral water, spring water and table water (Regulation, 53/2005) that is consistent with current requirements of the European Union in this area.

CONCLUSIONS

As it was presented in this work most of the examined parameters of tap water samples meet prescribed quality, so it can be concluded that tap water in Vojvodina is not bad as it was presented in media. Also, it was confirmed that bottled waters, artesian waters and purified waters can be use instead of tap water. However, people need to be informed how they can safely drink these waters, considering that their mineral composition is not adequate for all categories of the population. As the population on the planet increases rapidly, requirements for drinking water are growing. Since it is expected that demand for water will exceed its supply, we have to save water and keep it from pollution. Considering that in the rivers, lakes and water flows every day throw a millions of tons of waste, special carefulness must be given to wastewater treatment.

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THE INFLUENCE OF SEASONAL TEMPERATURE CHANGE RATE
ON THE RELAXATION PROCESSES IN THE RAW AND
CHLORINATED WATER OF ZRENJANIN URBAN WATERWORK

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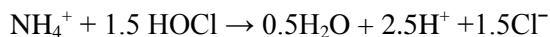
ABSTRACT

The standard laboratory monthly analysis of the raw and chlorinated water in the waterworks of the town Zrenjanin, indicate the stationary values during one year, of the color, pH chemical oxygen demand, COD ammonium ion, chlorides and electric conductivity, with the variability less than 12%. However the turbidity, nitrite, nitrate and iron content increase for the one order of magnitude compared to the raw water depending on the seasonal water temperature. In this work the indicators of the annual self-purification-aggregation of the colloidal particles are found.

Key words: Raw ground-water quality, Relaxation processes after chlorination, Seasonal relaxation processes, Indicators of the overall relaxation processes.

INTRODUCTION

Water disinfection achieves the maximum efficiency with the free chlorine by using commercial chlorinator has if the pH values are in the range 7.0-7.5 (*T.Rašić VMA, 1975, Beograd*). Maximal affinity of the chlorine to the hydrogen produce oxygen “in statu nascendi” which parallel with the enzyme dehydrogenase, oxidize the iron, manganese and other components, ammonium ion (*ammonium.chlorine has be 4:1*), substitution and addition reactions with the organic matter producing chloramine which longer time „conserve“ active chlorine due lower rate constants. The Volta potential in the end titration point determines the chlorine electrochemical potential with the maximal content 0.2-0.5 mg/l after 30 min. The secondary reactions are:

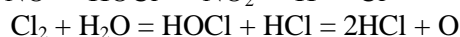
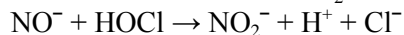


Production of the nitrate:

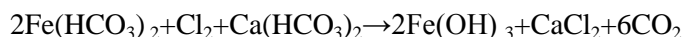
1-from ammonium ion:



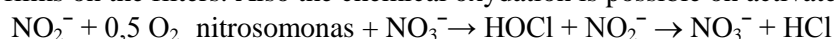
2-and nitrites:



In the end point of the fastest nitrogen reactions self-purification reactions in the raw water of the Fe (II)- bicarbonates activated in oxidation processes up to Fe^{3+} ions successive hydrolysis gives Fe (III) –hydroxide with increased pH, due released CO_2 .



The *nitroso-monas genus converse* ammonium in the nitrate in the aerobic condition in the bio-films on the filters. Also the chemical oxydation is possible on activated colloidal particles.



The objective in this work is the row seasonal water quality influence:

- on the indicators of the secondary contamination of the chlorinated water,
- and on the indicators content of the primary self-purification processes by the seasonal coagulation and aggregation.

EXPERIMENTAL RESULTS

The result of laboratory analysis are obtained in the Laboratory of the Institute of Public health as well as in the Laboratory of the Waterworks in Zrenjanin indicate the chlorination increases compared to the raw water contents of the pollutants: 7,1 times-nitrates content, 5,2 times-nitrites and 2, 4 times-iron (Isidora Mijatović, 2009).

Table 1: The average results of the standard examined parameters during 12 months and relative variance, ρ% and maximal allowed contents according to the law regulative, Sl. List SRJ Nb. 42/98 i 44/99

	<i>The average contents in chlor. water*</i>	<i>ρ%</i>	<i>The average contents in the row water**</i>	<i>ρ%</i>	<i>MAC Law. Reg.</i>	<i>γ_{av}/MAC chlor. water</i>	<i>γ_{av}/MAC row water</i>
<i>Temperature°C</i>		17,83	16,0383				
<i>Color, °Pt/Co</i>	55,6	11,85	58,92	7,25	5	11,13	11,8
<i>Turbidity, NTU</i>	0,39	61,02	0,192	105,7	5	0,08	0,04
<i>pH</i>	7,26	9,75	7,44	1,37	6,8-8,5	1	1
<i>COD, mg/l</i>	38,8	3,05	37,66	2,64	8	4,8	4,7
<i>NH₄⁺, mg/l</i>	1,35	11,11	1,55	18	1	1,35	1,5
<i>Cl₂ Residual, mg/l</i>	0,66	34,92			0,5	1,32	0
<i>Chloride, Cl⁻, mg/l</i>	22,86	11,89	19,83	10	200	0,11	0,1
<i>Nitrites, NO₂⁻, mg/l</i>	0,048	46,45	< 0,01	0	0,03	1,56	0,3
<i>Nitrates, NO₃⁻, mg/l</i>	2,424	71,07	0,35	0	50	0,05	0,007
<i>The dry mater, mg/l</i>	774,6	5,75					
<i>Elektric cond., S/cm</i>	1257,9	4,23	1204,75	0,83	1000	1,2	1,2
<i>Iron, Fe²⁺, mg/l</i>	0,56	24,63	0,25	18,8	0,3	1,9	0,8
<i>Ortophosphate P, mg/l</i>	0,65	11,61	0,77	56	0,15	4,4	5

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** Laboratory of the „Waterworks and Canalization” Zrenjanin

The zero variance is found for the stationary nitrates and nitrites content in the raw water and the approximately stationary contents is found for the pH and conductivity. The results in the table 2

indicate the seasonal water pH change rate constant enabled activation energy of the keeping of the stationary pH state to be determined base on the Arrhenius equation.

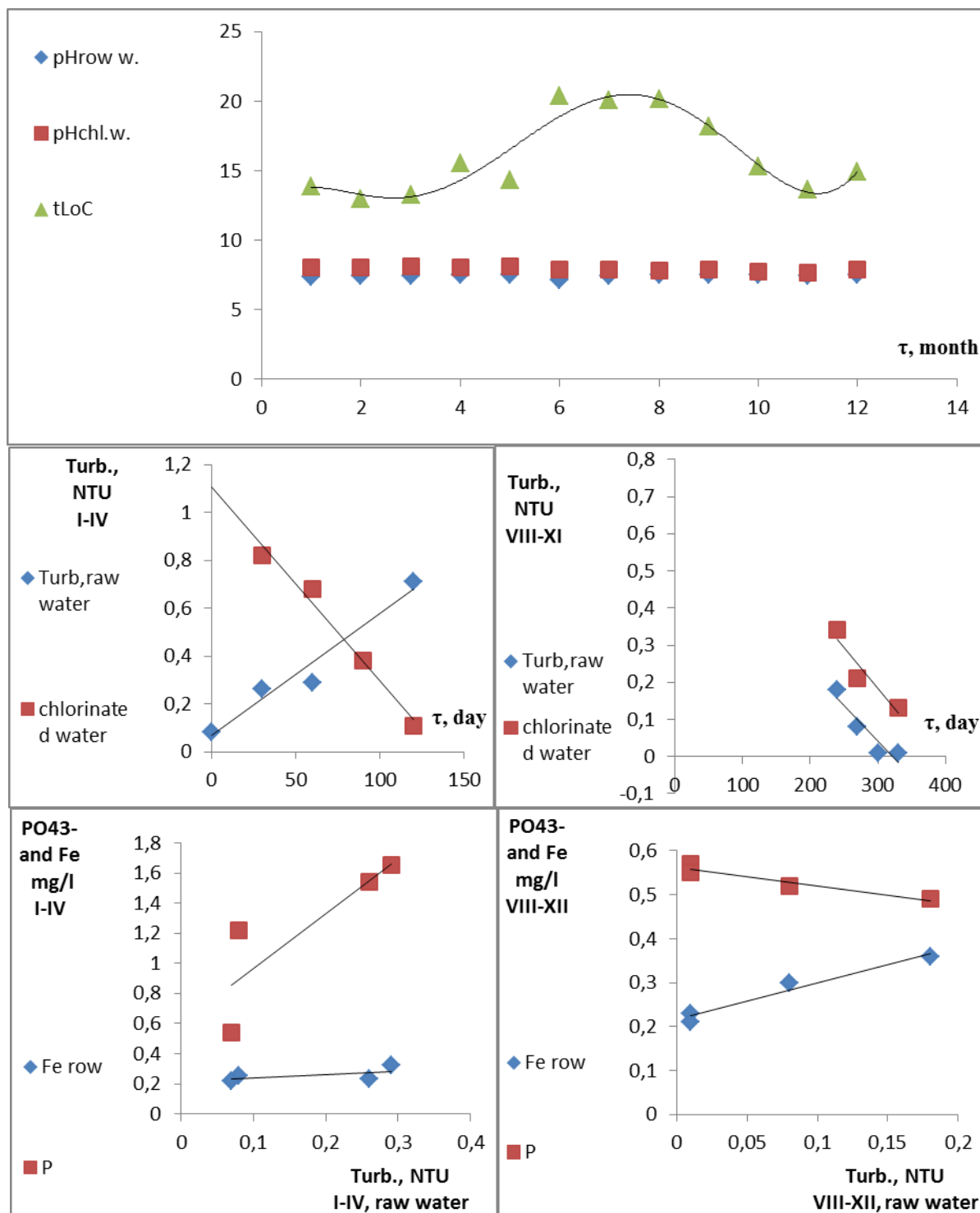


Figure 1. The diagrams of the functional dependence between the ions content of the seasonal turbidity from January to April (I-IV) and from August to December (VIII-XII)

The diagrams in figure 1 indicate:

1. The stationary temperature value in the first and forth winter season of the year, increased from march to the July and decreased from July up to November, indicating the fastest temperature change in May.

2. Temperature increasing in the first half of the year up to the May correlate with the reaction rates:
 - which produce the turbidity in the raw water,
 - and which decrease the turbidity in the chlorinated water.
3. The indicators of the increased turbidity in the raw water are:
 - up to May, the increased phosphate content at stationary Fe(II) ion content,
 - and after August to the end of the year, increased Fe (II) content at the stationary phosphate content.
4. In the second half of the year, the temperature decreasing correlate with the decreasing of the turbidity in the both, row and in the chlorinated water.

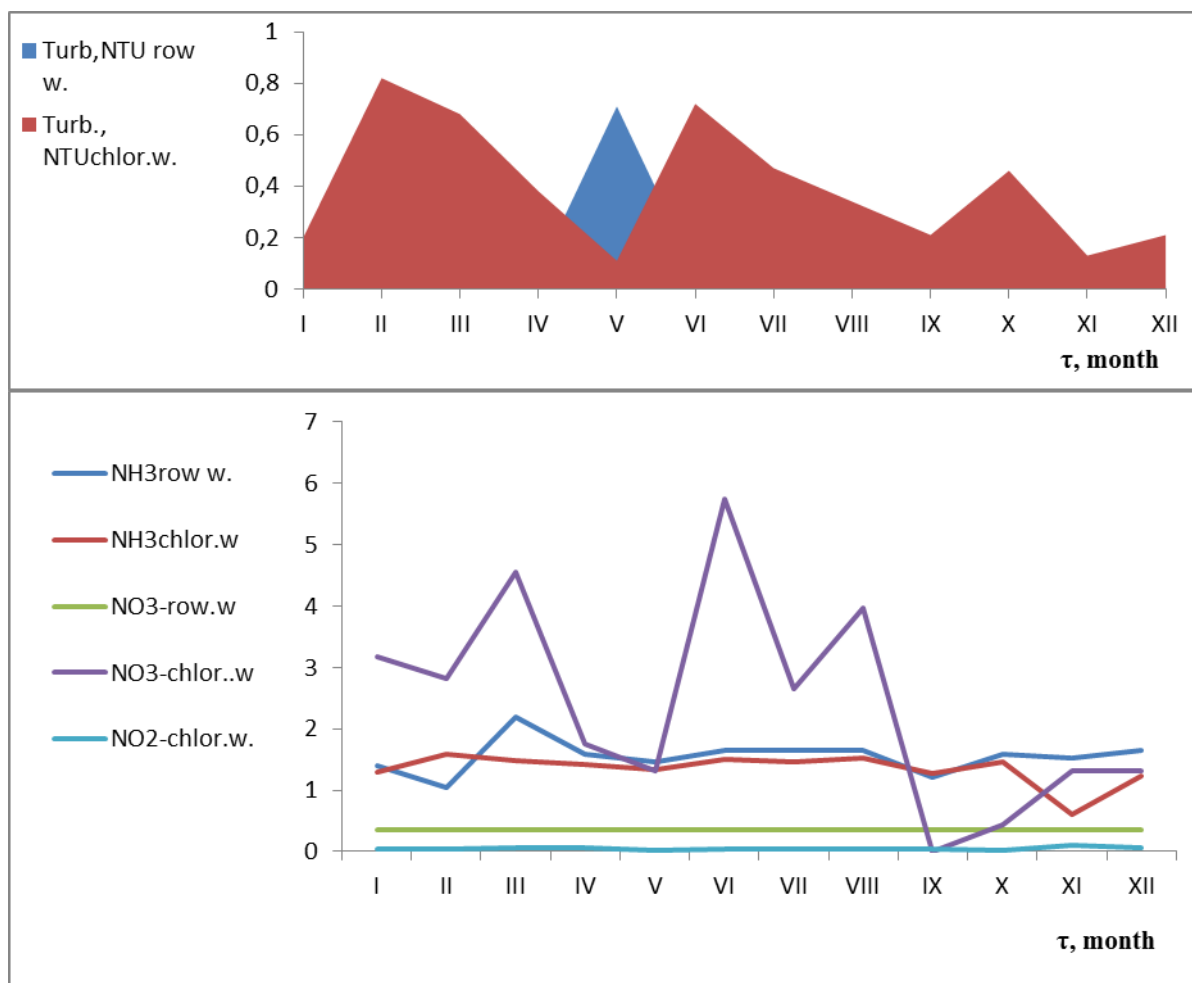


Figure 2. The diagrams of the seasonal changes of indicators of the ground water temperature influence on the relaxation processes

The results presented in the diagram 2 indicate:

1. The fastest temperature increasing in May cause peak, maximum of turbidity in raw water in the correlation which correlate with the minimum of the nitrate content in the chlorinated water at the stationary state in the row water as well as ammonium ion and nitrite content in the raw and chlorinated content.
2. In the row water in February and inversely in November, the maximum of turbidity in the chlorinated water correlate with maximum content of the ammonium ion which is the indicator of the fastest catalytic reduction in February, and inversely oxidation in November in the chlorinated water.
3. In the first half of the year, the maximum of the turbidity in the chlorinated water (March and June) correlate with the maximums of the nitrate content

4. In the second half part of the year and the two minimums (September and November) correlate with the minimum of nitrate content in chlorinated water (September) and with the minimum of ammonium ion content in chlorinated water (November).

CONCLUSION

Based on the results of ground water monitoring of the waterworks of the town Zrenjanin, during one year, it can be concluded:

- The seasonal water thermal energy change is not strongly dependent on the pH of the raw water (minimum in June) and the on chemical oxygen demand (with the variance to 3%)
- The raw and the chlorinated water contains up to five times larger chemical oxygen demand and phosphate content, compared to the maximal allowed values
- The chlorination of the raw water increased fastest, the nitrate and ammonium ions contents, up to 50 % and iron to 100 %, compared to the MAC, probably caused with the large content of natural organic matter, measured as COD
- The seasonal water thermal energy, increasing in the first half of the year up to maximum in the raw water achieved in May and in September correlate with the phosphate content increasing up to achieving the maximum of the turbidity due phosphates de-hydration and flocculation
- To maximum turbidity correspond maximum of phosphates at stationary Fe(II) content influence in the first half of year during temperature increasing, due relaxation with endothermic dehydration processes
- Maximum phosphate and minimum of Fe(II) content correspond to the minimal turbidity in the second half of year, during temperature decreasing due relaxation with the hydration exothermic processes
- the minimal ammonium content in raw water in February, and September is indicator of the slowest endothermic hydrogen titrations rates, which are maximal in March and stationary from April-August and November and December (or oxygen titrations in chlorinated water)
- In the chlorinated water after the disinfection the correlation are found between the temperature change rates and minimum of the exothermic produced nitrate content in May and minimum of endothermic produced nitrate content in September.

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**THE LATEST NANOMETAL OXIDES (NMOS) FOR THE
ADSORPTION OF HEAVY METALS FROM WASTE WATERS**

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ABSTRACT

The environment is exposed to emission and deposition of heavy metals, which are not biodegradable and tend to accumulate. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often present in industrial wastewater. Many methods have been proposed for removing heavy metals, including adsorption, which offers flexibility in design and operation and in many cases generates high-quality treated wastewater. Due to reversible nature of most adsorption processes and ability of adsorbent to regenerate, high efficiency and easy work have imposed adsorption as one of the main techniques for removing heavy metals from waste water. Adsorption of heavy metals on the latest nanomaterials may be a revolutionary process in water treatment. Characteristics of nanoparticles, such as high specific surface area, high reactivity and catalytic potential, make them excellent for water purification. Nanometaloxides (NMOs), including nanoparticles of iron oxide, manganese oxide, aluminum oxide, titanium oxide, magnesium oxide and cerium oxide have a large specific surface area and affinity to adsorption of heavy metals from aqueous systems in accordance with strict regulations. This paper presents an overview of the latest metal oxide nanoparticles and their ability to remove heavy metals from water.

Key words: Heavy metals, adsorption, nanometaloxides (NMOs).

INTRODUCTION

Since the advent of the industrial age, the environment is exposed to emissions and deposition of anthropogenic organic and inorganic substances. The daily increase in production and development of society increases demand for metals and leads to the increasing presence of different metals in the environment. Heavy metal pollution is a serious threat to aquatic ecosystems, since heavy metals are not biodegradable and tend to accumulate in living organisms and represent a special risk for the local biota (Adriano et al. 2005; Mulligan, et al. 1999; Onundi, et al 2011; Benavente, 2008).

Exposure to heavy metals, even to those that are found in trace amounts, is believed to be a risk for human beings (Jamil et al. 2010; Fu et al. 2011; Hua et al. 2012). Cadmium, zinc, copper, nickel, lead, mercury and chromium are often present in industrial waste-waters originating from mining, casting, battery manufacturing, petroleum refining, production of paints, pesticides, etc. Exposure to heavy metals may lead to a variety of neurological damage, organ damage and immune system deficiencies (Wan et al. 2010; Abdel-Halim et al. 2003). The issue of effective and permanent removal of unwanted metals from aqueous systems is an important and challenging task for environmental engineers. Numerous methods have been proposed for the effective removal of heavy metals from water, including but not limited to, chemical precipitation, ion change, adsorption, membrane filtration and electrochemical technologies (Fu et al. 2011; Hua et al. 2012; Wang et al. 2003).

This paper provides an overview of the latest NMOs and their sorption behavior from aqueous systems under varying experimental conditions, the underlying mechanism responsible for the sorption, as well as their reusability.

THEORY

In real terms, an advantage over other forms of treatment depends on many factors, including the shape and concentration of heavy metals in waste-water, other ingredients present in the effluent, the desired degree of removal, resources and operational costs associated with a particular treatment technology, environmental regulations governing the discharge of treated wastewater, as well as the quantity of sludge generated and associated costs. Selecting the best treatment option for particular waste-water requires a precise determination of the quantity and characteristics of waste-water (Jing, 2005). As one of techniques usually employed in wastewater treatment, adsorption offers flexibility in design and operation and in many cases generates high-quality treated wastewater. In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple use (Pan et al. 2009), leading to lower maintenance costs, higher process efficiency while many desorption processes are of low maintenance cost, high efficiency, and ease of operation (Mishra et al. 1996). Therefore, the adsorption process has become one of the major techniques for heavy metal removal from water/wastewater (Hua et al., 2012).

Adsorption has proven to be very effective for effluents with moderate and low concentrations of metals (Manohar, 2006). The efficiency of adsorption depends on many factors, including the free surface, pore size, charge distribution and functional groups of adsorbent (Ewecharoena et al., 2009). Adsorption process is limited by the size of the adsorbent particles. These limitations can be overcome by nanotechnology.

The application of nanomaterials for the wastewater treatment may prove to be a potentially revolutionary process. Nanotechnology uses specific phenomena and properties of matter at the atomic and molecular level. Characteristics such as high specific surface area, high specificity, high reactivity, the catalytic potential, make nanoparticles an excellent adsorbents for water treatment. Nanoadsorbents are quite effective for rapid adsorption of heavy metal ions and organic compounds from aqueous solutions due to their large specific surface area and absence of internal diffusion resistance (Watlington, 2005; Zhang et al., 2006).

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for heavy metals removal from aqueous systems (Vanbenschoten et al., 1994; Coston et al., 1995; Agrawal et al., 2006). This is partially because of their large surface areas and high activities caused by the size quantization effect. Recent studies have suggested that many NMOs show very favorable adsorption to heavy metals in terms of high capacity and selectivity, which would result in removal of toxic metals to meet increasingly strict regulations. However, as the size of metal oxide particles reduces from micrometer to nanometer levels, the increased surface energy inevitably reduces their stability. Consequently, NMOs are prone to agglomeration due to Van der Waals forces or other interactions, causing the high capacity and selectivity of NMOs to be decreased or even lost. Moreover, NMOs are unusable in fixed beds or any other flow through systems because of the excessive pressure drops (or difficult separation from aqueous systems) and poor mechanical strength. To improve the applicability of NMOs in real wastewater treatment, there were attempts to impregnate them into porous supports of large size to obtain composite adsorbents. The widely used porous supports include materials such as activated carbon, natural materials and synthetic polymers (Hua et al., 2012; Pan et al., 2009).

METHODS

Table 1 provides an overview of the methods that are usually used for preparation of NMOs, along with shape, size and surface area of NMOs. Table 2 provides techniques that are employed for their characterization (Hua et al., 2012).

Table 1: NMOs for heavy metal removal from water (preparation, shape and size, surface area and target metals)

Adsorbent	Methods of Preparation	Shape and size (nm)	Surface area (m ² /g)	Target metals
Goethite (α -FeOOH)	Fe(NO ₃) ₃ precipitation	Needlelike; length 200 nm; width <50 nm	50	Cu (II)
	Coprecipitation: HCl and FeCl ₃ solution at 100 °C for 2 days	Width, 10–15 nm; length, 500 nm	71.49	Cu (II)
Hematite (α -Fe ₂ O ₃)	Coprecipitation: Fe ₂ (SO ₄) ₃ + 2.5 M NaOH (4 h), heated at 40 °C for 2 days	Granular, with a crystal size about 75 nm	24.82	Cu (II)
Hydrous amorphous Fe oxides	Participation: Fe(NO ₃) ₃ + NaOH	Particles; diameter, 3.8 nm	600	Pb (II)
γ -Fe ₂ O ₃	Sol–gel method	Particles; diameter, 10 nm	178	Cr (VI)
	Sol–gel method	Particles; diameter, 10 nm	198	Cr (VI), Cu (II), Ni (II)
Hydrous manganese dioxide	Participation: Mn(NO ₃) ₂ + NaMnO ₄ + NaOH	Particles; diameter, 2.1 nm	359	Pb (II)
	Precipitation: MnSO ₄ + NaClO	Particles	100.5	Pb (II), Cd (II), Zn (II)
α -MnO ₂ (OMS-2)	Precipitation method (refluxing)	5 nm sized octahedras with 2 × 2 tunnel size of 0.46 nm	–	Cu (II)
α -MnO ₂ (OMS-1)	Precipitation method (refluxing)	Octahedras with 3 × 3 tunnel size of 0.70 nm	–	Cu (II)
TiO ₂	Hydrolysis	Particles with size of 10–50 nm	208	Zn (II), Cd (II)
	Commercially available	Particles, 8.3 nm	185.5	Pb (II), Cd (II), Ni (II),
Hydrous amorphous Al oxides	Participation: NaOH + Al(NO ₃) ₃	Particles; diameter 1.9 nm	411	Pb (II)
γ -Al ₂ O ₃	Precipitation	Particles with size of 7.5 nm	240	Ni (II)
γ -MPTMS modified γ -Al ₂ O ₃	Mixture	–	–	Cu (II), Hg (II), Pd (II)
DNPH modified γ -Al ₂ O ₃	Chemically immobilization	Particles, diameter 68–87 nm	42.62	Pb (II), Cd (II), Cr (III), Co (II), Ni (II), Mn (II)
ZnO	Hydrotherm	Nanosheets with square sides of about 1 μ m and thickness in nano-scale.	–	Pb (II)
	Solvotherm	Nanoplates of 10–15 nm in thickness and pore diameter of 5–20 nm	147	Cu (II)
CeO ₂	Precipitation	Hollow nanospheres, with a uniform size of 260 nm, composed of CeO ₂ nanoparticles of about 14 nm.	72	Cr (VI) Pb (II)
	Precipitation	Particles with mean size 6.5–12 nm	65	Cr (VI)

Table 2: Techniques used for characterization of samples

Characteristics	Techniques
Morphology	Transmission electron microscopy (TEM).
	Environmental scanning electron microscope (ESEM)
	Field emission scanning electron microscope (FE-SEM)
Particle size	Laser diffraction particle size analyzer
Crystal structure	X-ray diffraction (XRD)
Specific surface area	Triple-point N ₂ Brunauer–Emmett–Teller (BET) adsorption
pH _{pzc}	Potentiometric titration
	Zeta potential analyzer
Heavy metal-NMO interaction	Extended X-ray absorption fine structure (EXAFS) spectroscopy
	X-ray absorption near edge structure (XANES) spectroscopy
	X-ray photoelectron spectroscopy (XPS)
	UV–Vis diffuse reflectance spectrometer
	Diffuse-reflectance infrared Fourier transform (DRIFT) spectra
	FTIR
	Raman spectroscopy
C ¹⁵ peak	
Magnetic properties	Vibrating sample magnetometer (VSM)
	External magnetic fields

FINDINGS AND DISCUSSION

Nanosized metal oxides

Nanosized ferric oxides

Iron is one of the most widespread elements on Earth. The availability of resource and easy synthesis make nanosized ferric oxides (nFeOs) low-cost adsorbents for toxic metal sorption. Since elemental iron is environmentally friendly, nFeOs can be pumped directly to contaminated sites with negligible risks of secondary contamination. The intensively studied NFeOs for heavy metals removal from water/wastewater include goethite (α -FeOOH), hematite (α -Fe₂O₃), amorphous hydrous Fe-oxides, maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄) and iron/iron oxide (Fe@Fe_xO_y) (Hua et al., 2012).

The chemical nature and the high specific surface area of goethite make it an efficient sorbent for metal cations (Schwertmann, 1979). Grossl et al. (1994) evaluated the kinetics of Cu²⁺ adsorption/desorption on/from goethite using the pressure-jump (p-jump) relaxation technique, which provides both kinetic and mechanistic information for reactions occurring on millisecond time scales. Adsorption of Cu²⁺ increased with the increasing pH from 4.5 to 5.5. The process was insensitive to the background electrolytes. Cu²⁺ sorption on nano-goethite surface was found to form an inner-sphere surface complex, which was further demonstrated by the modified triple-layer model simulation with the experimental data. The calculated intrinsic rate constant for adsorption (106.81 L mol⁻¹ s⁻¹) was about two orders of magnitude higher than the intrinsic rate constant for desorption (104.88 L mol⁻¹ s⁻¹) (Hua et al., 2012). The rate of adsorption of divalent metal cation on goethite is directly related to that of water molecule release from the primary hydration sphere of a specific divalent metal cation. The conjunction of p-jump technique and surface complexation modeling is also employed to describe Cu²⁺, Pb²⁺, Zn²⁺, Co²⁺, and Mn²⁺ adsorption/desorption on γ -Al₂O₃ and Pb²⁺ adsorption/desorption on α -FeOOH (goethite) (Hua et al., 2012).

Hydrous ferric oxide (HFO) could be prepared by precipitation of ammonia with ferric chloride or nitrate solutions in carbonate-free environment by purging with N₂ (Fan et al, 2005). The sorption of heavy metals to HFO seems poorly sensitive to the variation of ionic strength. For example, Swallow et al. (1960) reported that Cu²⁺ and Pb²⁺ sorption to HFO was unaffected by different ionic strength from 0.005 to 0.5 M NaClO₄, or by change in the nature of the background electrolyte from NaClO₄ to a complex artificial seawater mixture. Trivedi et al. (2003) observed that Pb²⁺ sorption to ferrihydrite did not vary with ionic strength in the range investigated between 10⁻³ and 10⁻¹M NaNO₃. The resistance to variation in ionic strength might suggest the formation of inner sphere complexes between heavy metals and HFO. Intraparticle diffusion, a natural attenuating process, was observed to be the rate-limiting step in the sorption process of Pb²⁺ on HFO nanoparticles. The process could be described by two steps: a rapid adsorption of metal ions to the external surface followed by a slow intraparticle diffusion along the micropore walls (Fan et al., 2005).

Maghemite (γ -Fe₂O₃) nanogels can be prepared by a sol-gel method, that is, adding NH₄OH solution to the mixture of FeCl₃ and FeCl₂ in the purified water deoxygenated and bubbled by nitrogen gas. The product was red-brown γ -Fe₂O₃ nanogel and was collected via external magnetic field after adding ethanol. The prepared maghemite nanoparticles are expected to respond well to magnetic fields without any permanent magnetization, because the saturation moment of the synthesized particles, as determined by the hysteresis loop measured from vibrating sample magnetometer (VSM) was similar to the value of the bulky particles (3.3 emu/g vs 3.4 emu/g). The TEM images revealed that the maghemite nanoparticles synthesized in sol-gel method were multidispersed with an average diameter of around 10 nm. The BET surface area of the freeze-dried material was 178–198 m²/g (Fan et al., 2012). Hu et al. (2005) examined Cr⁶⁺ removal by nano-maghemite and found that the equilibrium period was independent of initial Cr⁶⁺ concentration, while adsorptive capacity increased when pH decreased. Nano-maghemite emerged a high selectivity for Cr⁶⁺ from water. Negligible competition was observed for many coexisting ions. The adsorption capacity of nano-maghemite for Cr⁶⁺ (19.2 mg/g) is higher than that of diatomite (11.55 mg/g), anatase (14.56 mg/g), commercial activated carbon (15.47 mg/g) and beech sawdust (16.13 mg/g). Based on X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopic techniques, it could be deduced that no chemical redox reaction occurred during Cr⁶⁺ retention, which also hints the stability of nanoscale γ -Fe₂O₃. The adsorption mechanism of Cr⁶⁺ onto γ -Fe₂O₃ is suggested to be electrostatic attraction particularly at a relatively low pH (Hua et al., 2012).

Nanosized manganese oxides, aluminum oxides and titanium oxides

Nanosized manganese oxides (NMnOs) exhibit an adsorptive performance superior to its bulk counterpart because of its polymorphic structures and higher specific surface area (Wang et al., 2005). In the past decades, NMnOs have been exploited (Larger-Trivedi, 1999; Mishra, 2007) for sorption of cationic or anionic pollutants from natural waters, such as heavy metal ions (Mishra, 2004), arsenate (Takamatsu, 1995) and phosphate (Kawashima, 1986). Such sorption processes significantly mediate the fate and mobility of the targeted pollutants in water. The widely studied NMnOs for environmental concerns include hydrous manganese oxide (HMO) and nanoporous/nanotunnel manganese oxides (Hua et al.2012).

Hydrous manganese oxide could be prepared by adding MnSO₄·H₂O into NaClO solution containing active chlorine. The precipitate is washed with HCl to remove excessive alkali, followed by rinsing with double-deionized water. Heavy metal sorption onto HMOs, including Pb²⁺, Cd²⁺, and Zn²⁺, usually results in the inner-sphere complex formation, and it can be described by an ion-exchange process. Divalent metals on HMO consist of two similar steps as that of HFO: rapid adsorption of metal ions to the external surface followed by a slow intraparticle diffusion along the micropore walls (Fan et al., 2005). The adsorption can be represented by the Freundlich model more reasonably than the Langmuir model, implying that the active sites of HMO surface are heterogeneous for metal sorption. HMO prefers metal sorption in the order of Pb²⁺ > Cd²⁺ > Zn²⁺, which might be caused by different softness of these metals. Compared to two commercial resins, D-001 and Amberlite IRC 748,

HMO exhibits more selective sorption toward these heavy metal ions in the presence of Ca^{2+} at high concentration levels. The BET surface area is around $100.5 \text{ m}^2/\text{g}$ (Hua et al., 2012).

Mixed-valence manganese oxides with 3–6 layers and 7–11 tunnel structures are classified as potentially interesting sorbents for cations. They are usually present as octahedral molecular sieve (OMS). Cryptomelane-type (K^+) and todorokite-type (Mg^{2+} and Ca^{2+}) manganese oxides, called OMS-2 and OMS-1, respectively, could be prepared by means of hydrothermal route. They have OMS structure constructed from edge sharing double chains of MnO_6 octahedra that build a 2×2 or 3×3 tunnel structure. The dimension of tunnels of OMS-1 and OMS-2 vary slightly depending on the type of the inside located cations. This feature enables small adjustments of the tunnel size and makes the material to be an adjustable molecular sieve. The size of the tunnels in 3×3 OMS-1(Mg^{2+}) and in 2×2 OMS-2(K^+) is about 0.7 and 0.46 nm (Hua et al., 2012).

Alumina (Al_2O_3) is a traditional adsorbent for heavy metals, and $\gamma\text{-Al}_2\text{O}_3$ is anticipated to be more active than $\gamma\text{-Al}_2\text{O}_3$ (Tsuji and Komarneni, 1993; Li et al., 2008). Nanosized $\gamma\text{-Al}_2\text{O}_3$ can be prepared by sol-gel method and has been employed as solid phase extraction material for separation/preconcentration of trace metal ions. Chemical or physical modification of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles with certain functional groups containing some donor atoms such as oxygen, nitrogen, sulfur and phosphorus is expected to improve their sorption toward heavy metals (Hiraide, 1994; Ghaedi et al. 2008; Dadfarnia et al., 2002; Shabani et al., 2009). When a modifier is immobilized at the surface of alumina, the removal mechanism is changed accordingly. The target metals are not only removed by adsorption on the surface of the alumina but also by a surface attraction/chemical-bonding interaction on the newly added chemicals. A very common procedure to deposit an organic coating on inorganic oxide is to mix the organic solution with inorganic oxide particles for a period of time, followed by evaporation of the solvent and air-drying the resultant adsorbent. For instance, fixing γ -mercaptopropyl-trimethoxysilane ($\gamma\text{-MPTMS}$) on the surface of $\gamma\text{-Al}_2\text{O}_3$ would improve its selectivity toward Cu, Hg, Au and Pd ions rather than other ions. The XRD pattern shows that the modified $\gamma\text{-Al}_2\text{O}_3$ tends to be amorphous possibly because of the formation of chemical bond of Si–O–Al, which is more stable than physical bonding. Three mechanisms were responsible for the adsorption of metal ions on $\gamma\text{-MPTMS}$ modified nanoalumina: (1) metal ions adsorbed through the bonding to –SH group, (2) the hydrolyzation of metal ions, and (3) electrostatic adsorption. In acidic media the first mechanism plays a dominant role while in basic solutions, the hydrolyzation and the electrostatic interactions play more significant role. Additionally, sodium dodecylsulfate coated nano $\gamma\text{-Al}_2\text{O}_3$ was modified with 2,4-dinitrophenylhydrazine (DNPH) as a new solid-phase adsorbent for removal of trace Pb^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} . SEM image showed that the naked alumina nanoparticles had a mean diameter of 53 nm, while that of the modified ones are in the range of 68–87 nm (Hua et al., 2012).

It has been reported that bulk and nanoparticle TiO_2 anatase exhibit different chemical behavior, catalytic reactivity, and surface acidity based on their different surface planes (Engates et al., 2011). Specific surface area of the nanosized and bulk particles were 185.5 and $9.5 \text{ m}^2/\text{g}$, and the nominal particle sizes calculated from BET measurements were 8.3 and 329.8 nm, respectively (Engates et al., 2011). The nanoparticles were able to simultaneously remove multiple metals (Zn, Cd, Pb, Ni, Cu) from a solution of $\text{pH} = 8$ and tap water. When adsorption capacities were normalized by mass, the nanoparticles adsorbed more than the bulk particles. Adsorption kinetics for heavy metals followed a modified first order model, and the nanoparticles had a faster adsorption than the bulk ones. Langmuir isotherm was suitable to characterize metal adsorption onto TiO_2 anatase. By comparing the distribution coefficient (K_d), TiO_2 nanoparticles performed better than other metal oxide nanoparticles and a commercial activated carbon (Engates et al., 2011).

Nanosized zinc oxides, magnesium oxides and cerium oxides

Zinc oxide (ZnO) was mostly applied to eliminate H_2S . Wang and coworkers (2010) have found that nanostructured ZnO could efficiently remove heavy metals. Lee et al. (2005) prepared nanometer size ZnO powder by “solution-combustion method (SCM)”. Compared with two titanium dioxide powders,

P25 and one prepared by a homogeneous precipitation process at low temperature, the ZnO nanopowder showed higher removal rate of Cu^{2+} ions from the solution. The plate-like nanostructured ZnO with high specific surface area was fabricated by various methods, such as hydrothermal, solvothermal, chemical vapor deposition, electrochemical deposition and microwave method. Besides some properties similar to TiO_2 , ZnO nanoplates has many unique advantages, such as ease to prepare and low cost (Wang et al., 2010; Hua et al., 2012).

Numerous works have focused on the synthesis of nanosized magnesium oxides of various morphologies, such as nanorods, fishbone fractal nanostructures induced by Co, nanowires, nanobelts, nanotubes and three-dimensional entities and nanocubes. Gao et al. (2008) developed a facile method to fabricate MgO of different morphologies and investigated their influence on the adsorption capacity for pollutants. By changing the concentration of Mg^{2+} and HCO_3^- , monoclinic $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2(\text{H}_2\text{O})_4$ with nanoflakes and flowerlike microspheres composed of flakes and hexagonal MgCO_3 with layer-like rhombohedra and microspheres composed of rhombohedra were synthesized. After annealing at 650°C , four kinds of nano-MgO of mesoporous structures were obtained. It is a good example for the tunable synthesis of morphological nanoparticles by adjusting the components and the crystal phases of the precursors. The highly supersaturation of the reactant species is believed to be the driving force for the hierarchical growth (Hua et al., 2012).

Among cerium oxides, ceria (CeO_2) is the most common and useful rare earth metal oxide in industrial applications, including catalysts, UV blocking and shielding materials, polishing materials, fuel cells, gas sensors, adsorbents and luminescence. The adsorptive properties of ceria vary significantly with morphologies, sizes, shapes and surface areas. Ceria nanoparticles are synthesized by oxidation of Ce^{3+} to Ce^{4+} under alkaline conditions using hexamethylenetetramine (HMT). In this process, CeO_2 nanocrystals in solution can be stabilized by HMT through formation of double electrical layer, which is expected to prevent agglomeration of nanoparticles. The CeO_2 nanoparticles have a mean size of 12 nm, zeta potential of 11.5 mV, and BET surface area of $65 \text{ m}^2/\text{g}$ (Bernal et al., 1999). During the adsorption of Cr^{+6} on ceria nanoparticles, no Cr^{+6} was detected in the solid phase and the total Cr obtained was Cr^{+3} . In the liquid phase only Cr^{+6} was obtained, suggesting an oxidation-reduction process on the surface of the nanoparticles. The reduced chromium remains at the oxygen vacancy on the ceria surface. The isotherm was well described by the Freundlich adsorption model with a correlation coefficient of $R_2 = 0.955$, whereas the kinetics corresponds to a pseudo-second-order equation (Bernal et al., 1999). However, according to the results of bioluminescent test, the toxicity of the treated solution is not significantly altered after this treatment. Besides nanoparticles, ceria has been successfully fabricated in other forms, such as nanorods, nanowires, nanotubes, nanopolyhedrons, three-dimensional flower-like structures, and hollow structures (Hua et al., 2012).

Composition of NMOs with porous supports

Host-supported NMOs

NMOs provide an effective and specific adsorption toward heavy metals. Nevertheless, they are usually present as fine or ultrafine particles, which often lead to problems such as activity loss due to agglomeration, difficult separation, and excessive pressure drops when applied in flow-through systems. An effective approach to overcome these technical bottlenecks is to fabricate hybrid adsorbents by impregnating or coating NMOs particles into/onto porous supports of larger size. The widely used supports include natural hosts such as bentonite, sand and montmorillonite, metallic oxide materials such as Al_2O_3 membrane and porous manganese oxide complex and synthetic polymer hosts such as cross-linked ion-exchange resins (Hua et al., 2012, Fan et al., 2005).

Natural supports

Bentonite is a kind of huge-deposited natural clay with basic structural unit of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions. The structure results in a net negative surface charge on the clay. Also, bentonite has

amphoteric pH-dependent surfaces, high exchange capacity and different modes of aggregation, which makes it a potential adsorbent for adsorption of heavy metals from aqueous solutions. Both iron oxide-coated bentonite (ICB) and magnesium oxide-coated bentonite (MCB) were prepared by precipitating the metal ions with sodium hydroxide on the surface of raw bentonite (RB), followed by thermal treatment. BET surface areas follow an order as $ICB > RB > MCB$. The Langmuir monolayer adsorption capacities of RB, ICB and MCB toward Pb^{+2} from 0.1 M KNO_3 solution were estimated to be 16.70, 22.20 and 31.86 mg/g, respectively (Sari, 2007, Bhattacharyya, and Gupta, 2006). All the bentonite samples showed a similar behavior of increased uptake of Pb^{+2} with gradually increasing pH because H^+ can compete for the exchange site with Pb^{+2} . Increasing the ionic strength from 0.01 to 0.1 M led to a significant decrease in Pb^{+2} adsorption. Besides, the adsorption of Pb^{+2} by the metal oxide-coated samples was influenced by the presence of Cl^- because $Pb-Cl$ and $PbOH-Cl$ complexes become the dominant Pb^{+2} species (Eren, 2009). Thus, the specifically adsorbed ligand enhances Pb^{+2} retention by the surface complexation of Pb^{+2} (Hua et al., 2012). Eren et al. (2010) also studied magnesium oxide-coated bentonite for the removal of copper ions from aqueous solution. The adsorption of Cu^{+2} ions depends upon the nature of the adsorbent surface as well as the Cu^{+2} species distribution solution, which are greatly affected by the pH of the system. The values of the adsorption coefficients indicate the favorable nature of Cu^{+2} adsorption on the MCB. The Langmuir monolayer adsorption capacity of MCB in 0.1 M KNO_3 solution was estimated to be 58.44 mg/g, whereas the adsorption capacity of RB was 42.41 mg/g, indicating that the treatment with magnesium oxide increased the number of adsorption sites to a large extent, which may be attributed to an increase in surface charge due to the formation of magnesium oxide on the bentonite surface (Hua et al., 2012).

Metallic oxide supports

Nanofiltration membrane techniques have been introduced to remove metal ions from water. One of the nanofiltration membranes, the anodic alumina membranes (AAM) has tunable holes, where NMOs of different size can be arrayed to fabricate composite adsorbents. The results of XRD spectrum and EDS pattern confirmed that hydrated MgO embedded on the AAM was crystalline. SEM images suggested that aligned nanotubes with uniform size and shape were obtained, and the diameters of the tubes were consistent with the pore diameters of AAM. This new adsorptive material was used for removal of Ni^{+2} from water. The equilibrium sorption capacity achieves 147.2 mg (Ni^{2+})/g $Mg(OH)_2$, due to the adhering OH^- on the wall of $Mg(OH)_2$ nanotubes. Also, nickel ions replace magnesium ions to form $Ni(OH)_2$ because the solubility of $Ni(OH)_2$ ($K_{sp298K} = 2.0 \times 10^{-15}$) is much lower than that of $Mg(OH)_2$ ($K_{sp298K} = 1.2 \times 10^{-11}$). In addition, $Mg(OH)_2$ nanotubes have a large amount of activity sites owing to their high surface areas, unique needle-like morphology and nanocrystalline/amorphous structures (Utamapanya, 1991). Thus, sorption of nickel to $Mg(OH)_2$ is greatly enhanced. Furthermore, the saturated $Mg(OH)_2$ -nanotubes/ Al_2O_3 composite membranes after sorbing nickel ions were thermally treated to convert $Mg(OH)_2-Ni(OH)_2$ to $MgO-NiO$. The $MgO-NiO$ -nanotubes/ Al_2O_3 composite membranes can be reused to remove Ni^{2+} from water with still high effectiveness (Hua et al., 2012).

CONCLUSION AND IMPLICATIONS

NMOs proved to be highly effective adsorbents for the removal of heavy metals from water and wastewater. Advantages such as fast kinetics and high capacity play an important role in sorption of heavy metals. However, by reducing the size of the metal oxide particles from micrometer to nanometer level, the increase in surface energy inevitably leads to poor stability. Accordingly, the NMOs are prone to agglomeration due to Van der Waals forces or other interactions greatly reducing or even losing the high capacity and selectivity of the NMOs.

In addition, how to efficiently and costly separate the exhausted NMOs from water/wastewater still remains an interesting but challenging task. As for column operation, the excessive pressure drop caused by NMOs should also be considered. Fortunately, fabrication of new NMOs-based composite adsorbents seems to be an effective approach to respond to all the above technical problems. However, it is still in the infant stage, and various issues need to be solved concerning the development of more facile processes to obtain the composite adsorbents, the answer to the interplay between the hosts and

the supported NMOs, the long-term performance of the composite adsorbents, as well as their field application in heavy metal contaminated water treatment. An increasing use of nanomaterials will be seen in the coming decade because of the significant contaminant removal potential that exists for improving the effectiveness of water purification systems.

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**THE APPLIED REMEDIATION METHODS OF SOIL AND
GROUNDWATER IN SERBIAN OIL INDUSTRY, NIS**

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ABSTRACT

This paper describes the application of methods of soil remediation, contaminated with oil, oil products and groundwater at few sites of the Serbian Oil Industry. When pollutants get into the soil and groundwater in any way, their further fate depends on a number of physical, chemical and biological factors which influence is intertwined. The form of compounds in which the pollutants are, is also very important, as well as characteristics of the soil and ground waters. As the causes, intensity, time of contamination, soil composition etc., of these sites are fundamentally different, the recovery and recultivation of these two environmental media, demand different approaches and techniques of remediation. Remediation is essentially a process of taking measures to prevent further pollution and environmental degradation to a level that is safe for future use of the site, including landscaping, prevention and remediation.

Key words: soil, groundwater, pollution, remediation.

INTRODUCTION

The rapid development of economic activity and the oil industry is the cause of increasing concern for many problems in the maintenance of the environment. In recent decades, great attention is paid to the risk of oil spills and its products into the soil and groundwater. Petroleum compounds cause serious physical, chemical and biological changes in the underground hydro system. Entering the pedological system, a compound of oil and oil products are linked to the land by changing its structure and physico-chemical characteristics. Later, the contamination comes in contact with groundwater, which is partly related to the collector rocks and spills into hydro. The effects of pollution to these compounds (oil and oil products) in total pedological-geological and hydro-geological system are large and long-lasting. Many years of research have discovered that there is a very small chance of biodegradation petroleum pollutants and it only goes to 10 - 30%.

OIL - COMPOSITION AND ITS DERIVATIVES

Crude oil is a complex and inhomogeneous mixture. It consists of a number of closely related sequences of complex hydrocarbon compounds - from gasoline to heavy crystalline compounds. The various components that make up crude oil can be separated by distillation at elevated temperature. In such a way petroleum products are derived in refineries - gasoline, kerosene, oil, grease, wax, bitumen, diesel fuel, asphalt, tar, liquefied petroleum gas (LPG), and many other components. Since petroleum often contains several percent sulfur, sulfur is often produced as a petroleum derivative.

Depending on the source from which it comes, crude oil varies widely in its chemical composition. However, its chemical content can be roughly divided into hydrocarbons and non-hydrocarbons. All hydrocarbons were built only from two elements, carbon and hydrogen, but they are building a wide range of complex and mutually entirely different compounds. It is believed that the crude oil contains

82 to 87% carbon and 12 to 15% hydrogen. Non-hydrocarbons content occurs in very small amounts, but it is important for the overall properties of crude oil. It consists of a sulfur (0.05 to 5.5%), oxygen (below 2%), nitrogen (0.1%), metals vanadium and nickel (trace). It is made up of thousands of hydrocarbon components and impurities, and can be grouped into three main chemical series: wax, oil and aromatics. Crude oil is lighter than water and does not dissolve it. A regular companion of oil in its deposits is a natural gas.

SOURCES OF CONTAMINATION

Contamination of soil and groundwater petroleum and petroleum products is caused by exploitation, processing, transportation, storage, use of oil, not in small part, and accidental spillage. Annually, 3.91 million tons of crude oil (2010., in the world) is produced, and it is estimated that 0.1% of that is due to contamination of the environment, as a background anthropogenic activities. Contamination of oil and petroleum products represents a risk to human health and the environment.

WAYS OF PREVENT AND REMEDIATION

Methods for prevention and remediation of soil and groundwater contamination from petroleum pollutants may be abiotic, such as physical, chemical or thermal and biotic as bioremediation in general. Also, remediation methods can be applied to the site (in situ) or outside of pollution (ex situ). For ex situ procedures soil and groundwater need to dig up and be exhausted, and then transported to the site for processing and decontamination.

For removal of oil contaminants, different lately remediation techniques are used. They are more or less based on the biodegradation processes that allow or facilitate it. These techniques can generally be divided into three major groups.

The first group consists of techniques which include translation of pollutants in the solid state, its stabilization and all necessary processes, in order to avoid the spread of the affected surface contaminants such as, for example, the oil slick. These processes are aimed at reducing their volatility and solubility and permeability of the medium. This group consists of the following techniques: increased sorption, in-situ precipitation/co-precipitation, in-situ soil mixing, asphalt processing, the addition of lime, add cementations materials, vitrification (glass formation matrix), recreational setting fixed barrier, setting up blankets and low - permeability of the walls, and others.

The second group consists of methods and techniques that include the separation of pollutants from contaminated media, mobilization and extraction. These methods are successfully applied for the removal of volatile and soluble oil derivatives. To effectively separate the contamination from the medium most commonly used high temperature, chemical reagents, vacuum or conducting current through the soil layer. This group consists of the following techniques: soil drench (solvents, surfactants, etc.), Soil washing, two-phase extraction, education leaked, in-situ soil mixing, two-phase extraction, electrokinetics and others.

The third group of methods is one that uses biological processes or chemical reactions to remove pollution through their degradation or transformation. Techniques based on the chemical reactions: chemical oxidation, substitution, barriers of elemental iron, incineration, thermal reduction and others. Techniques based on biological reactions are spontaneous bioremediation, technical in-situ bioremediation, composting, soil, phytoremediation and others.

The goal of the remediation process is to prevent the spread of contamination due to leakage into groundwater, hazardous materials entering the food chain, and the alike. Which variant of cleaning will be applied depends on the type of contamination, the nature of the terrain and others.

Very often the choice of remediation technology is not limited to a single technology but a combination of several of them, a combination of technical and spontaneous remediation or remediation mix with non-biological treatment.

INVESTMENTS IN THE FIELD OF REMEDIATION IN THE WORLD AND IN SERBIA

Throughout the world, as well as in Serbia, the area of environmental protection and remediation is increasing. The market value for the remediation of hazardous waste worldwide, in 2006 had gone to 11.7 million dollars in 2011, out of \$ 16.6 million, which is an increase of 7.8%. According to other assessors, in the international market, remediation sector is 30-35 million dollars worth. Only in the U.S. for the remediation of hazardous waste, \$ 12 million is allocated, accounting for 30% of the world market. In Western Europe, the total market for environmental protection is 227 billion dollars worth. For this purpose, the budget planned is 0.5-1.5% of the GDP. United Kingdom (England), France and the Netherlands invest most of the money. Countries of Central and Eastern Europe estimate that the total market for remediation is \$ 15 million, with an annual growth of 6.6%. The growth of the market for remediation in these countries is equivalent to economic growth and the introduction of legislation in the environmental field.

In Serbia, the adoption of new laws and regulations in the environmental sector created the conditions for the development of markets for remediation. Based on research by the Environmental Protection, 375 contaminated sites are identified, and soil contamination is confirmed by laboratory analysis of soil and groundwater in the vicinity of direct localized pollution sources. These are present in it for a long time. The largest share of the identified sites belongs to municipal landfills, and most of the industries belong to the oil industry.

The investment program of the Serbian Oil Industry – *NIS*, provides significant investment and substantial improvement of the environment, both from the point of impact of production on the environment, as well as from the position of producing fuels that meet the requirements of European quality standards. Defining long-term goals aligned with national strategies in the field of environmental protection, the company's strategy in the field of environmental management, in compliance with the obligations under the Integrated Pollution Prevention and Control of Environmental Pollution (Official Gazette of RS, no. 135/2004), obligations according to the Kyoto Protocol (cadastre of greenhouse gases), the program transitions of certain plants to renewable energy sources, using the best available technology (BAT). Strategic objectives by 2015 are planned to fully comply with European and national principles of environmental protection, promotion of technologies and products in order to reduce emissions, the construction of new facilities in line with European environmental standards. The realization of these objectives means that *NIS* invests almost 400 million dollars by 2015, which is 6.5 times more than the funds planned by purchase agreement for the protection of the environment. In addition to environmental projects, *NIS* will invest in infrastructure projects with environmental impact, as well as the modernization of gas stations and energy efficiency projects that directly affect the improvement of the environment.

LEGISLATION IN THE REPUBLIC OF SERBIA

The Law on Environmental Protection (Official Gazette of RS, no. 135/2004, 36/2009, 36/2009 - Dr. Law, 72/2009 - Dr. Law, 43/2011 - making U.S.) is the primary law governing the environmental protection in the Republic of Serbia, which states that the repairs or remediation process should take measures to stop further pollution and environmental degradation, to a level that is safe for the future use of the site, including landscaping, rehabilitation and reclamation. Article 16 provides that an individual or legal entity that degrades the environment is obliged to do a complete reclamation or otherwise rehabilitate degraded environment, in accordance with prevention and remediation projects.

The government adopted the Regulation on the application of systematic monitoring of soil quality indicators in November 2010, in order to assess the risk of soil degradation and a methodology for developing remediation programs ("Official Gazette of RS", No. 88/10) in which we discussed the

definition of contaminated sites: the locality of the confirmed presence of hazardous and pollutants caused by human activity in concentrations that may cause a significant risk to human health and the environment. The regulation stipulated limit values and remediation of hazardous and harmful substances in soil and groundwater. Implementation of the Regulation should ensure protection of land-based prevention of degradation by identifying areas at risk of degradation, whether degradation occurs naturally or is caused by human activity. The methodology for the development of remediation programs at contaminated sites is prescribed by Art. 13-16. In order to develop remediation programs (content prescribed in Article 13) on the basis of the established presence of pollutants in the soil the contaminated sites are determine. In Article 14, it is stated what contaminated sites include: landfills; site-operator businesses which cause pollution by the active or inactive installation operators, or the environment in which they deposited hazardous materials; accident locations and sites contaminated due to extraordinary events, including failures, degraded industrial sites (brownfield sites). Article 15 states that the contaminated sites perform additional research to determine the degree of contamination and remediation program development. Article 16 defines where to implement remediation programs and projects. Border (and remediation) concentrations of hazardous and noxious substances and values that may indicate significant contamination of soil and ground water are given in the Annex of this Regulation.

EXAMPLES OF REMEDIATION CONDUCTED IN SERBIAN OIL INDUSTRY

Serbian Oil Industry (*NIS*), a socially responsible company, being aware of its impact on all environmental media, manages the prevention of contaminated land, made by activities in the field of production, processing and transport of oil and oil products. In the process of exploration and production of oil and gas, large quantities of cutting transportation and waste drilling fluids are produced, and then disposed in the primary mud pit. Such places are subject to repair and restore the land to its original use. *NIS* is constantly conducting activities related to the remediation of soil and groundwater contamination at facilities where contamination is found. Measures to soil remediation and groundwater at contaminated sites and additional research to localized pollution are being planned and implemented. Remediation programs are reflected in the action plans, pilot systems and numerous other projects. In this paper we will mention some of the programs implemented to date remediation of soil and groundwater.

Project of prevent of historical soil contamination

Serbian Oil Industry (*NIS*) began the prevention project of pollution of historical land, worth 323 million RSD, in early 2010, and it will last until 2014. The aim of the project is prevention of contaminated soil that was created over a long period in the past when drilling oil, which is being extracted in Serbia since 1952. Also, this will include the reparation of absorptive pool, which is located within the *NIS* facilities in the Province. Remediation of contaminated soil and returning it to its original state will contribute significantly to the preservation of the environment, especially land, and will indirectly affect the conservation of groundwater.

Based on data collected in the field, prior to the commencement of the project of prevention of historical soil contamination, it was found that within *NIS* there were 142 primary non-repaired mud pits and three absorptive pools, created for years. In *Exploration and Production Block* the project for prevention of historical soil contamination is implemented. In 2011, 42 primary clean mud pits were prevented, a pilot project for the prevention of primary oily mud pit is implemented at the oil field Turija by bioremediation method, and the result is the elimination of further contamination of soil and groundwater remediation, where land can be returned to its original use.

By the end of the last year, about 4,000 square meters of cultivated land returned to farmers in Melenci: Mihajlo Babin, Zlatko Pajic and Rasa Kojcic. The ground was soaked with oil, sewage was replaced by the chernozem, brought from southern Banat, where the grade of the road in recent months. The waste is collected in addition to individual wells for decades.

Restoration of historical soil contamination include, above all, the primary mud pits, which are located close to the hole that is disposed in the mud used in the drilling process. Also, the repair will include absorbent pools layer that is disposed of waste water or warm water stimulation wells and oil (paraffin oil-water emulsion), which is essential for the smooth running of the production process, and oily soil after accidental spills of hydrocarbons pipeline.

Mud is a liquid, viscous fluid which is a flushed drilled material, while producing wells and coping with the pressures of layers that are pierced. The chemical composition is a fluid-based suspension of very active swelling clay, bentonite, with some additions that enhance swelling. Used mud contains material from the drilled rocks such as sandstone, marl, limestone. Mud is a necessity in performing activities of all production wells of oil companies in the world.

NIS has recently came into possession of landfill waste mud in Novo Milosevo, on which, at this moment, can be disposed only pure mud, which is loaded with hydrocarbons up to 5%. Since the start of commissioning of the landfill, waste is piled with mud holes that were active during that period, as well as the waste fluid from the process works, and in February 2010, as part of the project of rehabilitation of historical soil contamination, the clean disposal of waste drilling fluids from primary residual mud pit started. In the future, after the recovery of outstanding historical soil pollution, dumping of waste drilling fluids in the New Milosevo would be used for disposal of drilling new wells. This would be a shorter period ground around the borehole after drilling returned in its original condition, and the company will normally carry out its activities, in accordance with good oil practice.

The landfill in Novo Milosevo will cost a total of about 6.3 million. The first phase, five swimming pools, completed cost about 3.5 million euros. During operation of the landfill every precaution will be covered by the system for monitoring and controlling the quality of ground water and air. So far, the first phase of the project, which includes construction of a central part, including all general purpose facilities, the top five for the disposal of drilling mud pools, complete the fence, lighting and landscaping, and as the site to be used, will be followed by the next phase. Projected total of 17 pools to be built in five phases, for which the coating is to use extremely expensive, high-quality film, resistant to high mechanical forces at the disposal of solid materials.

Pilot system for providing the necessary data for the design of rehabilitation and remediation of groundwater and soil at the port Pancevo Oil Refinery (POR)

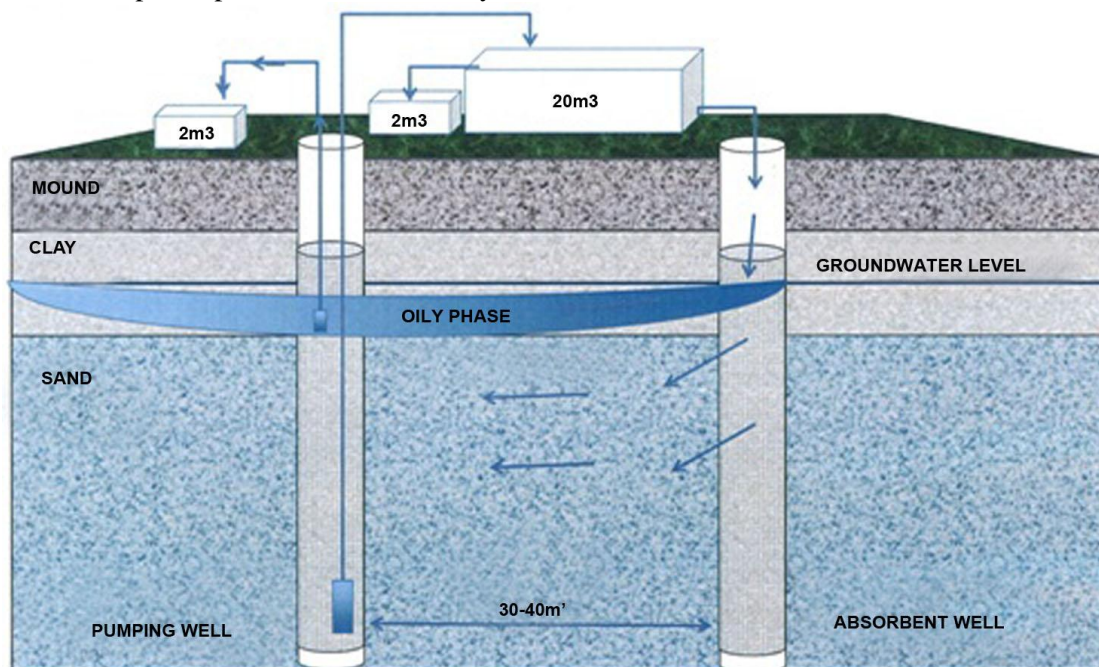
The pilot system is aimed at providing the necessary input parameters for the project of prevention and remediation of groundwater and soil at the port *POR*.

In order to solve the problem of soil pollution by oil and petroleum products in the zone of *Pancevo Oil Refinery* pier and expiration in the riverbed through the shoreline includes the Block Processing Directorate of MT and SP, Scientific-Technological Center Sector of Engineering and Block Services Section *Hidrosonda*.

For the purposes of the pilot system the necessary input data for the design of rehabilitation and remediation of soil and groundwater were collected at the site port *Pancevo Oil Refinery*, in period of January-March 2012. The works were carried out on the development of three wells. Wells B-2 and B-3 are derived as an extraction for the extraction of contaminated groundwater, while the B-1 well was made as an absorbent for drained groundwater hydrocarbon phase after separation. Drilling of three wells was performed using rotating, without the use of turbocharged fluid and at the same time covering the protection column.

During the pilot operation of the system Groundwater samples from seven sites were taken, in order to monitor the concentration of hydrocarbons and metals on every 10 days. The presence of hydrocarbons in high concentrations in all objects, and some objects were detected, as well as high content of lead. By fractional distillation of the oil phase, it was confirmed that pollution comes from diesel, Sulphur content was also present in high percentage. The pilot system worked from May to

mid-August 2012. A total of six buildings exhausted 96 903,60 liters of the mixture of water and hydrocarbon phases, while in the same period 118 400,00 liters of water and the mixture hydrocarbon phase of the separate pools were driven away.



Picture 1. Schematic view of Pilot System

Remediation of contaminated soil generated due to leaking pipeline in Pancevo Oil Refinery

During September 2009, the section near the northern border of the complex of *Pancevo Oil Refinery*, there was an accidental spill of crude oil from pipelines which supply contaminated soil and groundwater. It was estimated that the size of the affected area outpouring was 100x15m and contaminated depression near the surface was about 700m².

In order to choose the optimal method of remediation detailed tests of contaminated sites were conducted. The laboratory soil analyses were carried out by accredited laboratories and 11 piezometric wells were drilled to monitor groundwater quality. The analysis of the results showed the degree of contamination of soil and groundwater. It was found that oil generally retained in the soil layer in the vicinity of the pipeline at a depth of 2 to 5 feet as a result of physical and chemical properties of crude oil (high density and viscosity), and on the single piezometric wells, contamination of groundwater was determined.

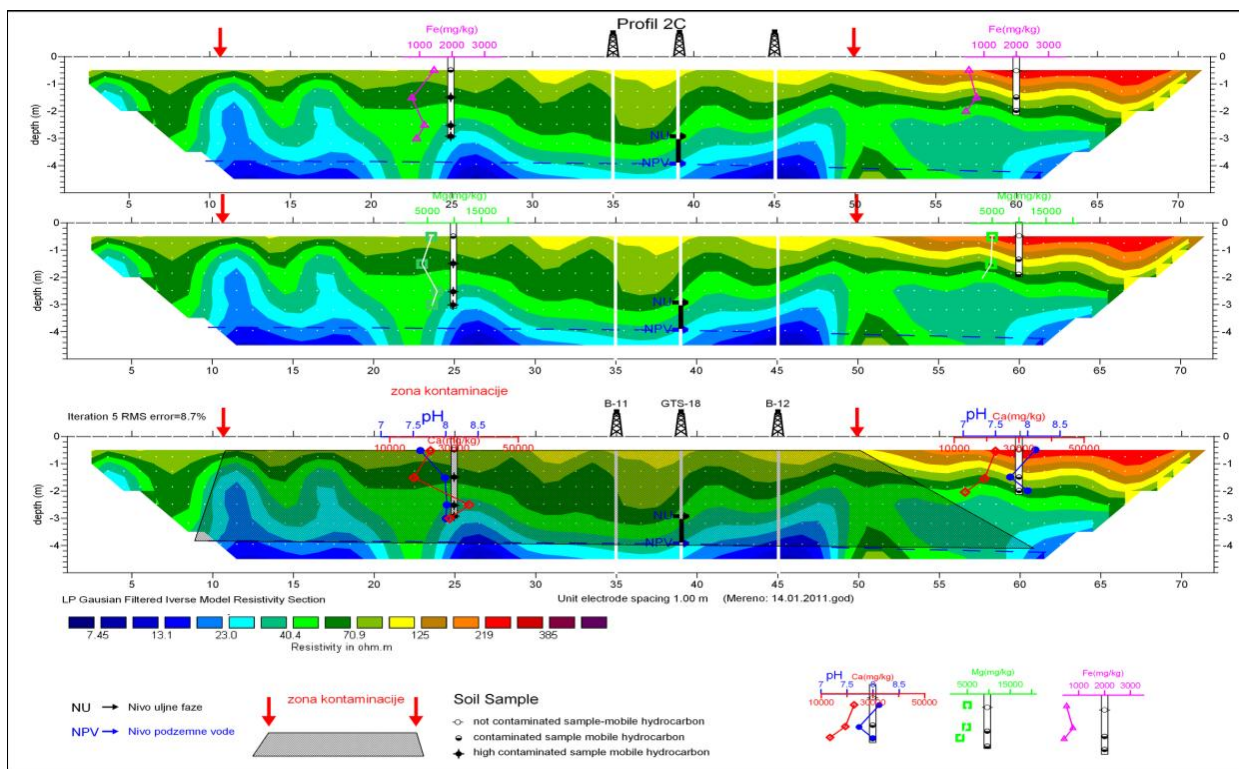
The optimum method for soil remediation method is chosen ex-situ bioremediation. The principle of bioremediation is based on the application of appropriate bacterial mixture and adding mineral and organic matter necessary to improve growing microorganisms in contaminated media. The technique of bioremediation is based on the characteristics of certain bacterial cultures that use organic compounds as carbon and energy source for the process of metabolism. As a result of the metabolic activity of microorganisms of different cultures, it comes to a complete breakdown of pollutants to carbon dioxide and water, or to a decrease in their concentration. In the process of remediation of contaminated soil was treated type Biostar Advanced Booster 1000 (bacterial nutrient, black and brown with the smell of ammonia, consisting of many components of fertilizers including urea solution, chloride, phosphate and sulphate, ammonium and potassium salts, caustic potash, and orthophosphate microelements solution of surfactants) and Biostar A 600 (preparation of active bacteria in the form of powders) Austrian manufacturer Applied Chemicals.

During application of the preparation cultivation of the land was done, by tumbling pile of earth working machines, or by hand, which made the contact of contaminated soil and bioproducts more

efficient, and air intake was enhanced. In 2010, the method of bioremediation in *Pancevo Oil Refinery* treated about 700 m³ of contaminated soil.

Goelectric survey

On the territory of the refineries in Pancevo and Novi Sad, as well as at a gas station Obrenovac city, in order to define the position of groundwater pollution, in 2011, for the first time in the region geoelectrical survey (geoelectrical scan) was realized. Geoelectrical scanning method is completely non-destructive and non-invasive, less expensive than exploration drilling, and allows one to create 2D models of electric resistance for different geological environments.



Picture 2. Geoelectrical scanning method

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**II International Conference
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**COMPARISON OF THE PRIMARY TREATMENT OF ORGANIC
MATTER REMOVAL EFFICIENCY FROM WATER, COMBINED
WITH OZONATION OR ADSORPTION ON CARBON POWDER**

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ABSTRACT

The urban area Northern Banat on urban area of Kikinda. is characterized with high content of natural organic matter in ground water measured chemical oxygen demand COD as permanganate number, PN , 19, mg /l . The work is concerned with the effects of the processes of urban under-ground drinking water treatment on the decreasing PN number with the combined primary treatment coagulation, flocculation using: - the invasive method – ozonation, - or (and) the un-invasive adsorption method on the added active carbon powder. Based on the 400 monitoring results during 8 months, it was shown that with the combination of processes coagulation, flocculation and adsorption may be come optimal technology for production of drinking water which pleasure all properly qualities.

Key words: *Natural organic matter, Coagulation, Flocculation, Adsorption, Ozonation, Potential of formation of THM and aldehydes.*

INTRODUCTION

The purification method for removal of the natural organic matter is necessary to apply due its influence on :

- odor, color and taste of water,
- the organic matter are precursor for the formation of the trihalo-metanes THM, and aldehydes
- the organic matter are substrate for the development of micro-organisms in distribution system
- can accumulate toxic matter and pollutants
- direct influence on the technological scheme of the purifying water treatment

For the removal of natural organic matter besides conventional primary treatment in this paper is examined and adsorption on active coal , destructive ozonation.

The effects of the examined technological procedure are examined in this paper, based on the 400 results of the water monitoring of the quality parameter PN (COD), during water treatment in the period of the eight months (Natalija Janković-Aćin, 2002).

EKSPERIMENTAL RESULTS

The coagulation, flocculation , adsorption and ozonation are examined on the pilot plant for the drinking water treatment capacity 2 m³h⁻¹ (the scheme presents figure 1), according to the plan of the investigation (figure 2 with the aim to decrease the used doze of the expensive coagulant).

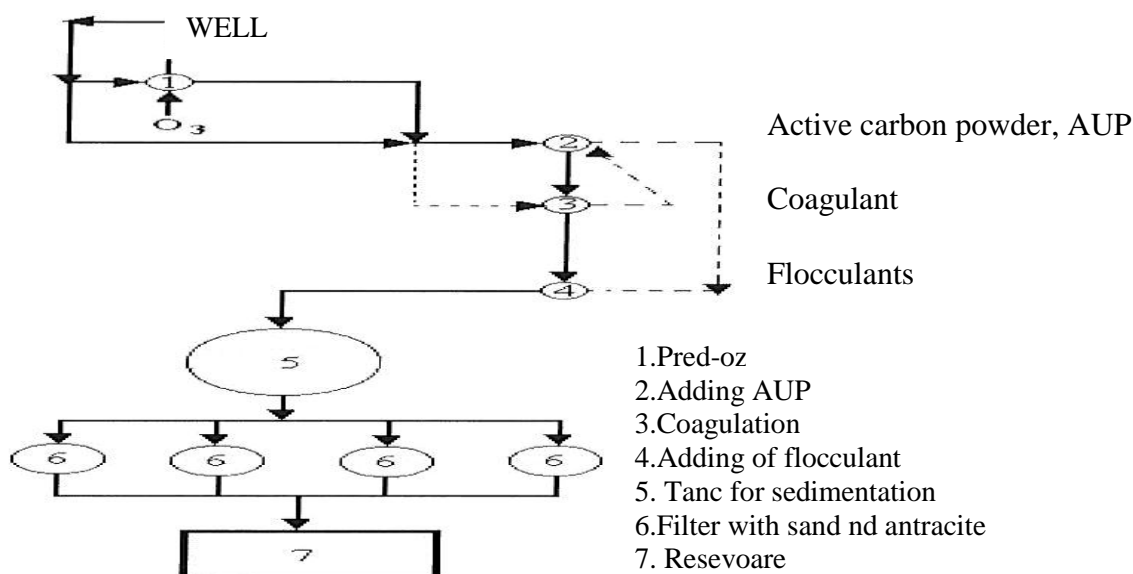


Figure 1. The pilot plant scheme

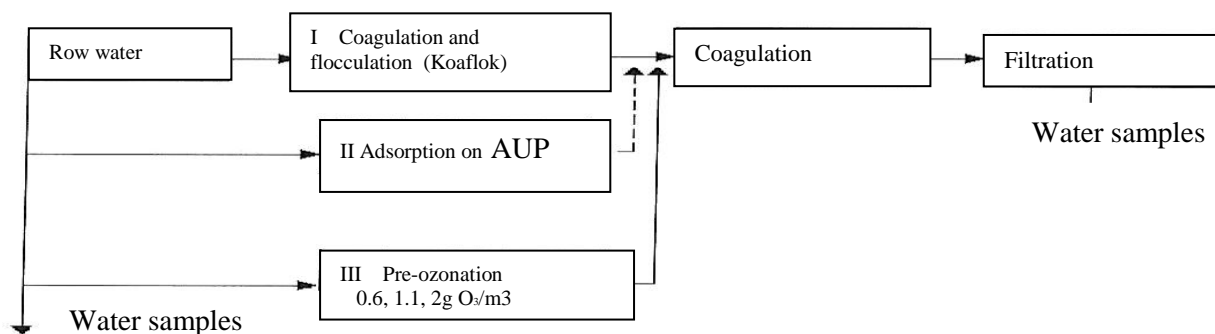


Figure 2. The scheme of the investigation plan (I, I+II, III+I, III+II+I, II+I)

The Koaflok dose 10-30 g Al m⁻³, PN decreased for 40- 70 %. That result agree with literature data (Vik and Eikebrokk, 1989). This primary treatment results were agreement with the literature data (Dalmacija et al, 1997) independent on the water turbidity, and pH change were less.

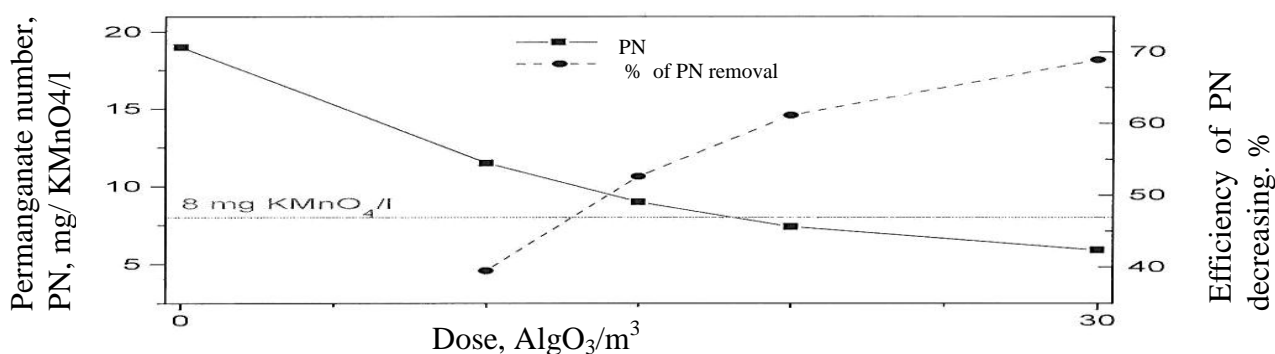


Figure 3. The PN decreasing with increased coagulant, Koaflok dose

The effects of the two combined methods invasive (with ozone) and un-invasive adsorption on active carbon powder were compared: with aim to decrease the costs with used increased Koaflok dose.

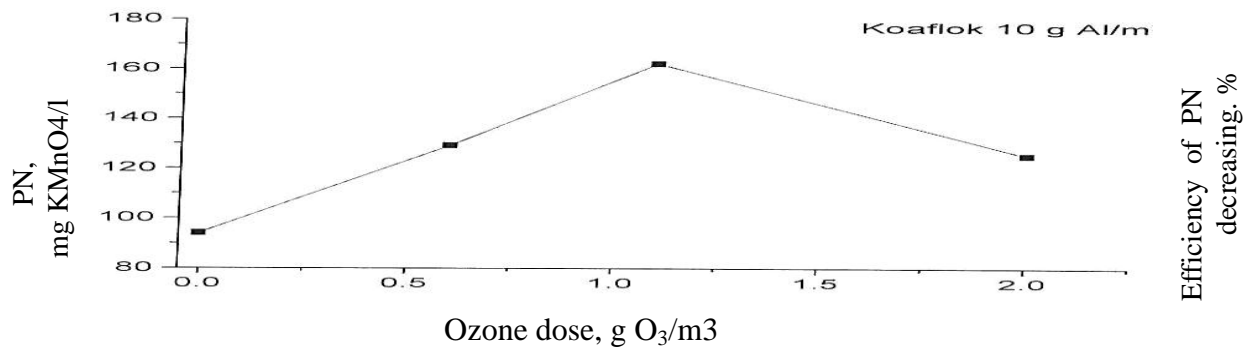


Figure 4. Influence of ozone concentration on the total potential of formation of THM Influence of ozone concentration in the ozonation pretreatment before coagulation with Koaflok on the content of natural organic matter in water, measured as permanganate number PN, mgKMnO₄/L

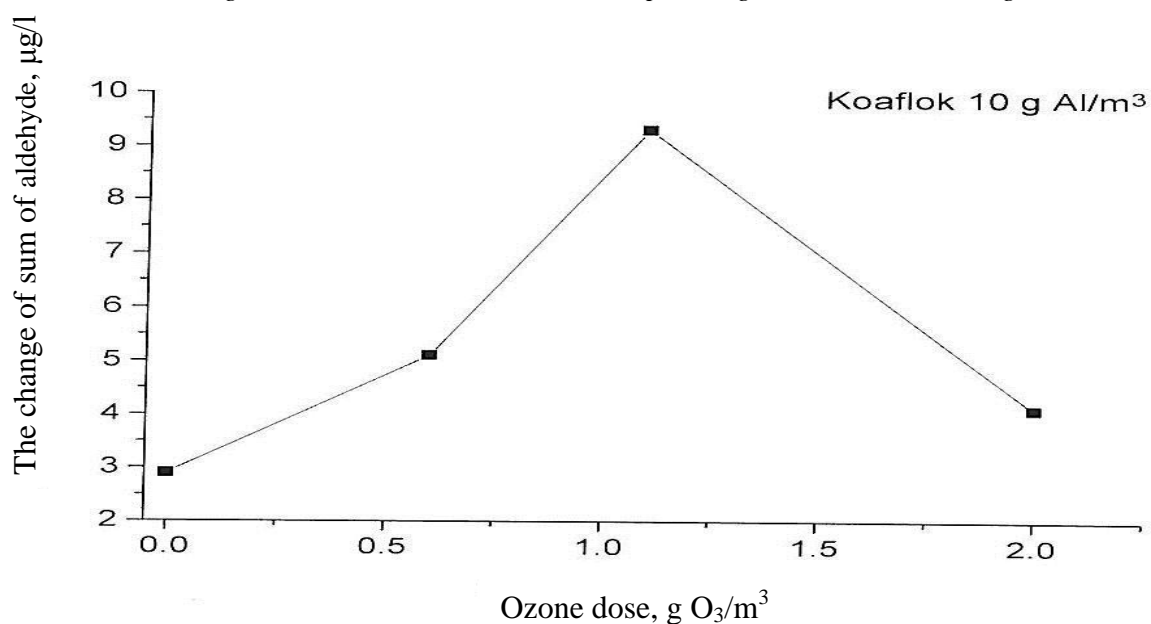


Figure 5. Influence of ozone concentration on the total potential of of aldehydes formation

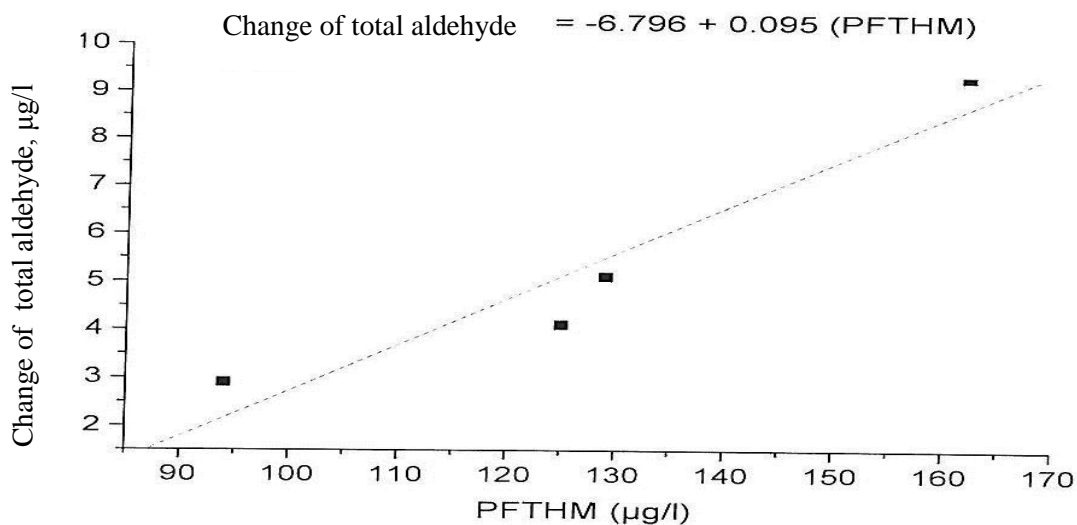


Figure 6. The functionally dependence between the total aldehyde content on the THM content in water after ozonation

Though PN with increased ozone dose up to 2 mg/l achieved 7 mg/l, the increased formatted THM due ozone presence became higher compared to maximal allowed content MAC. That means monitoring of water quality during ozonation beside PN has include the harmful increasing of THM and aldehyde content.

The second alternative the using of active carbon powder, AUP instead the part of the expensive Koaflok, without ozonation.

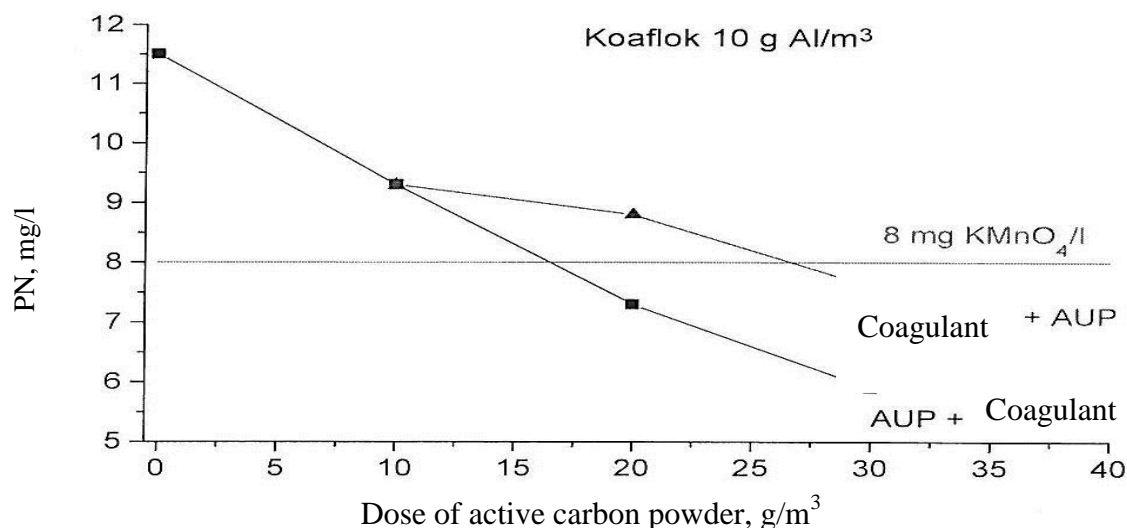


Figure 7. The influence of the concentration and scheme of the added active carbon powder AUP at Koaflok doze 10 g Al m^{-3} :

- a) previously added Koaflok (coagulant + AUP)
- b) previously added active carbon powder, AUP (AUP + coagulant)

The effect on the PN efficiency change of primary treatment were obtained at dose of the added active carbon powder 10 -30 g/l , at constant Koaflok doze of 10 g Al m^{-3} .

In *procedure a*) adding of active at dose 26 g/l of carbon powder after Koaflok, decreased PN up to the Law limited value 8 mg/l

In *procedure b* , adding at the same dose 26 g/l of active carbon powder prior Koaflok decreased PN up to 6 mg l^{-1} , and the Law limited value 8 mg/l could be achieved with added 16 g/ m^3 of active carbon powder prior Koaflok.

CONCLUSION

Based on the obtained results of experiments with aim to decrease the Koaflok dose in primary purifying of natural organic matter from water, the effects of the 2 combined methods were compared:

- Effects of the ozonation on the PN decreasing up to 7 mg/l-of the urban under-ground drinking water in the pretreatment applied before primary treatment is producing of the toxic pollutants, mesured as increasing of the formation of THM and total aldehydes.
- Effects of adding of the active carbon powder are examined in the two regimes, with the adding before and with the adding after ccoagulanf and flocculant.
- Previously adding of the active carbon powder increased the total suspended matter content in the treated water and decreased PN up to 6 mg l^{-1} and the efficiency of primary treatment from 50 % up to 70 %.

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**DECREASE OF THE CONTENT OF NATURAL ORGANIC MATTER
IN GROUNDWATER PREOZONATION PROCESSES AND
COAGULATION**

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ABSTRACT

Effects preozonation processes, coagulation and flocculation to remove natural organic matter in raw water were studied in groundwater from the territory of middle Banat. Groundwater from the aquifer to a depth of 100-150 m. As coagulant agent used FeCl₃. The applied process leads to loss of natural organic matter in coagulated water compared to their content in the raw water. Removing NOM best effects were achieved using a combined process preozonation dose of 2.2 g/m³ ozone, coagulation and flocculation, with the prior correction of pH values. At this dose, the reduction of ozone NOM content of 72% and 67% UV₂₅₄ PB compared to the raw water.

Key words: *Preozonation, natural organic matter, coagulation.*

INTRODUCTION

Natural Organic Matter (NOM) is the organic material present in surface or ground water. NOM are oxidized very slowly and their solubility in water may vary with pH. The dissolved fraction of NOM may not be fully removed using conventional water treatment practices. The presence of natural organic matter in the aquatic resources is not harmful, but problems arise when the source water containing NOM is treated with chlorine in the disinfection step. The organic matter reacts with the chlorine and forms chlorination byproducts (CBPs) in the drinking water, such as trihalomethane (THMs) and haloacetic acids (HAAs) which have been linked to cancerous diseases (Singer, 1999). Due to the heterogeneous and undefined character of the natural organic matter, it is measured through surrogate parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), specific ultraviolet absorbance at 254 nm (SUVA), colour and ultraviolet absorbance at 254 nm (UV₂₅₄) (García, 2011).

Ozone have been widely used as pre-oxidant before conventional water treatment processes, while some controversial results on the effects of preozonation on coagulation and particle stabilization, have been described (Li et al., 2009). The performance of coagulated flocs can be substantially influenced by preozonation which can be ascribed to the variation of particles or organic substances in water.

THEORY

Removing the NOM process of drinking water treatment

Natural organic matter are "large" molecules, which have a negative charge, which gives them the properties of colloids and can be removed by coagulation and flocculation secondary. Coagulation processes are used to eliminate the factors that ensure the stability of molecules of humic substances in

water, as humic and fulvic acids. Due to the size of colloidal humic substances prevented their deposition because the deposition rate is small, and because of the negative charge averted their agglomeration. To humic matter was settled in the technological treatment of drinking water need to be exposed to the process:

- Destabilization - translation given steady state dispersion or solution in an unstable condition. Destabilization influence the surface properties of the particles and thus increases their adsorption on the filter medium or provide conditions for agglomeration small particles into larger.
- Coagulation - the process by which colloidal particles, dispersed or dissolved in water loses its stability and begin to unite to form aggregates of several particles. When these aggregates reach a certain size, subject to the effect of gravity and begin to stand out from the dispersed phase (water).
- Flocculation - the process by which particles are destabilized, and, in turn, caused coagulation of particles interconnected and higher education in the agglomerates.

As coagulants are commonly used: aluminum sulfate, aluminum chloride, polyaluminum chloride or sulfate, iron chloride and iron sulfate, and organic cationic polymers. Coagulant task is to make destabilizing colloidal particles (diffusion layer compression, adsorption, neutralization, and precipitation), to those agglomerisale flocculation and as such was settled more quickly and easily. In the use of small amounts of coagulation agents turbidity removal is usually done via charge neutralization.

According to Pertnisky and Edzwald (2006), the coagulation mechanisms depend mainly on whether turbidity or natural organic matter is to be removed. They established that for conventional turbidity removal, two mechanisms are involved. The first involves charge neutralization of the negatively charged colloidal particles by adsorption onto positively charged coagulants species, and the second involves the enmeshment of colloids in precipitated $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ solids. However, Eikebrokk *et al.* (2006) pointed out that the presence of organic matter greatly affects the chemistry of coagulation. According with them, the destabilization of the colloids depends on the chemical nature and structure of the NOM.

Improving the processes of coagulation and flocculation

The advantage of the process of coagulation and flocculation is a low price, so it goes on its further optimization and the introduction of direct filtration, reducing the amount of residual coagulant and coagulant from the rest of the metals. The enhanced coagulation process is defined as an optimized coagulation process for removing DBP precursors or natural organic matter (NOM). In general, enhanced coagulation is practiced at higher coagulation dosages and lower pH values. Liu *et al.* (2006) studied NOM removal by enhanced coagulation and polymer aid, and found that both processes achieved UV254 removal greater than 90% and that enhanced coagulation removed preferably the hydrophobic fraction whereas polymer aid removed the hydrophilic fraction. Depending on the water quality effects of coagulation could be improved by applying preozonation or the addition of activated carbon powder. Based on a series of tests (Edwards and Benjamin, 1993; Ma *et al.*, 2001) concluded that ozonation reduces the need for coagulants and even 40% in the case of the removal process is carried out by precipitation when applied polymer coagulants and tends to increase the need for coagulant when such removal is dominated by the sorption mechanism (application FeCl_3 or $\text{Al}_2(\text{SO}_4)_3$, without the addition of flocculants.

The application of ozone in drinking water treatment

Ozone was first used in the preparation of drinking water 1893rd in the Netherlands (USEPA, 1999). However, since it was found that the use of ozone in addition to disinfection achieves a number of other positive effects, due to the oxidation of organic and inorganic substances present in the water, of its application may be different. Ozone can be applied as a biocide, as a classical oxidant or as a pretreatment for improving the process of coagulation and flocculation.

Preozonation water

Ozone is sometimes used as a primary step in the treatment of drinking water (preozonation), where the raw water is treated before the process of coagulation / flocculation and sedimentation processes or even before filtration (direct filtration). The effects of the removal process preozonation POM present in the water can be roughly divided into direct (direct reduction of POM, paint removal, taste and odor of water) and indirect (POM removal processes of coagulation, flocculation, direct filtration) (Agbaba, 2002). Regardless of whether it is implemented or preozonation main ozonation, organic matter present in the water is partially oxidized, whereas there is a significant structural change: reducing molecular weight, low molecular weight compounds increased content (such as aldehydes and carboxylic acids), an increase of biodegradability and polarity organic compounds, as a result of education compounds with carboxyl, aldehyde and keto functional groups.

METHODS

Effects were observed in the process of coagulation of natural organic matter content in groundwater from the territory of Central Banat, as well as the effects on the coagulation predozonizacije. We used an underground water from a depth of 135 meters (water characteristics are given in Table 1), which is used for the water supply of the town of Zrenjanin.

Table 1: Characteristics of raw water

Parametar	Unit of measure	Mean ± Sd
pH	-	7.8 ± 0.14
Total alkalinity	mg HCO ³⁻ /l	909 ± 15
Turbidity	NTU	0.52 ± 0.03
Conductivity	µS/cm	1202 ± 16
DOC	mg C/l	9.27 ± 0.92
Permanganate number	mg KMnO ₄ /l	37.7 ± 0.6
Ultraviolet Absorbance (UV ₂₅₄)	cm ⁻¹	0.497 ± 0.015
SUVA	l mg ⁻¹ m ⁻¹	5.36 ± 0.49
PFTHM	µg/l	555 ± 128
Sodium (Na)	mg/l	245 ± 54,9
Arsenic (As)	µg/l	134 ± 29
Boron (B)	µg/l	957 ± 153
Sd- standard deviation based on 5 measurements		

The quality of groundwater from aquifers used for water supply of the town of Zrenjanin does not satisfy the terms of use of this water for drinking, and to multiply. Among the main problems is the high content of natural organic matter. The process of preparing water features multiple functional method:

- pre-treatment of water (water preparation for further processing): correction of pH, aeration and preozonation;
- removal of all natural organic matter (POM) and micropollutants from water: coagulation and flocculation;
- separation of flocs from water: precipitation and filtration.

The dose of ozone in preozonation were 0, 0.2, 0.9, 1.2, 4.2, 4.7 g O₃/m³; FeCl₃ coagulant dose was 200 g FeCl₃/ m³ and the dosage of flocculants A 110 0 , 5 g/m³.

The content of natural organic matter in raw and treated water consumption was determined using potassium permanganate oxidation of organic matter. The procedure was performed according to standard procedure under acidic conditions (Škunca-Milovanovic et al., 1990). The content of organic

substances that absorb UV radiation at 254 nm was determined by measuring UV absorbance at 254 nm in a cuvette of 1 cm to UV spectrophotometer UNICAM SP600.

FINDINGS AND DISCUSSION

The dose of ozone in the preozonation ranged from 0.2 to 4.7 g O₃/m³, FeCl₃ coagulant dose was 200 g and the dosage of flocculant FeCl₃/m³ A110 was 0.5 g/m³. The change in total POM content in the water was monitored by UV254 absorbance and KMnO₄ consumption. Table 2 presents changes in content after preozonation POM (IV), and after coagulation, flocculation and filtration (VII).

Table 2: Content POM expressed through consumption of KMnO₄ and UV254 absorbance

Preozonation ozone dose in mg O ₃ /l	mg KMnO ₄ /l			Ultraviolet Absorbance (UV ₂₅₄) cm ⁻¹		
	I	IV	VII	I	IV	VII
0	37.4	37.7	24.8	0.495	0.492	0.300
0.2	37.8	33.4	16.4	0.487	0.480	0.175
0.9	38.3	35.8	17.0	0.470	0.185	0.175
1.2	37.9	31.1	16.0	0.508	0.550	0.212
4.2	37.4	30.8	16.2	0.500	0.395	0.180
4.7	37.8	33.0	14.9	0.512	0.442	0.177

I- raw water; IV- water after preozonation; VII- water after coagulation and flocculation and filtration

From the results it can be seen that the process of introducing preozonation in drinking water treatment, achieved a significant increase in the efficiency of the process of coagulation, flocculation, sedimentation and filtration to reduce the water content of POM. The mere process of coagulation without prior ozonation, the reduction of NOM content of 39% (measured over absorbance UV254) and 34% (in terms of the energy consumption of KMnO₄), compared to the raw water. The introduction of even very low doses of ozone (0.2 g O₃/m³) preozonation in the process, to a significant improvement of efficiency coagulation process in the removal of NOM from water (UV254 absorbance decrease by 64%, reducing KMnO₄ consumption by 57%, compared to the raw water). This result indicates that the use of preozonizacije achieves nearly twice as efficient reduction of NOM in the water than the process that does not apply previous oxidation with ozone. This is probably due to changes in the chemical structure of natural organic matter under the influence of ozone which they become susceptible to removal processes of coagulation and flocculation.

However, increasing the dose of ozone (0.2 to 4.7) in preozonation not lead to further increase the efficiency of reducing the content of NOM in water coagulation. Applying ozone dose of 0.9 g, the reduction O₃/m³ UV254 absorbance by 63% and reducing KMnO₄ consumption by 56%, compared to the raw water. Even increasing the dose of ozone at 4.7 g O₃/m³ achieved only a slight improvement effect of removing NOM coagulation (UV254 absorbance decrease of 65%; KMnO₄ consumption reduction of 61%, compared to the raw water).

Preozonation, at doses of 0.2 to 0.9 g of ozone O₃/m³ contributes to reduction of UV254 absorbance by 1% or 60% as the maximum reduction in UV254 absorbance, and the reduction of KMnO₄ consumption by 12% and 6%, compared to raw water. Increasing the dose of ozone at 1.2 g O₃/m³ achieved slightly better effect of reducing the consumption of KMnO₄ (18%) but at the same time, an increase in UV254 absorbance by 8% compared to the raw water. This increase is probably the result of reduced degradation of aromatic compounds absorbing at 254 nm. By further increasing the dose from 4.2 to 4.7 g of ozone on O₃/m³ UV254 absorbance percentage reduction was 21% and 14% while reducing KMnO₄ consumption remains at about the same limits as in other applied ozone dose (18% and 13%).

We can assume that a significant reduction of organic molecules coagulation and flocculation process and contributed to structural changes in the NOM oxidation by ozone, which results in the removal of NOM during coagulation and flocculation. The nature of organic matter present in the raw water is changed during their reaction with ozone, by restricting the content of functional groups responsible for the absorption of UV radiation at 254 nm with simultaneous formation of polar functional groups such as hydroxyl, carboxyl and keto functional groups.

CONCLUSION

One of the biggest problems in the preparation of drinking water is the presence of NOM in water resources. The presence of NOM in water is undesirable because those with disinfectants agents formation disinfection by-products, which are toxic and carcinogenic. Therefore, when designing the water treatment process must anticipate and prevent contact NOM present in the water and disinfectant.

The most frequently used methods for the removal of NOM from water as coagulation and flocculation, filtration, adsorption on granulated activated carbon (GAC) and powder activated carbon (PAC). In addition to these so-called, conventional methods of increasing application and get newer methods: ion exchange and membrane processes. Although coagulation processes have long been in use, and still is working on improving this process and the development and application of new coagulants. Coagulation and flocculation process can be improved by applying preozonation which is achieved by oxidation of NOM and its easier to remove these processes.

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**QFD METHOD AND SIGNIFICANCE OF ITS APPLICATION IN
DESIGNING QUALITY OF DRINKING WATER**

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ABSTRACT

Quality Function Deployment – QFD method is a methodology of customers’ needs and requirements identification, based on which a product should be designed, with paralel QMS improvement in accordance with the customers’ requirements. Respecting the customer’s wishes, QFD method initiates and directs QMS improvement with the aim to achieve business efficiency. Identifying and defining the relevant information for adequate decision-making on course and way of QMS improvement, QFD method as a modern quality system enables company’s strategic positioning for market progress through customer satisfaction, while making necessary conditions for feedback establishment and quality system’s achieved improvement assessment. This paper presents QFD method and analyses the significance of its application in designing the quality of drinking water. In order to fully meet the customers’ requirements, it is necessary to establish which characteristics are more significant than others and work primarily on their improvement.

Key words: *QFD method, QMS, quality house, drinking water.*

INTRODUCTION

Water is essential for everyday life. If it is bacteriologically safe, tap water is good for human body, while if we opt for bottled water, the producer has to be taken into account.

Hygienic drinking water in public supply or for production of food intended for sale (further: drinking water) is stipulated by Regulation on the hygiene of drinking water. (Official Gazette, 1999)

In accordance with this Ordinance, hygienic drinking water is the water regular by the following means:

- Microbiological features;
- The amount of chemical substances;
- The amount of residues of coagulation and flocculation funds;
- The amount of residues of disinfectants and disinfection by-products;
- Physical, physical-chemical and chemical features;
- Radiological features in normal and emergency situations and
- Amounts of battle poisons in emergency situations. (Official Gazette, 1999)

Hygienic safeness of tap water for public supply, food processing or production, is determined by systematic conveying of basic and periodic inspection of raw water in regular time intervals, in accordance with the positive legislature. The provisions of the Ordinance shall be applicable for both tap and bottled drinking water. Bottled drinking water is inspected in two ways, as follows:

1. Spring water and water from packaging is reviewed regarding the number of equivalent residents, in accordance with the provisions of Art. 6 of this Ordinance;
2. Review of the bottled water from the market (sales) is conveyed by taking two random packs, depending on the warehouse size. The basic overview of the water is done in these samples. (Official Gazette, 1999)

This paper presents the QFD method and analyses its application significance in designing drinking water quality. In order to fully meet the customers' demands, it is necessary to determine which characteristics are more significant than others and work primarily on their improvement.

QFD METHOD

Contemporary market conditions include certain goals reflecting primarily in business excellence achievement, leading towards making preconditions for long-term gratification of all society segments, from customers and business partners, to employees and company owners.

Current economic conditions require the integration of quality in all business aspects, which brings the companies turn to customer requirements. Company's marketing activities are the most important business philosophy in achieving these goals. Marketing unifies, coordinates and directs the company's activities towards recognizing and meeting the customers' needs and requirements. In order to do so, as well as achieve top quality of a product/service, information on desired quality has to be delivered from the customer to the producer, and has to be applied in the production process as well as in the process of product/service control.

Quality management represents the activities directed towards company managing with business excellence achievement as a goal and is the way to the future. (Institute for Standardization of Serbia, 2001)

Doing market research i.e. including the product/service consumers, the company gets the better overview of the market needs. The production is directed on the basis of this research and therefore the risk of sales failure is reduced.

Modern quality management process comprises using various methods for improving of both products' and production processes' characteristics. Customer demand on product/service quality is usually based on descriptive expression of sensory impressions. Customers describe the product's influence on their senses. The company and its engineers have to 'translate customers' demands to the language of production, i.e. product's/service's features. It is not an easy task. This means that value achievement through customers' wishes and needs understanding and realisation of these expectations, is the main task of quality management.

QFD method was developed in Japan, more precisely in Kobe in 1970s, in Mitsubishi shipyard, but it later found its application in other industry branches as well. Toyota uses it since 1973, and the following started using it later: Honda (1979), Ford (1983), Volvo and Saab (1987). Having seen the significant progress in Japanese industry, this method started being used since 1991 in developed European countries and USA as well. Today, Japanese industry sees QFD as just one of many standards with required application label. First QFD method application was related only for new product designing and development, but today it is used more and more often on different enterprise levels. It is interesting that it is being increasingly used when it comes to service (not product), while its newest application is related to improving a process within the company itself. (Đorđević and Čočkalo, 2007)

QFD means quality function deployment or quality function development. The aim of this method is to provide maximum quality with minimal investments, using various techniques of customer demands and requirements identification and through process of developing products, production planning and marketing activities,

This method has numerous advantages, reflecting in (Converse, n.d.):

- Shorter product development time,
- Less engineer interventions,
- Reduction of new product launching costs,
- Customer needs and requirements gratification,

– Future project databases development.

Using QFD method establishes the correlation between the customers' demands and organisation, i.e. company production functions. The correlation is established over certain matrices lined in a queue or a string (thus the term “deployment”, which basic meaning is development into a column), where the elements of previous matrices' columns are equal to elements of further matrices' rows.

QFD begins in the product concept development phase and is distributed over all the technical development processes, production preparation and quality management. Each phase focuses on processes, which are important for the customer. QFD method is most commonly described through its four phases, performed within four “quality houses” or matrix. Simply, QFD method contributes the strategic positioning of the company for market progress. Matrices or “quality houses” present relationships between the business system elements (Figure 1). These are:

1. Customer demand identification and defining characteristics of products and services significant for demand meeting;
2. Establishment of products/services critical components, which need more thorough research;
3. Establishment of critical production process, i.e. service parameters;
4. Establishment of realization procedures and instructions and product/service control

QFD method is based on series of matrix diagrams which are used for data collection and development, in the form of product team plan review. Based on the collected data the demand lists are formed (customer demands and technical demands).

Quality houses are matrices formed so that each their phase has the same basic look. The entrance in quality house in the left column always has the same question: “What is required?” and its exit always has the question: “How to meet the demands?”

Key element of QFD analysis is mutual working out of quality house in which the customer demands are placed – WHAT, and product-characteristic technical parameters – HOW.

Certain QFD method implementation phases have the same (Crow, 2000):

Phase 1: This phase is initial and essential. Customer demands are transformed into product characteristics – with clearly defined target values. First of all, all the demands posed by the customers are noted in the field WHAT, which have to be met by the product. Then, in the HOW field, product features important for customer demand meeting previously provided in the WHAT field are defined. After certain processing of these data, product characteristics from the HOW field in the first house are transferred in the WHAT field of the second house.

Phase 2: A product's components important for achieving product characteristics are established in the HOW field for all the product characteristics provided in the WHAT field. The product's critical parts and its characteristics are transferred into WHAT field of the third house.

Phase 3: The production technology is prescribed for achieving defined products. Processes, i.e. production technologies and all their parameters are established in the HOW field for all the product's parts and its characteristics. Thus, the required characteristics are obtained. Technological operations are transferred into WHAT field of the fourth house, along with their parameters.

Phase 4: Production instructions are written for ordered technological operations. For all of them, provided in the WHAT field, quality control procedures, i.e. measures to be undertaken are established, in order for the process to take place securely. Procedure defining goes up to the operation instructions.

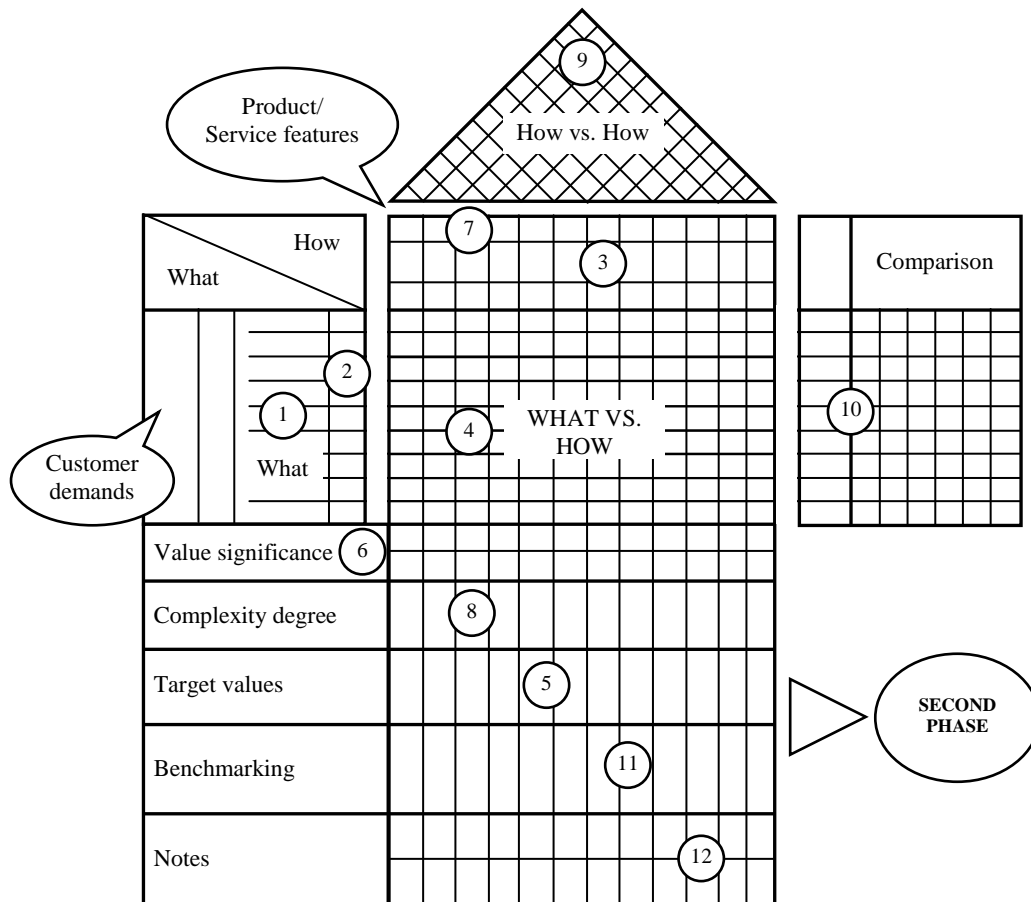


Figure 1. Quality house (Lazić, 2006)

In order to establish the order of element types that will be defined in these houses, all the business system elements influencing the quality of product/service are primarily defined, then the size of their influence is defined.

A successful QFD method application needs a multidisciplinary team. Their task is to develop the company's policy regarding the customers' demands, in that way that they become the decisive trigger of product/service development. Each quality house gets an expert team with the primary goal to establish the problem in the most concise and detailed way. It is important to extract and select the customer/buyer demands, which can influence the observed problem and analyse the competition in detail. This means that the following data should be collected:

- Characteristics of the existing product/service found satisfactory by the buyer;
- Customers' wants/expectations while using the product/service;
- Novelties on the market regarding the observed product/service;
- Emerging demands;
- New product/service characteristics in the similar, i.e. competing companies;
- The process of service realisation and the frequency of customers' complaints etc.

Data collection employs market research techniques like interview or questionnaire. These researches have to answer the basic question in the mere entrance of the QFD method: What do the customers want? The information gain process itself requires a previous classification of the users by categories – market segmentation needs to be done so as to define the target user groups which have to be particularly encouraged, since they potentially make the greatest company revenue or have the need for a service most frequently.

Quality Function Deployment – QFD method is a system for entire business system improvement, since a QMS elements' change is planned through the phase of product/service design, in order to influence the quality of the entire production process output. The result of using this method are reflected in getting the detailed plan of QMS elements' functioning, which can have control points with defined way of control, preventive and corrective activities apart from the process and necessary resources. From this standpoint, it can be seen as 'quality plan' of the product/service.

Results obtained through QFD method application are the management's direct responsibility, given that it decides on all the system changes. Also, change (development, improvement, growth) implementation quality directly depends on the way of organisation management.

QFD methodology is based on systematic engineering approach and is characterised by following four phases performed within the so-called quality house.(Đorđević and Čočkaló, 2007)

DESIGNING AND CONTROL OF DRINKING WATER QUALITY

Monitoring of quality of water is set with the goal to estimate the quality of water resources in order to perform the characterisation of ecological status and establish the condition for water cleaning on various purpose (water supply, recreation – swimming pools, agriculture – irrigation etc.)

Constant monitoring and care of maintaining a desirable quality state of water are the conditions for forming a successful water management system and planning of stimulating measures which prevent the polluted water and dangerous matters leak.

The type of data, sampling and analysis program and the way of treatment depend on the consumers' needs. Lately, local self-government invest more and more to ensure water delivery, which is in concordance with the quality standards, procedures and directives. However, recently an increasing number of people started using bottled water as an alternative solution which would replace tap water use. The quality of tap water was significantly increased due to the strong regulation which controls the availability of various technologies employed in the water treatment.

Hygiene of drinking water in public supply or production of food for sale (further: drinking water) is ordered by Regulation on the hygiene of drinking water (Official Gazette, 2005a and 2005b). According to this Regulation, hygienic water is the one appropriate regarding:

- Microbiological features;
- The amount of chemical substances;
- The amount of residues of coagulation and flocculation funds;
- The amount of residues of disinfectants and disinfection by-products;
- Physical, physical-chemical and chemical features;
- Radiological features in normal and emergency situations and
- Amounts of battle poisons in emergency situations.

Hygiene of tap water in public supply for drinking, processing or industrial food production, is established by systematic performing of basic and periodic inspection of raw water in equal time intervals, in accordance with the positive legislature. The provisions of the Regulation are applied to both tap and bottled water. Bottled drinking water is inspected in two ways, as follows:

1. Spring water and water from packaging is reviewed regarding the number of equivalent residents, in accordance with the provisions of Art. 6 of this Ordinance;
2. Review of the bottled water from the market (sales) is conveyed by taking two random packs, depending on the warehouse size. The basic overview of the water is done in these samples. (Official Gazette, 2005a and 2005b)

The increase of alternative solution use for tap water is directly linked to consumers' perception of water safety. This can be a feedback between the buyers' wishes and priorities while supplying with

water. The consumers are focused on drinking water quality and have zero tolerance towards any taste, smell or water shortage. (European Commission, 2012)

Rated by their importance, buyers' wishes are as follows:

1. Safe product in accordance with the regulations,
2. The product which does not contain any smell or taste,
3. Product with good characteristics (look-colour),
4. Certain quality of tap water.

Apart from that, main priorities or conditions necessary to be satisfied by water are:

1. Microbiological safety of distributed water,
2. Maintenance and quality disinfection of water remained in accumulations/reservoirs,
3. Odour, taste or colour prevention,
4. Minimisation of subproducts from the entire process.

The analysis of the water remained in reservoirs waiting for distribution can be a burden for its users. In order to maintain a certain level, it has to be disinfected properly, which increases the smell or taste of chlorine. This problem is the main trigger for using bottled water by consumers. It is crucial for communal enterprises to synchronise their priorities with the consumers' requirements, as well as the retention of consumers' trust in drinking water hygiene. In order to prevent this, it is necessary to develop a strategy or approach which would "foresee" which risk could occur for consumers of this water and "see" which is the current risk while consuming drinking water in its present state.

According to Franceschini (Full Professor of Quality Engineering at Politecnico di Torino) there are three types of product quality:

- Perceived quality – Q_p ;
- Offered quality – Q_o ;
- Expected quality – Q_e .

Perceived quality (Q_p) of a produce, given the example of drinking water distribution, is an effect of innovations applied to the product, according to the customers' requirements (water with less or without taste at all, with no odour, better look etc.)

Offered quality (Q_o) is the quality ensured by the producer itself. Based on the example of drinking water, it has to be:

- Without pathogenic organisms,
- Turby up to the prescribed limits,
- Coloured according to the prescribed conditions. (Francisque et al., 2009)

The rule is that the Q_p and Q_o values are not equal. The reasons lay in various measuring instruments used for product attribute estimation. The consumer's estimation is based on the obvious example based on which the competitors' products are compared to the used one. This can also be a good way for launching a product on market and threatening the competitors. This model leads to the expected quality (Q_e) of tap water compared to the bottled one, since the quality of this water does not live up to the expected quality (Q_p), required by the consumers.

QFD METHOD APPLICATION IN DESIGNING DRINKING WATER QUALITY

Each company producing drinking water has to direct its forces towards changing all the three quality dimensions in order to unify the perceived (Q_p) and expected (Q_e) quality. This should lead to maintaining and increasing market share.

Furthermore, companies also have to compare technical characteristics of tap and bottled water. In order to achieve this, various methods and procedures were developed. One of them is so-called QFD,

i.e. quality function deployment method. This method guarantees that the attention should be paid to the customers' requirements, in terms of good characteristics and homogenized water quality.

QFD is a functional planning method which unifies technical requirements and characteristics of a product through customers' demands. It is a tool, in which use responsibility for product quality lays on all the company's sectors. In water production, this refers to:

- Spring protection sector;
- Water purification plant maintenance sector;
- Production, management and distribution sector;
- Sector for continuous quality monitoring in distribution network.

QFD includes two basic aspects: customers' demands and product characteristics. Customer demands are usually expressed as qualitative characteristics:

- Taste- and odour-free water,
- Good looking water and
- Water with constant quality.

Technical characteristics of a product are successively coordinated with the customers' requirements during the process of product development. At that time, the following aspects transform and become measurable:

- Lack of pathogenic organisms,
- Certain level of turbidity,
- Certain Ph value,
- Chlorine amount etc.

This method has only been recently employed in analysing environmental protection by comparing the environmental issues with the costs and interest groups' requirements.

On the given example of drinking water, various parts of quality house are as follows (according to Francisque et al., 2009):

- **The first component 'WHAT'** – is the customers' requirements (water safeness, chlorine amount in water, water tastelessness and odourlessness, good outlook, homogenized quality etc.) Drinking water can be perceived as a product which the customers have certain expectations or needs for (expected quality – Q_e). Production chiefs have solutions for these expectations (offered quality – Q_o), which they achieve using QFD method mediating between customers' expectations and offered quality by the production management.

Water processing plants usually use the river water. Before distribution, the water is purified in accordance with the quality prescribed by positive legislature, most commonly in treatment chain, composed of coagulation, flocculation, sedimentation, slow sand filtration, ozonization and post-chlorification. (Official Gazette, 1999) Drinking water quality parameters constantly vary in the terms of space and time, from the output point in the processing plant, to the consumers' taps. Also, consumers' impressions vary depending on the location. Therefore, water quality projection has to be monitored from one location to another.

Customers' expectations are a list of basic needs (Figure 1 – the first part of quality house), which have the main role in QFD approach. In this case, the buyers are the consumers who use drinking water supplied through distributive network. They expect safe drinking water, with no taste, odour or bad look. In order to meet all the customers' demands, i.e. expected quality (Q_e) of tap water compared to the perceived quality (Q_p), the demands have to be noted i.e. lists of customers' demands have to be formed.

Customers' requirements are categorized as odor, taste and such. These requirements are used for establishing "WHAT", i.e. odorless and tasteless water, with good look and homogenized quality.

- **The second component** of quality house is “HOW” and it represents the product’s technical characteristics in order to meet the customers’ demands. These characteristics can be divided into two types:
 - The first type is related to water quality assessed during routine testing (water temperature, pH value, colour...)
 - The second type are hydraulic and structural integrity characteristics, like water age, material which the pipes are made of, pipe age, etc.Some of the parameters like pipe material, water temperature etc. have a significant influence on risk from water quality drop.

- **The third component** of quality house is the relation matrix. It represents the way how product characteristics influence the customer satisfaction. It is the relation between each “WHAT” and “HOW” requirement. Defining the relation between “WHAT” and “HOW” is the next step (the third part of quality house on Figure 1.) for prioritizing between “HOW” attributes. Relationships between “WHAT” and “HOW” in quality house are the relation matrix. It is calculated by Pearson correlation coefficients. These relations are defined on the (1, 3, 9) scale and represent weak, medium and strong relations. Observing values in the relations matrices, two different values are chosen for limit values. Relations lower than or equal to the first limit value are weak, ones higher than the first and lower than the second are medium, and in other cases, the relations are strong.

Franceschini (2002.) points out that one has to be absolutely sure that the customers’ demands, not the manager’s wish have greater significance. Thus it is necessary to establish relative significance of every “WHAT” perceived by the consumer.

Traditional QFD methodology prescribes priority degrees of “WHAT”, using the scale from 1 (unimportant) to 5 (irreplaceable) or from 1 to 10. For describing relative importance of conditions in group or category, they have to be defined. One of the methods for establishing the importance level for each new “WHAT” is the AHP method, i.e. analytical hierarchy process.

The classical method used in relationship matrix between “WHAT” and “HOW” attributes and preferential weight of each “WHAT”, is the method of independent sum addition. This method represents the main obstacle in certain cases, since it adds weak relative importance to certain “HOW” attributes which have strong correlation with certain “WHAT” attributes important to consumers, and vice versa. Normalization of relationship matrix values helps tackle these eventual flaws.

- **The fourth component** of quality house refers to competitive comparison and assessment (benchmarking). It is the comparison between product (in this case, distributed drinking water) and other products of the same type (bottled drinking water).

- **The fifth component** represents the ranking of technical characteristics of a product. They represent the influence of each “HOW” requirement on “WHAT” requirement.

- **The sixth component** of quality house is positioned as roof and represents the interdependence between each “HOW” requirement. It defines the number of “HOW”s influencing the forming of product price.

CONCLUSION

QFD method is a quality system for transferring customers’ demands into adequate company requirements at all levels including development, production, distribution, marketing, sales and service, as well as the way of achieving superior quality. It comprises elements of systematic thinking, given that the process of product/service development is looked upon as of system of synergistic action of all the business system parts. Thus, QFD method is a system for achieving quality in that way, which should achieve competitive advantage on market, through maximisation of recognizable

quality. QFD method application helps the entire business system direct towards improvement, in a way which should meet the customers' demands in the best possible manner.

The significance of QFD method application in designing drinking water quality is vast. It gives a great contribution in transferring customers' needs in adequate requirements for distributors of drinking water. It is obvious that the regular communication between the distributors of drinking water and consumers is essential and of vital significance. It helps progressive modification and effective adjustment of actions directed towards keeping and increasing drinking water quality, in order to raise the distributed drinking water quality (the offered quality – Q_o) to that level, where it also represents the perceived quality (Q_p) and expected quality (Q_e).

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SYSTEM OF ECOLOGICAL MANAGEMENT (ISO 14000)

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**ENVIRONMENTAL MANAGEMENT AND ENVIRONMENTAL
INFORMATION SYSTEMS IN EUROPEAN UNION**

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ABSTRACT

The interest for environmental management and environmental performances in organizations is constantly increasing. The paper points out the importance of environmental management systems (EMS) that enables organizations to manage and improve their environmental performance systematically. It should be noted that one of the main objectives of introducing the European Eco- Management and Audit Scheme (EMAS) is to promote balanced and harmonious ecological and sustainable development. The European Agency for the Environment (EEA) is of special significance for the management and control of environmental protection. The standard ISO 14001: 1996 which specifies requirements for environmental management is also very important. In contemporary world, solving environmental challenges depends on the assessment of environmental data from different sources. Therefore, it is crucial for the EU to have an information system based on the latest information and communication technology (ICT) which will provide updated environmental data to decision makers. Shared environmental information system (SEIS) is a joint initiative of the European Commission and European Environment Agency to establish an integrated information system for environmental protection in all EU member states. In this paper special attention will be devoted to this system, since it provides a number of advantages through storing environmental information in electronic databases in the whole EU.

Key words: *Environmental management, EMAS, EEA, SEIS, ISO 14001.*

INTRODUCTION

The interest for environmental management and environmental performances in organizations is constantly increasing. Humanity depends on the natural environment, natural resources and ecosystem services that sustain our health and well-being. Natural resources include both renewables, such as food and biomass, and non-renewables, such as fossil fuels, metals and other raw materials. Ecosystem services include the provision of clean air and water, fertile land and a stable climate. However, the provision of ecosystem services is limited. Some natural resources can be replaced by another. More often, however, this is not the case and once lost a resource may be irreplaceable. This suggests that it is necessary to use natural resources carefully, in order to ensure a safe supply of ecosystem services. European urban areas face a number of environmental challenges: poor air quality, traffic volumes and congestion, high levels of ambient noise and deprivation peaceful areas like sport, play and recreation areas, high levels of greenhouse gas emissions and generate large amounts of waste and waste water. These environmental challenges are serious and have a significant impact on human health, environmental and economic performance. These problems are caused by changes in the lifestyle of the population and less concern for the environmental protection. The EU environmental policy has an important role in the activities of the European Union. It is necessary to emphasize the importance of establishing the European standards in order to ensure the protection and enhancement of environmental quality and rational use of natural resources. One of the major problems facing modern society is certainly the protection of the environment and its improvement through appropriate mechanisms and measures.

THE IMPORTANCE OF ENVIRONMENTAL MANAGEMENT AND ENVIRONMENTAL MANAGEMENT SYSTEM

The importance of protecting the environment is an issue that has emerged as an imperative and a crucial question of modern society. It is necessary to find appropriate solutions for the rational use of natural resources. The protection and improvement of the environment increasingly come to the fore of EU policy with clearly positioned objectives: environmental protection and the improvement of its quality, protection of human health, prudent and rational use of natural resources, improvement of measures for overcoming the regional and global environmental problems. (Bjelajac, Dasic, Spasovic: 2011) An Environmental Management System helps organizations to achieve their performance related to environmental protection. (European Commission) ISO defines EMS as "part of a comprehensive management system which includes organizational structure, planning activities, responsibilities, practices, procedures, processes and resources for developing, implementing, achieving, reviewing and maintaining environmental policy." Multinational and domestic corporations around the world are adopting environmental management systems (EMS) and certifying them by international standards. An EMS enables companies to manage environmental issues in a planned and systematic way and thereby improving their environmental performance. The main objective of the environmental management system is an effective environmental management.

An environmental management system (EMS) is a tool to implement a structured program of continual improvement in environmental performance. The concept is straightforward. It means that large companies, small and medium-sized enterprises (SMEs), and privately owned organizations of various types and sizes can easily apply the principles of EMS. An EMS must include a cycle of planning, implementation, monitoring, and management review stages with regard to environmental risks and impacts. The planning stage includes the identification of environmental, social, health and safety risks and impacts. In the planning phase, the organization must decide how to best mitigate these risks and impacts given the resources available. The implementation stage encompasses the period of institutional learning. Almost in parallel with the implementation stage, the monitoring and review stages require that the organization check its own performance and act when that performance is not appropriate or needs enhancing. Management Systems are now widely adopted offering a number of benefits to public and private sector organisations. (Institute of Environmental Management and Assessment) There are many advantages of Environmental Management Systems: (The World Bank)

- **Environmental Performance.** Company can define and implement adequate environmental policy through EMS. In this manner, companies can identify and manage their impacts on the environment and ensure continuous improvement in the environmental area.
- **Compliance Awareness.** Adoption of an EMS can enable organizations to collect data that they did not previously have. An important benefit of an EMS is its capacity to help improve an organization's performance in developing countries where the regulatory framework may not be as robust.
- **Economic Performance.** An enterprise can make tangible savings quickly and visibly by using an EMS. Through the adoption of an EMS, enterprise can reduce costs such as those for energy, fuel, water, raw materials and waste disposal. Quantification of economic performance improvements due to the implementation of EMS is difficult, but these improvements are significant.
- **Trade Opportunities.** The implementation of an EMS is a way to demonstrate an acceptable level of environmental commitment, which in turn can assist with extending or developing new trade opportunities. Enterprises are using standards ISO 14001 to harmonize competition on the world stage and provide opportunities to trade with organizations in the developed world.
- **Changes in Environmental Attitudes and Environmental Awareness.** Core elements of an EMS, such as training and internal communication on environmental performance, have a positive effect on employee motivation and build the organization's reputation as a good employer, with positive impacts on human resources management and quality. The commitment to continual improvement in environmental performance sends a strong message to important external stakeholders, such as local authorities, regulators, and the local community, that the enterprise uses good practices and is a good corporate citizen.

- ***Risk and Liability Control.*** Financial advantages may include potential lower costs for insurance coverage for pollution incidents, and better control to minimize potential liabilities. This may increase the attractiveness of the organizations as a low-risk investment.

EUROPEAN ECO-MANAGEMENT AND AUDIT SCHEME (EMAS) AND ISO 14000

In the 1970s and 1980s, many corporations have tried to avoid costly and rapidly changing environmental regulations. Therefore, they began to adopt voluntary pollution prevention practices. As more companies began to use pollution prevention techniques and to recognize the relationships among them, some firms started to integrate their environmental management practices into more comprehensive systems. After the Rio Declaration on Environment and Development in 1992, it has become increasingly clear that sustainable development requires the implementation of new technologies in order to reduce the environmental impacts of human activity. Technical environmental innovations refer to the process, product and management innovations that enable the environmental impact of a facility to be reduced. Some environmental policies aim to link environmental management to technical environmental innovation and to improved economical performance in companies. (European Commission) Environmental management has become a core business issue for many organisations. Minimising the amount of waste that is produced, reducing energy consumption and making more efficient use of resources can all lead to financial cost savings, in addition to helping to protect and enhance the environment. (Institute of Environmental Management and Assessment) Environmental management systems have a positive influence on the environmental process innovation of companies. EMS is both an internal management tool and a tool to manage and communicate an enterprise's environmental performance to internal and outside parties, including its workers, partners, local communities, investors, bankers and the general public. Effective communication requires some level of standardization and common understanding. The best known international standards for EMS are the ISO 14001 series and the EMAS. (The World Bank)

It should be noted that one of the main objectives of introducing the European Eco- Management and Audit Scheme (EMAS) is to promote balanced and harmonious ecological and sustainable development. EMAS is a voluntary initiative designed to improve companies' environmental performance. EMAS has been established in 1993. year. This program is available to all companies since 1995. year, but was initially limited to companies in the industrial sector. Since 2001. The EMAS program is available to all sectors of the economy. (Privredna komora Beograd) The aim of EMAS is continually improvement of the environmental performance of companies and other organizations. The result is better management of the environmental issues. ISO 14000 is a set of international standards related to environmental management. ISO 14000 provides practical tools for businesses and organizations wishing to identify and control its influence on the environment and to continually improve its environmental performance. (International Organization for Standardization) ISO 14001 is a voluntary standard to provide a framework for a holistic, strategic approach to the organization's environmental policy, plans, and actions, thereby setting out the basic structure for an EMS. (The World Bank) By mid-2001 nearly 4000 companies have registered under EMAS guide lines in Europe. Many multinational corporations have designed, certified, and implemented environmental management systems under ISO 14001 because it provides a harmonized standard for managing a corporation's environmental impacts. The Eco-Management and Audit Scheme (EMAS) is similar to ISO 14001 in its components and requirements. The main difference between ISO 14001 and the European standard, until recently, was that EMAS was applicable only at the site level, and ISO can be applied to an object, business or organizational level. ISO 14001 and EMAS have different goals. ISO 14001 provides guidelines that can be applied in almost any type of organization in any country and is primarily intended to improve management. EMAS, on the other hand, is designed to bring about changes in environmental performance.

An increasing number of multinational corporations have adopted and certified their EMS. The Ford Motor Company was one of the first multinational corporations to accept ISO 14001 series guidelines. General Motors, Daimler-Chrysler, Toyota and other automobile manufacturers are also requiring all of their manufacturing facilities around the world to adopt EMS and to certify them by international

standards. Ford Motor Company claims to have saved millions of dollars and reduced its environmental impact as the result of having adopted ISO 14001-certified EMS. IBM reports that the worldwide registration of its EMS helped the corporation to validate the abilities of all of its manufacturing and design facilities to meet consistently and effectively the requirements of the corporate EMS and the chances for continual improvement. Certification allowed companies to adopt environmentally beneficial procedures and to emphasize their current and future customers on their environmental achievements. Honda educated its employees about the importance of environmental protection. As a result of EMS implementation, Honda reduced environmental incidents and significantly decreased costs associated with environmental incidents. (Morrow, Rondinelli: 2002)

EUROPEAN ENVIRONMENT AGENCY (EAE) AND ENVIRONMENTAL INFORMATION SYSTEMS (EIS)

The European Agency for the Environment (EEA) is of special significance for the management and control of environmental protection. The EEA is an Agency of the European Union (EU) and one of the decentralised EU bodies. The EEA aims to support sustainable development and to help achieve significant and measurable improvement in Europe's environment, through the provision of timely, targeted, relevant and reliable information to policy-making agents and the public. (European Environment Agency) Environmental policy has delivered significant progress in reducing environmental pollution. The key environmental challenges we face today are not significantly different from those a decade ago - such as air pollution, water stress, environmental protection and waste management. While immediate action is necessary in some cases to address the immediate crisis, the resolution of many of today's environmental problems will require rigorous, long-term efforts. (Environmental Indicator Report 2012) One possible solution of environmental problems is the sixth Environmental Action Programme (6th EAP). The aim of this program is to contribute to a better quality of life through an integrated approach to environmental protection. In addition, the program should contribute to the high quality of life and social welfare of citizens. (European Commission)

There are several software packages that support EMS, some of which are called EIS (Environmental Information Systems). The International Symposium on Environmental Software Systems (ISESS) define EISs as: "Environmental Information Systems is the umbrella term for those systems used for: monitoring, data storage and access, disaster description and response, environmental impact reporting, state of the environment reporting, planning, simulation modelling and decision making". The closing years of the 1960s mark the beginning of the environmental movement, and the arrival of the "Environment" on the international agenda. The Stockholm conference on the Human Environment (1972) is often used as a "starting point" for the development of environmental awareness among the people. The main result of this conference was the creation of the United Nations Environmental Programme - UNEP. A key goal of UNEP is to collect data and information about the state of the environment, in order to resolve potential problems as soon as possible. EIS are very important for environmental research and require the use of modern information technology. IT is a convenient term for including telephony, computer technology and embedded systems in the same word. By the end of the 1970s, GEMS (Global Environment Monitoring System) had created INFOTTERA - the International Environmental Information System. However, the use of computers for environmental research dates back to the late 1960s. Computers are increasingly used in various fields in ecology-from global warming to biodiversity in hydrology. Thus, modern technology is used in almost all aspects of environmental protection. Computers became more available, due to lower costs and ease of use. A large number of environmental data was collected, processed, stored and analyzed through the use of modern information technology. Information Technology (IT) casts a shadow over almost every aspect of the "Environment" debate: research, monitoring, management and, ultimately, decision making and public involvement in decision-making. EIS is a collection of data sets and information that have some relevance for the study and/or monitoring and/or exploration of the environment. The most important problems associated with the implementation of the EIS are: (Haklay: 1999)

- **Lack of money**- High costs of EIS- Information technology is expensive. The biggest expenses are costs related to the purchase of hardware and software, and costs of maintenance

- **Information overload**- A major problem is to get important information out of the huge amount of environmental information that is being collected every day.
- **Information sharing**- Information sharing can be divided into two aspects: organisational and technical. On the organisational side, there is a problem of accessing information that was collected by private organisations. A scientist or a group who have spent many years and resources in collecting environmental information usually regard it as their “own” and are reluctant to share it. The technical aspect is a combination of issues, including: data format, different observation sets, lack of documentation, data volumes etc.

SHARED ENVIRONMENTAL INFORMATION SYSTEM (SEIS)

In contemporary world, solving environmental challenges depends on the assessment of environmental data from different sources. Therefore, it is crucial for the EU to have an information system based on the latest Information and Communication Technology (ICT) which will provide updated environmental data to decision makers. Relevant and reliable informations about the environment are absolutely essential for decision makers to respond to the environmental problems of our time. It has to be a way to improve collecting and analyzing environmental information. Without improved collaboration between European public sector organisations, growth and security, jobs and freedom or health and a safe environment will be more difficult to achieve. Timely informations about the environment are very important, especially in an emergency. Tackling today's environmental challenges such as adapting to climate change, managing ecosystems and natural resources in a sustainable manner, protecting biodiversity, preventing and managing environmental crises such as floods, forest fires, and water scarcity depend on the assessment of data from a variety of sources. The main challenge for the EU is to integrate a large number of collected environmental data with existing social and economic data. These data should be presented in a way that policy makers and the public can easily understand and use them. In addition, Member States and institutions in EU should have effective and modern reporting system on the environmental data. Shared Environmental Information System for the European aims to address these challenges.

Shared Environmental Information System (SEIS) is a joint initiative of the European Commission and European Environment Agency to establish an integrated information system for environmental protection in all EU member states. This system should integrate all existing data collection systems and information related to environmental protection in the EU. Collecting data will be associated with technologies such as the Internet and satellite systems. In this way, the environmental information will be more accessible and comprehensible to users. The basic aim of SEIS is to move away from paper-based reporting to a system where information is managed as close as possible to its source and made available to users in an open and transparent way. SEIS will take advantage of the possibilities provided by information and communication technology. (European Commission) The Sixth Environment Action Programme (6EAP) confirmed that sound information on the state of the environment and on key trends, pressures and drivers for environmental change is essential for the development of effective policy and its implementation, and for empowering citizens more generally.

Timely, reliable and relevant informations on the state of the environment are essential for environmental policy. Public and policy makers need to know in a timely manner how the climate is changing, whether European waters are becoming cleaner or more polluted, how nature is reacting to pollution and whether policies are effective. This information should be available to everyone at the right time in the right place. As the environment is a public good that belongs to everyone, it is crucial that these informations are available to everyone. More than 70 of the several hundred pieces of environmental legislation in force in the European Union require Member States to report on specific aspects of the environment within their territory. EnvEurope was conceived synergistically dealing with several key targets and in response to challenges of research within the Long-Term Ecosystem Research in Europe site network (LTER-Europe). The project has been structured to play a role in the conceptual and operative context of the Shared Environmental Information System (SEIS) promoted by the European Commission and in the development of some components of the Global Monitoring for Environment and Security (GMES), a joint initiative of the European Commission and European

Space Agency. Within this context the project intends to lay the foundations for a more integrated system for successful long-term ecosystem research and monitoring at the European level, focused on understanding status, trends and changes of environmental quality and on the elaboration of relevant detection systems and methods. (EnvEurope Project)

THE BENEFITS OF SHARED ENVIRONMENTAL INFORMATION SYSTEM (SEIS)

Shared Environment Information System (SEIS) will improve the collection, exchange and use of environmental data and information in the EU. In order to facilitate the implementation of an integrated information system, existing processes have to be modernized and simplified. EEA is a leading proponent of SEIS, plays a crucial role in collecting and providing environmental information, and manages or participates in many current European and global initiatives contributing to the implementation of SEIS principles. Ecological data and informations are widely collected, analyzed, shared and used for a variety of purposes throughout Europe. This data and informations help European policy makers to develop and implement environmental policies. As the environment is a public good, citizens have a right to widely available environmental information. European businesses use environmental information to track their impacts on the environment; predict future supplies of resources needed for operations; or as an incentive to develop innovative solutions for environmental problems. Therefore, a key goal of SEIS is to maximize and expand the use of informations. The condition for the achievement of this goal is open and transparent share of data related to environmental protection. SEIS is based on the following 'principles': Information should be: (European Commission)

- managed as close as possible to its source;
- collected once, and shared with others for many purposes;
- readily available to easily fulfil reporting obligations;
- easily accessible to all users;
- accessible to enable comparisons at the appropriate geographical scale, and citizen participation;
- fully available to the general public, and at the national level in the relevant national language(s);
- supported through common, free open software standards.

SEIS is now a collaborative initiative of the EC, and the EEA and its „Eionet,, (European environment information and observation network) of 38 countries. In fact, its implementation is now at the centre of the EEA's 2009-2013 Corporate Strategy and daily operations. EEA plays a crucial role in collecting and providing environmental information with the help of Eionet. Since 2007, EEA has conducted around 50 „SEIS Country Visits,, to member and cooperating countries and European neighbours, to explain SEIS, its benefits, encourage implementation and identify existing SEIS-compliant activities at the national or regional level. The main benefits of SEIS are: (European Commission)

- **Better regulation, better policy** - SEIS will simplify the reporting and accessing of environmental information. Simplifying access to environmental information is an essential element of making better legislation. Relevant and timely information is crucial for better policy. Reducing the administrative burden must lead to an improvement in the quality of public policy and regulation. This will improve the effectiveness of environmental policy, lead to the management of natural resources in a sustainable manner and prevent ecological crisis. SEIS will provide European citizens with useful environmental information in their language, thus enabling them to make informed decisions on their environment, including in cases of emergency and to influence public policy.
- **Simplification and Efficiency** - SEIS is a decentralised information system based on data-sharing. It will offer Member States and EU institutions a modern and efficient electronic system to fulfil their reporting obligations related to EU environmental policies. By doing away with paper reporting, the process through which environmental information is made available will be easier, more flexible and more efficient. A system like SEIS will contribute greatly to international initiatives and programmes for collecting, managing, and using environmental data

and information such as GEOSS (Global Earth Observation System of Systems), biodiversity conventions, Millennium Ecosystem Assessment, UNEP's Earth Watch, and others. An additional benefit would be the reduction of the administrative burden and consequent cost savings from improved efficiency. SEIS should use all the advantages of modern information and communication technologies, such as the Internet and satellite systems. One of the major advantages is that ICT provides real-time data which can be used for fast decision making.

- **Boosting Innovation and Intelligent eServices:** eEurope, eGovernment, eEnvironment - SEIS will boost the development of intelligent e-services (e-Government, e-Environment, e-Reporting) by taking advantage of data sharing infrastructures.

CONCLUSION

One of the key goals of modern society is to increase ecological awareness on a global level. The adoption of environmental management systems (EMS) as a framework for the integration of corporate environmental policies, programs and practices is growing among domestic and multinational companies around the world. The growth of EMS as a process for integrating corporate environmental policies and programs has been quite rapid over the past decade. EIS play a major role in making decisions about the environment. The development of these systems is closely linked to the environmental awareness in past five decades. Today it is almost impossible to think about environmental research without relying digital technology. The use of ICT should improve cooperation between the organisation and to facilitate communication with civil society as a whole. According to the SEIS concept, environmentally-related data and information will be stored in electronic databases throughout the European Union. These databases would be interconnected virtually and be compatible with each other. The proposed SEIS is a decentralised but integrated web-enabled information system based on a network of public information providers sharing environmental data and information. The main goal of SEIS is to create a decentralized but integrated environmental information system based on a network of public information providers that share environmental data and information. This goal can be achieved through the rationalization of existing information systems and processes, thereby improving quality, availability, accessibility and understanding. It should be noted that there are many advantages that are achieved by implementation of SEIS: better environmental regulation and better environmental policy, simplification and efficiency, innovation and intelligent e-services.

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ECONOMICS OF SUSTAINABLE DEVELOPMENT OF URBAN AREAS

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**PARAMETERS OF MICRO-LOCATION AS A FUNCTION OF THE
ENERGY EFFICIENCY OF BUILDING**

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ABSTRACT

As architectural objects are large consumers of energy, primarily for heating and cooling, the energy efficiency of buildings is becoming increasingly important. Location and micro-locations are one of the primary determinants of the relatively high consumption or energy savings of buildings or neighborhoods. The parameters of the micro location, such as relief, orientation and others who contribute to the micro-climate of the location significantly affect the energy requirements of buildings primarily through the influence of temperature changes, wind and solar radiation. This is manifested through the heat losses and gains, which determine the energy consumption for heating or for cooling devices. This paper considers the parameters of the micro-locations, which lowers the energy needs of buildings and settlements, with a heat-providing comfortable and affordable health conditions.

Key words: micro-location, microclimate, energy efficiency.

INTRODUCTION

Even in the seventies began, the energy crisis on the global level, due to the rapid technological and industrial development, which has resulted in the high energy consumption, especially of fossil fuels. Thus there is the need for economical use of energy and energy saving and improvement of sustainable development, in line with the energy-efficient and environmentally sound technologies³.

Energy efficiency of buildings, as the status of buildings to consume less energy, while ensuring primarily thermal, and other comfort and to prevent the occurrence of building damage, is one of the most important aspects of sustainable construction. The less power consumption contributes to the economic stability of the country, to the environmental pollution reduction and ultimately higher living standards.

Favorable for achieving thermal comfort in winter, the heat needed for heating buildings depends on the size of the transmission and infiltration heat loss, and the degree of internal and solar heat gains. In the summer, potential required energy to run air conditioners depends on the heat gains. All gains and losses, other than internal, are conditioned, besides other, by climatic influences, most notably characterized by the location of temperature, wind intensity and the intensity of solar radiation. So the air as one of the main features of the sites, together with the geometrical and thermal-protective characteristics of the building envelope, affects the energy needed for heating in winter and cooling in summer.

Micro-location is characterized by particular microclimate with local climate impacts of space, derived from a set of factors such as exposure to sun and wind, and it depends on the configuration of the

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relief and micro-location and orientation of the building. Therefore, in this paper the methods of selection and organization of urban micro-location as the primary determinants in the design of energy efficient buildings and settlements are explored.

IMPACT OF PARAMETERS OF LOCATION' MICROCLIMATE

For buildings energy efficiency two groups of micro - location parameters are important: natural and created (Bogdanovic, 2005). The group of natural factors include climatic conditions: air temperature, solar radiation and wind, then the topographic characteristics of the location and configuration, and the group of created factors: building orientation, mutual position of objects, their architectural form and vegetation.

The air temperature is one of the basic elements of the climate, and it depends on the intensity of solar radiation reaching the Earth's surface. Low outside temperatures in winter cause the need for heating, and high outside temperatures cause the need for cooling the building. The amount of solar energy that reaches the surface of some of the day depends on the latitude, altitude, season, time of day, weather conditions, and orientation, slope, and surface area.

Insulation is an important factor in planning urban areas, which should be used properly and in the winter and the summer. In the winter, heat gains appear in buildings from the sun, which size depends on the orientation. In Table 1, the percentage of annual values of solar radiation in other orientations relative to the south, in Serbia, calculated with the corresponding values of the Regulations on energy efficiency in buildings RS are presented.

Table 1: Annual values of solar radiation

orientation	Qs (kWh/m ² g)	Qs /Qs south (%)
S-south	455	100
I-east, W-west	310	68
N- north	145	32

These data clearly show the advantage of orientation of objects in relation to the world. A similar conclusion can be obtained for the exposition site. If the site is located in the so-called southern slope, intensity of solar radiation will be higher, the temperature increased and microclimate favorable.

The necessary energy from the sun is affected by the relative position of objects, and the distance between them. It reflects the length of the shadow thrown on the objects. With sloping terrain to the south length of the shadow thrown is reduced and the on sites sloped to the north it is extended, so they are very adverse. In the summer, due to high environmental temperatures and insolation, the air temperature in the building can be high, and they need adequate protection.

Impacts from the building may be different, depending on the climate and structure of micro-locations. The effect of wind on the building depends on the speed and direction, composition, micro-location, possible protection by trees and other objects, as well as the height to the ground (Bogdanovic, 1997). At a certain micro-location on different building floors there are different pressures of the wind from the building, because the wind speed is different at different heights from the ground.

In addition to contributing to the exchange of heat between the outside air and the exterior surfaces of bulkheads, wind also causes the heat transfer due to air infiltration through the pores and exterior compartments' seals, as well as through the joints of the frame and sash windows and exterior doors. Infiltration heat loss can be very different, depending on the micro-location, type of construction and sealing windows. Influence of micro-location is reflected in the number of air changes depending on the wind exposure of the building, which can be seen from Table 2, according to the Regulations on energy efficiency in buildings RS. The table presents the percentage values of the number of air

changes per hour in wind exposure over a medium tightness of facades and windows, compared to a sheltered position.

Table 2: Relates of the number of air changes depending on the wind exposure of the building

Facade exposure to wind	Number of air exchange n (h-1)	%
Open site building	0,7	140
Moderately sheltered position	0,6	120
Very sheltered position	0,5	100

Data in the table show that there is a significant difference in the size of the ventilation rate, and therefore the infiltration heat loss in the event of exposure to different buildings wind. Wind adverse effect on the microclimate of the settlement and causes higher energy consumption for heating, which is particularly evident in the simultaneous effects of wind and rain. In addition to increasing energy costs, wind lowers temperatures and sensitive urban areas. The intensity of the wind on a building depends on its shape and position in relation to the wind direction (see Figure 1), (www.erg.ucd.ie). Favorable orientation of the object can reduce wind pressure on its facade, since objects can affect the movement of air currents by their shape, dimensions and mutual positioning.

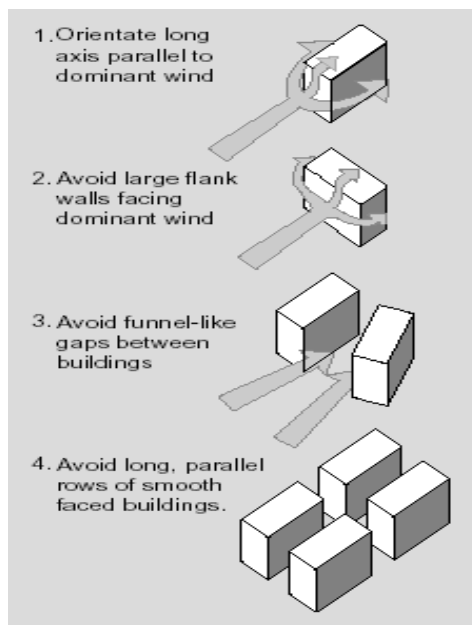


Figure 1. Effect of wind relative to the orientation of buildings

Objects that are placed in elevations are exposed to higher wind gusts. The influence of wind is most pronounced at the top of the hill, on the opposite sides are formed by wind leeward. Position of streets and buildings affects the change in the direction and speed of wind flow, creating a lee (Pucar, 1994). The microclimate of location is favorable if the temperature is higher in winter and wind speed is lower, and at the same time the energy for heating is also less.

Green space can improve the microclimate of urban sites paved with blocks, which are exposed to the winds and moisture in the winter and to the high temperatures in the summer. Screens facilities produced by other objects or by vegetation, can significantly affect the energy consumption. Properly planted vegetation can reduce energy consumption for heating and cooling by as much as 25%. U.S. Department of Energy is based on a computer model came to the forecasts that the average household tree planting only 3 save 100-200 \$ per energy basis, the return on investment for 8 years (www.eere.energy.gov).

PRINCIPLES OF MICROLOCATION' URBAN ORGANISATION

Given the impact of micro location parameters on energy efficiency of buildings, a set of principles should be followed when choosing the structure and organization of urban micro location.

From the standpoint of exposure to sunlight in order to have larger heat gains in winter, the slopes turned to the south are most suitable for settlement building, because they provide more exposure to sunlight, high temperature, and improved microclimate. According to Bogdanovic, 2005, an ideal location for building is faced 12° compared to the south, south-east-west, provided there is no interference on the southern horizon. South slopes in the winter gets about 10-30% more than the total radiation in the same northern climate.

Streets should be placed in an east - west, in order to be able to orient more objects with their long sides towards the south. At the same time, the building should be placed on the distance as large as possible so that those objects on the south side do not interfere with those of northern sunlight. If the street is set in a north - south direction it is important to provide more insolation to the objects that are oriented in an east-west direction, which can be achieved by shear objects, then placing the plot at an angle and turning the main part of the building to the south or southeast. Dual buildings along the streets of the east-west should be staggered so that buildings on the north side of the street were more sunny (see Figure 2), and the orientation of north-south streets can apply key subdivision.

If a street is running east-west, row buildings can get enough sunlight on the south side, and the buildings on the north side should be drawn to the inner courtyard and their balconies should be set on the south side. In the case of the streets set towards the north-east it is favorable apply shear objects (see Figure 3) (Pucar, 1994), and in the case of streets turned to the northeast-southwest direction it is necessary to withdraw the houses from the north-west side of the street facade and rotate them to the south.

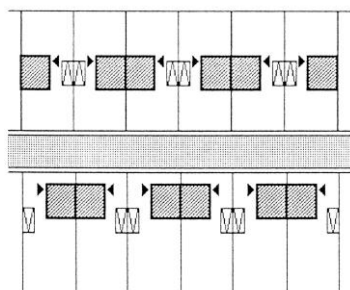


Figure 2. The position of detached houses along the street in the direction of E-W

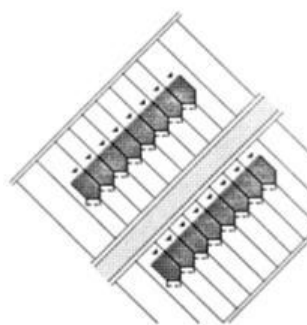


Figure 3. The position of row houses along the street in the direction of NE-SW

The best position of the lot is on the bottom of the street that runs in an east-west (see Figure 4). It is recommended that living rooms should be placed on the ground floor on the south side, to use as much solar insolation, and service rooms should be on the north side. Heat gains from solar radiation can be up to 10% in continental areas, and up to 20% in the south.

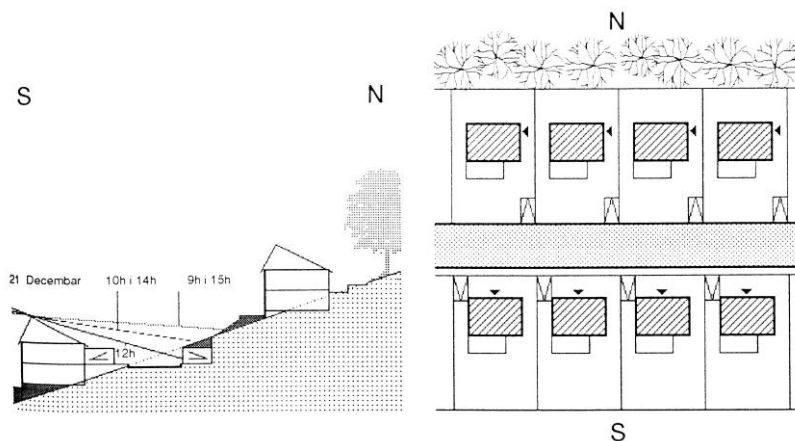


Figure 4. The objects' position on the south slope along the street in the direction of E-W

Different typological models of low-rise residential buildings should have different positions in order to energy efficiency. Thus, the individual housing plots have the best position on the south side of the street, because the living room is to the south, and the north side rooms. If the street is turned to the north - south, objects should be placed staggered so that all objects can use the winter sun. In the case of streets turned to the north-south direction, all objects are allowed to have the longer facade oriented to the south, and thus to receive a greater amount of energy from the sun.

In the case of south sloping terrains it is possible to reduce the distance between objects, while on the northern sloping terrains it is necessary to reduce the height and increase the distance of objects. Slope of 3-6% is optimal for the construction of buildings.

Heat gains should be used by appropriate intervention measures of passive solar energy. In order to maximize the energy of the sun, it is necessary that the southern facade of the building is not protected by anything.

Building should be avoided in particularly exposed windy areas. We should also not lose sight of the appropriate needed air infiltration from health and hygiene reasons, the purpose of ventilation of the building. In order to less expose objects to the wind, they should not be placed perpendicular to the direction of action of the wind, but at 45 ° (time pressure is reduced by 50%), or should be placed one behind the other.

In the hilly terrain configuration, close to the river and the sea, where there is greater exposure to wind, it is possible to set up firewalls, then an object as a windbreak for the rest (Bogdanovic, 2005), to plant high greenery as a protection, and it is preferable building houses in compact units.

Trees with high crown should be planted as close to the south side of the building to improve ventilation and to prevent the diversion of the flow of air upward. In this way, the roof temperature is reduced during the day and radiation is reduced during the night. Medium vegetation should be placed as close to the house to boost the flow of air to the interior. Trees should not be planted too close, because it can inhibit the penetration of sunlight to the object. Combining coniferous and deciduous trees maximum opacity can be achieved. It can also prevent wind blow and allow maximum penetration of solar radiation and light (see Figure 5), (www.erg.ucd.ie).

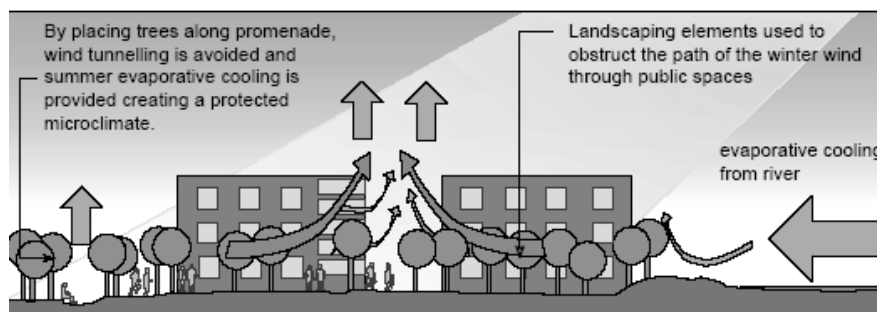


Figure 5. The influence of vegetation on air temperature

On windy sites, as on the upper floors, windows should have greater tightness. For this Adequate windows distribution can allow cooling in the summer and heat gains from the sun in the winter.

CONCLUSION

Significant micro-location parameters that are important for the energy efficiency of architectural structures, rational consumption of energy for working the heating and cooling systems, for achieving a favorable thermal comfort, are following: air temperature, solar radiation and wind, then the topographic characteristics of the location and configuration, as well as orientation and relative positions of objects, their architectural form and vegetation. In order to minimize energy consumption, it is necessary to maximize the potentials of the site, and to minimize the negative impacts, so that heat loss from the building are reduced in the winter and that heat gains from the sun are sloped, and in the summer it is necessary to prevent heat gains from the sun and allow maximum heat dissipation from the facility.

It is possible to contribute to greater heat gains from the sun and protection from the dominant winds by favorable orientation and the better use of existing configurations and other parameters of the micro- location, which leads to less energy requirements of buildings. Thus, when new buildings or settlements are constructed, site selection is the primary determinant of their energy performance and energy efficiency.

In line with the climatic conditions in our country, in the case of new planned objects and settlements these recommendations should be applied in order to create energy efficient buildings and for existing residential objects it is necessary to make energy recovery, which is the current trend in many developed countries.

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**STORAGE AND USE OF BIOMASS FROM MUNICIPAL SYSTEMS
FOR ENERGY PRODUCTION***

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ABSTRACT

Biomass as a renewable source of energy in the last ten years is a convenient and reliable way of obtaining energy in most EU countries. Numerous scientific and practical research is aimed precisely at the possibility of using various forms of biomass as a potential energy source. The paper provides basic guidelines for the storage of biomass, plants for pyrolytic combustion of municipal waste and system analysis for combined heat and electricity production using biomass as fuel.

Key words: *biomass, storage, energy usage.*

INTRODUCTION

One of the priorities of sustainable development is the replacement of fossil fuels by renewable energy sources including biomass, which is the first priority of the Energy Strategy of the Republic of Serbia until 2015. At the present level of development of technologies for the use of renewable energy, biomass has the greatest potential and prospects, primarily due to the energy crisis, the limited reserves of fossil fuels and environmental pollution due to the use of fossil fuels.

The energy obtained from solid biomass has multiple opportunities in different applications. Technologies of biomass use for energy purposes are focused on its direct combustion or gasification and then combustion. Certain technologies from biomass can produce liquid fuels (bio-diesel, bio-ethanol, etc.). Torefaction, palletization and pyrolysis can convert biomass with moderate concentration of energy in a bearer of concentrated energy that is easier for transport and handle. A well-planned biomass supply chain with appropriate preparation technology can significantly affect the cost of energy produced from biomass.

For energy use of biomass needs that available biomass be collected, prepared and transported to the appropriate location. The preparatory process of obtaining energy from biomass has a significant impact on the efficiency of the supply chain of bioenergy, particularly in logistics.

Some countries have lower population density than other, so they can be suppliers of renewable bioenergy, only. The production costs energy from biomass in such countries may be low, but we cannot ignore additional logistical costs, used energy and material losses. Research shows that opportunities for preparation technologies improvement and their new influence to the overall chain of bioenergy are not thoroughly tested.

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BIOMASS FROM MUNICIPAL SYSTEMS STORAGE

Storage we use for protection, preservation and arranging stocks in accordance with the requirements of delivery and dispatch (inflows and outflows). It can also be viewed as electrical substation of company logistics network. The main tasks of storage consist:

- providing continuity of production processes and the continuity of supply for consumers,
- preserving and protecting the goods from damage and loss,
- improving the utility of product characteristics (biomass dry),
- providing efficiency of procurement and so on.

The success of performing this tasks depends on several factors, the most important are: the location of the storage, storage capacity, storage technology and organization of storage operations.

The economy of the storage reflects in the choice of the correct storage form and type and in determining capacity and the level of mechanization and automation in storages. Storage economics contained in an economical exploitation of existing storages. The choice of the storage kind and of determination of their capacity is carried out during the design storage process.

With selecting storage according defined criteria and the type of storage we get optimum storage. Storage of biomass from municipal systems should be carried out in the most rational way, taking into account the volume of landfill space, volume and balance of biomass and transport routes. The basic functions of storage for biomass energy use are given in Figure 1. For biomass waste is characteristic that bulky - have a small bulk density and occupy a large volume in storage. In order to facilitate the collection, storage and exploitation of biomass is usually done baling, briquetting, etc. This significantly increases the storage density and energy density per m³, and also makes it easier to manipulate when dosing into the firebox.

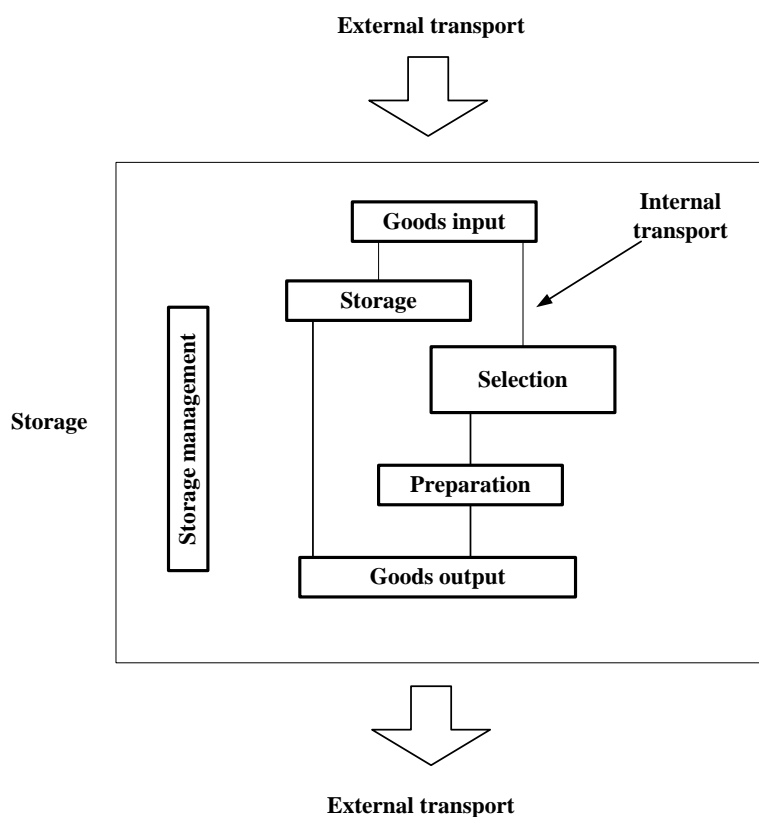


Figure 1. Biomass storage areas

TECHNOLOGIES FOR BIOMASS FROM MUNICIPAL SYSTEMS USE

More recently in Serbia there is a growing interest in biomass technologies, in particular in terms of solid fuel combustion. Due to the widespread availability of biomass, utilization systematically increasing, especially in the rural areas of Serbia. Growing interest in the use of biomass and co-generation of energy will follow the policy of the EU, which aims to increase the share of energy from renewable sources.

Biomass energy derived from the following processes: combustion of lattice or in fluidized bed co-combustion with other fuels, gasification and pyrolysis. Biomass combustion is the most popular technique for the production of energy, so because of that developed a different design of furnaces for burning solid biomass. Apparatus for combustion of solid biomass are different capacities, ranging from small domestic stoves from 1 -10 kW to large boilers used in combined plants (> 5 MW).

There are different types of biomass: firewood, chips, sawdust and other wood residues without any preparation, pellets, briquettes, biofuels that are produced specifically by increasing their bulk density, etc.

Sawdust is usually in sawmills and other wood processing firms. Larger chips can be manufactured specifically for use as fuel to produce electricity or heat. Intentional production is usually for domestic purposes. Typical technology for the production of wood chips are shown in Figure 2. These are the machines of different capacities and different options. Some of them are cutting thin branches for the needs of a household (Figure 2a) with a capacity of 6-10 m³ / h, while others are for cutting thin stems (Figure 2b) with a capacity of 100 m³ / h. The technology for the production of chips, according to the available information has not been implemented in Serbia (Energy Saving Group, 2008).

Lack of informations and promotion of biofuel use, particularly forest residues, is probably the main reason why these technologies almost not in use.

a)



b)



Figure 2. Machines for making wood chips (IEA., 2006)

Briquettes and pellets production is in expansion. Briquettes are larger in size, usually 60-100mm diameter and length of 20-200mm. Because of its relatively large size briquettes, unlike pellets, are not suitable for small and medium boilers with automatic feeding. Briquettes are suitable for boilers and furnaces with manual feeding. Because of its weight and size pellets are more prone to breaking and disintegration of the pellets. For this reason, pellets are the most interesting as fuel (Markovic, 2010). In Serbia today there are briquette producers, but their production is relatively small, although the production of wood pellets is in the expansion.

The pellets can be produced from wood waste that is pure wood, and can be produced with additives, again taking into account the maximum content of harmful substances. Pellets should have a declaration with the specification, and the pellet price in the market is higher if the raw material is pure wood pellets. However, the usual practice is that the pellets produced without the addition of a binding agent (a glue or resin). Technology of pellet production should fulfill the basic requirements of quality products, and it is resistant to breakage and decay in storage and transport. Some European countries, where pellets are consumed in large quantities, have adopted a very detailed standards for quality pellets (Sweden, Austria, Germany).

In Serbia mainly applied thermo energetic plants that burn biomass directly in furnaces with stationary flat grate. Although there have been attempts to modernize these plants, with built systems in which applied combustion technology on an incline and vertical grid, in the cyclone furnace or fluidized bed, none of these solutions has not found wide application in practice.

PYROLYTIC BIOMASS COMBUSTION

Biomass waste combustion should be carried out in specially for this purpose constructed boiler with a moving grate (Rosti) and special channels for the circulation and recirculation of air. The air required for combustion supplied below and above the grate and the combustion process realizes in one place and in a few time, including separated phases (Kozak, 2009):

1. drying,
2. evaporation,
3. combustion of volatiles,
4. combustion of related carbon,
5. final combustion.

Unlike conventional combustion, pyrolytic combustion biomass waste characterized by two simultaneous, but spatially distinct phases. In pyrolytic chamber which containing the entire waste that is incinerated realizes process of incomplete combustion. With insufficient amount of air at a high temperature evaporates volatiles and waste. These gases, along with other products of incomplete combustion going in the burning chamber where with sufficient amount of air completely burn and creating flue gas with high temperature. Due to the partial similarity with known chemical methods of pyrolysis (decomposition and evaporation of the fuel at high temperature in the absence of air), thus burning waste process named: pyrolytic combustion. The next phase realizes in the heat exchanger where flue gases are cooling and heating water or steam, releasing useful heat (Kozak, 2009).

A detailed scheme for the pyrolytic combustion plant and waste heat utilization of flue gases is given on Figure 3. These plants are important for the incineration of waste, energy use and environmental pollution, both air and ground and underground streams.

Plants for combined heat and electric energy production from biomass

Cogeneration is a common name for the simultaneous generation of usable heat and electricity in an process. Cogeneration principles have been known for a long time, and the technology is improving and developing for years. The application of cogeneration systems are primarily considered due to their high energy efficiency and related environmental and economic benefits.

The advantage of the combined facilities of the plant is its overall high efficiency (80%) compared to the levels of separate plants for the production of heat (85%) and electricity generation (35%). Higher efficiency means less fuel consumption and lower fuel consumption for a given amount of available wood waste means higher production of heat and electricity. Electricity produced in enterprises can be used to meet their own needs, or can be submitted online and sold. For this reason these companies are generally interested in increasing the production of electricity, after satisfying their need for heat.

Fuels that can be used in combined plants are different: natural gas, coal, light oil fuel, solid and gaseous biomass and waste fuels. Biomass in terms fuel for energy production (electricity and heat) is a biodegradable material made in agriculture, forestry, and supporting industry and household and includes: plants and parts of plants, plant residues and by-products created in agriculture (straw, corn stalks, branches, stones, shell), the remains of animal origin arising in agriculture (feces), the remnants of forest plants (residues deforestation) and biodegradable residues in food and the timber industry, which does not contain hazardous materials.

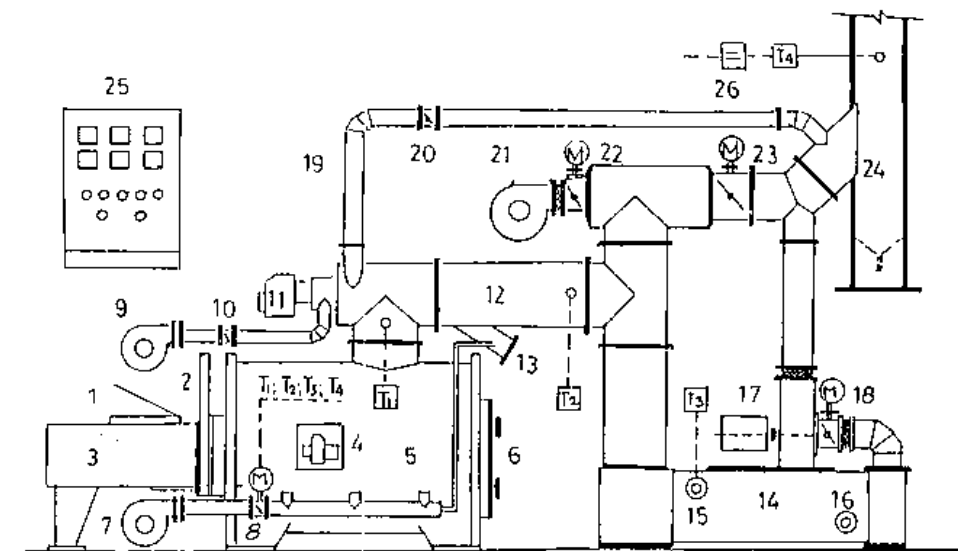


Figure 3. Pyrolysis plant (Kozak, 2009)

- | | |
|--|--|
| <ol style="list-style-type: none"> 1. The opening and cover for waste receiving 2. Sliding door between the press and the pyrolytic chamber 3. Hydraulic briquetting presses 4. The burner fire 5. Pyrolytic chamber 6. Large boiler door 7. Primary air ventilator 8. Motorized valve for controlling the primary air 9. Secondary air ventilator 10. Amount of secondary air manual control 11. Pilot burner to support combustion process 12. Flame chamber | <ol style="list-style-type: none"> 13. Visual flame control 14. The heat exchanger 15. Output of primary water 16. Input of secondary water 17. Flue gas ventilator 18. Open for regulating pressure in the system 19. Pipe for flue gas recirculation 20. Amount of recirculated gases manual control 21. Ventilator for flue gases cooling 22. Clamping louver 23. Clamping louver for air and flue 24. Flue gases in the chimney drain 25. Measurement - control road 26. Air pollution control |
|--|--|

The combined production of heat and electricity from biomass can be achieved through the following processes:

- Direct combustion of biomass in boilers with a grill or in a fluidized bed, which are associated with the low pressure steam turbine;

- The production of wood gas and its combustion in steam boilers that are connected to a steam turbine and a generator.

Other technologies including combined systems using Stirling engines, biomass direct combustion systems with gas turbines and heat regeneration, and the biogas systems which are still investigating. Combined heat and power production can be achieved not only in large installations, but also approved at small and medium-sized systems. The great potential of biomass, new energy policies and economic problems are the cause of increasing interest in the use of not expensive but reliable technology for combined heat and power production at the local level.

An example of the use of biomass for heat and power combined production shown in the following: the assumption is that it will produce energy that is sufficient to cover the required energy for a region that covers 18,060 hectares with 4000 people (European Commission Green Paper, 2006). Most part of the region is covered by forest area 4620 hectares and has a high yield of natural biomass: annual yield of wood (sawdust, wood waste, etc.) estimated at about 10400 t. Total energy needs and characteristics of consumers and their energy demands are the main factors that influence the selection of suitable biomass for heat and electricity. It is assumed that needs for electricity is 1.2 MWe and for heat about 6MWt.

The fuel that will be used for the combined production is biomass (wood residues). Total combined production level of usefulness depends on biomass conversion technologies, types of biofuels, conversion efficiency and techno-economic factors. Analysis for cogeneration system shown in Figure 4.

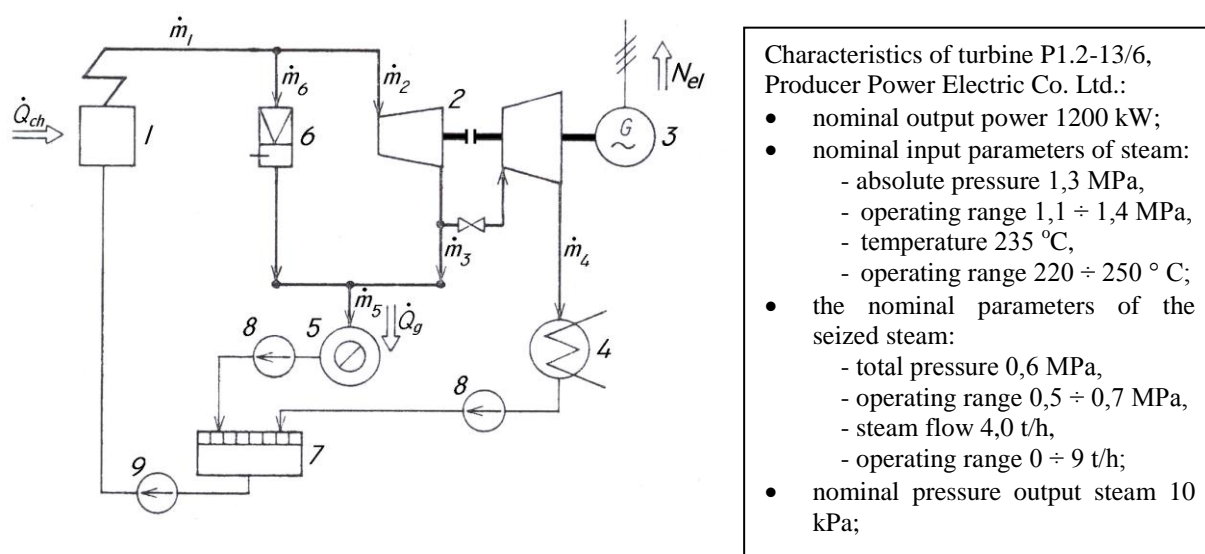


Figure 4. Biomass cogeneration system

1-boliler, 2-turbine, 3-generator, 4- condenser, 5- cooler, 6- reducer-cooling station, 7- condenser, 8- condensate pump and 9- feed pump

The calculation was conducted for the nominal parameters of the turbine. The resulting heat is using for heating and preparation hot water, with the assumption that 10% of the heat will be used for hot water preparation. To simplify the calculation, it is assumed that the system operates with an efficiency which corresponds to the average temperature of the heating period of 4° C. Calculated average amount of heat needed for a given system is 3000 kW. During the heating season seized steam was not enough to cover the required temperature for the heating, system equipped with a docking-station cooling, which is used to cover peak loads. Total system efficiency is 76.4%, and 63.7% thermal efficiency.

If we assume that the price of biomass (wood residues) 63 €/t, the annual amount of biomass that will be burned in a cogeneration plant 15,750 tons, the total operating costs of biomass amount will be €

992 250. Comparing biomass burning with coal burning that cost is 175€/t, we can conclude that the total annual cost of coal increased by 40% compared to the combustion of biomass. Incentive prices of electric power in Serbia which produced using renewable energy sources in cogeneration plants given in Table 1.

Table 1: Incentive tariffs for electricity production from biomass and biogas

Plant type	Installed power P (MW)	The purchase price (cEUR/kWh)
Power plants using biomass	to 0,5 MW	13,6
	from 0,5 to 5 MW	13,845-0,489·P
Power plants using biogas	from 5 to 10 MW	11,4
	to 0,2 MW	16,0
	from 0,2 to 2 MW	16,444-2,222·P
	over 2 MW	12,0

CONCLUSION

Regular realization of power supply is the main goal of any society and depends on the providing of safe and reliable energy sources. More intense and more streamlined development of renewable energy sources in Serbia could improve the energy situation and reduce costs of fossil fuels import. Requirements for energy in Serbia are in complete disproportion to the actual stocks, which causes great import. This problem can be partially solved using biomass energy at the local level, with the inclusion of utility systems for organized collection and storage.

EU rapidly implement the policy of increasing use of renewable energy sources. For biomass use for energy needs to the available biomass be collected, prepared and transported to the appropriate place for energy utilization. Renewable energy from biomass provides about 4% of the primary energy EU (Eurostat) and will require a significant amount of biomass in order to achieve future goals set by the EU. EU Plans to 2020 is the renewable energy share of 20%, which makes the 230-250 Mtoe of bioenergy depending on various scenarios (European Commission Green Paper, 2006). In addition, as an alternative for transportation fuel, the EU has set the goal of using the minimum mandatory 10% biofuels to 2020. Bioenergy participating with 22% in supply in developing countries with primary energy and about 10% of global energy needs (Wiesenthal, 2006).

The paper presents some aspects of the biomass storage, analysis of the system for pyrolytic combustion of biomass and combined heat and power production from biomass. Based on the costs analysis of the fuel use in the cogeneration system clearly demonstrated the economic validity of biomass use for heat and electrical energy production using biomass.

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**II International Conference
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ECO FASHION

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ABSTRACT

This paper analyzes the impact on the ecology of the fashion trends. Fashion has since long time become a way of life, and its original role of protecting the body has been replaced with a pace dictated by the fashion industry. Fashion has always been focused on sociability, in the last decades more and more an awareness of its social notes is appearing. Engagement of the individual companies and designers increased the awareness of certain aspects of the production of clothing, including environmental. Ecology as a discipline that has found supporters in all spheres of society did not pass the fashion world. Eco fashion is the most frequent term for the segment of fashion that deals with clothing that is produced in a socially responsible manner. The term Eco fashion define models made from recycled materials and materials that are produced in a harmless way, naturally dyed. The use of the term sustainable design is increasing and his intention is to determine environmental impacts that are negative, then eliminate and redirect them in a humane and intelligent design.

Key words: *Eco-fashion, sustainable design, slow fashion.*

INTRODUCTION

This paper analyses the influence of ecology on fashion design. "Green" wave that is very present in all spheres of society, found no exception in the fashion world. Fashion as an effective instrument, a platform for mass audiences served to awakening of many people. Originally it reflected in the products for the masses, such as cotton shirts and pants, and today it took a significant position in high fashion. The term fashion is not relating only to clothing but also in textiles, cosmetics, visual arts, photography, but to all the other areas that have a stake in the development of the fashion industry. Fashion companies for several years are trying, as a part of their production lines, to develop a line that refers to the eco - fashion.

Environmental movement is actively working around the world and very vigorously is making its way into the fashion field in the last decade. Each year growth among the supporters of the fashion world is recorded, and a growing number of companies are finding interest in developing and investing in this sphere.

This trend has taken its place at the most famous fashion brands, and its production lines which are developing for a long period, trying to follow global trends and rise to a higher level in home policy. As such, it became imperative for designers who have surrendered to the "green" movement. It leaves no one indifferent which was aimed at the rapid expansion of the ecological network and more people are joining this idea. In addition to the plants that are grown on the safe and environmentally sound manner, the process of coloration of yarn and fabric to the design solution and its presentation to the public, eco fashion trend is the everyday life now.

Eco fashion is a generic term that can mean many things. Companies that develop this concept are also supporting a healthier world view. It refers to the reduction or elimination of all those harmful environmental impacts throughout the product development, manufacturing and consuming. When it comes to fabric selection, importance is given to materials that are made from natural organic

materials. The advantage is given to natural vegetable fibers that are obtained from plants such as cotton, hemp, linen, and in recent years the bamboo and nettle. Followers of eco-fashion can be sure that the use of harmful chemicals during manufacturing is either off, or on the minimum. The significant fact is that the clothing items that are declared under the eco fashion, are made in human conditions, and that people who were part of the production chain are adequately paid and work in conditions that are relevant to the work environment. Use of natural resources that are not destructive to the environment makes design sustainable. Eco-fashion is a style and a way of life not only for those with deeper pockets, but for the masses. We have seen that fashion houses such as Zara, Mango, Esprit, H & M, Edun and others in their lines of production were listed with collections that belong to this area.

JEANS AND ITS ROLE IN ECO-FASHION

Changes in the atmosphere, climate change, rapidly expanding population, has only accelerated and deepened awareness among people about the appropriate changes in all aspects of life, including fashion. Many designers, who are inclined toward "green" wave, avoid dividing their collections into seasons. The division between spring and winter collection, requires the production of materials for the conditions of winter and of summer. With a designer for which eco-design became an imperative, there is no more rough collection division which leads to the use of one material for more seasons. It is now replaced with a collection that is adapted for all seasons. Today's designers use fabrics that are the base, and adaptable to all weather conditions. Typically, this is the fabric or twill weave fabric, which is acceptable and suitable to wear all year round. Materials undoubtedly play a major role in understanding what makes a sustainable fashion. Often they are the starting point for change, and key merchandise in the agricultural sense, then for designers, manufacturing industry, consumers etc.



Picture 1. Levi's brand campaign

If they were to choose one clothing (fashion) object, which in its characteristics, applications, and opportunities for subversion of meaning in everyday practice coexist in different semantic categories, giving each of them a new meaning, then surely the garment was jeans¹.

Levi's fashion house is well known for a long, long time and is the most famous in the production of jeans, has in the production chain a line of "eco" jeans. In addition to organic cotton grown, the production process is environmentally friendly. Levi's company has set, on its website a film about preserving the planet through the eyes of jeans. Also, there is a fact that 58% of electricity and 45% of the water used during the usage of Levi's jeans occur during the consumer use phase. Denim washed in cold water, drying it naturally, donating old jeans are just some of the things that consumers can do to save energy. Ironing and using the dryer increases energy consumption, and should be avoided whenever possible. The fact that 23.8 billion pounds of clothing a year end up in waste each year.²

There are more and more companies that use recycled cotton for raw materials used to produce denim. One of the leaders in this field is R.E.U.S.E. jeans, which use recycled cotton to produce jeans, and it makes 80% of the total production. In this way, savings are about 2560 liters of water for each pair.³

¹ Jestratijevec, I., The study of fashion clothing signs and meanings practice, Orion Art, Belgrade 2011, p. 273rd

² Levi's Strauss Company, www.levistrauss.com

³ Website <http://www.reusejeansblog.com/>

ECO-DESIGN

What is characteristic for models that fall within the field of eco-fashion, is that they differ by the texture and visual design apart from other models. Clothing initially looked like a continuation of the hippie fashion, which was hand-made, purchased at flea markets or secondhand shops.⁴ It is recognizable by a naturalistic feel and often pronounced texture. Models are usually in a form, of so-called earth colors that are: beige, brown, terracotta and green tones. Prints are often inspired by nature and the floral designs is present. We are meeting with slogans that symbolize and raise eco awareness. Labels on these products are the most visible and prominent, in order to be for seen by consumers. Companies can use the symbols that define a product is environmentally sound only if the company standards are approved. Some of them are defined by:

1. Origin - Where the product is made. And who is behind the production of these products.
2. Materials - What material is the product made of? Is it production compatible with clean air, clean water, recycling and resource conservation?
3. Charity - Eco clothing is considered "clothing with a conscience" and factories should help the community in some way, such as donating part of the profits to charity.
4. Recycling - Clothing should be recycled after use.



Picture 2. Symbol on label declare products on ecology that are environmentally friendly

Materials that dominate eco - collections can be divided into two groups. In the first group are natural fibers, while in the second group are materials generated by recycling. Back in the early 1990's, natural and recycled fibers begin to dominate trade shows; they predict trends and other industry segments. In the mid 2000's, the increasing application of organic materials is seen, fair trade and rapidly renewable fibers, which have led to innovations in design with many factories, basing its collections on the choice of alternative materials.⁵

What separates sustainable design from the rest is the fact that the conditions of production are much healthier and more humane to man. They are ethically correct. According to Oxfam estimates, less than half of women in Bangladesh in textile and garment production for export industries have a working contract, and most of them do not have health insurance or maternity leave, and they work on average 80 hours of overtime per month and receive an average of only 60 - 80% of the salary, having the rest of the profits retained in the factory⁶. Factory owners keep money for things like rent, food and water, and in particularly is the practice for women workers not to get paid on the first of the month, to keep them working t on the same place. Inhuman working conditions, mental and physical abuse, exploitation of women and children and all of that is stimulated by the production of illegal apparel, has prompted people to put some questions on, and the need for change.

In London, there are boutiques that support companies by donating a percentage of their sales. They send money to organizations for the protection of the planet, such as Friends of the Earth, Greenpeace and World Wildlife Fund.

Environmental awareness is growing among consumers, thanks to the designers that have, with their original eco-design, promoted one healthy idea. Many designers have adjusted their habits, attitudes and lifestyles to the movement. One of them is Stella McCartney, who dedicate 30% of the collection to the principles of eco-design. She never use leather or fur in her collections, and she is s prominent activist of PETA, dedicated to the protection of animals. As a vegetarian, through making the collection, she always takes care to use materials that are organic.

⁴ Pendergast, Sara. (2004) Fashion, Costume, and Culture. Volume 5. Modern World Part II: 1946-2003.

⁵ Sustainable fashion & textiles design Journeys, K. Fletcher.

⁶ 50 reasons to Buy Fair Trade by Miles Litvinoff and John Madeley, p.123.

Materials considered as the organic fabrics are the ones that are manufactured with minimal use of chemicals during the manufacturing process, from planting, growing, harvesting, dyeing, and finishing to the final product. She makes bags and shoes entirely of fabric. Biodegradable bags and recycled paper products used wherever possible. This influence is reflected in the complete organization of retail space, which is rounding the idea in total. When furnishing stores around the world, designers took a position on the idea in an environmentally friendly manner, and therefore sustainable use oak, solar panels, etc.. Stella McCartney has its own distinctive design, and by it she managed to attract many celebrities to give their help in the popularization of eco fashion.



Picture3. T-shirt with ecological message



Picture 4. Poster for Fashion week

More and more design houses and eco-conscious designers, try in their collections to avoid the use of synthetic fabrics and plastics. For the realization of buttons, buckles and supporting details are used more bark, shells, plants seeds, coconut, glass and others. Handbags and accessories, which are recommended for summer period, are made of wicker or recycled fabrics. For several seasons, fashion experts included wicker products in the necessary summer detail.

Fashion Week is often taken as the theme of ecology, and by so trying to raise awareness among the admirers of fashion. On New York's fashion week, never before so many designers were presented with the inspiration on this topic. They are trying to promote fashion and also to raise awareness of global eco. Belgrade Fashion Week in 2010. had the topic "Be Green In Any Color You Wear". Trying to pass the message from the fashion point of view, and show that this topic is a global problem. In addition to, and during Fashion Week shows, a variety of events, exhibitions, installations with the aim of obtaining clear conscious and social components is organized.

Conference titled RE / 8 Park Design - Eco Design Week 2012th was organized this year's In Novi Sat, with the subject of redesign, reconstruction, recycle, remake, reproduction, rejuvenation, renewal, modification. Time of event is aligned with the Exit⁷ festival, which has resulted in a large number of young visitors.



Picture 5. Eco Design Week, Novi Sad 2012.

It is defined as a multimedia expression of national and international designers of the WEEK dedicated to eco-design. As one of the exhibitors, I subordinated my own work to the idea of the event. I realized one dress using natural colors and stamp printing with objects from nature, such as acorn, stone, various fruits, etc.

Slow fashion is a term used as a symbiosis of sustainable design to a higher level of social responsibility. It opens up a world of creative possibilities in personal fashion, and the idea of personal expression through clothing. In a world where quantity has replaced quality goods at the mass market, Slow fashion is trying to convey the message that clothing that has significant value and high quality lasts longer. What makes a sustainable fashion is a change in the form of trends, colors, forms, etc. These seasonal changes we give to Fast-fashion, that because of quantity and pace of the market dried up in quality and poor working conditions. Slow fashion requires from the buyer more conscious decisions when purchasing, not to succumb to trends that are short-lived.

CONCLUSION

For many designers who have focused their work developing Eco Fashion, this is step out of mediocrity and raising social responsibility a few scales up. Today it is considered that the "Green is the new black" and many have accepted it. "This is not a trend," said Julie Gilhart, the fashion director of Barneys's, to *Women's Wear Daily*. "The trend is something that is dying. It is a movement"⁸ Therefore, it is interesting to observe the way in a consumer environment, meaning and symbolism of goods overcomes its use and market value. It takes on different ways to educate and inspire consumers to slow their spending and that their decisions should be more aware of, for a better life.

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⁷ Exit Festival, a music festival held since 2000 in Novi Sad.

⁸ "Barneys' Goal: Bringing Green to Luxury," by Sharon Edelson. *Women's Wear Daily*, 2007.

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**PROCESSES IN ECO MANAGEMENT FOR SUSTAINABLE
DEVELOPMENT**

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ABSTRACT

Environmental management system means that eco management or environment have to eliminate negative influence to health and environment function. On the hand the environment protection must not limit economic and social development. Environmental management system represents a basic strategic planning activity that defines principles and criteria of protection, maintenance and development of the environment. The environmental management has to run thought four mutually interacted and long-term processes: restructuring economy, environment pollution reduction, spatial planning and rational use of natural resources.

Key words: *management, environment, substation development, eco management.*

INTRODUCTION

Strategic planning has eco management necessary integrative potentials for management changes in space, long-term time horizon and the position of the catalyst for the harmonization of public, private and social interests. The concept of ecologically sustainable socio-economic development became the cornerstone of modern conditions of development planning, exercising influence over all spheres of human activity. However, the road to sustainability is a complex and lengthy process, requiring a change of thinking and behavior of all social actors, or the acceptance of the view that the environmental impact of development is as important as economic ones.

The concept of sustainable development is not new, but in our country eco management system failed to provide a balanced and spatial organization, which would adequately protect the environment. The opposition of opinions and interests of the relations "social and economic development-urban planning - Environment protection" resulted in the creation of partial and interrelated approach to environmental protection. Existing models of strategic planning eco management mainly include environmental protection as a separate sector planning, which in view of sustainable development can not give complete results.

These circumstances indicate that at present lacks many of the preconditions for the realization of the essential role eco management planning to protect the environment. However, regardless of the perceived limitations, and bearing in mind that planning is a key link in the system of management changes in the environment, to try to determine the framework for formulating strategies for environmental management in the planning of new and changed conditions. If you want to achieve overall positive development of the urban agglomeration of very important ecological factor makes the image of the town and environmental evaluation of its environment. The experience of developed countries and signed the global declaration, the cities and the area around them can find the proper path to sustainable development of its territory. At the same time, the assumption is that sustainable urban development is not just proper planning decisions, but also permanent training of decision makers (at local or national level) and overall (economic) informing the population about the necessity of a healthy environment. One way of approaching these people's attitudes and effective eco marketing authorities and institutions that promoted sustainable way of thinking. All these aspects would be

covered eco management system which has become imperative for the future development of urban areas.

SUSTAINABLE URBAN DEVELOPMENT

Sustainable development is a way that ensures the use of property in a way that meets the development needs of current generations and future generations and ensures that they meet their own needs. Concern for maintaining and improving environmental quality and protection of human health is growing. Achieve the effects of environmental demands that all stakeholders accept the obligation to introduce a system of systematic approaches to environmental management (Environmental Management System (EMS)) and its constant improvement. (Đukanović et al., 1996)

Ecological system has the characteristics of a dynamic and open system in which human influence is constantly undermines the existing balance in it and threatens to one day be a balance established at the expense of people. How to use the available space within the formation and development of urban settlements is one of the important factors which affect the human conscious state in its ecosystem.

Sustainable development of the city can be seen only through the integrity of economic, social, communal and environmental development, it is clear that the principles of sustainable development must be implemented during the planning and reconstruction of urban settlements, as well as the functioning of the city. In doing so should not be forgotten that the city is a separate entity and a complex of natural and physical conditions of built structures. In urban space dominated by economic, social, community and environmental issues and for that reason need to achieve consensus development of these four areas. Achieving the objectives of integrated and sustainable city development provides a balanced development of the relations between these four components. It is a prerequisite for achieving essentially quality level of life in the city.

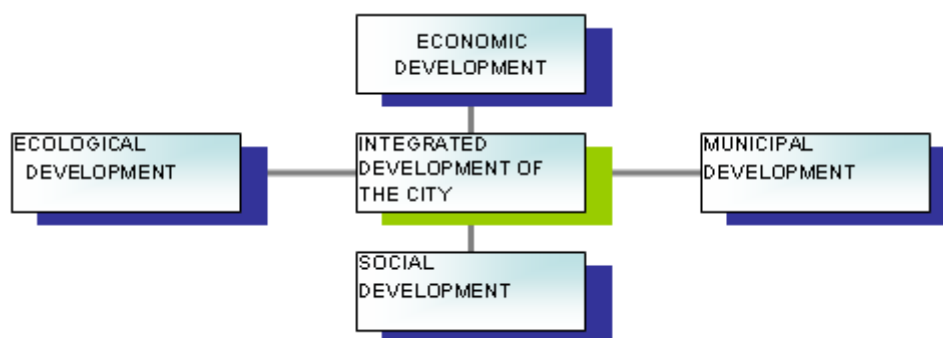


Figure 1. The components of sustainable development of urban settlements (Filipović et al., 2000)

It can be said that the goal of urban eco management improve environmental quality in cities. This implies the existence of a series of measures to ensure the optimization of natural and social factors that directly affect the quality of urban environment and quality of living conditions of people.

Environmental quality is defined by state standards and regulations and acts passed by local authorities. These regulations define the standards that must satisfy certain areas to be considered affordable to live, work and holiday residents.

PRINCIPLES OF MANAGEMENT ENVIRONMENT

Eco management must be one of the basic principles of urban planning since the city is a complex poly functional system performance. Therefore, the spatial distribution of elements and functions are very important to the functioning of the community and the quality of life in the city. Environmental management is not only related to the problem of water pollution, air and soil, but also to ensure balance in ecosystems and nature conservation, and resource management, development of

technological processes and equipment, improvement of legal acts, the system of ecological education, and more.

The basis for the functioning of an effective system of environmental management principles are agreed, separated powers and modern and effective social and administrative measures.

Taking into consideration the specific circumstances relating to an urban area can be distinguished five groups of activities, in mutual interaction, result in the efficient system eco management, namely: (Stošić-Mihajlović et al., 2007)

1. Spatial aspects of economic management,
2. Legal basis of management,
3. Technical and technological aspects,
4. Organizational (institutional) level of management,
5. Information system as a basis control.

What kinds of actions will be undertaken to improve the quality of the environment depends on the need for quality measures, the state of the environment, urban characteristics, organizational and technical capabilities of the community to implement the measures envisaged.



Figure 2. Activities in the system eco management (Stošić-Mihajlović et al., 2007)

In modern terms, the application of ecological principles in the strategic planning of sustainable urban development is imperative. According to many authors, the basic principles of this plan are:

1. Interdependence of environmental factors,
2. Tolerance limits, and
3. Complexity of relationships in ecosystems.

It is important to note that eco planning sustainable urban development must represent a qualitatively higher level of urban planning. City planners are usually not observed as an eco city, but in the technical design of the advantage of giving economic, hygienic and aesthetic principles. Without going into detailed analysis of advantages and disadvantages of this approach, note should be in accordance with international standards and principles of sustainable development emphasis must be placed on ecological principles in urban development. This means that the application of ecological principles in planning urban development and respect for environmental standards can make a synthesis between ecology and urbanism of management and planning for sustainable urban. Also respect environmental factors when planning to reduce the possibility of exceeding the capacity of environmental protection team provided a wholly better population health level.

CONSTRUCTION OF ECO MANAGEMENT

Quality management of the environment is a complex multidisciplinary task which constitute the basis of the strategic principles of sustainable urban development and which can be successfully achieved if there is a well-organized information system on environment. Information systems used for planning and environmental have more or less pronounced character control.

Modern approach to environmental management and development planning is not possible without quality, in detail and updated information on sources of pollution, the state of the environment in all

areas, the available technical and technological solutions, as well as economic analysis and legal regulations.

Privacy and management environment is an integral part of management at all organizational levels and on a continuous process that must be coordinated with social and economic processes (such as health, employee safety, quality, finances, etc.). Principles and elements of environmental management are: (Mihajlović et al., 2008)

- Environmental policy,
- Planning,
- The introduction and implementation,
- Measurement and Evaluation (checking and corrective action),
- Review and improvement, and
- Continuous improvement

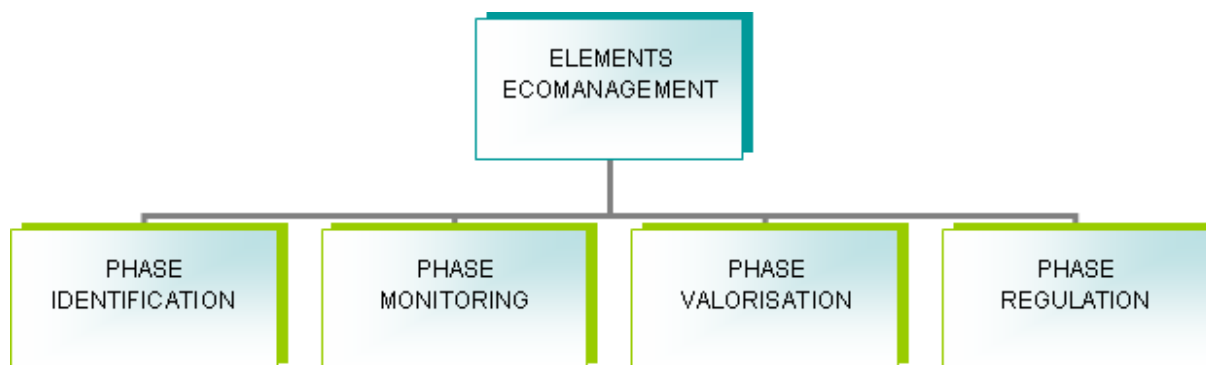


Figure 3. Components of management environment (eco management) (Đurić et al., 2008)

In the identification phase is a key element in obtaining information on which to arrive at knowledge of the potential effects of pollution. Identification of the substance is the most important phase, because at this point just need to identify and list all kinds of pollution sources, places, and chemical substances that participate in the pollution. An integral part of this phase should be a source of contamination and the cadastre. At this stage the immediate conduct of monitoring and measurement of pollutants, their distribution and localization. The aim of the monitoring system is to obtain a more precise picture of pollution of urban areas and to set control network of measuring stations in vulnerable territory. In the monitoring phase defines the unique parameters, units and method of measurement, monitoring period and methods of processing and displaying results. The third phase, which is defined as the phase of evaluation or assessment, completed in the sum of all information relating to the environment that are obtained in the earlier stages. In this way determines the actual level of environmental quality. As a special group method by issuing a valuation method which is particularly important for spatial and urban planning. The final stage is the stage of regulation or the application of various instruments and measures for effective environmental management.

To guide the desired state of the environment in the future must be used prognostic planning methods and models to manage led to an exact level. Therefore it is necessary to influence the development of methods of environmental management, both at the theoretical level and at the level of regulations, standards and guidelines. Management of complex systems, such as the environment, requires that highlight the basic concepts and procedures for the analysis of the environmental quality of an area. The management model must show a good relationship between the parties (competent authorities) and object management (elements of the environment), management tools (laws and plans), and position management instruments (Regulations, Standards,, standards, criteria and information). The implementation of planning decisions based on the harmonized application of instruments and measures in different areas of directing the development, construction and land use and environmental protection.

STRATEGY FOR ENVIRONMENTAL MANAGEMENT

Sustainability should not be, as it seems, considered over the concept, but it should be considered to develop. This is corroborated by the fact that the EU speaks of the "necessary changes in the economic structure in order to achieve a transition to a sustainable economy." In recent years there has been significant progress in clarifying the basic elements, relationships and approaches to the sustainable development strategy, based on the equal treatment of economic, environmental and social objectives. An integrated approach to the treatment of the interdependence of these factors can be expected only if the planning of development achieve balance all three aspects of sustainability. A sustainable community is, therefore, one that provides material and spiritual equality within a generation, assuming that such a community can not survive through the generations.

Environmental aspects of sustainable development relate to the formulation of strategies to preserve the ecological integrity and environmental protection and based on three main factors, namely: (Lješević et al., 1998)

1. The attitude towards the use of finite reserves of non-renewable resources. The degree of utilization of non-renewable resources should not be greater than the speed at which their respective renewable substitute.
2. How to use renewable resources. The degree of utilization of renewable resources does not exceed their regeneration capacity. Many of these resources are renewable, within the limits of the ecosystems in which arise, such as drinking water sources, land, forest stock, crops and animal resources.
3. Maintaining the volume of waste emission within capacity of the environment. The level of gaseous, liquid and solid wastes must be maintained within the limits of the capacity of local ecosystems and global systems of the Earth to absorb them, and that when it does not substantially disrupt the balance of flows of energy and materials.

In some countries in transition, there is the idea of the need for separation of economic and environmental development goals. This variant does not rule out the strategic objectives of protecting and improving the environment, but their solution is left for later, after arranging to achieve economic progress. This approach is promising, because if the new investment would not have taken measures to protect the environment and account for their costs, there would be unreasonably large damage to the environment and significantly higher costs later.

Regardless of the choice of development strategy, the price of its application must be paid either through the cost of the present generation, whether the costs are transferred to the account of future generations. Each of these alternatives will have long term consequences on the national economy, environment and social status citizens. The elements of sustainable development contained in the national investment plan which defines the goal of rational organization and spatial alignment of its use of the possibilities and limitations of the available natural and man-made values and the needs of long-term social and economic development.

The environmental targets are defined as follows:

1. Quality protection of the environment. This objective includes providing: clean air, sufficient quantities of drinking water, preserved farmland, eco systems and biodiversity, safe food, beach resorts and comfort in the workplace and place of residence.
2. Rational use of natural resources. This objective is reduced to the rational use of particular non-renewable or partially renewable, better utilization of raw materials and energy, reducing waste and increasing the level of recycling, safe disposal of all wastes, remediation of environmental and spatial consequences of the exploitation of raw materials.
3. To stop further environmental degradation. It is particularly topical in the critically polluted urban and industrial centers in ecologically valuable areas.
4. Protection of natural landscapes, scenery and landscapes.
5. Educational support and educational programs in the field of environment and natural environment.

MODELS ECO MANAGEMENT

The current approach to environmental protection has not given satisfactory results in improvement environmental conditions. Since the use of land and other natural resources in close relation with the state of the environment, the application of environmental criteria in the planning of land use, industrial activity, energy, transport, tourism and other sectors need to become a key factor for ensuring the quality of the environment. Therefore, the planning, especially planning and investment control documentation and activities, should become the main tool for protecting and improving the environment. To achieve this goal it is necessary to develop and refine tools and methods for managing and protecting the environment in the planning process, and in the process of implementation plans.

The main objective is to present management as a regulated system in which is pre-determined sequence. Modeling is one way of achieving the basic goal. Priority is to be a model of rational and efficient. Modeling can not exclude the possibility of "deviations" from a predetermined order of priority or unforeseen impacts, it is impossible to make a perfect model. (Stošić-Mihajlović et al., 2008) Conceptual models are observed brief description of the real world, expressed with text and images. Such models facilitate communication among participants in the planning and decision-making process; because it includes the basic structure of the system, define the limits of models and conditions for their further development. A conceptual model contains objects in the system and their relationships. Objects are basically a group of individual entities, which have similar functional properties. Facilities each have adequate functional links that point to the position of objects in the structure of the system, as well as the interaction of one object to another. Simplest conceptual model of the space covered by the limits a plan may be present theoretical model of the black box. The purpose of this model is to show the basics of the concept and process of managing changes in space using a feedback loop between the input and output factors of the system.

The ecological approach to planning is based on an assessment of the ecological capacity of the area, which requires the creation of comprehensive data base on the environmental, performance indicator environment, and more recently sustainable development indicators. A particularly important tool for preventive environmental protection is to apply the system of impact assessment planning decisions on the environment, which provides that in the plans provide various levels of the strategic framework, which requirements for harmonization of approaches to environmental protection at national, regional and local level. Planned activities and interventions in the area may represent sources of pollution and degradation of natural areas environment, due to changes energy, water, air and materials. Disturbances in the physical environment, which exceed the environmental capacity of the space, not necessarily cause adverse effects in humans, ecosystems, natural and cultural resources. By combining the above relations between individual objects are given a comprehensive and flexible model of environmental management.

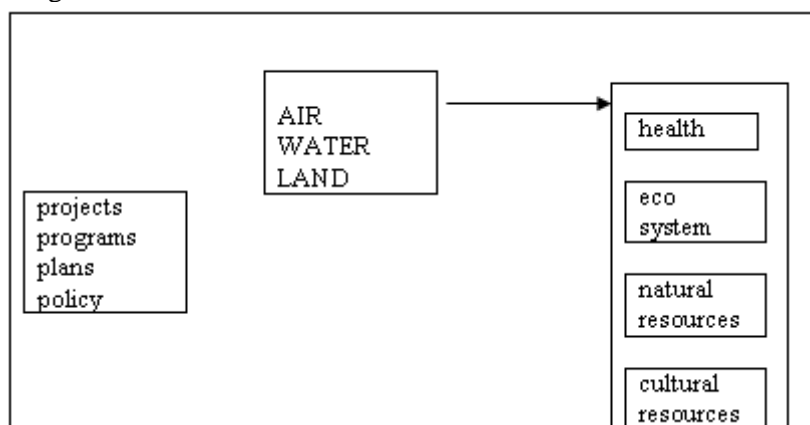


Figure 4. Integrated model of environmental management (Stošić-Mihajlović et al., 2007)

The planning process is interwoven with the process of decision making and the process of governance is unimaginable without the appropriate information system. The management process is essential to adequate and timely decision-making and based on reliable information. The higher the degree of openness and democratic model of decision making can be achieved by applying the principle of transparency.

METHODS AND INSTRUMENTS ECO MANAGEMENT IN PLANNING FOR SUSTAINABLE DEVELOPMENT

Increase awareness of the importance of the environment and the possibility of environmental impact is the increased interest in developing methods to better understand and reduce adverse environmental impacts. International standards (which are translated here) describe the principles and framework for the implementation of environmental protection with respect to the prescribed minimum requirements. Environmental management is one of the main tasks of present and future generations.

It is generally accepted that eco management has five basic functions: planning, organizing, staffing policy, management and process control. Developing skills in people who are dealing with eco management conditioned by education and training. It can be distinguished eco manager that can occur in six roles:

- Regulator - the behavior of other managers to create and influence on the behavior of others,
- Innovator - managers seek to create change and to adapt to changes caused by others,
- Catalyst - innovations that must be accepted as much as possible to meet the growing demands for efficiency,
- Assigned a guardian - management must be economically related to the consumption of resources,
- The mediator - mediate between system requirements and application environments,
- Leader - scientific management techniques, but also an emotional connection with subordinates to motivate subordinates to maximize their tasks.

Model of an ideal manager is shown that all the necessary qualities can never meet in one person, it becomes clear why there is no perfect manager, which can not be said for management. The following features can be easily completed in the management team:

- Manufacturer - "master of his craft," to achieve this must know all the secrets of their primary professions: technology, marketing, finance or other fields, but it has to be aware of when working well,
- Head - not enough to know how something is "produced" especially when it should be done by someone else. Must be an excellent manager, that the man who plans, coordinates and controls the implementation,
- The entrepreneur - it is necessary to realize the function of entrepreneurship, the need for a dynamic environment functions according to which it constantly emerging opportunities and threats. The manager must be able to change the goals and strategies to quickly decide the time and risk. Must be able to recognize, anticipate new trends in reality and to use it,
- Integrator - the integration means the process by which the risk of an individual becomes a risk group. The task of the integrator is to find a compromise between the requirements and capabilities of individuals and organizations, and thus closer to each other.

The planning process is expressed in an extremely complex activity, which can leave long-lasting effects on many people. In short urban eco management:

- a set of activities related to physical changes in the space being taken to improve the quality of life with economic, environmental and social aspects and raising the efficiency of utility systems and other urban functions,
- includes aspects of the land, housing, finance and social development,
- must be based on full information about the current situation and the available documentation, and decisions made based on the analysis and diagnosis of the current situation,

- to create a balance between economic, ecological and social development indicators and data which should be incorporated into the plans and standards,
- articulate the public interest and define measures for their protection, and any possible changes directed by parameters that serve to protect the public interest,
- a method of raising funds for the economic valuation of land as a resource and its reproduction and development in order to further more rational use.

Eco management is part of good business practice for all organizations that have a clear strategy and goal based on the continuous improvement of its processes. For organizations involved in planning the sustainable development of cities it is a challenge and a way to demonstrate its commitment to new approaches, new philosophies, new way of thinking, critical and scientific approach, willingness and ability to change, to leave and undertaking business and other ventures with efficiency better and the general promotion of effective practices.

Methods and instruments for environmental management are systematized means for obtaining information on the environment and help in making decisions about the environmental impact of current or planned activities to protect and improve the environment and achieving sustainable development goals. These funds may be used by all social actors (whether private or public sector), and activities at all levels, from local, regional, and national and international.

In practice applies more resources eco management and management of ecologically sustainable development. Some of the tools used as a legal requirement, some were standardized at level national or international standards and their application is voluntary, while others are under development and improvement. Methods and tools can be classified in different ways, depending on the interpretation of sustainability. In some approaches sustainability, the instruments are more technically oriented to the determination of the ecological capacity of the location and impacts of human activities on the environment, while in other approaches, in addition to technical tools important place occupied by political means, which are aimed at creating conditions for adequate public participation in decision-making processes on Environment and Development. Framework for this study, appear to be suitable methods and instruments for environmental management sorted into several groups:

1. Identification and analysis of environmental
2. Use of information for policy formulation and action
3. Assessment of policies and actions,
4. Management actions and information on issues of sustainable development,
5. Creating a social climate for sustainable development.

CONCLUSION

In recent years the problems of urban development and environmental protection in our country are becoming very complex, in order the dramatic political and social change, deepening socio-economic crisis and a very large population migration. Limitations realistic development strategy in the longer term, from the standpoint of efficient and rational planning, utilization, organization and legal structure is a major drawback, since in the space nothing happens that is not interacting with the socio-economic development processes. Bearing in mind that planning is a key link in the system of management changes in the environment, to determine the framework for formulating strategies eco management in new and changing conditions. In this regard, the proposed approach eco management plan, which provides a complex solution of environmental problems and greater flexibility in decision making.

Eco management planning as an element, which is based on ecological principles, possesses the necessary integrative potentials for management changes, long term time horizon and the position of the catalyst for the harmonization of development policies and strategies. In modern conditions and the time when the concept of sustainable development adopted at the global level, the role of planning in strategic eco management becomes even more important, since it is clear that the consequences of

current decisions as critical determinants of the cost of economic and social development, and for the cost of providing environmental quality .

Socio-economic situation and the attitude towards the environment here, indicate that at present lacks many of the prerequisites for the realization of the essential role of urban planning. However, regardless of the perceived limitations, and bearing in mind that planning is a key link in the system of sustainable management of change in the environment, the proposed framework for the formulation of strategies for environmental management.

Eco management strategies in planning for sustainable development of urban areas based on the following principles:

- Protection of natural values and cultural heritage is an absolute priority,
- Rational use of land, water, energy and natural resources of the total,
- Consistent application of the precautionary principle for those activities that can lead to risks and uncertainties or to cause environmental damage
- As a better and more elegant version of the resolution of environmental concerns access to use the "predict and prevent" approach instead of "react and cure"
- To ensure compliance of policies and strategies for environmental protection at all levels (from local to national)
- Ensure the implementation of models of environmental predictability and public participation in decision-making on urban, primarily spatial development.

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ECOLOGICAL CRISIS AND CORPORATE RESPONSIBILITY

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ABSTRACT

The link between economics and ecology has received significant attention. In particular, the relationship between economic development and environmental quality has come to the fore. In this era of great needs and unique opportunities, modern businesses intend to create positive change. They contribute to the well-being of communities through economic development. They are determined to use their strengths and their presence to help protect the health of our planet and to improve the lives of the people who inhabit it. This paper suggests that a very important part of today business is corporate responsibility. The mark we leave will have an impact for generations to come, so it is crucial to work with others to find viable solutions to global, social and economic challenges. Importance of this approach is substantiated with The Coca-Cola Company's data, the world's largest beverage company. This company is typical example of commitment to investing in a sustainable development through a focus on water stewardship, sustainable packaging and climate protection.

Key words: *economic development, environmental quality, sustainable development, corporate responsibility, sustainable packaging.*

INTRODUCTION

Environmentalism has essential importance for human society. It is the framework of his working and living conditions in general. Natural environment, its natural resources and natural conditions of the area in which economic activity takes place people, both productive and unproductive. According to the general theory of systems we can treat the economy as a subsystem of a large social system, so that while environmentalism is the economic environment, i.e. economic system, and essentially it determines.

Modern economic development is characterized by a strong acceleration of its pace and dynamics, which greatly influenced the escalation of environmental problems. Intensive industrialization and urbanization during the twentieth century had resulted in distortion of the natural balance and a negative impact on human health and the whole living world. The ecological crisis is a crisis of existence of the existing types of industrial society in relation to natural conditions in the contemporary period, emerging as a significant limitation. As such, it means exceeding the limit of self-reproduce global economic system, and is now almost generally accepted view that the ecological crisis socially conditioned. Namely, in the economy, as well as a large system, all processes of change have a cumulative result of the developed system of connections and interactions of all of its active elements, so that changes in each element leads to a change in all others. At the beginning of the twenty-first century allowed saying that human beings face environmental challenges that are unprecedented in the history of this planet. Mainly due to human activities, life on Earth is faced with the greatest mass extinction since the dinosaur age of sixty five million prior years. (Jardin et al., 2006)

Consumer lifestyles and environmentally destructive technologies have led to a growing ecological devastation. In industrialized countries like the United States, the environmental damage per capita is higher than in many less developed countries. So with less than five percent of the world's population, the United States used the thirty-three percent of the irreversible energy and mineral resources of the world and create more than twenty percent of the emissions of carbon dioxide. As for the

underdeveloped and developing countries, the more difficult the higher standard of living made by developed countries, represent a growing threat to the environment.

Global problems are manifestations of the crisis: the exhaustion of economic resources and the related energy crisis, pollution and deterioration in quality of life in every sense. Along with the growing exploitation and processing of natural resources increases the quantity of various waste materials and objects in the environment. It is therefore necessary that the worldwide radical change current rate of exploitation of natural resources, and direct the future direction of the direction of scientific-technical and technological processes. Also today, the industrial society, for that reason, develops a tendency of reduced use of natural resources in the form of a smaller share of raw material and energy inputs, and greater use of factors such as knowledge, information and new technologies.

THE CONCEPT OF SUSTAINABLE DEVELOPMENT

At today's level of economic and environmental sciences, it is widely accepted view of the necessity of integrating environmental requirements into the national economic policy, and global development policy, both at the level of individual countries, and global international level.

The practice of most developed countries and developing countries over the last decade proves the opposite: the traditional concept of development centered on the growth of production and also increase the consumption of natural resources has come to its limits. The value of the environment has long been underestimated, and the danger that threatened to jeopardize the development prospects of future generations. The so-called "External costs" that produces pollution, resource depletion and damage to human health are beginning to exceed the benefits that growth brings further. This rapid pace of economic development in the long run continuously proved to be unsustainable development", and concluded that the science is needed for the future development strategy which will ensure connections of growth of GDP and the use of natural resources on the one hand, and attracting greater public economy, individual firms and all other holders of economic life, to adopt less harmful patterns of behavior on the environment, on the other. Capital is now in most developed countries are increasingly investing in environmental protection, energy savings and other resources in the development of environmentally friendly technologies. It is in these areas are opened and many new jobs. Less developed countries have no choice, must follow this path. Sustainable development should be encouraged by fiscal measures at the local level, which are aimed at preventing pollution and waste of natural resources. Thus, for example, selective taxation, which modifies the relative prices of products depending on the effects on the environment, in some countries gave very good results and proved to be an effective measure (Finland, Sweden, and Switzerland).

Sustainable development is the harmonious relationship between ecology and economy, to the natural resources and preserves our planet for future generations. It can be argued that sustainable development is a general direction, striving to create a better world, balancing social, economic and environmental factors. Just over a decade, the World Commission on Environment and Development (World Commission on Environment and Development), also known as "Bruntlendova Commission" (Brundtland Commission) published a report entitled "Our Common Future (Our Common Future), which points to the danger to humans and the planet, from the politics of economic growth without taking into account the possibility of regeneration of the planet Earth. The action program" Agenda 21" of the United Nations Conference in Rio de Janeiro in 1992. contains the principles of operations in accordance with the achievement of sustainable development. Then they adopted the parameters of which companies should adhere to environmental protection. World Summit on Sustainable Development was held 2002nd in Johannesburg (Djukanović et al., 1995). Key issues discussed at the summit was just the eradication of poverty," sustainable production and consumption, energy efficiency, management of natural resources, promoting public health. The paradigm of sustainable development has become a leader in all economic sectors, and in the economy.

Sustainable development is based on an ethical approach and as such is a way out of the destructive and destructive activities of modern civilization, so it can be said that the main goal is survival. This

concept should provide a further progress of human civilization, with moderate use of resources and space. (Blagojević et al., 2001)

ENVIRONMENTAL POLICIES OF MODERN CORPORATION

Opportunities for sustainable use of natural resources and environmental protection should be harmonized with the aggressive application of technology in production aimed at achieving maximum profit. In the past, the practice in both developed and developing countries showed that under the influence of aggressive profit natural resources freely used, which leaves behind a tragic impact on the environment. The point is to find a more appropriate development programs that would enable protection of the environment on one hand and achieving optimal economic outcomes on the other. The development policy of the company environmental goals should have a much more important place than they had before. Due to the improvement of ecology should become a permanent process, each company should approximate its environmental programs with the current trends of technology development, taking into account local environmental conditions and consumer demands. Commercial enterprises have an essential role in sustainable development for their business and production policy should fit into the basic strategic directions of development set by the state, and that by investing in new technological processes and modern filters prevent environmental pollution. (Berber et al., 2004) environmental policy guidelines must be an integral part of long-term development policy of the company and therefore an integral part of its strategic planning.

An example of environmental policy guidelines of the company Coca Cola

Found in 1886. Its headquarters is in Atlanta (USA) Coca Cola operates in over 200 countries and produces over 2600 different kinds of soft drinks. Improving quality of life in countries where it operates has always been one of the main strategic goals of the company: the promotion of active lifestyles and well-being of the community, minimizing the impact on the environment, accelerating economic growth and a lot of similar tendencies. Commitment to environmental protection began in the early days of business with what was at first most of the attention paid to water quality and reduce waste components to be in the future continued efforts to minimize his imprint, which leaves the natural environment. The vision of sustainable growth, contained in the Manifesto Corporation, is based on several key areas: 1. Personnel - to create a place to work where people are motivated to reach their maximum; 2. Portfolio - offer the world a number of different brands of beverages to suit and satisfy various human needs and desires; 3. Partners - to form a winning network of partners-colleagues and build mutual loyalty; 4. The planet - to be responsible global citizen that will make a positive contribution; 5. Economy - maximizing yields and taking care of all the above responsibilities.

Coca Cola company is listed on the FTSE4Good Index-a (an independent company owned by The Financial Times and the London Stock Exchange-a), which includes companies that meet globally recognized corporate responsibility standards. The criteria governing the FTSE is regularly updated and modernized in line with the evolution of how opinions and trends in corporate responsibility.

The system of environmental protection carried out by the manufacturing giant to focus on areas that are under the strongest impact: water management, recycling, packaging and energy and climate protection. Such actions have become an integral part of business processes than ever. Of course, even though much has been done in each of these areas, the company is still a lot in terms of further investment in the sustainable future of the planet. Commitment to responsible business, the company is publicly committed itself by signing the UN General Agreement, in March 2006. year. With this agreement, Coca Cola is committed to include the public, support and implement a set of core values of human rights, employment standards, environmental protection and anti-corruption. Many of its business partners are also signatories to the agreement.

Numerical data will be listed below were taken from the company's corporate responsibility report for 2006. year, and refer to the period from January 2006. to July 2007. year.

Water Resources Management

Water is a limited resource in many parts of the world that is constantly faced with problems of over-exploitation, increasing pollution and poor management. Today, more than one billion people lack access to clean water, safe drinking water. And more than 2.6 billion people lack basic sanitation. Taking into account the current situation in this world, and given that water is an essential ingredient of any beverage produced by Coca Cola, not forgetting its importance to ecosystems, the preservation of human health, prosperity and development, here the emphasis is on conservation and protection of water for people and plant and animal species worldwide.

The objectives of water resources management in the company include three components: restricted (consumption) - recycled - refilled.

Among other things, the five year period and were expended considerable efforts and funds in the amount of twenty million dollars to preserve and protect water resources. So the company has organized projects in forty different countries, bringing together local people about solving the problem of clean water, sanitation, hygiene, use of water resources in the production of informing and educating local people. Today there are many communities where the company has launched similar actions:

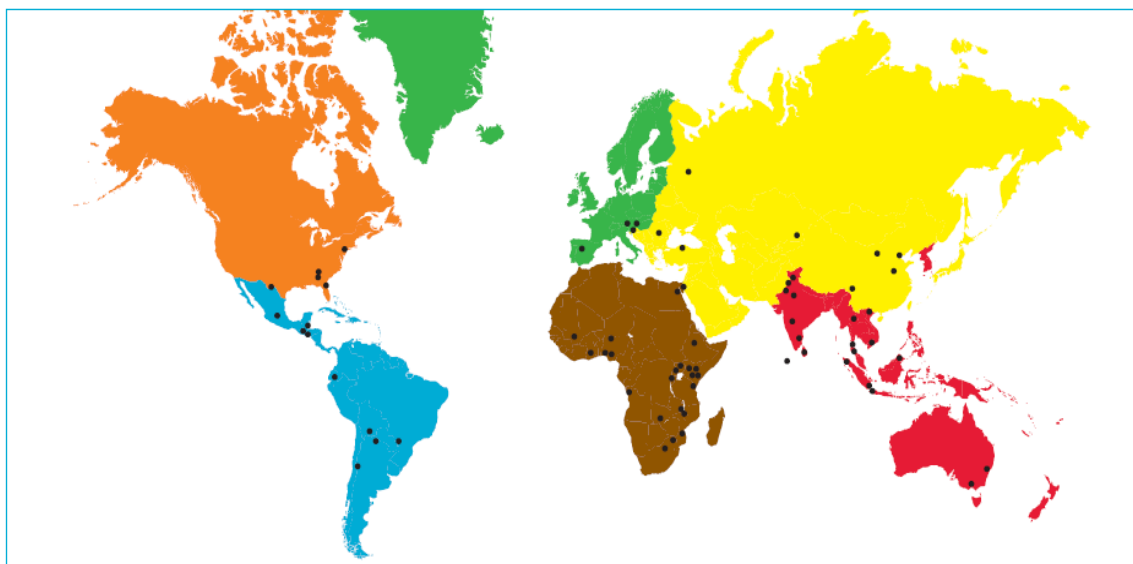


Figure 1. Graphical display of locations (there are a total of 68, items are presented) in the operation of the company to preserve and improve water resources (Despić et al., 1989)

Coca Cola - the system has improved water use efficiency by over 19% compared to 2002. Although the ratio of water use significantly improved over the previous five years, since the reports began to be published, it is anticipated that in future, due to changes in product mix, increase the consumption of resources, as confirmed by the slight increase in water consumption in production in 2006. year.

In 2006. 83% of the factory plant of the company has met the standards on the treatment of wastewater. This trend continues, with the aim of this objective is fully realized by 2010. year to meet the strict standards of the company, which often exceed state laws in the field of environmental protection.

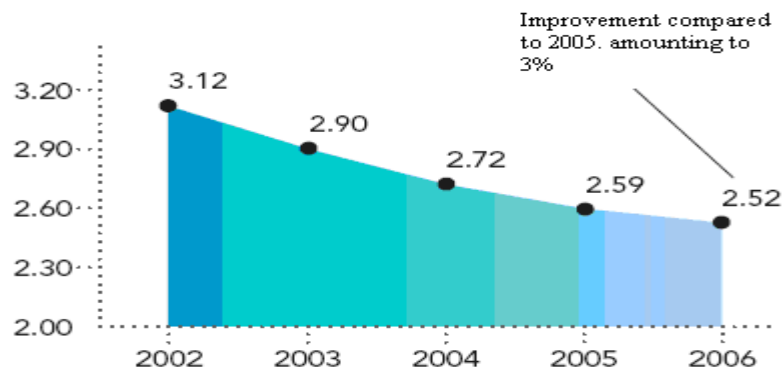


Figure 2. The ratio of water use (l/l product) in the period 2002-2006. (Mitić et al., 1991)

We see that the ratio decreases from year to year, which is the goal, and that the minimum value reaches 2006th year. However, for a more complete analysis must take into account the total water consumption in production (absolute value):

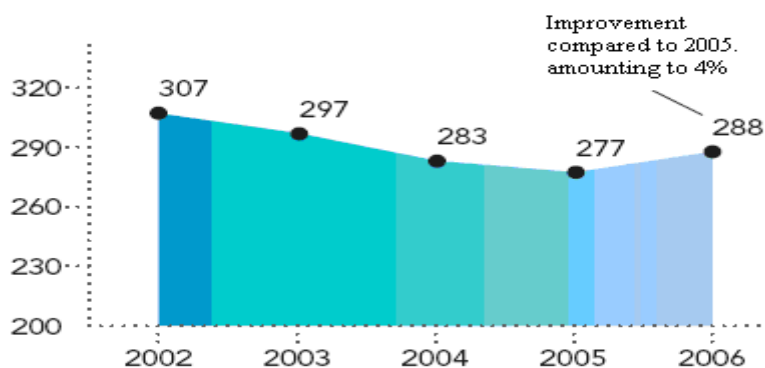


Figure 3. Total water consumption in production (l billion) in the period 2002-2006. (Mitić et al., 1991)

As already mentioned, due to changes in the product range is an increase in water consumption in 2006. years and it is anticipated that this trend will continue in the future.

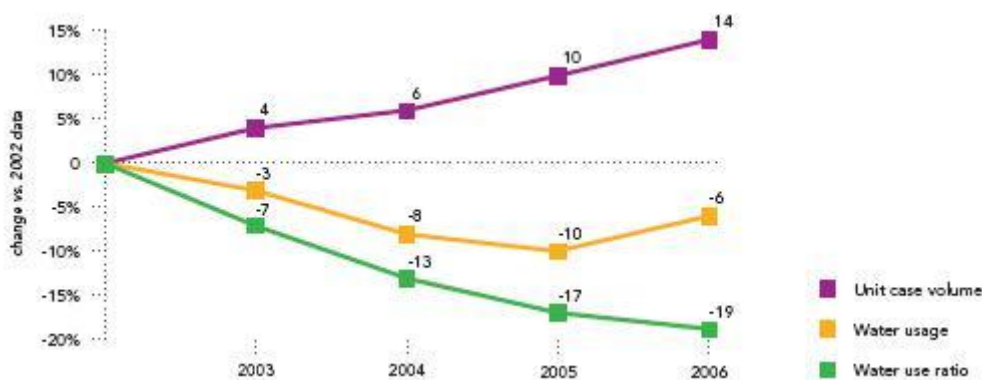


Figure 4. Water consumption and production volume (Janković et al., 1995)

A significant increase in production volume and sales (Unit case volume) led to a significant jump in the consumption of water (Water usage) in 2006. compared to 2005. year. It's also led to a decline in water use ratios, i.e. decrease in efficiency.

Recycling of packaging

Company envisions an environment in which the packaging it produces will be treated as a valuable resource for future use. The goal is to simultaneously reduce the amount of waste and consumption of natural resources. For example, thanks to computer software to design the packaging, effectively reduced the negative impact on the environment, so that the production of new bottles "Ultra" save 89 000 metric tons of glass in 2006. year. (Čobeljić et al., 1981)

The level of recycling beverage containers Coca Cola is the largest in relation to competing producers, since it involves designing a package of high utility value and helping local communities to improve their systems for sustainable development that will take this advantage. In general, it is believed that the education of the key process in changing attitudes and behavior related to recycling and preventing the accumulation of waste, which contributes to the selection of high-quality materials and reusable packaging. Approximately 85% of the total production of these corporations is delivered in the materials that can be fully recycled: PET, plastic, aluminum, glass and steel. The remaining 15% is mainly delivered through high-efficiency systems support a large packaging capacity. In addition, substantial resources are invested in the construction of facilities for recycling of PET bottles to be produced from recycled materials in Australia, Austria, Mexico, Philippines and Switzerland.

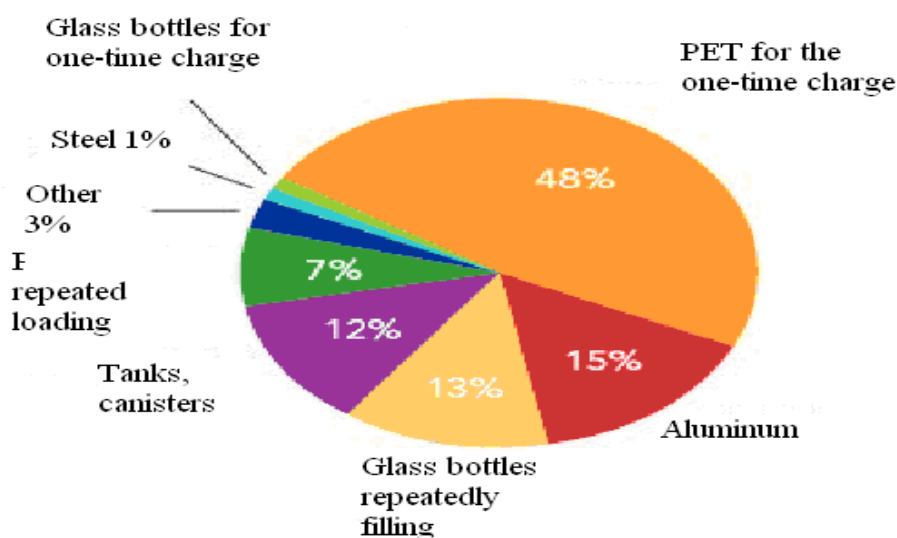


Figure 5. Packaging used by the company in 2006. year (data obtained from the 21.4 billion products shipped worldwide) (Vujičić et al., 2003)

Protecting the environment

It is known that the greenhouse effect leads to drastic climate changes at the global level, with consequent negative impact on biological diversity of the world, water resources, agriculture and human health. These climate changes may have multiple direct and indirect effects on the operations of the company and its supply chain. Through continuous improvement in business, this system has improved the efficiency of energy use in the production process by 16% compared to 2002. year, when the Coca Cola and began reporting on performance.

Given that the largest impact on the environment, this company achieved using cooling devices, which produce an estimated one third of greenhouse gases at a company level, great care had to pay a reasonable, i.e. Sustainable cooling. Thus, in 2002. eco program was launched for the development of commercially viable refrigeration technologies that do not contain harmful HFC (hydro fluorocarbon), which normally causes the greenhouse effect.

The energy management system used within the company, EMS-55 is able to reduce energy consumption up to 35%. By mid-2007. year, more than half a million of these EMS-55 devices

purchased by the Coca Cola Corporation, in accordance with the planned reduction in annual energy consumption amounting to more than 640 million kWh and the planned reduction of greenhouse gases in the amount of 300 000 metric tons.

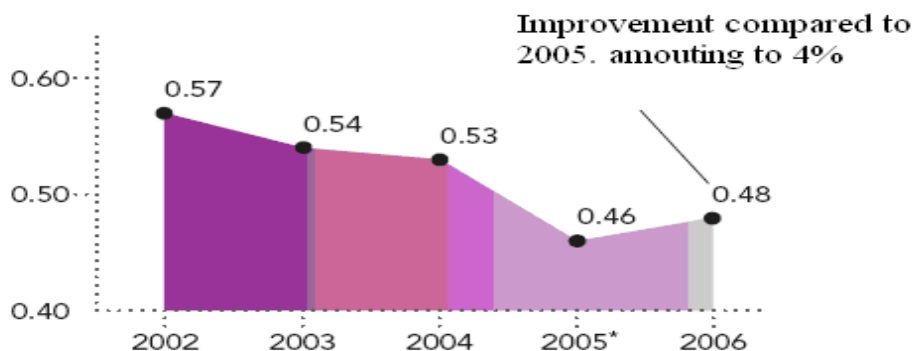


Figure 6. The ratio of energy use (efficiency) in the period 2002-2006. (Mitić et al., 1991)

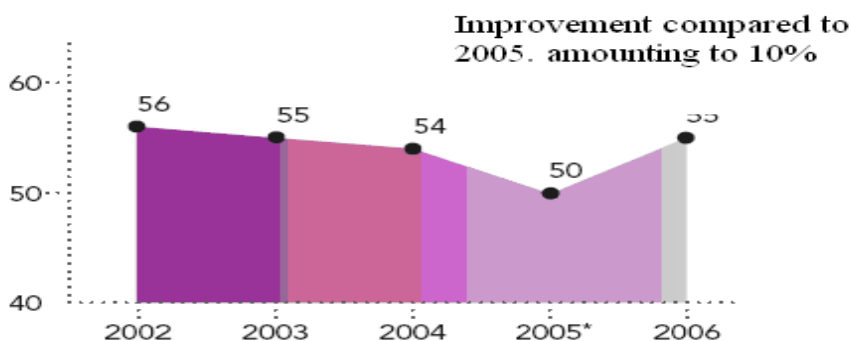


Figure 7. Total energy consumption in the period 2002-2006. (Mitić et al., 1991)

As you can see from the enclosed and the energy consumption in 2006. year has increased over the previous year, according to some estimates led to the direct and indirect CO₂ emissions amounting to 4.86 million metric tons, an increase of 0.33 million metric tons compared to 2005. year.

In the period since 2005. The improvements observed parameters recorded by the factory for the production of concentrates and raw materials, which are also owned by the corporation. Thus, for example, the ratio of water use increased by 13%, the average level of recycling by 2% and the average ratio of energy used 7%. The amount of waste produced and disposed no changes.

CONCLUSION

It is obvious that not only in developed countries than in developing countries, the public is increasingly being against all forms of environmental degradation. For the environmental awareness of the population is in constant growth, primarily due to growing environmental concerns current events, and changes in global thinking in general.

The study of consumer behavior has been determined that a growing segment of the population is willing to pay more for environmentally oriented products. It is this knowledge used by large multinationals, but smaller ones, and their operations are introduced environmental management system. A typical example of such a company is the manufacturer of Coca Cola, the world's leading corporations in the production of soft drinks. The company is aware of the huge shift in consumer preferences, a new situation and the current trend is not considered a threat, and not seen as a problem and the additional cost impact, but as a business opportunity and the challenge of gaining competitive advantage in the international market.

In this sense, this work is an example of a specific business firms show possible directions of movement in the creation of a modern office politics, which must include a system of environmental management, research and development strategy in which incorporated the environmental dimension, the concept of sustainable development and a similar preference of modern times. All that must be followed regularly notifying the public with the aim of forming a positive attitude towards Products Company, and a positive company image at all, as if the company is fully implemented. It is not only environmentally oriented, but also affects other businesses-its subcontractors, to transition to the ecological system, asking them the correct and environmentally friendly raw materials and intermediate products.

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NOISE AND VIBRATIONS IN URBAN AREAS

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NOISE MEASUREMENTS IN THE BELGRADE ZOO

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ABSTRACT

With the Industrial revolution many different types of environment contamination became a part of everyday life. Noise is increasingly becoming one of the largest problems because of the negative effect on the sense of hearing and the brain. Attempt to reduce traffic noise, street noise, noise in plants and urban areas depend on many technical, financial, sociological and cultural factors. Noise source identification and noise measurements are prerequisite for defining safety measures. Technological development has reached substantial level so that satisfactory solutions for environment noise contamination have been established. Financial and sociological factors are still a burrier. Satisfactory solutions can not be produced without applying law regulations and acoustical standards. In this paper the noise in Belgrade Zoo is going to be analyzed and some suggestions for reducing that noise are going to be discussed.

Key words: *acoustics, noise, noise reduction.*

INTRODUCTION

Noise as an undesired sound plays an increasingly important role in everyday's life. Just a half of century ago people have realized that in addition to the other forms of pollution (air pollution, water pollution etc.) noise and sound pollution in general are becoming a serious issue. Increase of overall social needs has caused intensive development of industries, traffic systems and megacities. In such environment, the noise pollution (paradoxically called 'silent polluter') become a serious problem that requires a dedicated attention as well as steps and measures for the mitigation of its negative effects (Long, 2006).

Dedicated medical research as well as research in the field of acoustics has shown that sound has a profound influence on people, animals and plants, in particular of functioning their nerve systems.

Belgrade as well as the majority of large cities in Europe has experienced a major influx of people from the rural areas, in the period of economic development. This caused increase of the industrial facilities.

The Belgrade Zoo has been chosen as the topic for this paper as it has a specific location in the very center of the city. It can be assumed that in the times it was built (1936), sound on this location did not have any particular impact on the surroundings as the intensity of local traffic was substantially lower. However, as the result of transportation developments and influx of the new citizens the impacts of the noise have become very high.

As animals are more sensitive on sound and vibrations than humans, measurement of the noise impact on them will be a good indication on the impact on the Belgrade citizens living in the neighbourhoods of the Belgrade Zoo.

METHODOLOGY

Noise measurements are done with the specialized equipment that confirms to the related ISO standards (see also Figure 1). Noise is measured in dBA units as they are the closest to the human perception of sound. In almost all countries use of the dBA units has been standardized methodology.

Some of the initial research on the human hearing and sound perception on various levels has been done by Fletcher and Manson. Corrective sound levels (dBA) are disregarding to a high degree lower frequencies, as it is done in the human hearing system as well (see also Figure 2).

The device for sound level measurements is a basic acoustic apparatus used for measurement of the noise levels as well. It comprises microphone, pre-amplifier, range controller and level indicator. Different filters are usually connected as separate external modules. It often features an internal processor that automates many of the measuring functions.

An ideal method for the traffic sound measurement is placing the measuring device on a specific place and conducting continuous measurements for a full day. This method is often not practical for the safety, financial or some technical reasons and is frequently replaced with the method of single hourly measurements. Measured level is L_{eq} - the equivalent sound level during the measuring period.



Figure 1. Device for sound level measurements

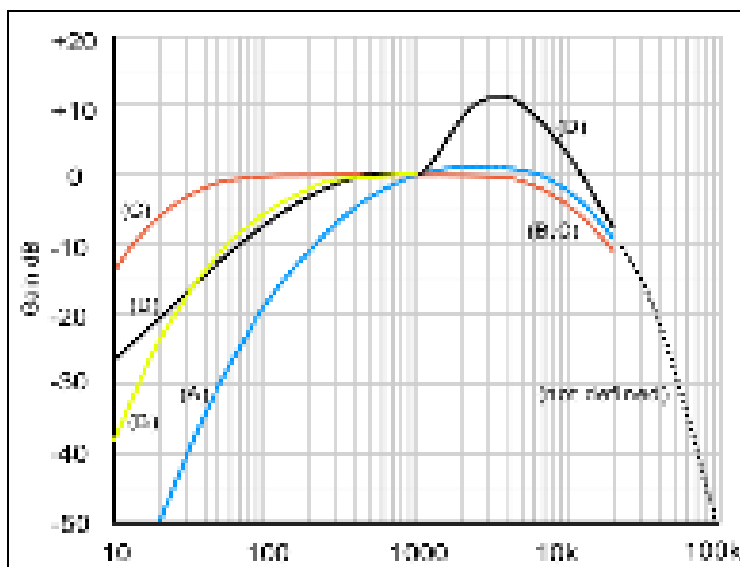


Figure 2. A, B and C corrective measurement results

MEASUREMENTS AND MEASUREMENT RESULTS



Belgrade Zoo is located within the Kalemegdan Fortress in the very center of Belgrade city. In its neighborhood there is a major crossing of two very large roads. Next to the Zoo perimeter there are tram tracks for several tram lines that cause noise as well as vibration disturbances. Such disturbances are perceived by the Zoo management as serious problem for most of the animals. Vibrations are caused not only by trams but also by large trucks which are using the mentioned roads as their major transportation route, particularly in the morning hours. There are several clubs on the other side of the Zoo that are causing additional noise through the day.

The noise measurement points were placed in accordance with the opinion of the Zoo management. The additional criteria for the determination of the measurement points were: perimeter fence height, traffic flow and appropriate distances that would provide for a complete noise chart.

Four measurement points were placed on the equidistant locations next to the fence and the main road (see also Figure 3). Hourly measurements were taken. Measurements results showed that Zoo visitors had minimum contribution to the overall noise levels.

The results were grouped to cover four distinct day periods (morning, afternoon, evening and night). For all of the four periods hourly average noise levels were calculated.

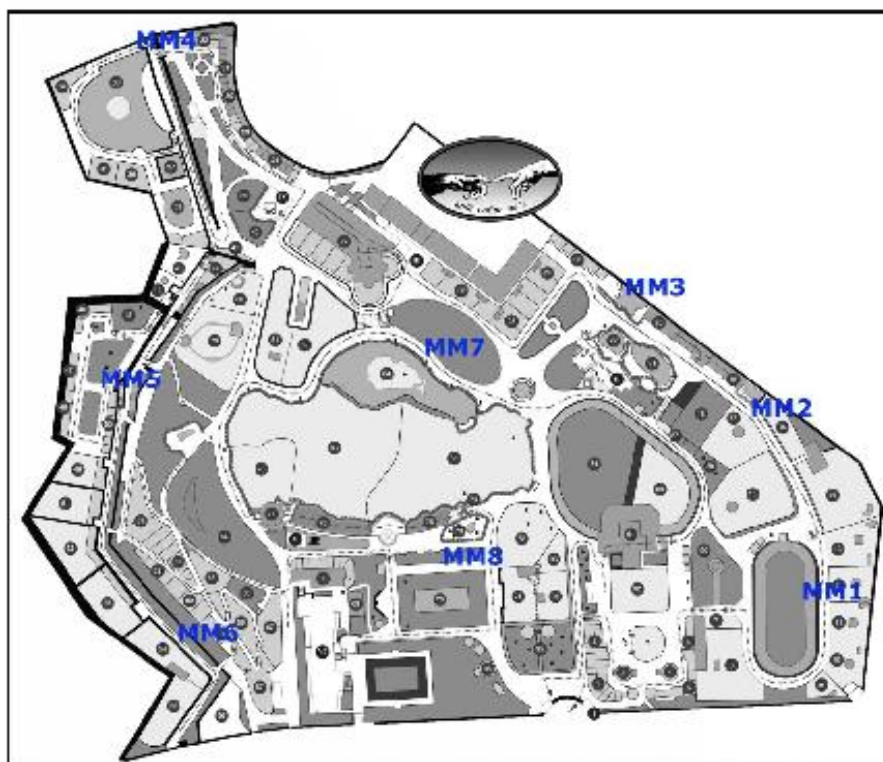


Figure 3. Zoo map with measurement points

The part of the Zoo near the main road and tram tracks has a constant daily noise that exceeds 65 dB at all time periods (this is shown in table 1). Relevant standards consider the areas with the noise higher than 65 dB as critical zones. During the working days the level of noise gradually increases from 6 a.m. to 10 a.m., mainly due to increase in traffic. In the instances of simultaneous passage of trams and large trucks, the level of noise is temporarily rising to the level of 90 dB (this is shown in table 2). After 11 a.m. the level of noise gradually decreases to 62 dB and keeps more or less the same value until 6 p.m. In the period from 6 p.m. to 8 p.m. the noise level increases to the traffic intensity. After 8 p.m. the sound level drops to the average of 55 dB and after midnight takes even lower values (see also Figure 4).

Table 1: Measurement results within and out of Zoo perimeter

	Morning	Afternoon	Evening	Night		Morning	Afternoon	Evening	Night
MM1	68,3	64,9	64,7	53,5	MM1	71,5	69,2	67,2	54,6
MM2	65,8	65,7	64,3	52,8	MM2	68,3	68,4	66,8	55,8
MM3	63,1	64,7	62,3	50,4	MM3	63,2	67,1	64,2	52,3

Table 2: An example of out of the Zoo perimeter noise measurement

Band [Hz]	L_{EQ} [dB]	SPL [dB]	Min [dB]	Max [dB]
A-WTD	68.2	71.5	36.9	79.2
31.5	76.8	79.5	40.2	92.3
63.0	78.0	78.2	40.6	96.0
125.0	73.1	72.4	41.6	91.3
250.0	68.9	69.8	41.6	84.3
500.0	65.5	72.1	41.9	78.6
1000.0	62.1	64.1	42.0	71.4
2000.0	59.8	60.8	42.1	69.6
4000.0	56.3	59.0	42.0	68.4
8000.0	50.3	53.2	42.1	64.7
16000.0	45.6	43.7	42.0	62.7



Figure 4. Measured areas (MM1, MM2 and MM3)

Additional noise through the day is caused by the clubs (this is shown in table 3), (see also Figure 5 and 6).

Table 3: Measurement results (MM4, MM5 and MM6)

	Morning	Afternoon	Evening	Night
MM4	56,7	59,2	55,4	50,3
MM5	48,3	51,7	52,5*	50,4*
MM6	46,8	49,2	47,1*	46,9

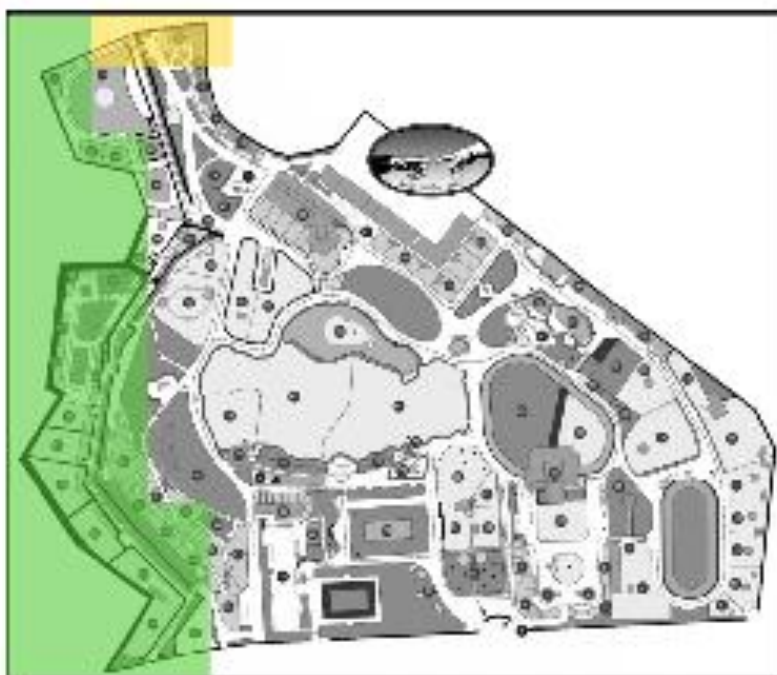


Figure 5. Measured areas (MM4, MM5 and MM6)



Figure 6. Periodical noise area

Table 4: An example of a periodical noise measurement

<i>Band [Hz]</i>	<i>L_{EQ} [dB]</i>	<i>SPL [dB]</i>	<i>Min [dB]</i>	<i>Max [dB]</i>
A-WTD	70.1	61.4	58.7	84.2
31.5	78.7	77.5	67.4	94.3
63.0	78.3	74.4	65.7	94.7
125.0	72.3	68.1	56.5	91.8
250.0	69.7	62.1	55.1	84.8
500.0	67.9	56.6	54.5	82.0
1000.0	64.7	55.6	52.6	80.8
2000.0	61.7	54.1	49.9	75.2
4000.0	57.3	49.9	46.6	68.7
8000.0	49.8	43.8	42.6	61.4
16000.0	45.2	42.3	42.1	63.0

Measuring points MM7 and MM8 were placed in the center of the garden and they are showing overall noise in those areas (this is shown in table 5 and 6), (see also Figure 7).

Table 5: Measurement results (MM7 and MM8)

	Morning	Afternoon	Evening	Night
MM7	52,4	57,8	50,2	46,3
MM8	53,3	59,6	50,8	47,4



Figure 7. Measured areas (MM7 and MM8)

Table 6: An example of noise measurement in the center of the Zoo garden

<i>Band [Hz]</i>	<i>L_{EQ} [dB]</i>	<i>SPL [dB]</i>	<i>Min [dB]</i>	<i>Max [dB]</i>
A-WTD	61,9	64,0	54,7	76,0
31,5	67,5	59,4	53,2	88,9
63,0	65,0	63,0	53,0	86,0
125,0	59,5	51,8	47,4	80,2
250,0	58,8	55,9	45,9	77,5
500,0	60,1	56,4	45,4	74,0
1000,0	55,2	61,2	45,6	73,4
2000,0	54,4	56,8	46,1	72,2
4000,0	53,4	56,5	47,4	61,3
8000,0	45,0	46,4	42,5	55,7
16000,0	42,3	42,7	42,0	50,1

The complete noise map based on all of the measurements done indicates that two sound sources and two locations are more critical than the others (red shaded). On the critical place of the road it is not possible to decrease the level of traffic. On the other side (Kalemegdan Fortress), rather high level of noise have been registered, particularly in the summer period (see also Figure 8).



Figure 8. Complete noise map

DISCUSSION

As mobile sources of noise which are critical in the particular case are difficult to control, the proposed measures include erection of the sound-absorbing barriers (see also Figure 9). Such barriers would serve the purpose of isolating the animals and Zoo visitors from the excessive noise. It is assumed that the sufficient noise reduction would be decrease of 10 to 15 dB (Egan, 2007).

The most suitable place for erecting the barriers would be next to the Zoo’s perimeter fence, from the inside of the Zoo (see also Figure 10). Placing the barrier from the outside of the perimeter fence would be very difficult, due to the existing infrastructure (tram rails, electric poles, cables, etc.). The

problem of the tram rails vibration could be solved by replacement of the rails themselves and their foundation as well as with the asphalt replacement.

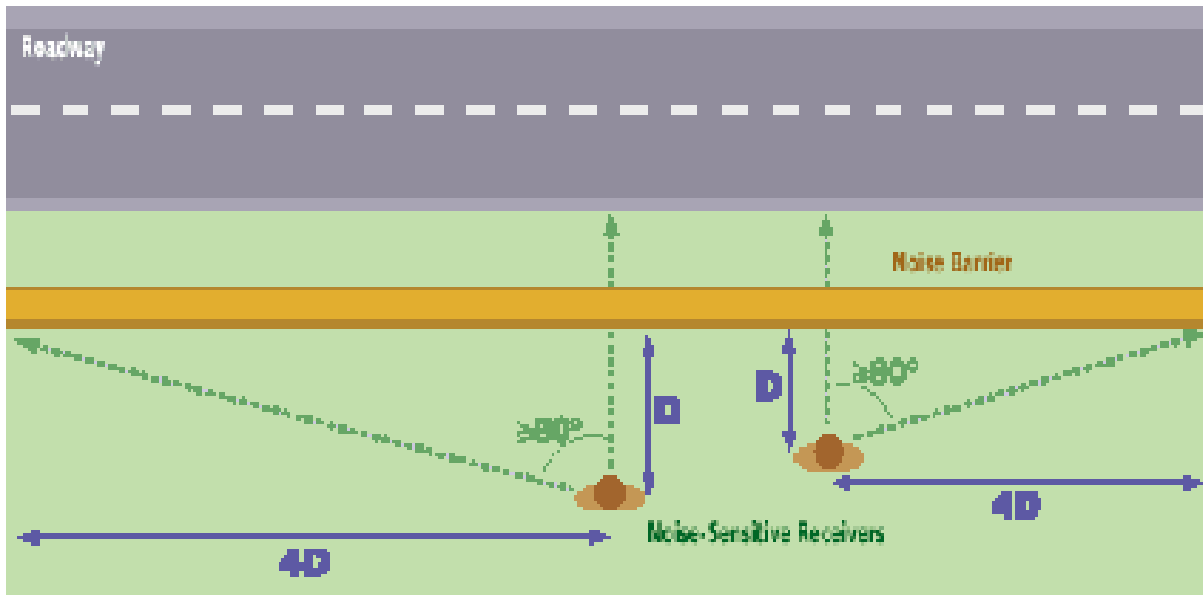


Figure 9. An example of a noise barrier protection

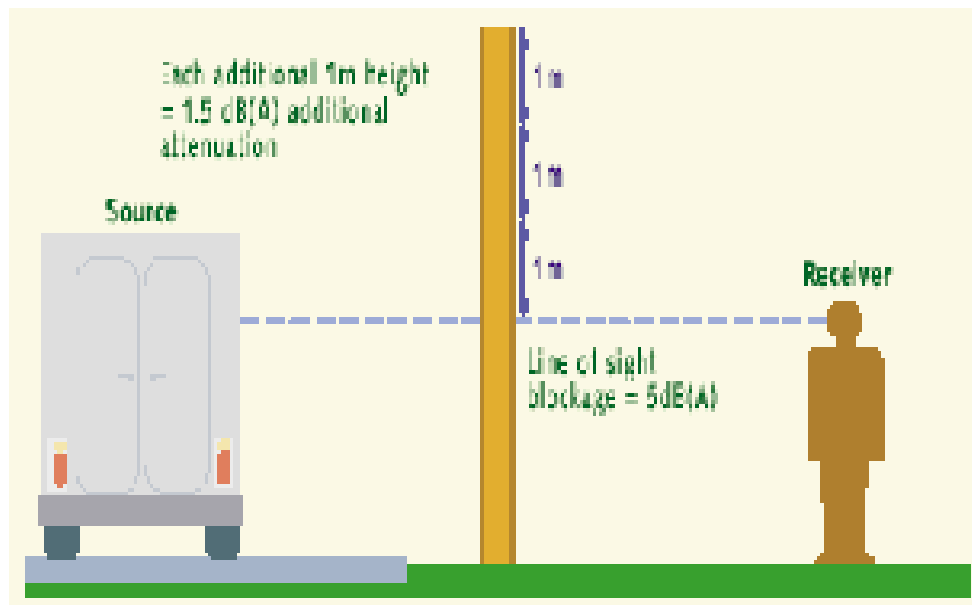


Figure 10. An example of the noise barrier placement

The measurements have shown that the noise is most prominent in the low frequency spectrum, which indicates that the noise barriers should be made of a specific material that is able to absorb such low frequency noise (high absorbing barriers).

It is also proposed that the noise barriers are decorated with plants (‘vertical gardens’), in order to give them more natural and friendly looks. Such vertical gardens further contribute to noise reduction as well as to the human subjective perception of the lower noise (see also Figure 11, 12 and 13).



Figure 11. An example of the vertical garden placed on the noise barrier

In the case of Belgrade Zoo, sound barriers and vertical gardens are expected to produce additional positive effects such as:

- Zoo visitors will have more intimate contact with the natural environment as they will lose the sight on the city
- Decreased level of noise will come close to the noise levels which animals experience in their natural habitats
- The sound barrier will also substantially reduce to intensity of the sound coming from the Zoo that some of the residents in the vicinity might find disturbing.



Figure 12. An example of the fence acting as a noise barrier



Figure 13. An example of the vertical garden

On the second critical location with respect to the noise intensity, noise is the most intensive during the summertime, due to the music from clubs, restaurants and coffee shops that work until the late hours. Sound barriers applied to such noise sources would prevent noise to spread around the Zoo, but would be rather ineffective in the areas next to these facilities. Additional measures would be establishing the limits of the allowed sound levels, particularly in the later evening hours.

CONCLUSIONS

It is widely accepted that noise is one of the key ecological factors that has detrimental influence of the various life forms. In the recent years a wide variety of steps and measures have been taken with the view of limiting such negative effects. It is estimated that in more than 90% of all cases human activities are causing excessive noise and people should face their responsibilities to control the noise and to keep it into the recommended levels.

Within this paper it has been shown that the communal noise is rather constant for the most of the day (in average 8 hours/per day), and as such that it has a strong negative effect on the Belgrade Zoo animals as well as on the people that are living in the close neighborhoods. In their natural habitats animals are exposed to the noise level of up to the 40 dB. Due to the traffic infrastructure already put in place, it is not possible to design an ideal solution for the Belgrade Zoo animals. However, some of the compromise solutions would bring great improvements in terms of reduction of the noise animals are exposed to.

Application of the noise barriers, combined with vertical gardens on one side and tougher regulatory measures related to the allowed sound intensity in coffee shops on the other, would be the most suitable for the given situation. It is expected that the noise would be reduced for 12 – 15 dB, which would substantially change the noise map of the Zoo and the vicinity. The noise intensity, which is as high as 65 dB on some of the most critical spots, would be reduced to the acceptable 50 dB level. In addition, reconstruction of the traffic infrastructure (tram rails, roads) would further contribute to the noise level reduction.

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TECHNICAL ASPECTS OF REQUIREMENTS REGARDING
 EXPOSURE TO VIBRATION AT WORKPLACE

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ABSTRACT

The paper deals with two types of occupations exposure to vibrations: whole-body vibration (WBV) and hand-arm vibration (HAV) as well as with techniques currently implemented for assessment of risks arising from exposure to vibration. The dominant and widely accepted lumped parameter models for human body and filters which enable acceleration measurement in accordance to human sensitivity to the vibration were exposed. The presented analyses has demonstrated that the technical procedures for measurement and assessment of the HAV as well as WBV were well established and defined in international health regulations while technical regulations don't prevent lurching of technical systems which are with inherent vibration risk.

Key words: Whole body vibration, Hand-arm vibration.

INTRODUCTION

For a long time vibrations have been known as cause for different psychological, physiological, pathological and biodynamic effects to the humans. Exposing the human body to the vibration disturbances above particular limit in the amplitude, frequency and duration causes the serious acute or chronic diseases. Acute affects are mainly related to high amplitudes at particular frequency rang while chronic diseases are related to long exposure to the vibration.

In spite of complexity of human body, it is obvious that the predominant approach in human vibration investigations is related to modelling of human body as mechanical system. The main problem in that approach is nonlinearity of human body models as well as variation of parameters from one to another person. Based on long history of the human vibration researching, nowadays, it became possible to use already established models of the human body as models with acceptable accurate.

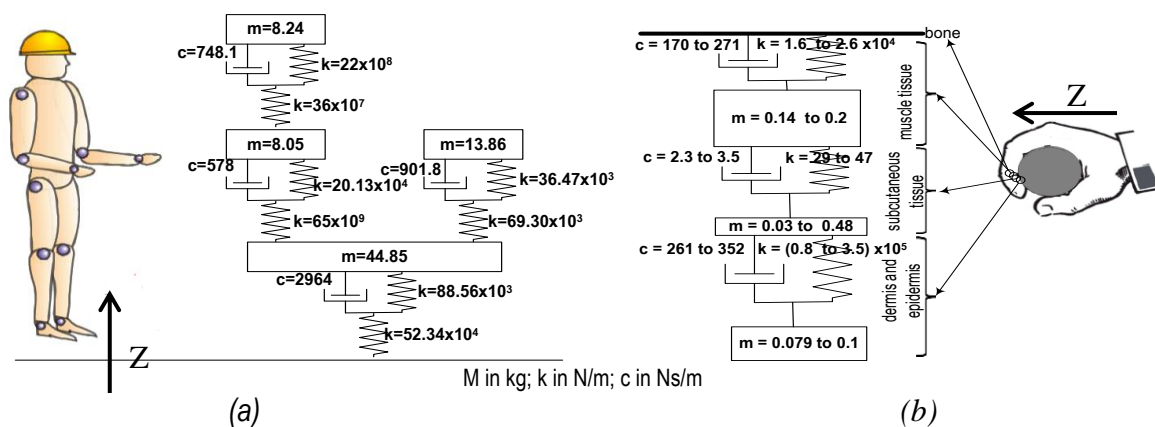


Figure 1. Spring-mass-damper models of the human body (a) and human hand fingers with the parameter values - parameters are valide for disturbance in vertical i.e. Oz direction

HAV AND WBV AND FILTERS

Based on huge amount of researches which have been done, it has been found as possible to define specific filters which would correspond to the human sensitivity to the vibration. Applying the filters to the acceleration signals enables appropriate weighting of the same. Consequently, the adequate weighting of the accelerations gives good picture of the vibration which corresponds to human sensitivity. This approach has been standardised in EN ISO 5349-1, and ISO 2631-1:1997.

For the whole body vibrations the two filters are in use. The first one is dedicated to the horizontal directions (forth–aft i.e. along 0x axis and left-right i.e. along 0y axis) – see Figure 2. As it is given in Figure 2, the humans’ sensitivity to the horizontal whole body vibrations, in the frequency band between 4 and 10 Hz, match to „technical vibrations“ while, in the frequency ranges: below 0.2 Hz and above 80 Hz is negligible. In opposite to that, in vertical direction (0z axis) the human’s body sensitivity is located in the frequency range 0.6 to 2 Hz. The same can be taken as negligible in the ranges below 0.15 Hz and above 20 Hz. Since, the hand and arm are with very different dynamic characteristics, related to the whole human body, the filter applicable for hand-arm vibration have to be different to the previous two.

The human’s hand-arm is with the same sensitivity to the vibrations in all directions. Consequently, the same filter can be used for vibrations in all three directions. That filter has to imply hand-arm sensitivity in frequency range from approximately 1 to 2 Hz and negligible sensitivity at frequencies below 0.25Hz and above 200 Hz. The filter which has been accepted for hand-arm vibrations is defined through EN ISO 5349-1. The magnitude of frequency weighting, along with referent axis is given in Figure 3.

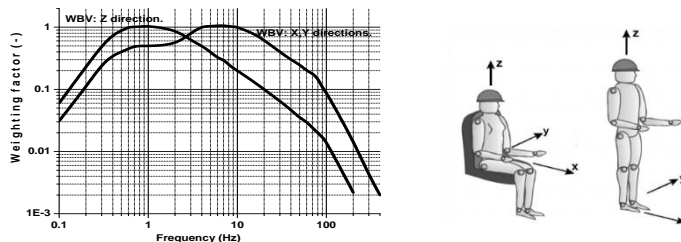


Figure 2. Amplitude-frequency characteristics WBV filters

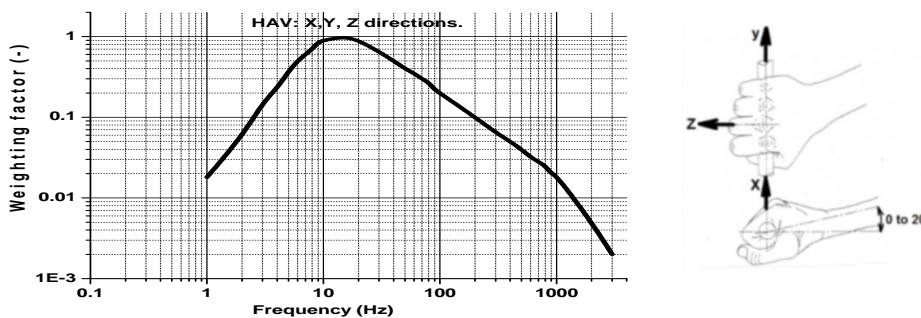


Figure 3. Amplitude-frequency characteristics of VBV filter

ASSESSMENT METHODS

Data evaluation

It comes out that applying the weighting as per ISO EN ISO 5349-1 and ISO 2631-1:1997 in investigations related to the human vibrations enables accelerations to be weighted in frequency domain as per subjective sensitivity of the humans. But, it is not in the practice, that humans are exposed to the same i.e. constant level of vibrations through the day. Consequently, some kind of additional evaluations have to be taken in consideration. All of them include different approaches to the hand-arm vibration (HAV) and whole body vibrations (WBV).

Basically, all measurements are based on acceleration measurements and data evaluation as given in Figure 4a. For clear understanding of Figure 4a it has to be noted that its' top part is related to WBV as well as HAV. For that purpose, at the top part of the Figure 4a (above dashed line) all signals are with index “.” which can be “h” – for hand-arm vibrations or “w” – for whole body vibrations. In that way, the top part of Figure 4a (from the top to the to the dashed, horizontal line which splits Figure 4a) can be taken as general (with exception of 6 boxes with dashed frames), while the bottom part is related to WBV (bottom, left) and HAV (bottom, right), only.

At the top part of the Figure 4a, signals marked with a_x , a_y , a_z represent raw signals from the accelerometers. Since they can be taken as general acceleration signals they still don't have “.” in the index. These signals have to be filtered with the filters given in Figure 2 and Figure 3. At the output of the filters the acceleration signals (based that particular filter was applied) can't be taken as general acceleration signals. Consequently, they are marked as $a_{.x}$; $a_{.y}$; $a_{.z}$ (where index “.” can be h – for HAV or w – for WBV). After filtering the root-mean-square values for time of integration of 1 s and for all signals have to be defined – see equation (1a), (1b), (1c).

$$a_x^{rms1s} = \sqrt{\frac{1}{\tau} \int_{t-\tau}^t a_{.x}^2 dt} \quad \text{where } \tau = 1s \quad (1a)$$

$$a_y^{rms1s} = \sqrt{\frac{1}{\tau} \int_{t-\tau}^t a_{.y}^2 dt} \quad \text{where } \tau = 1s \quad (1b)$$

$$a_z^{rms1s} = \sqrt{\frac{1}{\tau} \int_{t-\tau}^t a_{.z}^2 dt} \quad \text{where } \tau = 1s \quad (1c)$$

where index “.” can be “h” or “w” – for HAV or WBV.

After filtering and rms the acceleration signals are marked with a_x^{rms1s} ; a_y^{rms1s} and a_z^{rms1s} . In the literature this signals are frequently named as rms whole body acceleration (for particular axis) or rms hand-arm acceleration (for particular axis). The same have to be differentiated from “running rms values” of the signals which come as next in the order of raw acceleration signals evaluation – see equations (2a), (2b) and (2c). The “running rms values of acceleration” are nothing else but rms values for integration time from the beginning of measurement till its end. In Figure 4a running rms values are marked with $a_{.wx}$; $a_{.wy}$ and $a_{.wz}$. The first index can be “h” or “w” (as noted above). The second index “w” is to identify that weighting in frequency domain i.e. filtering was done, while the last index is to identify the axle along which the acceleration was measured.

$$a_{.wx} = \sqrt{\frac{1}{T_{exp}} \int_0^{T_{exp}} (a_x^{rms1s})^2 dt} \quad (2a)$$

$$a_{.wy} = \sqrt{\frac{1}{T_{exp}} \int_0^{T_{exp}} (a_y^{rms1s})^2 dt} \quad (2b)$$

$$a_{.wz} = \sqrt{\frac{1}{T_{exp}} \int_0^{T_{exp}} (a_z^{rms1s})^2 dt} \quad (2c)$$

where index “.” can be “h” or “w” – for HAV or WBV and T_{exp} is effective time of exposure to vibrations.

By definition the “running rms” of acceleration is not always increasing function. Figure 5 (with results of WBV measurement and data evaluation of the acceleration along 0z axis) gives clear picture of that. In the periods of time when a_z is at the higher than common level, or with the significant picks, the $a_{.wz}$ increases. But, if after that, for significant period of time a_z is with lower level that will reduce $a_{.wz}$ - the running rms of a_z . It can happen that human's body is exposed to the significant peaks of acceleration in short time, while in all other periods the acceleration is with extremely low level. As result of that, at the end of measurement the running rms would be very low and will not be good represent of that what was the vibration history to which the body was exposed.

To enable better identification of total value of acceleration absorbed by human body the dose value, defined as fourth power of weighted, running root-mean-square value of acceleration (noted as VDV) has been introduced – see equations (3a), (3b) and (3c). In Figure 4a the same is defined in the boxes with dashed frames (since that is applicable to the WBV, only).

$$VDV_x = \sqrt[4]{\int_0^{T_{exp}} (a_x^{rms1s})^4 dt} \quad (3a)$$

$$VDV_y = \sqrt[4]{\int_0^{T_{exp}} (a_y^{rms1s})^4 dt} \quad (3b)$$

$$VDV_z = \sqrt[4]{\int_0^{T_{exp}} (a_z^{rms1s})^4 dt} \quad (3c)$$

Based on different sensitivity of humans to the acceleration along particular axis, the next sequence in data evaluation is to multiply already calculated values with k_x , k_y and k_z where index “.” can be “h” for HAV, or “w” for WBV. In line to humans’ sensitivity to vibration the following levels of k factors are defined through standards:

$$\text{HAV: } k_{hx} = k_{hy} = k_{hz} = 1 \quad (4)$$

$$\text{WBV: } k_{wx} = k_{wy} = 1.4 ; k_{wz} = 1 \quad (5)$$

Assessment methods for HAV

Overall hand-arm vibration level can be derived as per scheme given in Figure 4a, bottom right, while the overall whole body vibration can be derived as per Figure 4a, bottom left. For the assessment of HAV the only important is a_{hv} - value which has to be derived for the period of 8 h. In that way a_{hv} would become “daily exposure value” $A(8)$ as it is given in equations (6) to (8).

$$a_{hw} = \sqrt{a_{hwx}^2 + a_{hwy}^2 + a_{hwz}^2} \quad (6)$$

$$A(T_{exp}) = a_{hw} \sqrt{\frac{T_{exp}}{T_0}} \quad \text{where } T_0 = 8 \text{ h} \quad (7)$$

$$A(8) = A(T_{exp} = 8h) \quad (8)$$

where T_0 is the reference duration of 8 hours for calculating the “daily exposure level” and T_{exp} is the effective time of exposure to the vibrations.

General approach related to the permissibly levels, accepted worldwide and already included in various regulations is as follows:

- daily exposure action value of 2.5 m/s^2 and
- daily exposure limit value of 5 m/s^2 .

The meaning of terms “action value” and limit value” has to be explained. As long as $A(8)$ is below 2.5 m/s^2 no actions to eliminate or reduce vibration have to be done. If the vibrations are above that value (and below limit value) the programme of measures to eliminate, or reduce vibrations to the minimum risks, must be implemented. If overall daily exposure value is above 5 m/s^2 the immediate action to prevent exposure above the limit value has to be done.

In addition to assessment exposed above another one, named “exposure point system” can be implemented. The assessment of the HAV in „exposure point system“ is nothing else than simplification of the $A(8)$ approach. For any condition, the number of exposure points accumulated can be calculated as given in equation (9).

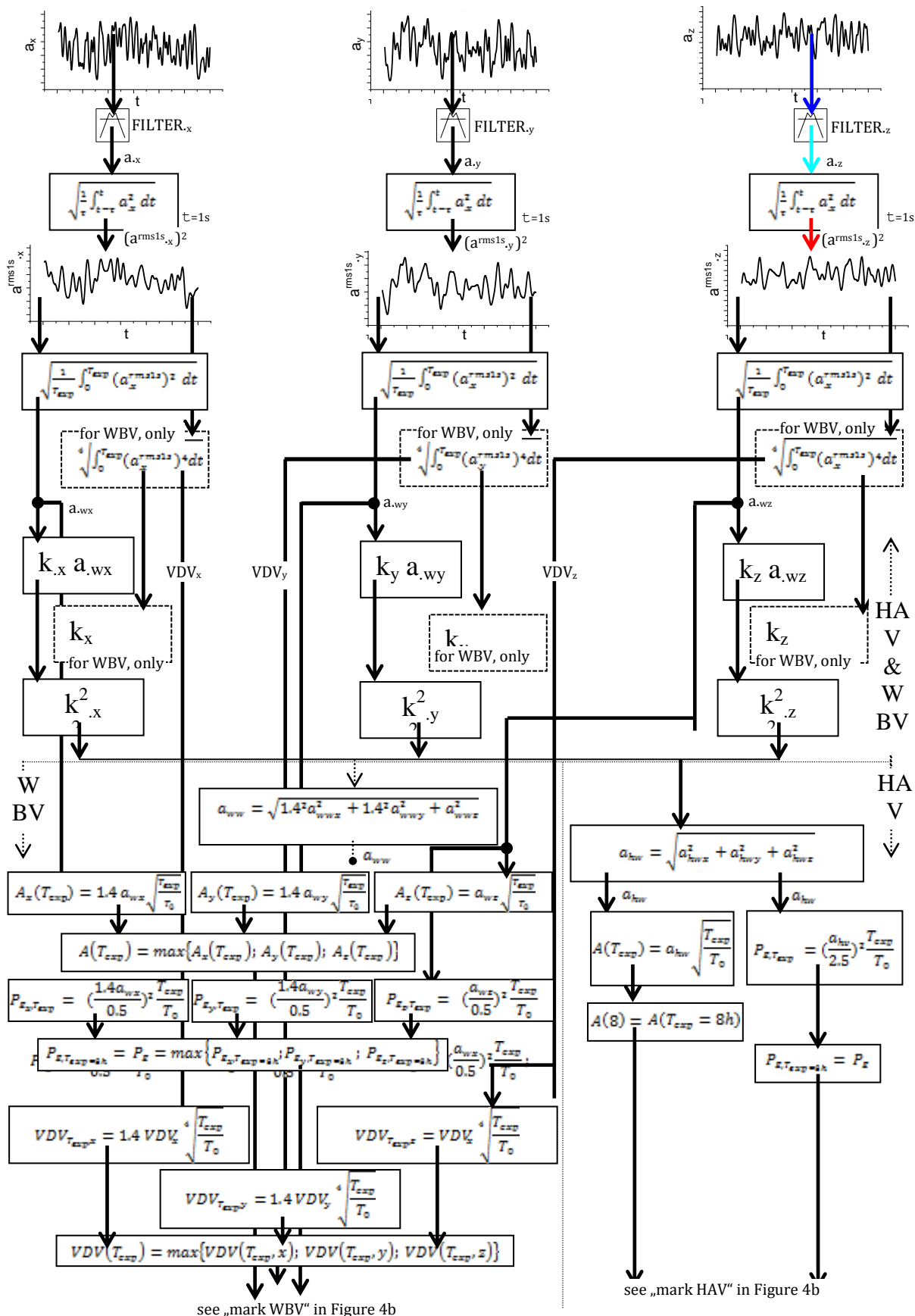
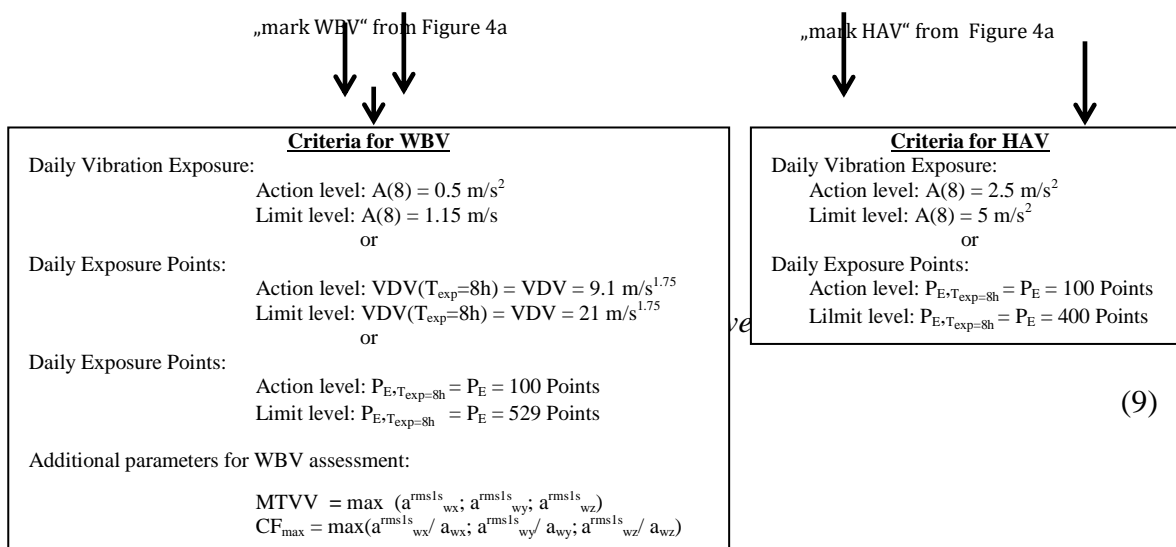


Figure 4a. Data evaluation flow chart for HAV and WBV (for coloured lines see Figure 5)



Based on

$$A(8) = 2.5 \sqrt{\frac{PE}{100}} \quad (10)$$

it comes out that the:

- daily exposure action value = 100 points and
- daily exposure limit value = 400 points

Assessment methods for WBV

Opposite to the hand-arm vibration the assessment of the whole body vibration is more complex and sometimes, it becomes appropriate to be assessed not only through one parameter.

The most important difference in WBV risk assessment (related to the HAV) is that arbitration total value is not criteria for the assessment. Instead of total value the vibration daily exposure value for each of the three axes separately has to be calculated and the highest of the three has to be placed in relation to the „action“ and „limit“ values (see Figures 4a and 4b and equations (11a) to (11d) – limit and action values are given in the text in next page.

$$A_x(T_{exp}) = 1.4 a_{wx} \sqrt{\frac{T_{exp}}{T_0}} \quad (11a)$$

$$A_y(T_{exp}) = 1.4 a_{wy} \sqrt{\frac{T_{exp}}{T_0}} \quad (11b)$$

$$A_z(T_{exp}) = a_{wz} \sqrt{\frac{T_{exp}}{T_0}} \quad (11c)$$

$$A(T_{exp}) = \max\{A_x(T_{exp}); A_y(T_{exp}); A_z(T_{exp})\} \quad (11d)$$

or, for $T_{exp} = T_0 = 8 \text{ h}$ it becomes that the daily exposure value is:

$$A(8) = \max\{A_x(8); A_y(8); A_z(8)\} \quad (11e)$$

Important phenomenon regarding WBV is a human sensitivity to the high accelerations with short duration (transient acceleration). From the exposed above it is obvious that vibration daily exposure values are based on weighted, running mean-square-root values and in that way can't give clear picture in case where high amplitude vibrations are with duration relatively short to T_{exp} .

There are two ways for assessment of transient vibration. First one is defining the maximum transient vibration value (notation: MTVV) which is maximum weighted, running root-mean-square value of acceleration found over each measurement period i.e. T_{exp} .

The second method is to define the cumulative value which increases with the measurement time. This has to be the fourth power of weighted, running root-mean-square value of acceleration. This value is named “Vibration Dose Value” (VDV) - see equations (12a) to (12d) and figure 5.

$$VDV_{T_{exp},x} = 1.4 VDV_x \sqrt[4]{\frac{T_{exp}}{T_0}} \quad (12a)$$

$$VDV_{T_{exp},y} = 1.4 VDV_y \sqrt[4]{\frac{T_{exp}}{T_0}} \quad (12b)$$

$$VDV_{T_{exp},z} = VDV_{xz} \sqrt[4]{\frac{T_{exp}}{T_0}} \quad (12c)$$

$$VDV(T_{exp}) = \max\{VDV(T_{exp},x); VDV(T_{exp},y); VDV(T_{exp},z)\} \quad (12d)$$

where VDV_x , VDV_y and VDV_z are defined in equations (3a), (3b) and (3c), respectively.

As it is recommended in ISO2631-1:1997, the following criteria has to be used in defining the parameter(s) which would be taken as the referent for the assessment of the WBV. In case that $MTVV^*/a_{ww}^* > 1.5$ the MTVV should be considered in addition to criteria based on a_{ww}^* i.e. $A(T_{exp})^*$, where * change x, y or z. In case that $MTVV^*/(a_{ww}^* T_{exp}^{(1/4)}) > 1.75$ the VDV should be considered in addition to criteria based on a_{ww}^* i.e. $A^*(T_{exp})$, where * change x, y or z.

The additional recommendation given in ISO2631-1:1997 is: if ratio of peak of weighted acceleration to maximum of running rms value (MTVV) over T_{exp} i.e. $\max(a_w^*) / MTVV^*$ is > 9 then VDV should be considered as criteria in addition to running rms. Defined ratio was named as crest factor (CF). In more precise approach it would be noted that, defend in that way, CF is ratio between max. values of two signals which may have occurred at a different time. It has to be recognized that the defined in technically more correct way: the crest factor (CF) is ratio between local peak values of filtered acceleration i.e. a_w^* and local rms peak values i.e. a_w^{rms} which must occur in the same time – see Figure 6. To make distinguish between two approaches in defining CF the last one will be named as local CF (local in time domain).

The action and limit values which are accepted for WBV are:

- Action level (above which the risks from vibration exposure must be controlled) is defined as $A(8) = 0.5 \text{ m/s}^2$ or daily VDV of $9.1 \text{ m/s}^{1.75}$.
- Limit level (above which person should not be exposed) is defined as $A(8) = 1.15 \text{ m/s}^2$ or daily VDV of $21 \text{ m/s}^{1.75}$.

Same as in HAV the point approach can be implemented to WBV in which the number of exposure points can be calculated as per equation:

$$P_{E_x,T_{exp}} = \left(\frac{1.4 a_{wx}}{0.5}\right)^2 \frac{T_{exp}}{T_0} \quad (13a)$$

$$P_{E_y,T_{exp}} = \left(\frac{1.4 a_{wy}}{0.5}\right)^2 \frac{T_{exp}}{T_0} \quad (13b)$$

$$P_{E_z,T_{exp}} = \left(\frac{a_{wz}}{0.5}\right)^2 \frac{T_{exp}}{T_0} \quad (13c)$$

$$P_{E,T_{exp}=sh} = P_E = \max\{P_{E_x,T_{exp}=sh}; P_{E_y,T_{exp}=sh}; P_{E_z,T_{exp}=sh}\} \quad (13d)$$

Based that

$$A(8) = 0.5 \sqrt{\frac{T_E}{100}} \quad (14)$$

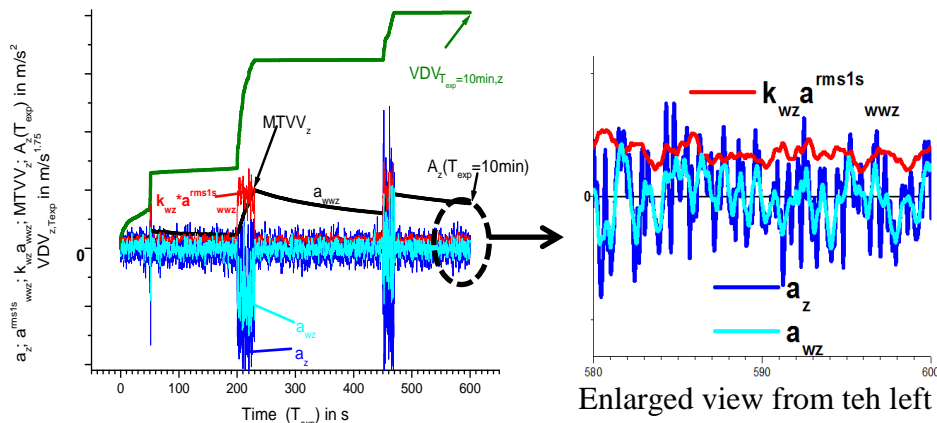


Figure 5. Sample from WBV measurement along 0z axle

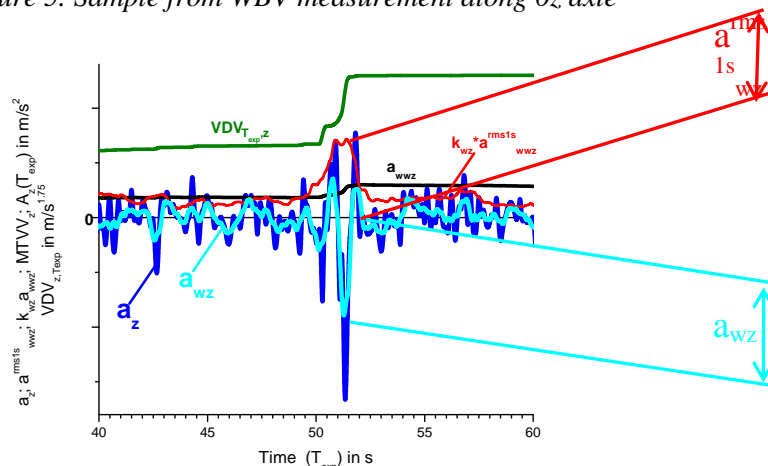


Figure 6. "Local" Crest Factor: $CF = a_{wz} / a_{rms}^{rms1s}$ (shown in this figure) is not same as $a_{wz} / \max(a_{wwz})$ i.e. $a_{wz} / MTVV_z$ since they may have occurred at a different time (For $MTVV_z$ see value in Figure 5)

It comes out that, in point approach:

- Action level value is $P_E = 100$ points, while
- Limit level value is $P_E = 529$ points.

HVB AND WBV REGULATIONS VS PRODUCT CERTIFICATION REGULATIONS

The product certification process considers the set of procedures, testing and audits which has to be performed with positive results. The purpose of certification process is to check does the product meet qualification criteria.

Since the humans are exposed to the vibration mainly in contact with technical systems i.e. by use of technical systems, it can be assumed that the certificated technical system would be safe for humans including WBV and HAV. Unfortunately, that is not case with many products. The reason is related to the service condition i.e. the different ways in which health regulations and technical regulations take in to account service conditions. There are many products which vary with vibrations based on service condition. Clear examples are all public transport vehicle, passenger cars, forestry, construction, agricultural machines, etc.

Based that service conditions are not uniform, it is impossible to predict accurately what would be the impact of the particular machines to the humans in terms of vibration. That is the reason based on which certification technical regulations are not harmonized with health regulations related to the human vibration

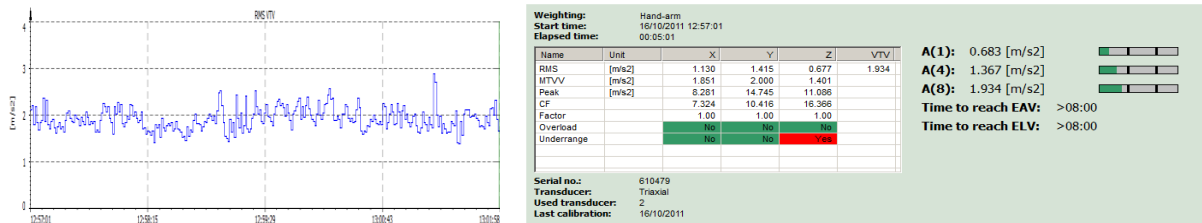


Figure 7. Record (a_{hv} in time domain – on the top) and evaluated data (bottom) for HAV on AGT's steering wheel – service condition 1 (in-field operation); RMS has meaning of running rms

The general approach in certification regulation is to define particular service condition in which technical system has to be tested. Unfortunately, that is only one among many very different conditions. To solve the problem, and to protect person from high level of vibrations all health directives related to HAB and WBV call for measurement in real service which is typical. It is clear that in some cases the same technical system can give acceptable level of vibrations while in some others it would be different. That opens the problem of responsibility. If the system is certificated and placed on the market and if, in particular service, it will be found that human vibrations are above action or limit value, who has to take the responsibility and do correction actions?

European health directives call for management staff to do the same. That looks as a good approach since they manage the process. The problem is that directives ask for action from management in process where the technical system is in service, not from the management responsible for lunched the technical system. It is obvious that in some cases i.e. in particular service conditions it would be unavoidable to have high level of vibration with particular technical system. For those who are named as holders of the responsibly the situation can be explained in the following way. If the technical system is certificated and placed in service for which it has been designed, in which way one can have problem with human vibrations?

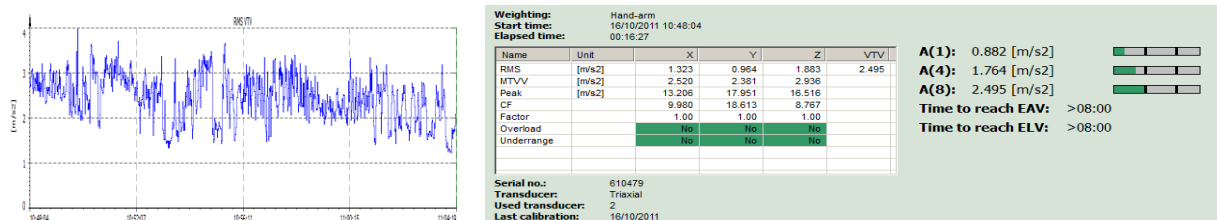


Figure 8. Record (a_{hv} in time domain – on the top) and evaluated data (bottom) for HAV on AGT's steering wheel – service condition 2 (in-field operation); RMS has meaning of running rms

The next example – example of HAV on an agricultural tractor's steering wheel, can be good illustrative example for problem of un-harmonized health regulation for human vibrations and technical regulations for product certification.

As it was given in Figure 8 to Figure 10 in the different service condition the same vehicle, agricultural tractor (AGT), shown acceptable level of HAV at its steering wheel. As it can be recognized all service conditions were very typical. Based on technical directives the product has been certificated and lunched to the European market.

As it was declared buy the manufacturer, and found through certification testing, the product was found vibration safe in various applications. But, in spite of the manufacturer declaration a few owners reported the problems. One of them has conducted the assessment for daily exposure to HAV for his employee and has found that in many cases the value A(8) was above 2.5 m/s².

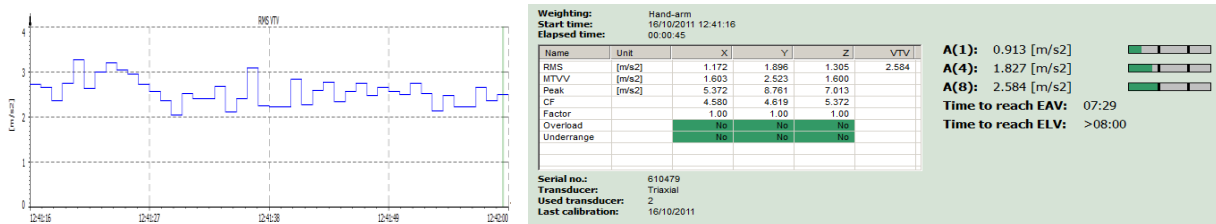


Figure 9. Record (a_{hv} in time domain – on the top) and evaluated data (bottom) for HAV on AGT's steering wheel – service condition 3 (on road service, max. speed); RMS has meaning of running rms



Figure 10. Time history (a_{hv} in time domain) for HAV on AGT's steering wheel – service condition 4 (vehicle speed 0 km/h, no load, and partial to full throttle).

To solve the problem, certification authorities have conducted in detail investigation. The finding was that in particular engine rpm bands the HAV on the steering wheel was above 2.5 m/s^2 – see Figure 10. Consequently, it has found necessarily to redesign product.

As it was given in previous example there is no guaranty that certificated system would not cause problem in real service.

CONCLUSION

The paper reviews the significant improvement in monitoring human vibrations. In the main the improvement is consequence of implementation of various regulations which are mainly harmonized through the world. Clear technical procedures for measurement and assessment of the hand-arm vibrations (HAV) as well as whole body vibrations (WBV) were established and defined in international standards. Since the limits for HAV and WBV are harmonized through the world, the significant improvements in protecting humans against vibration were done. It was found that there is no better way to protect humans in their working ambient other than to improve testing specification for certification purposes. This means that it would be no one service condition in which technical system would cause HAV and WBV above action level, or at list above limit level. Only in that way it would be possible to harmonize all health and safety directives i.e. technical regulations which are applicable for new system certification.

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**THE MAPPING THE RAILROAD NOISE ACCORDING TO
STANDARDS**

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ABSTRACT

The main aim of this work is to point out that with our own resources and knowledge we can organize and accomplish the mapping of railroad and industrial noise according to the contemporary standards and legal acts in the European Union. Precisely in this example, a way of modeling the railroad noise according to ISO 9613-2 and RLM2 standards is processed. It presents a way of mapping railroad noise, whose methodology can be used for mapping of the other sorts of traffic (road and air transport for example) with certain variations, and for mapping of the industrial noise. A part of the work refers to the use of the LIMA software for the prognosis of the noise and vibrations, and which is also in accordance with contemporary standards and rules.

Key words : *Model, mapping, noise, standard.*

INTRODUCTION

To be able to do the mapping of traffic noise (noise road vehicles, rail vehicles, noise, noise cheap), or industrial noise, a prior series of measurements of noise at the very beginning. These measurements are organized in accordance with applicable standards and regulations, with precisely determined measurement locations and the method of measurement (selectable read out scales and weight measurements).

In this case is elaborated railway noise emission modeling, where we want to show the methodology, without the input and processing of measured values of sound. So, it is a methodological approach to railway noise mapping, with respect to standards ISO 9613-2 and RLM2, since we do not have a national standard for the area.

Here will be described briefly railway noise mapping using LIMA software for prediction of noise and vibration. The above software is used in Western European countries, and provides a very clear and useful results, based on which further work on the design of protective barrier and other noise, due to the volume which will not be detailed in this paper.

STANDARD ISO 9613-2

Standard under the label in the title refers to the fact that direct research toward engineering acoustics, and the method of calculation and forecasts emissions outside noise at a distance from the sound emitters. This method predicts the equivalent continuous A - weighted sound pressure level values based on the weather condition is favorable for the spread of sound from sound emitters whose emissions known (previously measured).

Noise emission from the broadcasters to the recipient depends on the transmission medium (terrain), transfer the sound environment (air, water, earth ...), air pressure, air temperature and wind strength

and direction (which are the main factors when measuring noise emissions) and other conditions under which transmits audio broadcast. For each of these conditions, which may have an impact on the final value of the emission of sound, there are some fixes, listed in the appropriate tables. Standard ISO 9613 specified that the exact measurements performed in octave algorithmic scale with a nominal frequency range between 63 Hz and 8 kHz. Here is the source of the sound, which can be stationary or mobile. Typical methods are given in the accompanying algorithms for physical effects:

- Geometric deviation,
- Atmospheric absorption,
- The effects of land
- Rejection of the substrate,
- Protection from obstacles.

DUTCHSTANDARDRLM2

Since 1996., this standard is applicable in Europe for the calculation of rolling noise and was adopted by the European Commission. This standard describes the method and the results are obtained using noise emission of appropriate software for noise prediction. It is the LIMA software, which supports the RLM2 with that really get graphic review of the noise emission. It should be noted that this standard is also used to map the external noise.

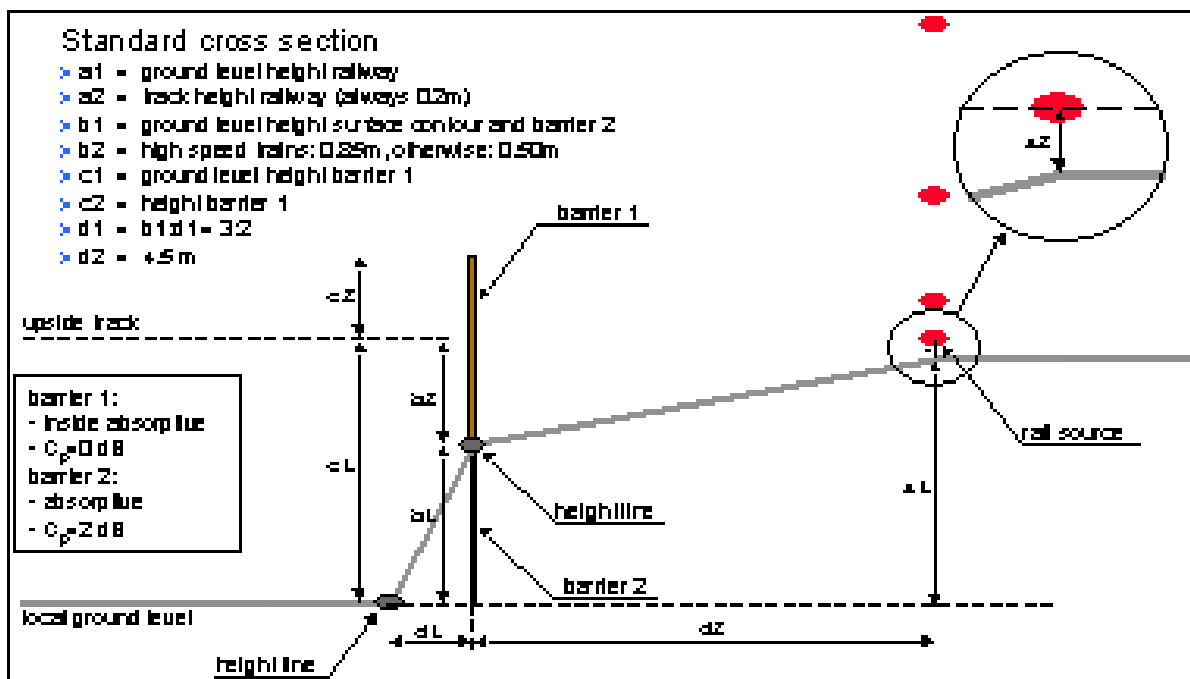


Figure 1. Standard model rail way sources noise is defined under RLM2

In Fig. 1 shows the real source of the sound propagation direction encountering some barrier and has a certain value upon them. Page measurement of reflectance and source model are standard specific values that off set the differences in different software for noise mapping. This gives approximately the same results, which do not deviate from the real value.

RLM2 the octave scale model with frequency range from 63Hz to 8000Hz, which is defined nine categories of trains (Fig.2) shows similar characteristics to define in terms of speed of movement of the track, stopping trains per cent and average traffic density in a given period (day, night).

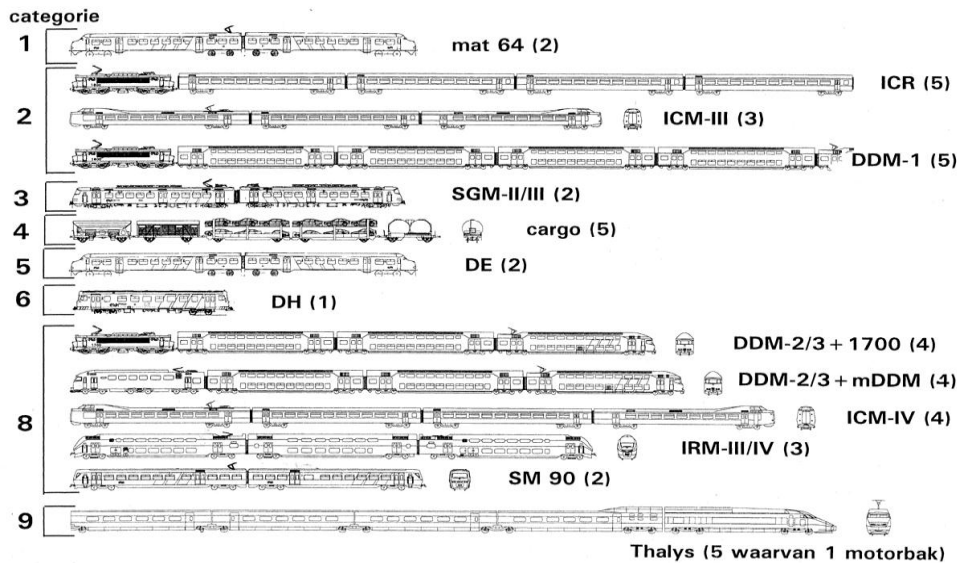


Figure 2. Categories defined by the standard of trains RLM2

Figure 2 shows how the car has a composition similar to the numbers that determine the category of the train.

Figure 3 presented five sources of noise for the category of the train at different positions.

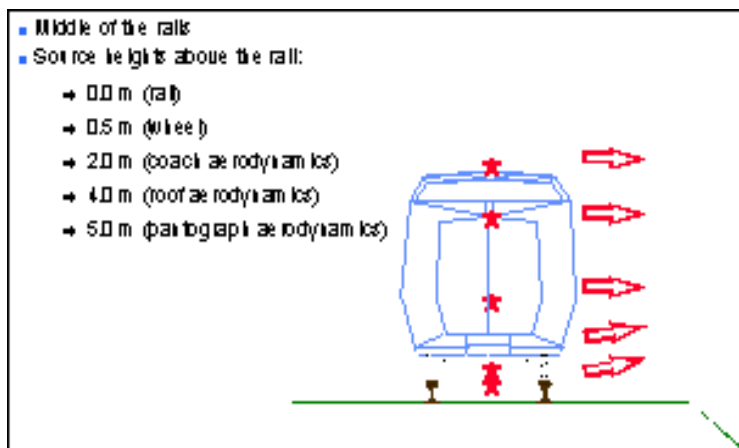


Figure 3. Noise sources and their position with respect to gauge

In most cases, only the bottom two sources are used for mapping (4m and 5m). Similar to ISO 9613 and here in the calculation of emissions must take in to account the geometric deviation, absorption of air and land barriers, reflections and meteorological condition at the time of measurement noise.

LIMA SOFTWARE FOR MAPPING NOISE AND VIBRATION

In Figure 4 presents the organization of the concept of server computing to perform operations, forecasting and presenting the results of emission of noise and vibration.

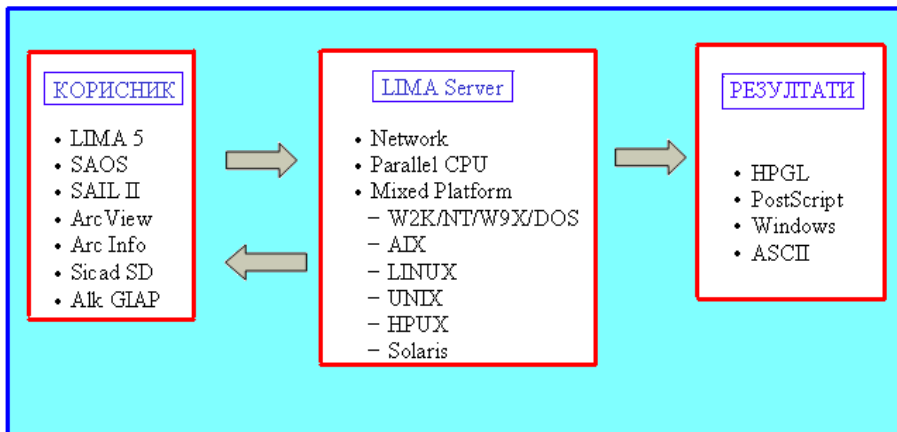


Figure 4. Server organization for computing the prediction of noise and vibration

All the data can be displayed in 2D or 3D. In this way we get a very clear computer simulation output data, followed by a very high graphics.

RAIL WAY NOISE CALCULATION TECHNIQUE LIMA IN SOFTWARE

In order not to go into the details, because of the scale of the process of preparation and computation train noise will be a brief description of the methodology used for this mapping. In the work place LIMA software necessary to open the working folder for this calculation. Furthermore, based on the ortho photo image to enter the facilities, if any, and to gauge if they are at a distance that is taken for computation, for example. 150 meters from the track axis. In Figure 5 the red and orange objects on display gauge.

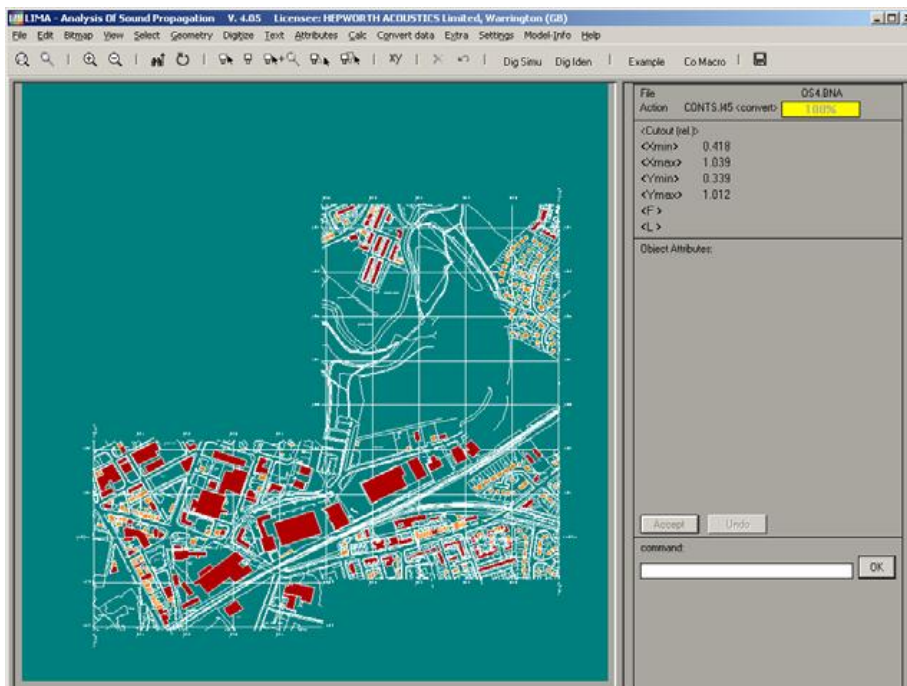


Figure 5. Desktop Software LIMA and labeling facilities

Continue to be done counting railroad trestle (which in this case are called lines). Depending on the number of track sand so it draws the line, and later marks and numbers.

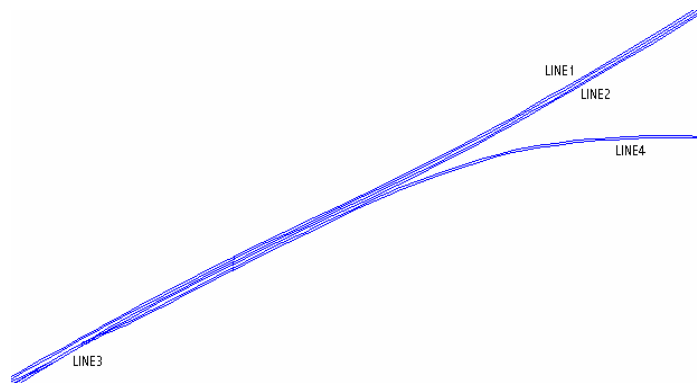


Figure 6. The lines indicate the four tracks

Computation technique is such that the line should be matched by providing direction can be connected together to count, if you are the same initial conditions, for example. lines1 and 2 maybe the same source. This combination maybe only along certain sections, where they match some other characteristics such as the speed of the train, daily traffic density, number of stop and routes and more.

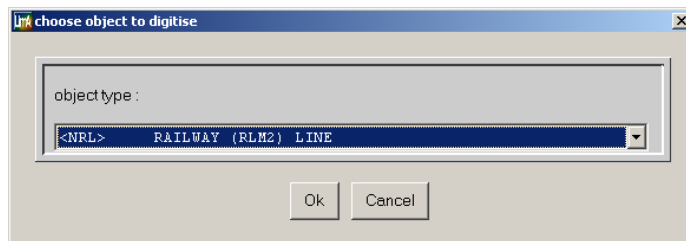


Figure 7. The choice of object counting

To Figure 7 be noted that for the selected object counting coaster where counting will take place on the principle RLM2 standards, where the rail is considered as a line source. Further approaches to assigning attributes, as shown in Table 1.

Table 1: Assign attributes for tracks (lines)

	Train Line Data			
	Line 1	Line 2	Line 3	Line 4
<NRL>	Line1	Line2	Line3	Line4
<RQ> Geometry	1	1	1	1
<Z> Height	0 R	0 R	0 R	0 R
<EH> Emission Heights	Do not alter this attribute			
<EHD> Displayed Height	0	0	0	0
<VAD> Admitted Speed (kmh)	100	100	80	80
<MSW> Track Type	1	1	1	1
<IBB> Index BB	1	1	1	1
<REG> Regulation	RLM2_TA B	RLM2_TA B	RLM2_TA B	RLM2_TA B

When you add the required attributes only need to start the server I still perform calculations. Upon completion of the calculation of track, trains approach to the formation of the addition of trains on the track.

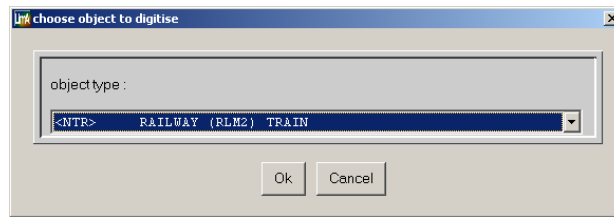


Figure 8. The choice of object counting

Here we notice that it is now the selected object computing train, which his now added to its attributes. It is necessary now to add attributes to the working surface of train tracks (lines) and can begin the process of calculating the train noise. The software also allows subsequent amendments for a given computation, and the adjustment of the obtained values as could be represented graphically.

Table 2: Assign attributes for trains

Attribute	Train 1
Runs on Lines	1
<BTR>	Train1
<ID> ID of the Train	1
<RQ>	0
<ND> Number of trains per daytime period	32
<NN> Number of trains per night-time period	15
<NE> Number of trains per evening period	20
<CAT> Category of Train (Type)	9 High Speed Train (TGV or Thalys)
<NLW> Number of Motor Units and Wagons	2 8 Default setting for a TGV or Thalys
<VMX> Speed (kmh)	100 V
<EH> Emission Heights	Do not alter this attribute
<REG> Regulation	RLM2_TAB

More detailed view of the train noise emission calculations will be described in this paper.

CONCLUSION

The aim of this paper is to briefly clarify the standards ISO 9613-2 and RLM2, and to describe the LIMA software for prediction of noise and vibration. Here are the basic requirements that must be complied with in order to get a noise map which will be in accordance with current EU standards. This way, with us able to perform a mapping of the noise in the larger space, which is in the world today has become a legal obligation. Data obtained from the measurement and prediction, in this case the train noise can have many benefits, including:

- Determine the value of an equivalent level noise acting on the surrounding buildings, which mission a point.
- Based on the values of noise can beto calculate the speed of the train where there is less noise emission.
- Based on the data obtained in this way calculation can be made of protective barriers to mitigate the adverse effects of noise the surrounding objects and people in general, and more.

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ELECTRO AND ELECTRO-MAGNETIC POLLUTION IN URBAN AREAS

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**MOTHERBOARDS AND OTHER CIRCUIT BOARDS IN WEEE
RECYCLING PROCESS**

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ABSTRACT

Reuse and recycling have become crucial because the rapid advancement in technology has led to the accelerated obsolescence of electronic equipment. Disassembly is the first stage in the recycling process. Manual disassembly has proven to be the most efficient although cost-effective method. Automated systems find their implementation only when relatively uniform-type equipment or assemblies are disassembled. Layout changes can enhance the disassembly speeds by efficient material movement.

Key words: *motherboard, disassembly, reuse, recycling, hazardous materials, layout.*

INTRODUCTION

Motherboards and other circuit boards are popular items for recycling since circuit boards can contain 40 to 800 times the concentration of gold ore and 30 to 40 times the concentration of copper ore mined in the United States.

Dangerous substances in circuit boards

Circuit boards contain a variety of materials and components, including some which are qualified as dangerous substances. These harmful substances are usually found in the circuit board conductors including solder, plastic with flame retardants, batteries, capacitors and resistors. These components contain materials dangerous to the environment, such as mercury, lead, cadmium, chromium, chlorofluorocarbons (CFC), polychlorinated biphenyls (PCB), polychlorinated naphthalenes (PCN), brominated flame retardants (BFR). Some of these elements, with their harmful effect on the environment, people and animals, are described here (Koch and Kasper, 1996; NN, 2003; Kljajin et al., 2006).

Cadmium (Cd) is a heavy metal, scientifically proven to be a health hazard. It is a toxin which deposits in the body, damages kidneys and can be harmful to fragile bones. It is an integral part of many solders, as well as a pigment and plastic stabilizer. Computer batteries, which memorise system time, are partially made of cadmium. It has been established that 9 % of all cadmium ends up in municipal solid waste: 95 % of this are batteries and 0,1 % cathode tubes.

Lead (Pb) – the sources of lead are circuit board solders, pigments and plastic stabilizers. It has been established that 17 % of the total amount of lead in municipal solid waste comes from e-waste (further 65 % comes from lead-acid batteries and rechargeable lead batteries). In EU, that number is even higher – as much as 40 % in municipal solid waste. Lead has many ill effects on human organism, especially on the nervous system, vascular system, kidneys and reproductive system; it inhibits mental development of children as well as fetuses. It is accumulated in the environment and can cause acute and chronic human, animal and microorganism diseases.

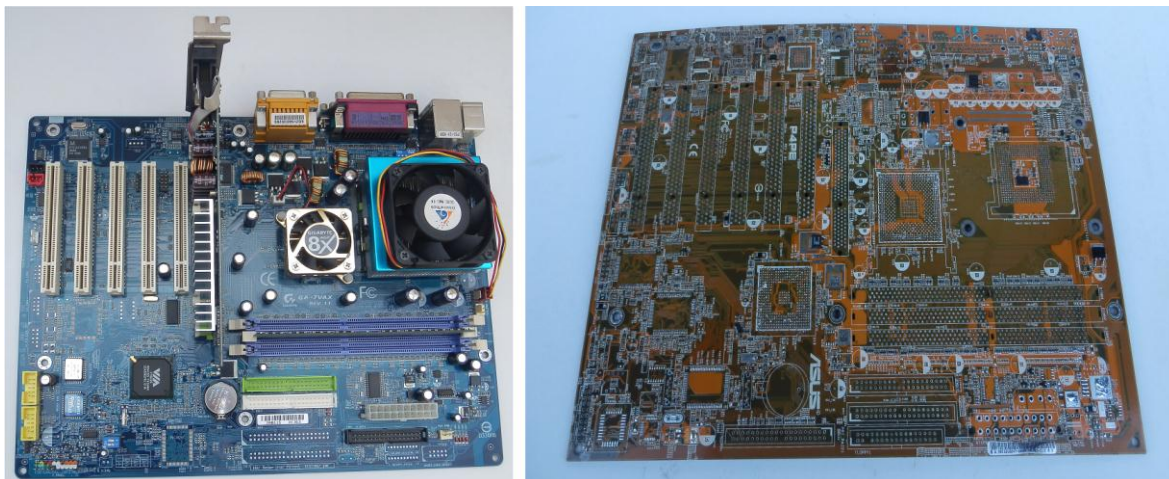


Figure 1. Motherboard before and after disassembling electronic elements

Hexavalent chromium (Cr) is commonly used for coating different parts of casings, for anticorrosive coating of steel plates (hexavalent chromium is ductile metal and does not oxidate) and in manufacturing printed circuit boards. Hexavalent chromium is very mobile and can move a great distance from its source. It is highly toxic for plants and animals and, under certain circumstances, for people as well. Hexavalent chromium can cause damage to the DNA and asthmatic bronchitis.

Brominated flame retardants (BFRs) are used as protection from burning of electronic equipment. They are mainly used in printed circuit boards, connectors and plastic casings. Plastic with flame retardants makes up about 5,5 % of the total mass of e-equipment, or about 25 % of total plastic used in e-equipment. About 80 % of this plastic is treated with BFRs. Some BFRs are organic bromine derivatives which are very long-lasting and prone to accumulating in human and animal fat.

Legislative regulations state that they have to be disposed of in a manner not harmful to the environment and on special landfills.

MOTHERBOARD RECYCLING METHODS

Manual disassembly is the best method for preserving the function of motherboard elements. However, it is the least cost-effective process, since it is difficult to make it automated – boards are disassembled one element at a time.

Mechanical methods are mainly based on grinding whole motherboards (with components) after which different materials are sorted. It is not possible to reuse motherboard components. More valuable parts, like gold and palladium contacts, are sometimes detached prior to grinding. This method is questionable from the ecological point of view.

Chemical methods are based on applying corrosive substances to solder, thus freeing all soldered motherboard components so they can be detached easily. This is one of the so called "cold procedures", so no thermal damage is expected. This process has to be executed following the strict control procedures because the process itself is dangerous (hazardous) to the environment.

Thermomechanical methods – since the melting point of circuit board solder is around 250 °C, hot air or hot air atmosphere can be used for this purpose.

The prototype has electrical heaters and fan for producing hot air built into the bonnet. Hot air temperature within the bonnet is around 300 °C. Only the side of the circuit board without any electronic components is heated. Directly under the bonnet, motherboard is held by jaws and they

vibrate together vertically and horizontally. Vibrating forces ($F = m \cdot a$) which act vertically on the soldered elements of the circuit board (Figure 2), for some typical elements amount:

$$m_1 = 3,5 \text{ g} \rightarrow F = 0,35 \text{ N}; A = 1 \text{ mm}; f = 50 \text{ Hz}$$

$$m_2 = 2,7 \text{ g} \rightarrow F = 0,27 \text{ N}; A = 1 \text{ mm}; f = 50 \text{ Hz}$$

$$m_3 = 0,5 \text{ g} \rightarrow F = 0,05 \text{ N}; A = 1 \text{ mm}; f = 50 \text{ Hz}.$$

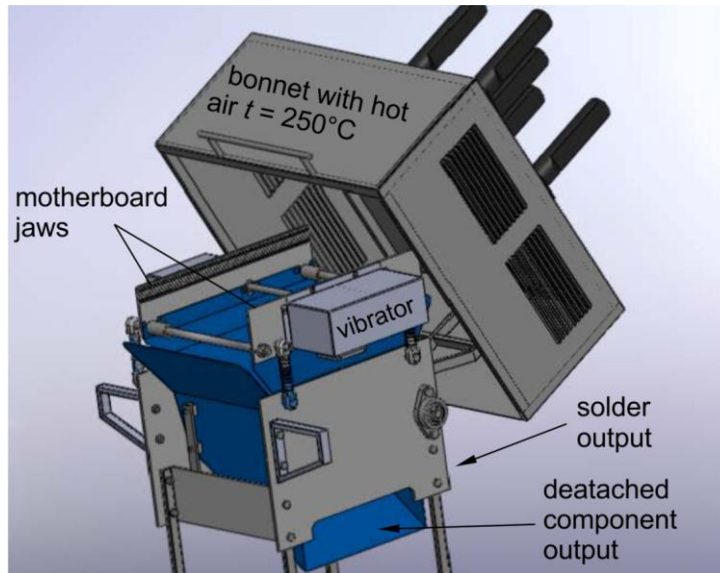


Figure 2. Prototype of electronic components detaching device

Even though these forces seem small (they can be increased), the experiment has proven them sufficient, since most elements detached under their own weight, however small it was (Figure 3 and Figure 4).

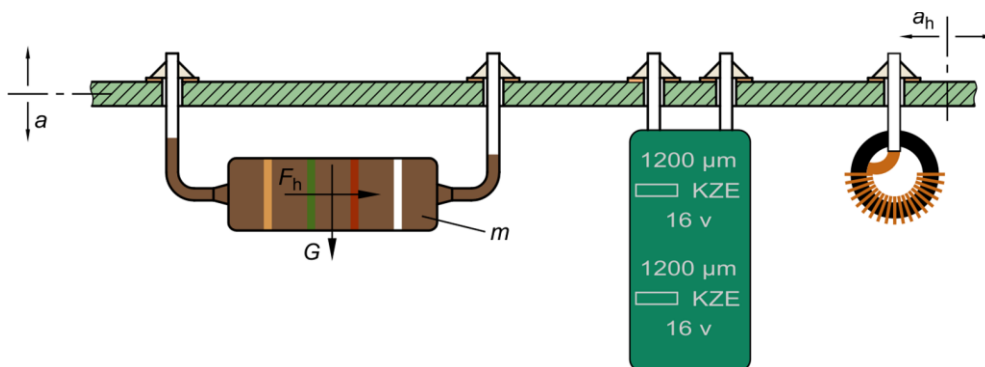


Figure 3. Vibrating forces acting on electronic elements



Figure 4. Some disassembled electronic components detached under their own weight

There are two panels on the bottom side of the device. The upper grate-like panel gathers detached electronic elements. It is placed at an angle so that gravity leads those elements to a container letting through only solder drops which are collected on the lower panel.

In order to preserve the integrity of the built-in elements, it is essential that the temperature on that side of the board is kept low enough so that those elements and circuits of the motherboard remain functional.

A portion of the disassembled elements underwent testing. Over 80 % proved to be in working condition. Some thermoplastic elements were slightly damaged by the heat.

END-OF-LIFE OPTIONS FOR MOTHERBOARD

The electronic equipment is assumed to have reached the end-of-life (EOL) status when it has served its useful life and/or is no longer functional or when technological obsolescence renders it unusable (Leet Socolof et al., 2001). In the past, landfill has been the prevalent method for the disposition of post-use electronic equipment (i.e., those re-used after being resold or donated). However, with the increasing awareness of potentially harmful life-cycle environmental impacts, dwindling natural resources, government regulations against disposal of toxic substances in landfills, and the consequent development of markets for recycled components and materials, more options are now available for the disposition of post-use electronic equipment (e.g. PCs, computer monitors, motherboards, etc.) (Leet Socolof et al., 2001). The EOL options for the electronic motherboard are graphically depicted in Figure 5.

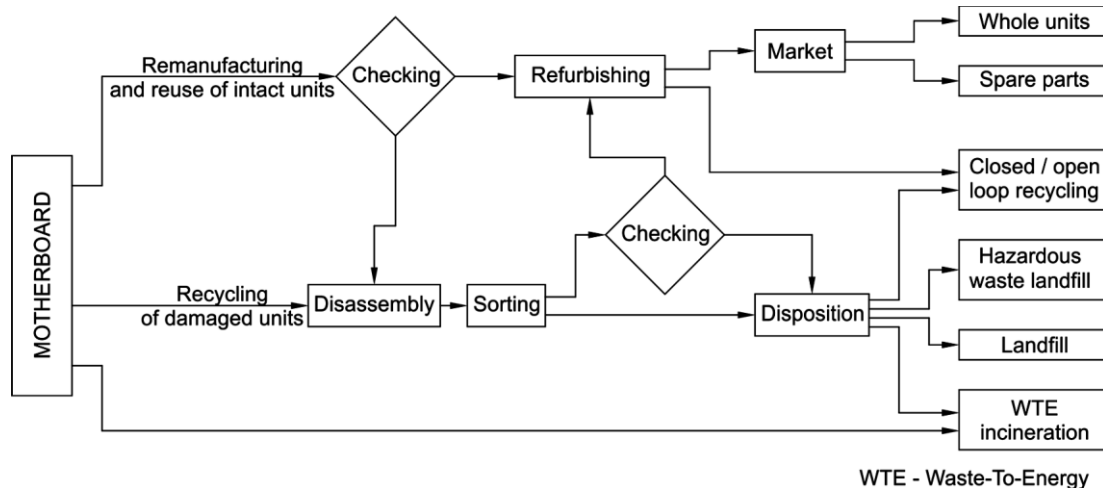


Figure 5. EOL options for motherboard

Environmentally preferred EOL disposition options are reuse, recycling and remanufacturing. Reuse, often as a result of reselling, involves continued use of the electronic equipment for the purpose for which it was built, and is considered to occur within its originally intended useful life. Remanufacturing is a viable option for the electronic equipment that is no longer functional but could be refurbished (upgraded or restored to working conditions) at a cost lower than that of manufacturing a new electronic equipment, to be sold again in domestic or foreign markets. Recycling involves recovering the individual materials from EOL electronic equipment, to be used in the production of new electronic equipment (closed-loop recycling) or in other products (open-loop recycling). Two other disposition options are waste-to-energy (WTE) incineration in incinerators or municipal WTE facilities and landfilling as the most undesirable option (Leet Socolof et al., 2001).

CONCLUSION

Layout changes can enhance the disassembly process by efficient material movement. The new disassembly concept introduces some solutions for known problems in the existing layouts. Focusing on the disassembly of motherboard found in residential waste stream and sorting it by type prior to disassembly enhances the disassembly speed because the operators disassemble similar equipment per time unit. The closed loop conveyor is introduced so that the operator could pick a certain type of unit which is the most similar with the last one disassembled. The disassembly process can be further enhanced by implementing automatic operations for specific processes, such as punching out screws, or unscrewing screws. Manual sorting operations can be replaced with an automatic vision recognition system but its effectiveness must be enhanced.

The material flow, in the above described disassembly system, is physically carried out by means of a conveyor system and all drives, sensors and actuators are operated using a modern control system. An efficient utilization of this equipment requires a computer aided planning approach, which can be supported by a bundle of simulation tools (Kernbaum et al., 2006).

Based on the conducted experiments, it can be concluded that the researched method gives encouraging results. However, some caution is needed because not all components have been tested, so it cannot be stated with absolute certainty how many of them can be returned into the production cycle or used in other products.

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RECYCLING OF ELECTRONIC WASTE IN REPUBLIC OF SRPSKA

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ABSTRACT

Contemporary technology and technique and their constant improvements have enabled quality products to be produced by processing waste substances. There is a constant progress that leads to an increasing level of utilization of resources, and results in an increase in cost-effectiveness and profitability. In many developed industrial countries, the processing of waste materials has grown into a modern state-of-the-art industry. In this paper we will analyze the recycling of solid waste in the Republic of Srpska and region, with an emphasis on electronic waste. One of the reasons why this type of waste is considered hazardous is its toxic substances, so one can refer to a discarded computer as a chemical bomb. In order for a recycling program to be successfully implemented, there should be an expressed demand in recycled substances the market value of which should be sufficient to cover the expenses of collecting and transportation.

Key words: *recycling, solid waste, toxic substances.*

INTRODUCTION

The economic development has been so far solely based on resources from nature. With the general belief prevailing that there were enough natural resources, no alternative solutions were sought. The raw materials and energy crisis in the seventies of the last century was a first warning pointing out at non-sustainability of the current process of economic development. It was this knowledge of exhaustion of natural resources and the need for their rational use that imposed a new approach on designing a future economic development based on long-term sustainable development and high stability in business operations. The first reaction came from the developed countries, which adopted the programs of saving and rational use of natural resources as well as of preserving mineral resources and energy. The use of waste materials has a special place among these activities. Recycling ensures protection of natural resources, contributes to making significant economic effects, provides for broader social interests, primarily through preservation of the environment.

By recycling both the waste problem is solved and different consumer goods are produced. In certain cases the quality of such goods is higher than the products obtained by processing the primary materials. In addition to that, there are many analyses that show the economic justification for recycling waste materials which is reflected in the decrease of operating costs, energy savings and other possibilities (Brunner and Fellner, 2007).

In this paper we analyze recycling of the products the shelf life of which expired. In the first part of the paper we outline the main elements of waste, of recycling, of the products that can be recycled as well as of electronic waste. In the second part of the paper recycling of electronic waste and the examples of recycling electronic waste in the region are discussed.

WASTE

Protection and promotion of the environment, as an inseparable part of work and life in general is of vital importance for future survival of people in certain areas. The growth of consumption of all kinds is directly influenced by an increase in population, urbanization and industrialization; this in turn results in increasing quantities of waste which, in order to exist, must be collected, transported and

processed in a manner that should first of all be complaint with sanitary requirements, and then technical and technological, economic and many other requirements relevant for the protection of the environment.

Classification of waste according to the state of matter is the simplest and shows that waste can be solid, liquid and gaseous. Although such a classification does not show much, it points out at the complexity of task.

Another classification, made according to the activities, classifies the waste as: energy waste, metal, non-metal, biological, industrial, organic, waste of basic chemical industry, waste of oil industry, and mixed waste – municipal waste or waste from used products.

Generally speaking, waste can be regarded as:

- Controlled waste, which includes household waste, commercial waste, clinical and industrial waste, and
- Non-controlled, which includes agricultural waste and waste from mining and quarries.

RECYCLING

Recycling implies reprocessing waste for the purpose of its use as a raw material in the production of the same or similar product, and includes collecting, extraction and processing, whereby it is very important to sort out the waste according to the types.

Recycling is not only a means of preserving the environment, but also an important branch and the activity that can significantly generate lasting economic benefits, because as much as 70% of waste has use value. As much as 160 million dollars a year are generated by the developed countries from recycling, and about 1.5 million of people are employed throughout the planet (Ilić, 2002).

Additionally, it is important to note that recycling:

1. results in lower use of raw materials, thus protecting non-renewable natural resources or natural resources that are hardly renewable, against uncontrolled consumption;
2. decreases the impact of waste on pollution;
3. makes the environment more livable and cleaner;
4. saves the space in nature that would be destroyed if used as landfills;
5. saves the money, and
6. contributes to a decrease of energy quantity that would be spent for generation of a new product.

Both consumers and suppliers, especially in industrial countries, make the decisions on buying the products based not only on the key factors relating to quality, price and availability but also on ecological aspects. Ecological certificate or „ecolabelling“ as it is often referred to, is finding a way to reduce destruction of the environment that occurs in all the fields of human activity (Gašić and Mirjanić, 2006). These activities include production, marketing, consumption, use and disposal of products.

We can differentiate primary and secondary recycling. Primary recycling represents separation at the source and collection of the components of solid waste separated in such a way, while secondary recycling implies centralized separation of recyclable components from delivered integral waste.

The experiences of the European Union countries show that the extraction at the point of generation and separated collection of recyclable material from municipal waste, the so-called recycling of „clean components“ has immeasurable advantages over extracting the recyclable materials from the total mass of dirty waste, the so-called “dirty recycling” (Caroll and Essicik, 2009).

The waste management hierarchy, that was established by the European Union has resulted in the fact that the separation at the place of generation becomes a priority. Primary recycling is based on separated collection of usable waste fractions at the place of its generation. In that way, separated flows are formed made of different material types that can be used on the one hand and hazardous waste components on the other hand. For effective and quality establishing of the system of primary waste separation, it is necessary to conduct education at all levels of the society, through the projects in which the individuals, organizations, educational institutions, public and governmental institutions as well as the local self-governance units will take part.

Electronic waste

Electronic waste has become a large scale problem, due to two main characteristics: it is hazardous because it contains over a thousand different substances, of which many are toxic and create severe pollution during disposal, and it is being created in alarming quantities due to fast outdateding of products.

There are about 40 million tons of PCs, monitors, faxes, video game consoles, mobile telephones and other e-waste created in the world every year. Of that highly toxic waste, only 20% has been properly treated and recycled. Non-regulated trade with e-waste is affecting even the world's biggest populations. China, which is one of the largest e-waste processors, has exported jewelry that contained toxic lead from e-waste.

Hazardous substances in electronic waste include the following:

- lead – causes damage to the central and peripheral nervous systems, of cardio-vascular system, kidneys and reproductive organs. It can be found in monitors (1.5 – 4.0 kg per monitor) and motherboards;
- cadmium – causes irreversible consequences for human body and is deposited in kidneys. It can be found in different chips, and is also a stabilizer for plastic;
- mercury – can cause damage to different organs including the brain and kidneys, as well as to fetus. The biggest danger is presented by the pollution of water with mercury that is easily deposited in living organisms through the food chain, most frequently through fish. 22% of the world's consumption of mercury is estimated to be used in electronic equipment. It is used in thermostats, sensors, relays, mobile devices, batteries and LCD monitors;
- hexavalent chromium – is used in anti-corrosion protection and as decoration or the case fixer. It is easily absorbed in cells and can cause damage to DNA;
- plastic (including PVC) – there are about 7 kg of it in an average computer. The most used form of plastic is PVC (polyvinyl chloride). During burning it can create carbon-dioxide;
- brominated flame retardants (BFR) – are used in plastic cases in order to prevent flammability;
- barium – soft, silvery-white metal used in CRT monitors to protect users against radiation. Researches have shown that a brief exposure to barium causes brain swelling, weakening of muscles, damage to heart, liver and spleen;
- beryllium – very light metal, hard and non-magnetic. Due to these properties it is used in mainboards. It has been recently classified as carcinogenic as it causes lung cancer;
- toners – pigment is the main ingredient of the black toner. If inhaled it can lead to irritation of air ways. Classified as carcinogenic;
- phosphor – is used as coating on CRT monitors for image resolution. It is toxic, so medical aid should be sought after coming in touch with it.

Due to quick technology development, consumers less and less frequently have their defective devices repaired and simply replace them with the new ones, because it is simpler and very often less expensive. Most mobile phone users buy their new phones every two years. As a consequence, there are many old phones ending up as waste, and as much as 90% of the material mass can be reused. Also, the batteries that represent 15–30% of phone mass can cause significant damage to the

environment. Consequences are two-fold: disposal of a mobile phone also means the disposal of precious metals (palladium and gold), and such waste pollutes the environment, as it releases the mentioned toxic substances. According to the European studies, the quantity of electronic waste grows 3-5% on the annual level, which is four times more quickly compared to the waste from households. This waste accounts for 5% of total quantity of the world's waste, with the growth rate increasing annually. Suffice to say that an average UK citizen disposes of as much as three tons of electronic waste during his/her lifetime.

In statistic terms, the United States of America produce the highest amounts of technical waste in the world. In 2005 alone, about 4.6 million tons of popularly called e-waste were disposed of. In the same year about 130 million mobile phones were discarded, which makes approximately 65 thousand tons of hazardous waste. We should add here a big number of TV sets, fax machines, VCRs, etc. (Johansson and Bjorklund, 2009).

There are about 50 million tons of electronic waste created in the world on the annual level, whereby the biggest part ends up in the developing countries, which is a problem in its own right. North America is a leading continent in the annual production of this hazardous waste, with about 20 million tons; it is followed by Europe and Asia with about 14 million tons each, while the other continents are at the level of about 5 million tons. China, which imports about 70% of world's e-waste, has developed a huge industry for its recycling (Barba-Gutierrez, et al., 2008).

Trading e-waste in India, more precisely, in New Delhi, is flourishing. The Indian tradesmen sell the waste at the auction to the best bidder who sorts it and resells it later. It has been recently reported that as many as 25 thousand workers, in New Delhi alone, work on disassembling, as an illegal employment, between 10 and 20 thousand tons of electronic waste a day. The waste arrives at this town daily, with small quantities of copper, gold and other useful metals being extracted from it. 500 containers filled with the used electronic equipment arrives each month to the Nigerian port Lagos, which is 400 thousand computers, having in mind that each container has about 800 of them on the average. Even 75% of this equipment is unusable, beyond repair and cannot be sold.

Basel Convention and the European Union Convention

Basel Convention is an international multilateral contract, drawn up in Basel (Switzerland) in March 1989, which regulates the treatment norms, i.e. waste management criteria in the manner compliant with the requirements of protection and promotion of the environment as well as the procedures with transboundary movements of hazardous and other waste.

According to the Basel Convention, waste management was based on an integral approach that implies the control of creation of both hazardous and other waste, storing, transport, treatment, re-use, recycling, recovery and final disposal.

Based on the Basel amendment of 1995, export of hazardous waste to the countries that do not have authorized capacities for the treatment of this type of waste, i.e. to the countries outside the European Union, was banned. Serbia signed the Basel Convention in 1989 and ratified and became a member in 2000.

In addition to this, there are the directives relating to electric and electronic waste:

- 2002/96 Directive on Waste from Electrical and Electronic Equipment (WEEE) aims at promoting re-use, recycling and other forms of recovery of electrical and electronic waste, in order to reduce the quantity of this waste and improve environmental performances.
- 2002/95 Directive on Hazardous Substances in Electrical and Electronic Equipment (RoHS) (Restriction of Hazardous Substances) prescribes restrictive use of certain toxic substances in electrical and electronic equipment. According to this Directive, the sale of devices in which the content of certain substances such as lead, mercury and cadmium is not within the prescribed limits, was strictly forbidden after 01 July 2006.

RECYCLING OF ELECTRONIC WASTE

The known companies for recycling e-waste have authorizations, usually ISO 14001. This standard belongs to the group ISO 14000 for waste management and aims at reducing the negative impact that certain activities have on the air, water or soil. ISO 14000 is similar to quality standard ISO 9000, which does not relate to the end product, but to the manner of its production.

ISO 14000 is generic and can be applied to any organization, production and processing of any product or rendering of service anywhere in the world. It also covers special aspects of environmental protection, including labeling, performance evaluation, life cycle analysis, communication, audit. Inadequately treated e-waste can entail a fine of 25.000 USD due to the disposal at the public utility landfill (Barba-Gutierrez, et al, 2008).

ARC Company, which deals with recycling of e-waste in the USA, develops infrastructure, including its own software for working within the legislation frames. This company offers expert knowledge in recycling activity. ARC removed and processed more than 25 million tons of e-waste disposed to public utility landfills and takes full responsibility for its users, who have an online access at any time, which enables them to watch in real time the processing flow of their waste and, following an adequate treatment, to print the certificate and report on the process.

Typical machines used for sorting e-waste are based on the magnet (Eddy Current Separator ECS) for the separation of iron components and operate on the principle of electro-magnet which is driven by the alternate current for attracting non-magnetic metals: copper, aluminum, stainless steel. The remaining inert material, such as glass and plastic, are being sent to another separator.

Some devices use x-rays for the separation of certain components. X-rays have a different possibility of passage through certain materials, which depends on the crystal lattice density.

The international ecological group „Greenpeace“ published a report under the name „Your Guide to Green Electronics“ announcing the results of the evaluations on how much care is taken by each specific mobile phone and computer producer in terms of protection of human health and the environment.

On this scorecard from 0 to 10, the manufacturers are mainly categorized by the fact whether they use hazardous PVC and BFR materials in their products. So, „Nokia“ and „Dell“ won 7 points each, while „Apple“ and „Motorola“ found themselves on the very bottom of the scale. „Nokia“ was declared a leader in eliminating toxic chemicals, as none of its new models contain PVC or BFR substances. Companies „Nokia“ and „Dell“ are followed by „Hewlett Packard“ (HP), „Sony Ericsson“, „Samsung“, „Sony“, „LG Electronics“, „Panasonic“, „Toshiba“, „Fujitsu Siemens Computers“, „Apple Computer“ and „Motorola“.

As an example of practical application of e-waste recycling, we can use the experience of the renowned company „Siemens“, which has been upgrading and applying the recycling of its products for a number of years already. Thus, in 2007, the Company „Siemens Nixdorf“ recycled 5700 tons of its old components, saving about 30 million Euro. The reason for such a big saving is also in the fact that „Siemens“ makes products in which 88% of components are reusable, and each year they try to increase this percentage.

RECYCLING ELECTRONIC WASTE IN THE REGION

In the Republic of Srpska, enacting of the law on waste management, that will be in line with the European Standards, is underway. There are only a few companies in BiH that collect secondary raw materials also working with electronic and technological waste from time to time; however that processing is not adequate. In Spionica near Srebrenik the first modern factory for waste recycling „OS Petrol“ started operation; among other, it will be able to recycle electronic waste too.

There are about 280 companies in Serbia today that process secondary raw materials on different technological levels (Vujić, et al., 2011). Three factories for recycling electrical and electronic waste are among these companies: „BiS-reciklažni centar“ in Omoljici near Pancevo, „S.E. Trade“ in Visnjicka banja in Belgrade and „Eko-metal“ in Vrdnik Municipality, near Novi Sad. Although more than one million Euro was invested in each of these factories, that was not sufficient for full recycling to take place in these factories. The recycling of non-recyclable materials requires extensive financial investments, special infrastructure and sophisticated technology the value of which reaches a few hundreds million Euro. Something that is common for all the three factories is that they perform recycling of recyclable elements in the devices such as plastic, metal and glass. 25 kilograms of quality material is returned to the production based on recycling of one 30-kg heavy computer. The waste of the second and the third category makes 4.7 kg, and 0.3 kg of the material cannot be recycled in Serbia remaining. Non-recyclable components, such as mainboards, cathode ray tubes, processors and hard disks are stored in special containers and finally exported abroad, because only very few recycling companies in the world perform final recycling.

For operations on the secondary raw materials exchange, the minimum offer is within a range of 200 tons a month, which is still unfeasible for the factories in Serbia. Another reason for that is that the citizens still do not know what should be done with the old computer equipment, so that, instead of being placed in some recycling centers, it ends up in cellars and garages.

The state is the one that should have a key role in the development of recycling in Serbia. Until this year there has been an Agency for Recycling, but it stopped working with coming into force of the Law on Waste Management. In the Ministry of the Environment and Physical Planning, they believe that passing of the new legal solutions, based on which both the producers and importers of packaging and products would pay a fee to the Environment Protection Fund, and consequently, allocate the Fund's funds for the development of recycling industry, would have an impact on the development of that industry in Serbia.

In Croatia, the Ministry of Protection of the Environment, Physical Planning and Construction, issued, in accordance with the European Union Directives, on 13 July 2007 (Caroll and Essicik, 2009), a Rulebook on Management of the Waste Electrical and Electronic Devices, based on which a system of separated collection of e-waste and its processing and treatment was put in place. The system enables the citizens to call the authorized collector by phone, who comes to the house or business premises and collects, free of charge, a device that a citizen, i.e. the company wants to be rid of, on the condition that it weighs more than 30 kg. This practically relates to all electrical home appliances – fridges, washing machine, dishwashers, stoves, water heaters. Authorized collectors will also collect small electrical or electronic waste at the same time when collecting the big ones from households: TV sets, computers, irons, boring machines, radios. In that way bigger quantities of e-waste are collected.

The provisions of the Rulebook on Management of Waste Electrical and Electronic Equipment (Official Gazette, no. 74/07), define the following: holders of e-waste as legal entities (companies) and holders in households (physical entities and households). This Rulebook also lays down the obligation of each holder to separate e-waste from municipal waste and other types of waste that he/it intends to hand over to the authorized collector. Electronic waste that is given to the collector must be in a state that clearly shows that it has not been previously disassembled for the purpose of extracting separate components.

When collecting e-waste, along with the waste, the holder is required to hand to the collector filled out accompanying sheet PL-Oo/ PL-No/Io, and, upon delivery, confirm the handover by signing the PPEEO form. The collector brings this form with him. In case where e-waste represents hazard in terms of health or safety, the holder shall notify the collector thereof in advance. By fulfilling this procedure, the provisions of the Rulebook on Management of Waste Electronic Devices and Equipment are complied with, as the waste has been handed over to the authorized collector.

Despite the efforts of relevant institutions, the situation in Croatia regarding collecting and recycling e-waste is not satisfactory.

CONCLUSION

Due to increasing quantities and hazard for health, waste is considered as one of the most significant ecological problems of the modern world. With his activities, man is a decisive factor in changing the environment. By polluting the environment and spending natural resources man disrupts the natural balance without realizing that at the same time he harms himself. Waste is a boomerang – once thrown it comes back through polluted water, air and land, damaging human health. Therefore, it is important to understand the problem of e-waste and the ways of its treatment, i.e. reducing, starting from the producers themselves to the end users.

Electronic waste is ecologically hazardous waste, which must be addressed very seriously from the moment of collection to the moment of final treatment, so that the secondary raw materials are used most properly. This would help minimize the harmful effect on the environment.

Recycling is a job from which everyone would benefit: producers – from savings of raw materials, consumers – from cheaper electronic devices, and thus discarded computers would not end up on landfills polluting the environment. The researches carried out on removal of e-waste suggest that 86% of waste is recycled by Japan, 60% by the European Union countries, only 10% by Serbia, while the Republic of Srpska is in the process of passing the legal regulations in the field, and in BH Federation started working the first factory for waste recycling.

Electronic waste treatment should be approached in a system manner, because the amount of this waste is higher and higher year in year out.

In addition to this, there are limiting factors for collection of electronic waste, such as undeveloped collection network, inadequate legal regulations in force governing the waste disposal and the problem of non-compliance with these laws.

Legal regulations are necessary for further system solutions, including developing the recycling centers, the construction and management of which in the world are primarily based on private initiative.

By recycling waste materials quality cheap raw materials are obtained that are necessary for the economy, as well as appropriate energy sources and consumer goods. At the same time, primary resources are protected and healthy environment ensured. Additionally, processing of secondary raw materials grows more and more into a separate industry with significant production capacities, production volumes, staffing potentials, developed high profitability in operations. With constant application of modern technical and technological achievements in operations, this field of economy can be realistically expected to have increasingly prominent effect on the economic growth and the development of national economies in the future.

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**THE RADIATION OF ELECTROMAGNETIC FIELDS OF VERY LOW
FREQUENCY**

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ABSTRACT

This paper analyzes the impact of very low frequency electromagnetic fields to human environment. Humans exposure to the electric and magnetic fields at very low frequency VLF (Very Low Frequency), primarily is related to the working environment, electrical grid as well as to various electrical energy application. Different sources of VLF fields are found in environment, houses and the workplace. These sources can be divided into two groups: DC (Direct Current) and AC (Alternating Current).

Key words: *Electromagnetic Radiation, Very low frequency, Biological effects.*

INTRODUCTION

The human environment comprises various sources of non-ionizing radiation. These consider: power lines, cable and satellite communications, power stations, electric transportation vehicles (electric trains, trams and trolleybuses), TV, radio repeaters, etc.. As a result there is an interaction between the electromagnetic fields and biological tissue. The effects of these fields can be harmful to humans if the field strength exceeds certain threshold values which are defined by the corresponding regulations and defined based on harmful effects. In order to analyze the biological effects of electromagnetic radiation and to make assess of the associated hazards in a particular situation, it is necessary to know strength of the field in frequency domain. The same has to be compared with the corresponding allowed value. The field strength values can be reached by applying analytical calculations, numerical methods, or by using the appropriate measurement equipment. Despite the fact that the non-ionizing electromagnetic phenomena have been well studied, interactions between electromagnetic fields and organic matter, and especially human body, are still not fully clarified.

SOURCES UNIDIRECTIONAL ELECTRIC AND MAGNETIC FIELDS

Electric fields caused by direct current (DC) are known as static fields, because they do not change over time. Their frequency is equal to zero and the wavelength of the atom. In this case, the circuit transmits all the energy and does not radiate at all. Therefore, we have only field. Since the field is static, there is no excitation of surrounding molecules and there is no heating. The electromagnetic field produced by direct current can cause a burning sensation when standing close to the source or high voltage source straightened hair. As an example we will present the natural and man-up one-way source of electromagnetic fields.

Magnetosphere

The Earth produces an electromagnetic field, which is almost static. This field makes the Earth with its magnetism, Solar activity and atmospheric discharges in the form of electrical and lightning storm. Earth's static electric field depends on the conditions in the atmosphere. During the calm and clear

weather conditions, the field has a strength of about 150-300 V / m, but during an electrical storm may reach a value over 10.000V/m.

Intensity of the magnetic field ranges from 30 μ T to 70 μ T depending on latitude and composition of the Earth's crust (magnetically conductive ore or local mountains). The volume density of the Earth's magnetic field at latitude of 50° is 58 μ T, and on the equator (0 ° latitude) is 31 μ T. The average volume density of Earth's magnetic field is 45 μ T.

It is interesting to note that human movements within the Earth's magnetic field caused by induced electric field inside its body. For example, a quick run around 8 m / s creates an internal electric field of 400 μ V / m. Such strength of the electric field can induce a low frequency magnetic field magnetic flux density of 20 μ T.

Magnetic field lines extending between the north and south poles as well as between the permanent magnet poles. At the north pole of the Earth, the lines of magnetic induction are directed toward Earth, the Earth's south pole directed away from Earth. Charged particles are trapped by this field, forming magnetosphere, which is part of the near-Earth space, just above the ionosphere. Earth's magnetosphere is a dynamic plasma floating belt-driven magnetic field, which sometimes comes into contact with the sun's magnetic field magnetosphere extends into space from the Earth approximately 80 to 60.000 km on the side toward the Sun to 300.000 km on the side facing away from the Sun.

The force pushes the magnetosphere solar wind, clutching the side toward the Sun and dragging on the night side of the long tail. This effect is called magnetic tail, which extends thousands of kilometres into space. Solar activity causing geomagnetic induced current that can flow in and out of the mains through various earthing points. The frequency of the current is very small (below 1 Hz) and can be placed in almost direct current. These currents measured in North America amounted to 184 A, while in Finland the measured value is 200 A.

Magnetic Resonance Imaging

Magnetic Resonance Imaging has become an important diagnostic tool for getting good insight into the human body. Stationary magnetic field creates a device called a MRS (Magnetic Resonance Scanner). Any system of magnetic resonance is composed of three main components that are necessary to obtain diagnostic images of soft parts of the human body. These three components been developed and perfected over the last 25 years that have passed since receipt of the first image, the soft parts of the human body magnetic resonance diagnostic method.

Three main components of the MRS system:

- Magnet that produces a homogeneous static magnetic field,
- Radio frequency transmitter and receiver and
- Gradient (magnetic) system in the X, Y and Z axes.

The physical principle of MRS consists of the following: the human body is exposed to a constant magnetic field of high-power (0.2 - 4 Tesla). On these circumstances, there is a reorientation of protons so that their magnetic axes placed parallel magnetic lines of outer magnetic field. Over gradient (additional powerful electromagnet) defines the cross-section image projection that is desired, whether it be coronary, sagittal or lateral. Certainly, the stronger gradients and higher scanning speed and resolution Get protected images. Intensity gradients are limited due to the negative impact on the patient's neural system stimulation. Gradient system for measuring 100 mT / m is set to 1 meter long tunnel and a field strength of 1.5 T in the center. the difference from the beginning to the end of the tunnel ranges from 1.45 T to 1.55 T. RF system for MRS, consisting of part of the emission and reception parts. Today the real RF transmitters are of the power of 35 KW with electronic tubes or less power - about 15KW with semiconductor devices. RF transmitter coil is fastened around the

tunnel magnet and it can be linearly or circularly polarized. This coil is transmitting and receiving at the same time.

Outside broadcasting of radio frequency waves (frequency 21 MHz - 128 MHz) leads to disruption of basic positions and creation of magnetic lines of force lines of magnetic another direction. The frequency of this process depends on the strength of a homogeneous magnetic field, thus giving the larger magnetic field and frequency higher than frequency of the RF waves.

Cessation of broadcasting radio frequency waves at the outer side a gradual reduction of the magnetic lines of force that can be registered and the time to return to the ground level is measured. These signals are recorded, evaluated by different software and finally presented as figures. It is that MRS examinations devices have harmful effects on human health. However, it should be noted that due to the use of radio-frequency pulses very high power (12.000-15.000 W), each section of footage, human body temperature increases by 03 ° C.

A static magnetic field of the use does not cause any visible effects, especially the strength of the magnetic induction of 1.5 T. The magnetic field of 4 T may cause dizziness, light effects when moving the eyes and a metallic taste in the mouth. Magnetic resonance can be recognized only by patients who have a pacemaker installed it (on purpose) or acquired (incident) ferromagnetic foreign bodies in the body.

SOURCES TIME VARYING ELECTRIC AND MAGNETIC FIELDS

Time-varying electromagnetic fields generated by time varying AC (Alternating Current) electricity during transmission, distribution and use of electricity. The main sources of time varying electric fields in the work area are electric cables. The strength of these fields is in the range from 1 to 100 V/m. Flow of electrical current through a conductor produces a magnetic field. These fields always form a closed loop around the conductor which caused them. As the basic unit of magnetic flux density Tesla [T] is very large, it is the practice of using smaller units: microtesla [μ T] and nanotesla [nT]. Under normal conditions in the workplace time-varying magnetic fields caused by electric grid ranging from 10 nT to 1 mT.

Frequency of a VLF field depends on the field sources. Although the dominant frequency of 50 Hz and 60, people are generally exposed to a mixture of frequencies, some of which may be much larger. For example, the frequency of certain parts of electronic equipment or TV monitor can go up to 120 kHz. In addition, during turning may occur sudden peak in the waveforms of current and voltage, leading to a high-frequency transient conditions that can cause the radiation frequency of a few MHz. Also, the non-linear characteristics of electrical devices can cause the creation of significant harmonics at frequencies of a few kHz. Electric and magnetic fields are components of the EM field. Electric fields are generated in apparatus involved in network installation, ah, these devices do not have to be in operation.

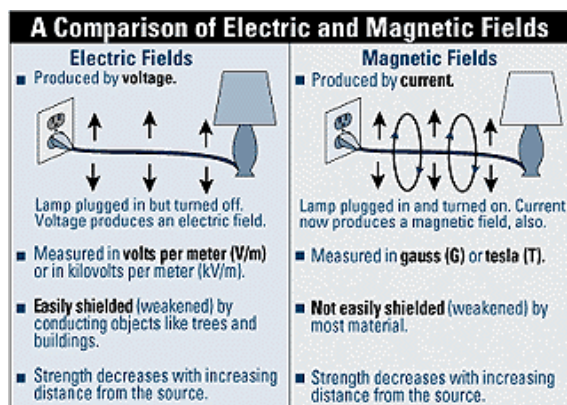


Figure 1. The characteristics of the electric and magnetic fields

The Figure 1 shows an example of a table lamp. Although table lamp is not in function i.e. switched off, the outlet along the power cable the electric field exists.

This example applies to all other electrical devices that are put into operation with a switch on the device. One can be protected against these electric fields by physical disconnection of the device from the network (removing the plug from the socket), installation of special switches on the enclosure to which certain power circuits may occasionally turn off (for example circuits bedrooms). For protection against electrical fields of this type there are various readily available and inexpensive materials.

Putting into operation the device (Fig. 1-b) the current will produce the magnetic field. The magnetic field passes through the Earth, people, and most of the material. They were severely restricted. VLF magnetic field strength decreases with distance from the source. For example, a conductor for the magnetic field strength is inversely proportional to the distance from the source code of the source. Which consists of multiple conductors strength of the magnetic field decreases with the square of the distance.

Magnetic field strength decreases with distance from the roots third source, which is in the form of coil windings. These relationships are important when it is necessary to reduce the strength of the magnetic field.

ELECTROMAGNETIC FIELDS AT VERY LOW FREQUENCIES IN OUR ENVIRONMENT

Given that the above sources of device components in our environment, we'll just consider these devices as sources of electromagnetic fields of very low frequency VLF. In this sense, we are exposed to VLF magnetic and electric fields originating from many sources: the transmission lines connecting power plants and households through distribution lines and cables that distribute energy into our homes, schools and workplaces, substations, transformers, installation of our homes and buildings, and various other electronic devices.

Electric power system

An electric power system is a network of electrical components used to supply, transmit and use electric power. An example of an electric power system is the network that supplies a region's homes and industry with power - for sizable regions, this power system is known as the grid and can be broadly divided into the generators that supply the power, the transmission system that carries the power from the generating centres to the load centres and the distribution system that feeds the power to nearby homes and industries. Smaller power systems are also found in industry, hospitals, commercial buildings and homes. The majority of these systems rely upon three-phase AC power - the standard for large-scale power transmission and distribution across the modern world. Specialised power systems that do not always rely upon three-phase AC power are found in aircraft, electric rail systems, ocean liners and automobiles.

Electric power is the mathematical product of two quantities: current and voltage. These two quantities can vary with respect to time (AC power) or can be kept at constant levels (DC power).

Most refrigerators, air conditioners, pumps and industrial machinery use AC power whereas most computers and digital equipment use DC power (the digital devices you plug into the mains typically have an internal or external power adapter to convert from AC to DC power). AC power has the advantage of being easy to transform between voltage levels and is able to be generated and utilised by brushless machinery. DC power remains the only practical choice in digital systems and can be more economical to transmit over long distances at very high voltages .

The ability to easily transform the voltage of AC power is important for two reasons: Firstly, power can be transmitted over long distances with less losses at higher voltages levels. So in power systems where power plant is distant from the consumer, it is desirable to step-up (increase) the voltage of

power at the generation point and then step-down (decrease) the voltage near the load. Secondly, it is often more economical to install turbines that produce higher voltages than would be used by most appliances, so the ability to easily transform voltages means this mismatch between voltages can be easily managed.

Solid state devices, which are products of the semiconductor revolution, make it possible to transform DC power to different voltages, build brushless DC machines and convert between AC and DC power. Nevertheless devices utilising solid state technology are often more expensive than their traditional counterparts, so AC power remains in widespread use.

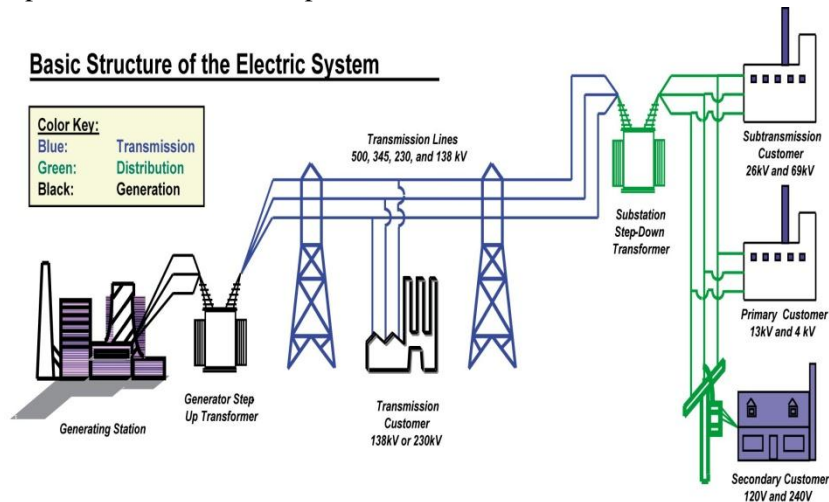


Figure 2. Basic structure of the electric system

If you look at the picture of a typical power system, (Figure 2) you will recognize come to the conclusion that the transmission system (transmission line) is the main source of the electric and magnetic fields, because of the great length of the conductor and the high voltage line. But other elements, such as electrical device in industry and households, electrical installations and distribution part of the system, are very important sources of electromagnetic fields in our environment.

Electrical energy produced in power plants is distributed to consumer areas via high voltage power lines from 35 kV to 400 kV. The voltage is reduced by transformers to 400/230 V for local distribution. The general population is exposed to magnetic fields at the network frequency, 50 Hz in as, via three individual sources: high voltage transmission power lines, the local system for the distribution and low voltage electricity at home and at work, and electrical household appliances. The first two sources create basic, so-called background magnetic radiation, known as the magnetic flux density of the environment.

Overhead power lines

Transmission and distribution lines can be called by one name - power lines. Overhead power lines are the less expensive way to transfer electricity. Usually consist of parallel conductors, which carry most of the energy with very few losses or small radiated energy. Field between the conductors is intense, but it is usually closed between them. The strength of the magnetic field line is determined by the rate of electricity, the proximity of the transmission line, the transmission line height above ground, distance between phases, column geometry and distance from other lines.

Highest levels of electric and magnetic field lines are located in the area where the conductors are closest to the earth, and it is midway between the two pillars. Because of the ambient temperature, the

height of the lowest conductor (h_2) was flying lower and higher in the winter, because the levels of the fields in the area flying higher and lower in winter (Figure 3).

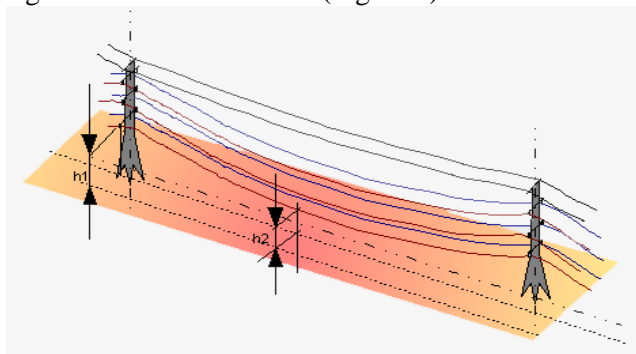


Figure 3. Distribution of the field lines between the columns. Darker red zone with a higher level in the field or in a brighter colour

Lately, most take account of the distribution and geometry of the column conductors to significantly reduced magnetic field.

At any point the field can be determined by superimposing fields of each wire. If, for example. the three-phase line, then the voltages and currents of each phase conductor to move in, and the resultant field vector calculated based on the sum of the fields of each of the conductors.

The only point fields are added which produces a relatively high field strength, while the other points may cancel each other. Thus, the field wires can be very complex prostomu distribution. Addition to these normal variations in field strength electric field under the conductor is changing depending on their surroundings. In the picture shown is 4 phenomenon of concentration of the electric field above the person's head beneath the conductors.

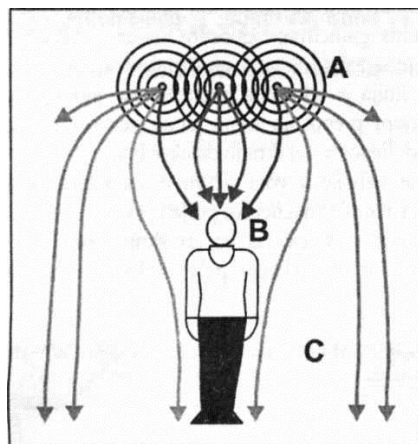


Figure 4. Concentration of the electric field above the person's head beneath the conductors

Because the electric field tends to end up in (or shift to) a grounded object, and because the human body is electrically conductive and near potential electrical field surrounding the Earth is directed toward human head (B). Urinary areas (C) with a weakened electric field strength. All over the world there are vast energy network. That means that almost complete human populations exposed to various fields of power system components. The only difference is in the degree of exposure that varies in the day, days in the week, the season, and depending on the ambient temperature. Most fields are usually located beneath high voltage transmission lines, however, the field strength depends on the strength of the current.

Transformer stations

Transformer stations (Fig.5) are one of the most important parts of the energy system, which is used to change the voltage level, and perform other functions in the transfer of control and flow of electrical energy. There are several ways to build substations in order to achieve a reliable electricity system. In essence, they are complex equipment such as circuit breakers, high voltage switches, grounding, transformers intended course with the changing voltage control. Since the substations are often located near schools and homes, must be considered as sources close to the electric and magnetic fields.



Figure 5. Transformer station

Transformers are sources of strong magnetic fields because their principle of operation is based on a time-varying magnetic fields. The problem of the magnetic field near cells is more complex, since the current entering or leaving the station, in the general case are not symmetric. Field produced by equipment weakens with distance and does not spread outside the physical boundaries of stations. However, the magnetic field near the station is stronger than in other parts. Approximate values that can be found near the fence of transformer cells depend on the level of voltage: $10 \mu\text{T}$ for 275-400 kV cells and $1.6 \mu\text{T}$ station for 11 kV.

Transformer as standalone devices found in rural areas (Column transformers), and in urban areas, mostly inside residential buildings. Transformers in buildings adversely affect the people in the apartments above them. These transformers create an extremely strong electric and magnetic fields. Unfortunately, to enable lower expenses of their installation, they are frequently installed in the buildings. That is not in line with technical recommendation which allowed that kind of installation in exceptional cases only. This radiation is stronger than transmission radiation.

Electromagnetic fields in the apartments directly above the transformers were even a hundred times stronger than allowed through regulations. This radiation, which half a meter from the floor becomes harmless, is dangerous for pregnant women and children and is a common cause of "unexplained" leukaemia. Such transformers reduce the voltage to 380/220 V, that is used in home installations. VLF fields in the vicinity of the transformer can be strong, based on small dimensions of the coil through which the current passes. Values measured at the street, directly below the pole-mounted transformers are not much higher than those measured under overhead power lines.

Electrical installations

Average value of the magnetic fields in homes which are away from power lines and transformer stations is small. The mean value of the magnetic fields in the houses in major cities is around $0.1 \mu\text{T}$. Values in the smaller towns and villages are of half of the noted value. In cities, about 10% of homes have at least one room where a field value exceeds $0.2 \mu\text{T}$. If a house is near power lines and substations, the strength of magnetic fields is even greater. It was found that 0.5% of houses have values of magnetic

fields in excess of $0.2 \mu\text{T}$. For commercial buildings, transformers and distribution boxes are placed in separate rooms in the buildings. Field values in areas around such premises or buildings have a value from $1 \mu\text{T}$ to 10 mT .

Vehicles on electric power

Electric trams and trains (Figure 6) are also sources of static and VLF fields. For traction they somewhere use direct current somewhere alternating current. Near the coaches floor the static magnetic fields can reach 0.2 mT , and time-varying magnetic fields can reach several hundred μT . At the headquarters of passengers, electric fields can reach up to 300 V / m and magnetic field reaches values of a few tens μT .

Values are highly dependent on the level of design and location of electrical equipment and machinery within the train composition. Traction motors and equipment are often placed under the floors in the coach. They create a ver intense fields in the area of the floor below which they are located. Passengers were further exposed to magnetic fields from sources that are close to the tracks.



Figure 6. Radiation Sources in the traffic

Television screens and computer monitors

Monitors or video display terminal are output unit of the computer equipment which is used to display data from the computer. There are two basic types of monitors : monitors cathode CRT (Cathode Ray Tube) and TFT monitors (Thin Film Transistor).

CRT monitors work on the principle of TV technology. The main part of the monitor is cathode ray tube CRT (Cathode Ray Tube). On the back of the picture tube set, there are three electron guns, which emit beams of electrons through a metal mesh or a screen to be placed on the inside of the glass monitor. The screen surface is covered with phosphor strips, which counts them bright red, green, Combination of these colours enable any other colour. By the the coils (vertically and horizontally) the image on the screen is drawn point by point and the horizontal lines from left to right. The lines are drawn respectively from top to bottom, and when all the sails are delineated single image. In cathode ray tubes that are used in standard TV sets, the images are drawn 50 times per second (50 Hz), which is due to the inertia of the human eye is almost impossible to detect. In a monitor draws a picture every 50-85 seconds (50-85 Hz), and the quality as much as 120 times per second (120 Hz), and therefore are characterized by a still picture.

TFT monitors operate by LCD (Liquid Crystal Display) technology. These monitors have cathode ray tubes, liquid crystal, but between two glass plates, two polarizers, colour filters and two layers for alignment. Behind these layers of backlight which usually consists of more fluorescent lamps.

Bringing power to the alignment layer, it generates an electric field that smoothed liquid crystals, which prevents the light to pass through them, while eliminating voltage allows the passage of light. This technology uses an FET (Field Effect Transistor) transistors to control liquid crystal states of molecules. Since the monitor does not have this type of electron gun and bail coils, the radiation is much lower. Consequently, TFT get much more information about any of these harmful radiation monitors.

Classic CRT video display terminal that is still the most widely used, include the following categories: optical radiation (ultraviolet, visible, infrared), radio frequency electromagnetic fields, low-frequency time-varying magnetic fields, low frequency electric field time-variant and electrostatic field.

As a response to growing concern for the effects caused by radiation of very low frequency, the Swedish government has developed a set of standards that should minimize exposure to such radiation while working with video terminals. Norms are named after the initials of the Swedish Institute for measurement and testing (Swedish Board for Measurement and Testing), MPR II. Sometime later TCO 92 standards are set which initially reduce harmful radiation by 50 to 70%. These standards deal with frequency oscillator for horizontal and vertical removal of the monitor's cathode rays, as frequency power supply lines. In determining the standards certain measurements of electric and magnetic fields at different points around the monitor were performed.

TCO in 1995. expanded its regulations on environmental protection and became the first global environmental regulation also contains TCO 95 and a much larger set of regulations for the CRT and FPD (Flat Panel Display) monitors.

The current and most stringent standard for monitors is TCO 99th.

CONCLUSION

The paper discusses the radiation of electromagnetic fields of very low frequency. All natural as well as “man created” sources were analyze. The electromagnetic fields of extremely low frequency in our environment are related to overhead power lines, electrical vehicles, TV and computers. Although the electrical and magnetic fields often occur together, the emphasis is on the negative impact of a magnetic field. This is because the magnetic field is difficult to avoid based that it propagates through the buildings and people while electric fields have little ability to penetrate through building them even human skin.

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**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

LASER TECHNIQUES APPLICATIONS IN ECOLOGY

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ABSTRACT

Contemporary laser applications in the fields of ecology and environment monitoring are considered in presented paper. One of the first is remote atmosphere control and human environment monitoring connected to fundamental approaches to scattering, absorption and reflection phenomena. The use of LIDAR, DIAL, LADAR, COLIDAR and RDAR are in use for several decades, with different names, but essentially the same phenomena are at stake: laser beam targeting and detecting transmitted, reflected or scattered photons. Devices and systems followed the progress in electronic, automatics and other complementary disciplines. After considering some possibilities of remote control in various parts of electromagnetic spectra and comparing their possibilities in IR, VIS and UV bands, some of the uses will be analyzed to compare laser based remote control side by side with thermo-vision techniques, ultrasound and other measuring techniques. Some nonlinear phenomena linked with intensive laser beam propagations will be analyzed concerning to space waste and defense by using quantum generators, as well as laser isotope selection and enrichment. Author's simulation and measurement results, in those complex group of problems will be presented, as well as the further directions considerations. The questions linked to laser dosimetries and relationship with other respective dosimetries will be analyzed, too.

Key words: *laser, lidar, ecology, scattering, fluorescence cultural heritage.*

INTRODUCTION

Urban, Building Climatology And Topic Investigations And Techniques

Hundred years ago some very known scientists have written about temperature increase in Earth and ozone role, but in this time they were exotic for the most of the people. But today... we remember... Urban, building climatology and topic investigations and techniques, blending height, flux aggregation, urban atmospheric pollution, urban heat islands and climates from Japan through Mexico, Rome, North and South pole etc. are the object of analyses in different periods of the past and future climatology on Earth and wider in Space from very different points of view. In the periods 1981-1991 and 1992-1995, 1996-1998 the tremendous number of national institutes for Urban/Building/Climatology/Atmospheric Sciences and National Universities from all continents held world conferences. Depending on the place on earth, different problems appeared, but ecological point of view was one of the unique interest for humane beings, water and air surfaces and spaces. Many stated terms of reference (Res. 9/5 CCL-XII) and systematizations of data were collected on urban and building climatology covering both mid-latitude work and dealing with the tropical urban environment. Previous bibliographies on urban climate were obtained by the World Meteorological Organization: WMO/TD No. 552 and WMO/TD No. 759 .

Main source of information has been in previous bibliographies the J. Meteor.&Geostrophys. Abstr. and Proc. of various meeting organized by WMO, the Am. Meteor. Soc. -AMS, the Intern. Geogr.Un.-

IGU, the Assoc. Amer. Geogr.-AAG, etc. Activity in urban climate studies steadily increased comparing 1990's with the previous decade (Tab. 1). Urban climate in the tropics is still a small fraction of mid-latitude activity in this field; it has doubled with respect to the 1980's. Fig. 1 shows the evolution of urban climate studies during the last decade of the century and Tab. 1 activity on urban climate studies in tropics. Proliferation of descriptive screen-level urban heat island studies (air pollution) in the tropics, a gradual diversification of topics during the chosen decade and physical modeling, remote sensing, energy issues, physical urban climatology are more frequently seen.

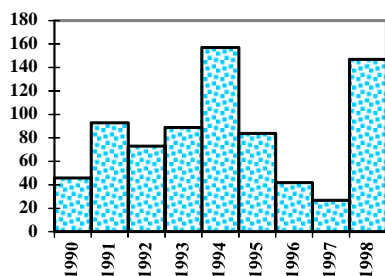


Figure 1. Summary of statistics papers published on urban climate for period 1990-98

Table 1: Activity on urban climate studies in the tropics

N° of papers on UC. Period 1981-98		
Period	Tropics	Mid-Lat. %
1981-89	63	630 10
1990-98	158	758 20

The city **Fukushima** becomes drier every year, and cool islands appear more clearly at the time of the appearance of T_{max} . The center is 1.2°C cooler than its suburbs. Cool islands appear in spring and autumn as relatively dry seasons. Heat islands appear at the time of T_{min} . The center of the city is 0.8°C warmer than the suburbs. Heat islands appear clearly in the autumn and winter. The diurnal range of temperatures is 1.7°C larger in the suburbs than in the city. The environmental problems in the city of **Nairobi** (1992) are legion and are constantly on the upward trend. They cannot be understood without the knowledge of geography, climate and population. Whatever environmental problems are in city, those are a product of the interaction between the geography and climate and the population trends. The growth of slum areas is a result of poor land use planning, coupled with an apparent lack of a comprehensive policy to regulate human settlements. The rising population has led to spontaneous and unregulated settlements that have occasioned various environmental problems. There are no water facilities, no roads to enable the vehicles to collect garbage. Eyesore, the garbage not fouls the air and provides breeding ground for disease carrying insects. Noise is an environmental problem that is generally on the increase in the city. The quality of the air in the city does also present a serious environmental problem. During peak hours one observes a “train” of fumes over these routes, as well as from industry as smoke and fumes. The fumes and smoke is such that they form a thick blanket of smoke over the city which is easily visible as one flies over the city at a low altitude. The problems are in homogeneity of air temperature measurements **Prague-Klementinum** with respect to the intensification of the urban heat island is followed in the series of monthly and annual mean air temperatures in 1771-1990. The in homogeneity caused by intensification of the urban heat island is particularly emphasized. They have to be compared for Central Europe.

Here is also a study of the weather records from **Athens** (1860-1988) including climate variation. Weather record from 1860 to 1882 from Athens, on the southeastern coast of Greece supports the evidence that a warming trend took place in the middle latitudes beginning in the middle of the 19th century until 1990. A cooling occurred ~ 1925. A new rise continues until the 1940s, followed by small fluctuations. It is evident that the climate has varied over the past century. The meteorological observation records from **Lódz** compared temperature from stations Lódz-LER, in the central part of the city, and Lódz-Lublinek, outside of the city, with those from the reference stations Pulawy and Bydgoszcz. From them, temperature urban effects were estimated using data from period 1903-1930. The influence of the city on hourly sunshine duration distribution was monitored. Urban effects on summer convective precipitation in **Moscow** are considered. The mean summer precipitation amount is higher than in its environs by 7%, the maximum summer time excess being 27% (70 mm). The rainfall excess was caused by a higher frequency and intensity of convective precipitation. Radar

observations of precipitation identified three types of situations with the increased convective precipitation in the area. The urban influence on the diurnal and annual patterns of absolute humidity in **Szeged**, Hungary was monitored with measurements of vapor pressure. The data was acquired four times daily over a 3-year period and there from diurnal and annual patterns of urban-rural absolute humidity differences were estimated. The city was more humid than its surroundings. Variation of humidity surplus can be explained by energy balances and additional sources of moisture. Good relationships exist between urban-rural absolute humidity differences, nocturnal heat island intensity, variation of aridity index, and the variation of the temperature of the River **Tisza**. The diagnosis of climate change in **Cracow** against a background of circulation and local conditions had similar problems and conclusions with the above mentioned cities (Bibliography_1986_1988).

Listing the chosen places the aim was to unit the ecological common problem independently on geographical position of the place and to point some specific problems. Before laser invention (near 60's) many methods were established and used to monitored temperature, pressure, wind, turbulence, (atmospheric performances), volcanic eruption, seismic movements, food quality control, wastewater control, etc. But with the laser invention almost all listed and unlisted items could be and are solved by laser based techniques. Some of them used replacement of the optical source (spontaneous electromagnetic radiation) with some stimulated source (quantum generator). This statement is valid for laboratory control (locally), for *sample* characterization but also for remote control of many parameters and processes including traffic control, etc.

In the period of 1980-1990-2000 in spite that LIDAR was invented more classic methods were used for analyzing and monitoring world's ecology situation. In more than 100 papers the word lidar was mentioned only three times. Note that in the same time many strictly lidar conferences were held in Europe, USA, etc (Vujkovic 1987, Sreckovic 2010, Sreckovic 1986, Weibring 2001)

Tasks for LIDAR investigation in ecology and other areas

Laser pulses from Earth detected at Mars, performance of the GLAS Space lidar received trough its Seven-Year space mission, lidar remote sensing of the Parma cathedral and baptistry and many other lidar missions were and are in the area of actual events. From the first lidar (Light Detection And Ranging) more other devices were designed and manufactured for endless list of tasks which could be solved with laser beam, transmission, signal detection and signal processing. Colidar (Coherent Light Detecting and Ranging), dial (Differential Absorption LIDAR), rdar, laser rangefinder, fiber lidar, flidar (Floating lidar), fluorescence lidar, represent the devices practically in the UV, VIS and FIR, NIR, MIR, part of the spectra which accomplish further some of microwave radar tasks. The name of devices originates from the principal method chosen for working conditions i.e. what kind of information will be drawn from the transmitted, reflected, scattered electromagnetic radiation from chosen quantum generators. As first, we think to linear phenomena but with the increase of laser power when the air break down phenomena start, many other processes could be used for laser application in ecological purposes (lightning control and provoking, estimation of microparameters of atmospheric content, and ionization constant, etc.). Lidar based systems could monitor macroscopic parameters of the atmosphere and aqua sphere (temperature, pressure, turbulence, volcanic dust movement, space dust movement, pole movements including Sagnak effects in laser gyroscopes, etc. Depending on the degree of the resolution and possibility of some monitoring station, laser controls are in competition with more classic but reliable methods including balloons, acoustic methods, etc (Vujkovic 1984, Letokhov 1986, Kaiser 1996, Currie 1987, Milic 2008, Sreckovic 2008, Sreckovic 2009, Sreckovic 2012, She 2011).

Some of the lidar based devices use the previously laboratory data about chosen material on the level of atoms, molecules, ions, radicals, micelle, lattice type, etc. i.e. on the data obtained by classic spectroscopic methods. On the other hand, many laser spectroscopies are developed and they are included or in laboratory work or for remote monitoring and control of the aqua sphere, atmosphere and Space. In presented paper we will give some our measurements which could be the bases for material characterization as well as for the basis of lidar used for recognition of material which could

be of interest for common life, pollution, water content, etc. We will present also some of other non laser techniques as thermography which could be used for the same task - atmosphere and processes monitoring. The principal difference between laser and the other techniques is that with laser we obtain local characterization in the scale of laser used wavelengths.

LIDAR REMOTE SENSING OF THE CULTURAL HERITAGE

In spite of the fact that the lidar application was not as first used for cultural heritage we start with very small history of the first use of fluorescence laser for sensing in the beginning of this millennium. Explicitly they were the first experiments of remote sensing of historical buildings using fluorescence lidar in collaboration of IROE and other Italian and foreign institutions. Work was carried out to remote monitoring of biodeteriogens and the lithological characteristics of the building materials. The best results of the field experiment carried out at the Parma Cathedral and Baptistery in Sept. 2000. In the fig.2 one of the most interesting medieval buildings in northern Italy, the Cathedral and the baptistery is presented.

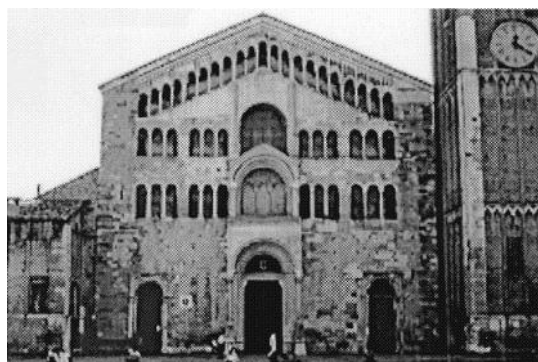


Figure 2. Medieval monuments of the Cathedral Square in Parma, Italy. The Cathedral and the Baptistery (Weibring 2001)

Two systems, based on Nd³⁺:YAG (higher harmonic) lidar and excimer laser XeCl lidar are used in estimation of both fluorescence point measurement and fluorescence thematic imaging in the remote non-destructive monitoring of buildings. Apart from confirming the possibility of detecting biodeteriogens, for the first time the processing of the fluorescence data made possible the detection of restorations and the distinction between pigments having the same color.

OPTICAL CHARACTERISTICS FOR DECISION OF CHOOSING PREFERRED PATTERN FOR LABORATORY AND REMOTE LASER METHODS IN ECOLOGICAL PURPOSES

Specific and common water characterization

Performances of Bedford tap water purified by various common techniques, were given in tab. 3. There from and from our measurement we can conclude that the optical purity of water is the highest level of confirmation of quasi ideal water sample. We measured integral scattering in four components with the devices for integral scattering and we have controlled angular distribution, too. It means that we used HeNe laser line of 632.8 nm (the most known) and in cylindrical cell we put water which was three times distilled, centrifuged and filtered with special fine/narrow filters. The incident beam was polarized and we measured component of the same polarization and normal to incident beam. After that incident polarization was changed the to 90 degree by polarization rotator and the both analogue components were measured. When the water was not optically pure the great asymmetry was in angular distribution (central asymmetry relative to 90 degree). These asymmetries were due to the large dust particles or macromolecules from the cells during the centrifugation processes or bimolecules (germicide action of UV radiation is commercially confirmed technique for water-disinfection, but this technique does not remove these particles from water and they remain as centers of scattering). For very small water quantities germicide action in water samples could be more

effective theoretically. The organic solvents are often used for solvent in different processes but some of them are used for calibration (benzene, toluene) processes or for refraction index matching processes with glasses or plastic components in scattering devices. Cyclohexane is one of them with very small depolarization degree close to water. We will present data of interest in tab 4. and figs. 3 and 4 for cyclohexane.

Table 3: Characteristics of water purified by various techniques

	Bedford water	1 time distilled	3 times distilled	System Milli Q2	Deionized strong acid or alkali (basis)
Inorganic materials dis. [ppm] (eq.to CaCO ₃)	170	1.0	0.3	0.025	0.025
Specific resistance MΩcm, 25°C	0.003	0.5	2	18	18
Silicates [ppm]	1	0.1	0.05	0.01	0.01
Heavy metals [ppm]	1	0.1	0.05	0.01	0.01
Organic materials disud. [ppm]	12	1	1	1	10
Microorganisms/ml	100	10	10		100
Particles 5µm/ml	10000	200	100		10000

Table 4: Rayleigh integral scattering of cyclohexane; all polarization combinations by incident parallel and horizontal and depolarized issues. Angular distribution for 632.8nm incident laser line.

	30°	45°	60°	75°	90°	105°	120°	135°	150°
I_{vv}		1.1397	0.7946	-	0.7545	0.7260	0.7200	0.7463	-
I_{hv}	2.89	0.0022	0.0161	0.01489	0.0117	0.0134	0.0162	0.0177	0.02
I_{hh}		1.5998	0.7944	0.2413	0.1036	0.2374	0.6672	1.2625	1.997
I_{hv}	2.67	0.0845	0.081	0.07488	0.02575	0.0606	0.0651	0.0733	0.065

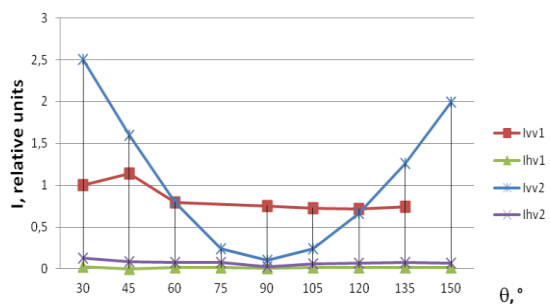


Figure 3. Angular distribution for Rayleigh component 632.8nm HeNe laser for cyclohexane

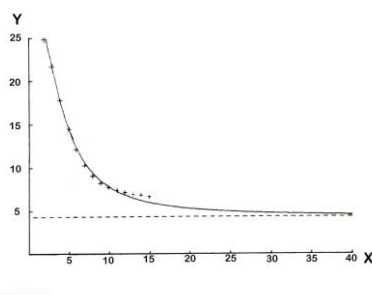


Figure 4. Rayleigh line obtained by dynamic light scattering devices for cyclohexane

The water processed by deionization in strong acid milieu and weak basis, by osmotic processes or by some other technique shows much worse performances.

Laser wavelength tuned systems

Many laser lines exist today starting of the first days when all working laser lines could fill a few pages. Now the detailed laser lines, not only of commercial types have to be read. In excimer area the most popular are, as in medicine and in industry the types: 193nm ArF, 248nm KrF, 308 nm XeCl, with various cavities and linewidths. In IR area: Nd³⁺:YAG with various pumps including diode lasers, and nonlinear elements for higher harmonics, CO₂ (10.6µm) with tuning possibility. Very known are

N₂ laser in UV and dye lasers with metal vapor pump lasers, with various possibility of tuning range. In tabs. 5, and 6 some data about excimer lasers are presented.

Table 5: Excimer laser transitions

Laser	Transition	λ [nm]	Bandwidth [GHz]
ArF	B→X	193	17000
KrF	B→X	248	10500
			2583
XeCl	B→X	308	374
			204
			393
		308.2	223
XeF	B→X	351	187
			353
			330
	C→A	456-514	

Table 6: Gas mixtures for Excimer lasers

Rare gas	Halogen gas	Wavelength [nm]
xenon	fluorine	351
xenon	chlorine	308
xenon	bromine	282
xenon	iodine	253
krypton	fluorine	248
krypton	chlorine	222
krypton	bromine	206
argon	fluorine	193
Argon	chlorine	175
fluorin	fluorine	158

Thermovision aspects

In many areas detecting of IR radiation from old photography by IR possibilities up to modern process diagnostics, thermovision based devices have important role in ecology, industrial monitoring, and applications in power distribution systems up to monitoring of the small electrical circuit dissipation. Some of the example are presented in fig. 5. a) and b). This issue deserves special discussion about the laser scanning techniques and results of these visualizations with this infrared presentations. Protection against atmospheric lightning processes is also solved by microwaves and rockets but modern investigations for lightning lasers initiation to prevent unwanted natural discharges phenomena exists.

Excimer lasers and lidars

Excimer lasers are the relatively well known laser types today but lasing processes belong to 'exotic' processes. It's not so common fact that molecules of noble gases exist but in *lasing processes* they could be *real* in the higher energy levels (excited states). Excimer and exciplex systems are today in competition with visible and IR quantum generators (tabs 7, 8, 9 and 10). Due to interesting processes with UV stimulated radiation where they have emission lines they are of interest from ecology trough military, medicine, biomedicine and industrial applications. All these applications contributed to development of relatively intensive sources. In UV range most of biosystems posses excitation lines for fluorescence (luminescence) and the matching with specific lines is complicated without use of tuning laser systems. Therefore different lidar systems, fluorescence processes could be and are very valuable in recognition of chosen target (sample). A major breakthrough is ahead of them (semiconductor technology and material processing in general), but in presented multidisciplinary area lidar- laser radars have both many common as well as specific (*exotic*) tasks. Note that contemporary problem were O₃ dynamics should be monitored in troposphere is and could be analyzed by lidar, colidar, dial, flidar, etc. tasks where are. The first data about ozone hole were that it exists only on Earth's north hemisphere. The other very important pollution including volcanic activity and volcanic dust spreading patterns trough Earths atmosphere (continents) could be and it was monitored by same adequate devices from earth, airplanes or from space stations (Ready 2001).



Figure 5. Thermographs of the a) car and b) the people

Table 7: CALIOP transmitter characteristics

Laser	Diode pumped Nd ³⁺ :YAG
Pulse energy	110 mJ:532nm, doublet, 110mJ:1064nm
Repetition rate [Hz]	20.16
Pulse length [ns] Qswitch	20
Linewidth [pm]	30
Polarization purity	>1000:1 (532nm)
Beam divergence	1000 μ rad (after beam expander)

The most important advantages of excimer lasers are: emission in UV range where the square cross-section from scattering is larger than in visible range. Characteristics of excimer and other laser types which produce UV radiation by various nonlinear processes could be the basis of many other applications including isotope selection and enrichment. The efficiency of frequency conversion with Raman shifter is relatively high, signal-noise ratio is favorable; and various laser lines as well as continually tuned lasing material exist. These advantages have shown good performances for investigation processes for vertical profiling of interesting parameters. In tab. 10 are data about existing excimer systems.

Lidar equations

Myriade of measuring methods could be of interest for remote monitoring of various air and water ecosystems. Similar to them are the systems for ground monitoring where the principal are the coefficients of reflection of the rock, soil, plants, canopy, sand, etc. If the systems are equipped with tuning or multispectral sources the monitoring is more reliable. In references there are many solutions for laser monitoring and for target recognition. Of interest are the methods which follow the shape and linewidths of incident beam and compared with scattered or transmission beams and their angular dependencies (Fidanovski 2011).

Depending on the chosen processes i.e. Raman, DIAL (difference absorption lidar), LIDAR with parametric processes, LIDAR with linewidth monitoring there are more that one of LIDAR equation. The equation linked with backscattering and different absorption coefficient depending on targeting species (pollution molecules) has limiting wavelengths for starting and stopping of absorption processes. From the chosen complexity of devices, beside the laser power, and transmission optics, detecting systems and adequate software packages the issue of monitoring depends. Developed systems could be used for meteorological data, pressure, temperature, wind (Bose 2010), turbulence as well as for microparticles monitoring (missile gas patterns), fire monitoring, etc. Special systems follow pole movements, tectonic and seismic movements.

Table 8: The chosen laser types as candidates for sources in UV range.

Type	Jet propulsion Laboratory USA
Wavelength[nm]	308
Pulse energy[mJ]	700
Mean power [W]	100
Rep. rate[Hz]	150
Linewidth [cm ⁻¹]	0.5
divergency[mrad]	0.5
sinhr.eff. [%]	10 ⁶ pulses
Application	aerosole monitoring

Table 9: Typical Excimer Laser parameters

Parameter	Value
Wavelength [nm]	193, 248, 308 or 351
Pulse energy [mJ]	400-500
Repetition rate [Hz]	100-200
Average power [W]	40-100
Pulse duration [ns]	15-30
Peak power [MW]	10-30
Peak fluence [mJ/cm ²]	100-200
Beam divergence [mrad]	1-3
Beam size [mm]	8-15 x 25-30

Some of data from references are presented in figs. 6-10. Depending of various reasons, wind, temperature, ozone or other gas monitoring in atmosphere and water sphere will be presented in other paragraphs. The examples will be with chosen wavelength based on elastic or inelastic scattering processes, Raman, CARS) different absorption or other processes.

Table 10: Excimer Laser Wavelength

Gas	Wavelength [nm]	Comments
ArF	193	Requires high operating voltages to transfer energy to the discharge efficiently. The laser beam is absorbed by O ₂ molecules in air so beam path requires N ₂ flush for efficient propagation. Usually the shortest absorption depth in organic materials of all excimer wavelengths.
KrF	248	Generally the best combination of power and lasing efficiency. The most commonly utilized transition for machining polymers due to combination of absorption characteristics in plastics and overall average power from laser.
XeCl	308	Very long lived gas lifetimes. Longer absorption lengths in polymers can lead to higher etch rates than KrF but lower average powers generate slower rate of material removal overall. Often used for marking applications.
XeF	351	Lower absorption in polymers. Less attractive for machining tasks.

HYBRID REMOTE SENSING LASER BASED METHODS AND SYSTEMS

Imaging lidar system and K-meter employing tunable and fixed frequency laser transmitters.

One of the inventions uses tunable and fixed frequency lasers as an optical light source in imaging laser detection and ranging (LIDAR) systems. It provides a high energy, short pulse laser output which is tunable to or set at a desired wavelength. The tuning is used for performance optimization of lidar system; and for scientific investigations carried out using these systems. An example of performance optimization is the tuning (setting) of the laser at the *Jerlov minimum*. It depends on the optical characteristics of the water. The improved system serve for scientific investigation: such as determining the frequency-dependent optical attenuation coefficient in the ocean at depth, and imaging various opaque objects under battlefield conditions. The invention significantly improves the optical S/N ratio for all of these applications (Norris 1992).

Quasi-phase-matched parametric chirped pulse amplification systems reduces the pump peak power and brightness, allowing exploitation of spatially-multimode and long duration pump pulses. It removes restrictions on pump wavelength and amplification bandwidth. This allows simplification in pump laser design for a high-energy PCPA system and, the construction of compact diode-pumped

sources of high-energy ultra short optical pulses. It allows elimination of gain-narrowing and phase-distortion limitations on minimum pulse duration, which arise in a chirped pulse amplification system. Example of a compact source of high-energy ultra short pulses is a multimode-core fiber based PCPA system. Limitations on pulse energy due to the limited core size for single-mode fibers are circumvented by using large multimode core. Limitations on pulse duration and beam quality are due to multimode core (Galvanauskas 2001).

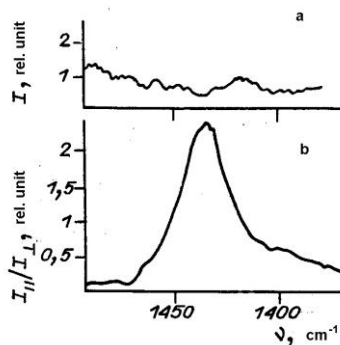


Figure 6. CARS of cyclohexane without and with calibration of resonance signal b); line 1445cm⁻¹

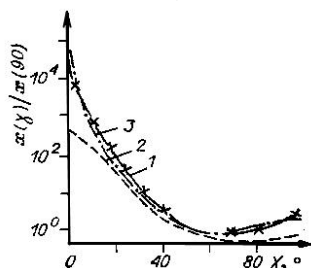


Figure 8. Angular scattering recorded by laser for various water: ocean, sea 1, sea 2

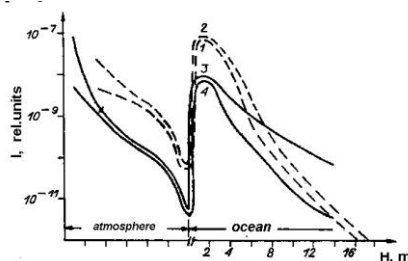


Figure 9. Lidar echo signal. 1, 2, h=200m, 3, 4 h= 600m, field of view 6 i 20min, H- depth in the water

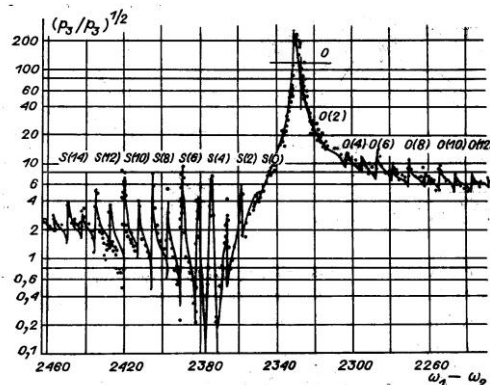


Figure 7. KARS spectrum of atmosphere nitrogen in the flame

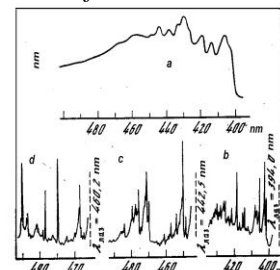


Figure 10. Benzene fluorescent spectra, 4.2 K, a) excitation with Hg lamp, 365 nm, bcd laser excitation

Parametric study of an Excimer-pumped, Nitrogen Raman shifter for Lidar Application

KrF excimer-pumped, nitrogen Raman shifter was studied for use in a wavelength-optimized solar-blind Raman lidar. First Stokes conversion efficiencies (248 ? 263 nm) as high as 12% have been observed in N₂:He gas mixtures. Both oscillator-amplifier and self-seeded configurations were investigated. Wavelength-dependent effects were investigated with a Nd³⁺:YAG laser operating at 532 and 266 nm. A comparison of KrF- and Nd³⁺:YAG-pumped Raman shifting has shown that the beam quality of the excimer laser was a major factor in limiting the maximum first Stokes conversion efficiency.

Methodology for the independent calibration of Raman backscatter water-vapor lidar systems

A method for the independent calibration of Raman backscatter water-vapor lidar systems is designed. Particular attention is given to the resolution of instrumental changes in the short and the long terms. The method reposes on the decomposition of the instrument function, which allows the lidar calibration coefficient to be re-expressed as the product of two terms, one describing the instrumental transmission and detection efficiency and the other describing the wavelength-dependent convolution of the Raman backscatter cross sections with the instrument function. The origins of changes in instrument response necessitate the experimental determination of the system detection efficiency. Two external light sources for calibration are assessed: zenith observation of diffuse sunlight and a Xe arc lamp. The results favor use of the diffuse-sunlight measurement but highlight the need for

simultaneous sunphotometer measurements to constrain modeled aerosol optical properties. Quantum mechanical models of the Raman cross sections and errors and convolution with the instrument function are of interest. The calibration coefficients deduced by using the independent method are compared with coefficients deduced from radiosonde measurements. Changes in the calibration coefficient in the short and the long terms should be comparable or better than precision of existing dependent methods of calibration.

CONCLUSION

The contemporary laser roles in ecology are numerous but all potential possibilities are not used yet. The favorable fact is that many of them are of multidisciplinary interest and that all crossing areas in medicine, industry, traffic, meteorology and general measurements (sensing) are in progress as the components of lidar systems. New laser types, new electronic and signal processing devices as correlator or spectral analyzer, computers and next generation of all of them are of interest. The choice of optimal laser techniques and processes is still the task for further discussion. Only very common applications are recommended in references, but the competitions between resolutions, rate of issues, good statistics, universal tasks, or very specified e.g. chosen pollution components, resolve our decisions. Nonlinear phenomena occur by high power laser beam propagation and atmosphere breakdown phenomena. The projects concerning space waste and defense by using quantum generators, as well as laser isotope selection and enrichment have basic idea that laser mechanical effects change the path of space waist. Multiphoton processes are the basis for laser isotope enrichment and selection and in a principal more of them are included in different nonlinear spectroscopies based on scattering and fluorescence processes.

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CLIMATE CHANGES AND URBAN POLLUTION

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**MITIGATING THE CLIMATE CHANGES THROUGH
LIGNOCELLULOSIC BIOETHANOL PRODUCTION: THE
ENZYMATIC HYDROLYSIS CHALLENGE**

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ABSTRACT

Mankind raising awareness of the risks of dramatic global climate changes due to anthropogenic greenhouse gases, especially to those associated with fast-growing transportation sector of urban areas is the main driving force for biofuels production. Compared with fossil fuels biofuels combustion can help mitigate the greenhouse effect throughout their life cycle, considering that part of the emitted CO₂ returns to the atmosphere where it was fixed from by photosynthesis in the first place. Within bioefules, production of bioethanol from lignocellulosic biomass represents promising options due to its abundance and availability. During this process the most challenges are addressed to the enzymatic hydrolysis which has the objective to overcome recalcitrance of the biomass and provide monomer sugars in high yields, which subsequently will be fermented to the ethanol. In this work enzymatic hydrolysis as the crucial step in conversion of lignocellulosic biomass to bioethanol is reviewed through its challenges, environmental impact and economic contribution to the overall production process.

Key words: *Climate change, Fossil fuels, Lignocellulose, Bioethanol, Enzymatic hydrolysis.*

INTRODUCTION

Global consumption of primary energy (i.e. energy in its naturally occurring form such as coal and oil) from all sources in 2008 was 514 EJ (EJ = exajoule = 10¹⁸ J) and it is projected to rise to 1000 EJ or more by 2050 if economic growth continues its course of recent decades. Today, over 80% of world energy is being from fossil fuel, while the transportation sector worldwide is almost entirely dependent on petroleum-based fuels and it is responsible for 60% of the world oil consumption. The dramatic increase in the price of petroleum and the depletion of fossil fuels along with mankind increasing concerns regarding environmental impact, especially related to greenhouse gas (GHG) emissions and health and safety considerations are forcing the search for new energy sources and alternative ways to power the world's motor vehicles. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available (Moriarty and Honnery, 2012). Bioethanol obtained by biochemical conversion of lignocellulosic biomass is showing a great potential to fulfill listed demands.

The most challenges in respect of unlocking plant cell wall sugars, efficiency and cost effectiveness are addressed to the enzymatic hydrolysis as crucial step in production of second-generation bioethanol from highly complex and recalcitrance lignocellulosic biomass as substrate.

A FOOTPRINT OF FOSSIL FUELS IN ERA OF CLIMATE CHANGES

The use of fossil fuel energy for electricity, transport and other requirements of industrialized lifestyles plus emissions from changes in land use and forestry, is currently putting CO₂ into the atmosphere faster than natural environmental processes can remove it (Chicco and Stephenson, 2012). Today fossil fuels take up 80% of the primary energy consumed in the world, of which 58% alone is consumed by the transport sector (Nigam and Singh, 2011) which accounts for more than 70% of global carbon monoxide (CO) emissions and almost 20% of global carbon dioxide (CO₂) emissions. Emissions of CO₂ from a gallon of gasoline are about 8 kg (Balat, 2011). Other greenhouse gases, for

example CH₄ and N₂O, also contribute to warming, but the relative quantity and extreme longevity of CO₂ in the atmosphere makes it the dominant influence (Chicco and Stephenson, 2012). About 56% of the CO₂ emitted as a result of human activities is accumulating in the atmosphere (Seinfeld, 2011) and some estimations say that 20–40% of anthropogenic fossil fuel CO₂ emissions may remain in the atmosphere for periods up to tens of thousands of years (Chicco and Stephenson, 2012).

Atmospheric carbon dioxide concentrations are higher today than at any time in at least the past 650,000 years. They are about 35% higher than before the Industrial Revolution. Concentrations of CO₂ have increased steadily from about 315 parts per million (ppm, or molecules of carbon dioxide per million molecules of dry air) in the late 1950s to about 390 ppm now. The amount of CO₂ in the air is currently increasing about 2 ppm per year. Continuing on to date established trends in use of fossil-fuel energy and accounting for projected population growth, the CO₂ level will be 900 to 1100 ppm by the end of this century (Seinfeld, 2011). In addition, the present and future levels of urbanization, particularly the rapid urbanization of developing countries, have clear linkages to the global greenhouse gas emissions. International Energy Agency (IEA) estimated that the urban areas contributed 71% to the energy-related CO₂ emissions for the year 2006 and estimated increase to 76% by 2030. On a national and regional scale, carbon emissions from urban energy usage for China, USA and Europe are estimated to 85%, 80% and 69%, respectively (Dhakal, 2010), while transportation is responsible for one-third of the USA carbon footprint, or 534 million metric tonnes of carbon emissions in 2005 (Brown et al., 2008).

The rapid transfer of carbon from the lithosphere to the atmosphere over the last century associated with the burning of fossil fuels is an unprecedented force in the climate system, driving change on a time scale of decades, not millennia (Seinfeld, 2011). Global temperature change shows a near-linear relationship with cumulative carbon dioxide emissions (Matthews et al., 2009). Limiting global temperature rise to 2 °C has been widely adopted in international policy as a target for controlling global warming. Recently the practicality of staying within a 2 °C threshold has been questioned and warming of the order of 4 °C is considered likely before the end of 21st century (Chicco and Stephenson, 2012; New et al., 2010).

The dramatic increase in the price of petroleum, the finite nature of fossil fuels, increasing concerns regarding environmental impact, especially related to GHG emissions, and health and safety considerations are forcing the search for new energy sources and alternative ways to power the world's motor vehicles. Within all energy alternatives, biofuels are the most likely to accomplish environmental and economical demands. As concern about global warming grows, there is increased interest in biofuels, to which also contributes the fact that home-produced fuels mitigate, to some extent, the dependence on imported oil and political variations in its supply and price (Nigam and Singh, 2011).

BIOETHANOL HELPING MITIGATION OF CLIMATE CHANGES

Biofuels are referred to liquid, gas and solid fuels predominantly produced from biomass. Biofuels have emerged as one of the most strategically important sustainable fuel sources and an increasing number of developed and developing countries found biofuels as a key to reducing reliance on foreign oil, lowering GHG emissions and meeting rural development goals. Between 1980 and 2005, worldwide production of biofuels increased by an order of magnitude from 4.4 to 50.1 billion litres, with further dramatic increases in future. The European Council in March 2007 endorsed a mandatory target of a 20% share of energy from renewable sources in overall energy consumption by 2020 and a mandatory 10% minimum target to be achieved by all Member States for the share of biofuels in transport sector by 2020 (EU. Directive 2009/28/EC, 2009). The key advantage of the utilization of renewable sources for the production of biofuels is the utilization of natural bioresources (that are geographically more evenly distributed than fossil fuels) while utilization of agricultural residual and waste substrates as raw materials would minimize the potential conflict between food and fuel. Renewable and carbon neutral biofuels are necessary for environmental and economic sustainability (Nigam and Singh, 2011).

Although biofuels are emitting less greenhouse gases primary throughout their life cycle, considering that part of the emitted CO₂ returns to the atmosphere where it was fixed from by photosynthesis in the first place, they are not carbon neutral (Bessou et al., 2009). One way to determine the impact of bioenergy is to use the environmental management tool, Life Cycle Assessment (LCA). LCA is a methodological tool used to quantitatively analyze the life cycle of a product or an activity within a generic framework provided by ISO 14040 and 14044. It examines the environmental burden of a product or process over its entire life, from production, through use and on to disposal or recycling (Borrion et al., 2012).

Given the objectives of reducing fossil fuel use and GHG emissions, LCA permits evaluation of the net contribution of biofuels. There are several ways to express the relationship between fossil fuel energy inputs used to produce biofuels and the energy contained in the fuel itself. The ratio of fossil fuel inputs to energy in fuel provides a succinct indicator. For fossil fuels themselves, of course, this ratio will be greater than one since some fossil fuel is needed to extract, transport and refine gasoline from crude oil. Central estimates of those ratios are 1.23 for gasoline and 1.15 for petroleum diesel. For biofuels, these ratios vary considerably across fuels, reflecting a wide range in net energy contributions, the most cited values being 0.66 for corn ethanol, 0.38 for soy biodiesel, and 0.08 for cellulosic ethanol. Considering that part of the emitted CO₂ returns to the atmosphere where it was fixed from by photosynthesis in the first place, biofuels can emit less greenhouse gases compared with fossil fuels throughout their life cycle but they are not carbon neutral. Similar to the LCA energy accounting life-cycle carbon emissions can also be evaluated for biofuels. Carbon LCA depends greatly on technology and types of fossil fuel used (Jaeger and Egelkraut, 2011). Different studies have reported different sources contributing to GHG emission through the whole life cycle chain: some report that the majority of GHG emissions come from the biomass cultivation stage; others argue that significant GHG emissions are from ethanol conversion process (Borrion et al., 2012). There are estimates that suggest a 20% reduction in CO₂ emissions per MBTU (million British Thermal Units) when substituting corn ethanol for gasoline, while reduction for biodiesel in the U.S. and Europe is 40%, and 78% for Brazilian sugarcane ethanol (Jaeger and Egelkraut, 2011).

A recently popularized classification for liquid biofuels includes first-generation and second-generation biofuels. The primary distinction between them is in the feedstock used. The first-generation liquid biofuels are the type of liquid fuels generally produced from sugars (Love et al, 1996), grains or seeds (Suresh et al., 1999) and requires a relatively simple process to produce the finished fuel product. Second-generation liquid biofuels are generally produced by biological processing from agricultural lignocellulosic biomass, which are either non-edible residues of food crop production or non-edible whole plant biomass (e.g. grasses or trees specifically grown for production of energy). It is believed that the basic characteristics of feedstocks holds potential for lower costs, and significant energy and environmental benefits for the majority of second-generation biofuels (Nigam and Singh, 2011).

Use of bioethanol as biofuel is both renewable and environment-friendly. Ethanol can be combined and blended with petrol or burned in its pure form within modified spark-ignition engines. Although a litre of ethanol contains less energy than a litre of petroleum in blends it improves the fuel combustion in vehicles, thereby reducing the emission of carbon monoxide, sulphur, unburned hydrocarbons and carcinogens (Nigam and Singh, 2011). In addition, reviewed studies show a range of GHG savings from 4% to 15% when shifting from conventional gasoline to E10 (blend with 10% of ethanol), from 12% to 96% with E85 (blend with 85% of ethanol), and from 46% to 90% with E100 (pure ethanol fuel). They show energy savings from 4% to 8% when moving from gasoline to E10, and from 45% to 76% with E85, and 56% to nearly 100% with E100 (Borrion et al., 2012).

To ensure that “good” bioethanol is produced, with reference to GHG benefits, the following demands must be met: (1) bioethanol plants should use biomass and not fossil fuels, (2) cultivation of annual feedstock crops should be avoided on land rich in carbon (above and below ground), such as peat soils used as permanent grassland, (3) by-products should be utilized efficiently in order to maximize their

energy and GHG benefits, and (4) nitrous oxide emissions should be kept to a minimum by means of efficient fertilization strategies, and the commercial nitrogen fertilizer utilized should be produced in plants which have nitrous oxide gas cleaning (Balat, 2011).

Ethanol, if it is produced using a renewable biomass, is named as bioethanol, while one produced from lignocellulosic biomass is referred as second-generation bioethanol or cellulosic bioethanol. As mentioned before, lignocellulosic biomass includes agricultural waste i.e. non-eatable parts of plants or whole plants that are non-eatable. Lignocellulosic biomass is generally composed of two fermentable carbohydrate polymers, cellulose and hemicelluloses, and one non-fermentable polymer - lignin. These polymers together make complex and recalcitrant biomass structure which makes process of production of second-generation bioethanol more complicated than the one of first-generation. Generally, production of bioethanol from lignocellulosic biomass is carried out through four major steps. Pretreatment, as first step, has the objective to prepare biomass for enzymatic hydrolysis through disturbance of its complex structure by lowering degree of cellulose crystallinity and lignin removal. Second step, enzymatic hydrolysis, biochemically converts biomass polymers to the fermentable sugars. During third step obtained cellulosic and hemicellulosic sugars are being fermented to ethanol by yeasts and/or bacteria, while final step includes distillation and formulation of final product, (bio)ethanol.

Considering that enzymatic hydrolysis converts biomass to the substrate that will be fermented to the ethanol, it probably represents the most crucial step in whole lignocellulosic bioethanol production. In addition, enzymatic hydrolysis has the most challenges to overcome in respect of enzyme production, efficiency of hydrolysis and overall cost effectiveness.

The enzymatic hydrolysis challenge

Enzymes play a critical role in the conversion of lignocellulosic waste into fuels and chemicals, but the high cost of these enzymes presents a significant barrier to commercialization. In the simplest terms, the cost is a function of the large amount of enzyme required to break down polymeric sugars in cellulose and hemicelluloses to fermentable monomers. In the past decade, significant effort has been expended to reduce the cost by focusing on improving the efficiency of known enzymes, to identify new, more active enzymes, to optimize enzyme mixtures for selected pretreated substrates, and to minimize enzyme production costs (Merino and Cherry, 2007).

Cellulose is typically hydrolyzed by the group of enzymes called cellulase. These enzymes are produced by several microorganisms, commonly by bacteria and fungi while commercial products of various *Trichoderma reesei* isolates have been available for a long time (Balat, 2011).

Although cellulose is a homopolymer, a number of enzymes are needed to degrade it. These can be divided into the following three types: endoglucanases (EG) which hydrolyse internal β -1,4-D-glucosidic linkages randomly in the cellulose chain; exoglucanases or cellobiohydrolases (CBH), which progress along the cellulose line and cleave off cellobiose units from the ends; celobiases or β -glucosidases (BG), which hydrolyse cellobiose to glucose and thus prevent exoglucanases being inhibited. These three groups of enzymes act synergistically in degrading cellulose polymer chains by creating new sites for each other and preventing product inhibition.

The exact understanding of mechanisms involved in enzyme systems required for hydrolysis is complicated by a number of factors that include the insoluble nature of cellulose and heterogeneous nature of lignocellulose. However, recent years have shown important advances in revealing mechanisms of improving and producing synergistic cellulases. Although both enzyme systems and the understanding of cell walls are still subject of improvement, it is believed that knowledge of the mechanisms and interactions between these two areas is needed in order to further increase the viability of bioethanol production (Kristensen, 2008).

Other challenges of efficient enzymatic hydrolysis of lignocelluloses biomass are addressed to the biomass origin, type and thus characteristic structure and type and severity of pretreatment. Ultimately the selection of biomass feedstock will be based on local availability and economy of supply. The substrate characteristics that have been shown to impact the rate of enzymatic hydrolysis according to Alvira et al. (2010) include degree of cellulose crystallinity and polymerization (as indication of substrate complexity), available surface area of substrate (i.e. area that enzyme could be attached on), hemicelluloses content (as indication of decreases accessibility to cellulose) (Chandra et al., 2007; Hendriks and Zeeman, 2009) and the type and distribution of lignin as physical barrier and non-productive binding of enzymes (Chang and Holtzapple, 2000; Börjesson et al., 2007).

Thus, the variation in composition of a given biomass requires specific tailoring in the enzymatic conversion as well as pretreatment method (Merino and Cherry, 2007) which has the aim to decrease all above mentioned substrate related limitations of enzymatic hydrolysis. Pretreatment is a balancing act that involves unlocking the cell wall structure without forming inhibitors, which affect hydrolysis and/or fermentation. Choice of type and severity of pretreatment can have a profound impact on enzyme dosage required for hydrolysis, and therefore on the cost of enzymatic hydrolysis (Merino and Cherry, 2007).

Despite all of the above it must not be forget primary parameters of every enzymatic reaction: substrate and enzyme concentration (Alvira et al., 2010). Researches are focused on optimizing the hydrolysis process and enhancing the cellulase activity in order to obtain high yields and rates in reasonable time course. A low substrate and enzyme concentrations give low yield and rate. A high cellulase dosage may increase the costs disproportional (Balat, 2011), while high substrate concentrations may be useful to some extent due to more biomass being process and less water inputs, which is environmentally. Thus balancing between substrate concentration that will be high but will not provoke limiting of hydrolysis rate, and enzyme concentration that will provide high hydrolysis yield in reasonable time course without unproductive consumption is the key factor for energy savings and cost reduction in both enzymatic hydrolysis and overall bioethanol production.

This is crucial considering that enzyme and hydrolysis cost have great share of the overall cost per litre of bioethanol produced. It is estimated that cost of enzymatic hydrolysis should be 0.341 US\$/L or 22% of minimum ethanol selling price when implementing second-generation ethanol production in existing plants of first-generation. This value could be up to 0.47 US\$/L accounting for more than 40% of ethanol price depending of different scenarios and process modifications. Scenario that involved hydrolysis time reduction increased process energy efficiency but lower yield resulted in increased ethanol price. On the other hand, increasing enzyme dosage and adapting biomass concentration resulted in increase in yield hydrolysis and fermentation yield. The final ethanol concentration prior to distillation also increased, reducing the energy demand as well as the capital cost for the distillation stage. This is also confirmed by the increase in energy efficiency and decreased selling price. In case of combining these two scenarios a decrease in time did not pay off in spite of higher enzyme loading, and the minimum ethanol selling price increased (Macrelli et al., 2012).

Impact of lignocellulosic bioethanol production on environment with special reference to water resources

Bioenergy production generates large amounts of wastewaters with different characteristics (Šćiban et al., 2011) and can have both positive and negative effects on water resources. Bioenergy production generally consumes more water than gasoline production (Fingerman et al., 2010). However, this relationship and the water impacts of bioenergy production are highly dependent on location, the specific feedstock, production methods and the supply chain element. Feedstock cultivation can lead to leaching and emission of nutrients that increase acidification and eutrophication of aquatic ecosystems (Menon and Rao, 2012). The decrease in acidification potential after 2005 is due to the increase of lime use in pretreatment process, but primarily from the improvements in efficiency from 2010 and beyond. Eutrophication steadily decreases from 1999 to 2015 - this decrease is primarily due to improvements in enzyme production. Further, the other main contributors to eutrophication are

pretreatment and wastewater treatment and gradual decrease in eutrophication from these sub-processes is due to the improvements in the efficiency of the process (Pawelzik and Zhang, 2012).

Air pollutant emissions from bioenergy production depend on technology, fuel properties, process conditions and installed emission reduction technologies. Compared to coal and oil stationary applications, sulphur dioxide (SO₂) and nitrous oxide (NO_x) emissions from bioenergy applications are mostly lower. When biofuel replaces gasoline and diesel in the transport sector, SO₂ emissions are reduced, but changes in NO_x emissions depend on the substitution pattern and technology.

As for the biofuels impact on the soil it includes soil carbon oxidation, changed rates of soil erosion, and nutrient leaching. However, these effects are heavily dependent on agronomic techniques and the feedstock under consideration for biofuel production (Menon and Rao, 2012).

The overall performance of bioenergy production systems is therefore interlinked with management of land use and water resources. Environmental impacts of biofuels and bioethanol depend on the type of chosen feedstock, the way it was cultivated, and overall technology employed for its conversion.

CONCLUSION

Bioethanol obtained by biochemical conversion of lignocellulosic biomass is showing a great potential to become feasible, economically competitive, environmentally acceptable and readily available fuel that will replace fossil fuels in the future. Furthermore, lignocellulosic bioethanol could help mitigating climate changes caused by fossil fuels combustion, especially in transportation sector. Although there is still a lot of challenges to overcome, the enzymatic hydrolysis of lignocellulosic biomass has the crucial influence in production of bioethanol in respect of achieving its future viability, sustainability and cost effectiveness. Blending or substituting fossil liquid fuels with bioethanol produced through second-generation technologies will reduce GHG emission on global level, while its environmental impacts should be additionally perceived through diminished influence on wastewaters due to improvements in management of the most important step - enzymatic hydrolysis of lignocellulosic biomass.

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**OPEN SPACE DESIGN AS A TOOL FOR ADAPTING CITIES TO
CLIMATE CHANGE: POSSIBILITIES FOR INTEGRAL APPROACH**

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ABSTRACT

Adaptation to climate change is a challenge that all countries and cities are currently facing. In local climate adaptation policies, open spaces are recognized as an important action area due both to their vulnerability and their potential to respond to various climate-related problems. Though various practical open space design solutions were recently introduced in different areas of climate sensitive action, they remain isolated and fragmented. The theoretical basis for open space design as a tool for adapting cities to climate change is still missing. Starting with premise that "fragmented understanding of problems only generates fragmented solutions" we argue that for open space design to be a useful tool for adapting cities to climate change - an integral approach is necessary. Therefore the capacity of Nan Elin's theory of integral urbanism is evaluated in relation to the complex role open space is supposed to play in adapting cities to climate change. Using case-study methodology, qualities of hybridity, connectivity, porosity, authenticity and vulnerability of urban open spaces are analyzed in climate sensitive design solutions, and discussed in relation to the three strategic areas of climate-adaptation action: flood, overheating and droughts/water management. The research results imply that dealing with adaptation to climate change through open space design requires a shift in mindset- from fragmentary and problem-solving way of thinking, towards an integral and proactive one. Theory of Integral urbanism provides the valuable basis for this task.

Key words: *open space design, climate adaptation policies, cities, integral approach.*

INTRODUCTION

Climate change is widely recognized as one of the most challenging and complex problems facing humanity. At the same time, it affects and is affected by development at different levels. Various pragmatic tools were developed to incorporate climate change into development planning, along with longer term strategic envisioning tools to enable development organizations to consider global futures. It is believed that actions taken over the next decade will have an enormous influence on the rate and magnitude of climate change over the next centuries. In recent years, numerous cities and towns across the world are integrating climate adaptation policies into their strategic documents.

Urban areas, where the majority of the population lives, are especially vulnerable to the impacts of climate change due to their high population density and physical structure (EEA, 2009). They will warm more than rural ones because buildings absorb heat. The concentration of buildings and hard surfaces leads to the formation of a specific climate, characterized by higher night time temperatures, restriction of wind which disperses pollutants and increased run-off, i.e. 'urban heat islands'. (NCRA, 2007). On the other hand, increased coastal, fluvial and pluvial flood risk (stimulated by sea level rise, increased storminess and increased winter precipitation) are also key threats of climate change to building integrity as well as for all forms of life in the city.

The way that climate changes are related to urban environment shows that the urban built environment is not only exposed to climate change risks but also has an impact on it. On this basis urban and open space design issues are related to climate adaptation policies and measures. These policies recognize urban open spaces as an important action area, due both to their vulnerability and their potential to

respond to various climate-related problems. Therefore climate-sensitive design of open spaces in urban areas becomes an important task for urban development.

This task is mostly approached in a practical way, without developed theoretical basis. In recent years several useful guidelines were produced (TCPA, 2007; NCRA,2007) worldwide in order to integrate climate issues into urban and open space design. Proposed adaptations interventions typically involve measures such as: water conservation, rehabilitation of coastal and riverside areas to increase their physical resilience, etc. (Brooks N., Grist N.,2008) Although various practical open space design solutions were recently introduced in different areas of climate sensitive action, they still remain isolated and fragmented.

Starting with premise that "fragmented understanding of problems only generates fragmented solutions" (Elin N. 2006) we argue that for open space design to be sustainable tool for adapting cities to climate change - an integral approach, based on strong theoretical foundations, is necessary. For that reason, in this paper the capacity of Nan Elin's theory of Integral Urbanism is evaluated in relation to the complex role open space is supposed to play in adapting cities to climate change. This theory is chosen for its proactive, sensitive and optimistic approach toward restoring valuable connections between human and non-human, between people, between culture and nature. At the same time it acknowledges the need for reaching this aim in a sustainable way.

THEORY

Nan Elin's theory of Integral Urbanism (Elin N. 2006) aims to heal the wounds inflicted upon the landscape by Modern and Postmodern eras, that manifest as sprawl, declining sense of community and environmental degradation. It searches to restore connections between people and nature and among humans that have been broken by previous modes of development and design. It extends the normative path that Jane Jacobs paved in *The Death and Life of Great America Cities*– "that urban vitality and public safety are complementary-not contradictory-features of the city, achieved through adjacencies of uses and people along with other generators of diversity". (Jacobs J. 1961)

The main goal of Integral Urbanism is to achieve vitality ("flow", "anime" fr.) By distilling the principal qualities of the more sustainable practices it aims to achieve new functionality of urban space that enables vitality. This functionality is understood more holistically to include not only classical urban functions (uses, activities) but emotional, symbolic and spiritual functions as well.

Main qualities for places to enable urban vitality include: hybridity, connectivity, porosity, authenticity and vulnerability. These qualities describe a shift from emphasizing isolated objects and separating functions to considering larger contexts and multifunctional spaces. It adopts the logic of ecology, that the health and well-being of places derive from optimizing numerous variables rather than trying to maximize one variable.

Hybridity & Connectivity

Hybridization as a quality connects people and activities at points of intensity and along thresholds. While Modern Urbanism espoused the separation of functions in urban form, Integral Urbanism reaffirms their symbiotic nature by combining and linking them. In search for optimizing numerous variables, it learns about relatedness, simultaneity, juxtaposition and synergies from ecology and city-building wisdom, and adapts it to contemporary needs. It asks for programed hybridity in urban design that can be described such as complexity, density, congestion, and thematic intensification. (Koolhaas,1996). Transposing programmatic hybridity onto the urban and regional scales can increase density of activity without necessarily increasing building density. The outcome is that resources conserved this way include time, water, energy, building materials, space, and nature. ... "Integrative design solutions add long term value and offer collateral benefits related to sustained economic capacity, enhanced ecologies and improved public health – the foundations of creative development"(www.uacdc.uark.edu)

Connectivity is important quality because this theory recognizes and emphasize that vitality is based on quality and complexity of relations and connections between entities. Connections are various and include: people, places, programs, resources... center-periphery, city-region, nature-culture, material-digital, global-local, future –past...

Forms of connectivity and hybridity are numerous and can be regulated by shifting from use-based zoning to integrated land use, mixed use zoning or form-based coding. Connections are based on networks and nature as models and include various nodes and different links. Links can be permanent or temporal, functional, physical, emotional.

Porosity

Porosity is the quality of “being able to see through” to what lies beneath or beyond the surface. It is in its maximum when it is transparent; it is minimum when it is translucency. Both extremes- no porosity or too much porosity- diminish the quality of life. Various types of porosity exist: visual, functional, provisional, temporal, historic, ecological, administrative, spatial, symbolic...¹

Emphasis on a various levels and types of porosity are in contrast to both Modern aspiration to transparency (that resulted in overexposure, homogeneity and lack of legibility) and Postmodern reaction to it - in form of opacity (resulting in “fortress urbanism”). Integral Urbanism favors translucent urbanism that glorifies borders that exist in natural systems, more adaptive, unpredictable, thresholds where ecosystems meet and is ultimately sustainable. Accent on borders induces a movement from objects to relationships, from projects to places, from opposition to synergy.

Authenticity

Authenticity is the quality of Integral urbanism that is based on search for self and meaning in city life. It is a reaction to the words most commonly used to describe urban spaces: abandoned, vacant, generic and anonymous. Elin recognize that »this loss of sense of place contributes to feelings of emptiness, anxiety and insecurity« and identifies numerous efforts to rekindle a sense of place and with it a sense of interest, meaning, security, and community. She analyses contemporary urban design theory and practice through different intellectual lines that correspond to Mis Van der Rohes »form follows function« and reveals their reactive nature. These new lines of thought are »form follows fiction, finesse, finance and fear« (Elin N., 2002).

As opposed to existing reactive theories Elin suggests proactive approach that »responds creatively and compassionately by remaining connected to our environment, to our communities and to ourselves by being authentic«. Therefore it embraces the reality as a basis for action. The city becomes and stays real through ongoing meaningful connections, not through cosmetic quick fixes or massive razing and rebuilding urban fabric. Becoming real is a transformation from isolation to integration, form numbness to feeling, from boredom to excitement, from cynism to caring, from complacency to engagement. »Our search for the real reflects a desire for interconnectedness with places we live and with a community of people.« (pp.117) It lays in our ability to reveal »latent qualities within imperfect spaces«. An Authentic-city results from a combination of large scale and small scale interventions, both systematic and the serendipitous. It is based on the ethic of taking care – of self, others and environment.

¹ *Visual porosity* – allows us to see through but not move through a space., *Functional porosity* – allows access to a place or modulates our relationship with it; *Provisional porosity* – allows access on a temporary basi, *Temporal porosity* - occurs when a place transforms over the course of a day, a week, or a yera, *Historic porosity*- preserves remnants of the paat while building new; *Ecological porosity*- integrates nature and natural processes into the built environment; *Experiential porosity* - allows us to discover the place; *Administrative porosity* - occurs when administrativ eunits communicate and collaborate with each other ; *Spatial porosity, or programmatic porosity*, occurs when activities seep into each another; *Symbolic porosity* – occurs when a permeable membrane is perceived although there may be no separation at all (Elin N.,2006, pp.63-93).

Vulnerability

Desire for creation and control (of nature, people, environment...) lay at the heart of Modern urbanism. Modern master planning ultimately have fallen short in achieving cities and buildings as »living machines«, based on pure rationality. Realized only partially these ideas produced fragments of cities that do not congeal into an urban fabric, and run counter to integration and dynamism of the life lived in them. This problem could not be solved by just looking for another kind of technical, planning or design solutions. A new approach was needed to the overall attitude to human activities.

Integral urbanism thus »features a willingness to relinquish control. To let things happen, and to play – vulnerability«. By emphasizing relationships rather than isolated objects, complementarity rather than opposition, substance rather than surface, it emphasizes process rather than product. In this way buildings and city are always works in progress. And »as process becomes product so the journey becomes as important as destination«. (pp.120) Therefore a vulnerable urbanism» allows things to happen things that may be unforeseen«. (pp.121) It embraces change and accepts imperfection and irrationality. It is soulful and poetic and in integrates culture and nature

This is translated into a shift from all-inclusive master plan (in which land use considerations are primary) to a more project oriented, site and client specific, incremental, catalytic form of intervention.

METHODOLOGY

Relation between theory of Integral Urbanism and problem of sustainable adaptation to climate change through open space design is first analyzed at theoretical level, by comparing concepts, goals and principles of Integral Urbanism to complex demands of climate adaptation policies in urban areas in the field of open space planning and design. For that purpose qualitative content analysis of main climate adaptation related research and policy documents was done in order to map and classify main forms and field of action, as well as to understand the character of climate adaptation as a problem of urban development.

At the empirical level, by using case study methodology, integral design qualities of hybridity, connectivity, porosity, authenticity and vulnerability of urban open spaces were analyzed in 3 cases of climate sensitive design solutions and compared to conventional approaches to combating climate-related problems in urban areas. Further, they were discussed in relation to the three strategic areas of climate-adaptation action: flood, overheating and droughts/water management.

FINDINGS

Adaptation to climate change as a problem of urban development

- In scientific community climate change is recognized as a multidimensional, complex, vague and dynamic problem.(IPCC.2007a, 2007b; Esbjörn-Hagens, S. (2010) This means that different areas are affected by and can influence climate change, and that effects of climate change are at the same time interdependent and more or less unpredictable. Since it depends on various development scenarios, it has been suggested that it should be approached in relation to overall developmental issues. (Brooks N., Grist N.,2008). Therefore, as a challenge for development, climate change mitigation and adaptation is usually seen in the context of search for sustainable development or/and in the context of integral development.(Lalovic, Zivkovic, Milovanovic, 2012).
- Scientific reports recognize three main exposure units to climate change in urban areas: *building integrity, urban green space and human health and comfort*:
- *Building integrity* means that both buildings and infrastructure are at risk to increased coastal, fluvial and pluvial flood risk; shrinking and swelling of the ground erosion. This is stimulated by sea level rise, increased storminess and increased winter precipitation. These impacts are increased

by type of urbanization, which alter natural hydrological regimes through reducing the infiltration capacity of the ground. (Handley J., Carter J., 2006);

- *Urban green spaces* are important for improving the climate conditions and combating the threats induced by climate change, but they can also be affected by climate change. It is expected that climate change will lead to more droughts in summers, and this will mean a greater need for urban green spaces to be watered. (Barber, A., 2006). Yet it can be expected that limited water resources will cause the problem in managing and effectiveness of urban green space so different methods which allow rainwater harvesting, the re-use of grey water and making use of water in rising aquifers under cities should also be employed. (Gill.S, J.Handley,Ennos R,Pauleit S.,2007
- *Human comfort and health* in urban areas are threatened by climate change due to rising temperatures and more intense rainfall events with associated flooding. With the prospect of climate change, people will need to be aided in their efforts to adapt to the different expected new climatic conditions within urban areas (Handley J., Carter J., 2006). The adaptive capacity of different communities and groups also varies. Vulnerable groups, such as elderly and poor inner-city residents will be disproportionately affected. It can be expected that climate change will affect people's demand for, use of, and experience of open space. (Cabe, 2008) Natural venting and shading, accessibility, quantity and quality of green and blue space areas, which can moderate temperatures and enhance human comfort, are for that reason of main importance (Zivkovic J., Lalovic K., 2011)

Complex role of open spaces in adapting cities to climate change: fields of action

Taking into account the main exposure units to climate change in urban areas, content analysis of general adaptation recommendations and specific local urban climate adaptation strategies indicates three main adaptation policy areas: flood, overheating and droughts/water management in which open space planning and design plays significant role (TCPA, 2007; Kamal-Chaoui, L., Alexis R.(eds.)2009; The World Bank, 2010)

- **Flood:** Increases in average winter precipitation and in the frequency, duration and intensity of heavy downpours will increase flood risks. Measures for reducing and managing flood risks include: a) Safeguard of land that is required for current and future flood risk management - holistic approach, b) Creation of hard, permanent flood defenses and barriers where necessary) Reducing flood risks to new development through location, layout and flood resilient design; d) Use of sustainable drainage systems (SUDS) to manage and slow down surface water run-off and release it to the natural water cycle. e)Understanding flooding pathways in urban environments - making space for water (use of green infrastructure for flood storage, re-creation of functional floodplains, provision of temporary water storage capacity during flood , creation of flood retarding basins, upland land management, diversion of flood flows away from vulnerable areas or constructing a second flood channel.
- **Overheating:** Since average annual and seasonal temperatures are likely to continue to rise planning and design should aim for integration of water, open space and built form through green space and blue space strategies. Local microclimate is essential for human health and wellbeing. Related policies and measures are: a) good quality green infrastructure, b)Making blue space accessible, such as rivers, lakes and urban canals, c) shading and orientation to reduce excessive solar gain (e.g. through narrow streets, canopies of street trees). d) Passive ventilation captured through location, orientation and morphology of buildings streets, green and blue areas. e) Cool pavement materials on roofs, roadways or large parking areas – to increase surface reflectivity or increase rainfall permeability
- **Droughts/water management:** Changing patterns of rainfall will have a significant impact on water resources and water quality. In the summer, warmer temperatures will mean that demand for water grows just as supply declines due to lower rainfall. Low river flows during dry summers can lead to restrictions on water abstractions, with consequences for cooling processes when the need for cooling is highest. Also urban areas have little capacity to store drinking water and are more likely to experience shortages during droughts. Spatial policies and measures for managing droughts and water shortage include: a) creation of upland and lowland reservoirs, both natural and manmade that can also have important aesthetic, recreation, ecological and flood storage roles, b) Providing

space for treatment of storm water and waste water (e.g. by platooning and micro-filtration) and increasing use of reclaimed and recycled water. C) Use of sustainable drainage systems SUDS for groundwater recharge, d) Greater use of separate drainage systems for surface and foul water; e) Use of low water , underground storage and accessing new supplies of lower grade ground water in order to sustain the evaporative cooling function of vegetation in times of drought.

Integral Urbanism qualities in climate – sensitive urban open space design

Adaptation to flooding

Conventional approaches to flooding in open space design – Conventional flood control design methodology seeks to minimize the right-of-way required for flood control channels by increasing flow velocities. This allows narrower channel to be built that reduces flood elevations. It is done by lining the channel with smooth reinforced concrete. With a suitable slope in a uniform channel, the low roughness of the concrete can allow "super-critical flow" to develop very fast-moving shallow flow. When super-critical flow occurs, the channel cross-section and right-of-way can be significantly reduced. (Williams P.B, Swanson Mitchell L.,1989) These engineering methods of flood control design focus narrowly on the efficient conveyance of water, with little regard for environmental resource planning and natural geomorphic processes. Consequently, flood control projects are often environmentally disastrous, expensive to maintain, and even inadequate to control floods. Besides, they don't take into account variety of functions that border between water and culture can have in contemporary urban life. (fig.1a)

Integral approaches to flooding in open space design – This approach is based on understanding of both physical and social system. It utilizes an integrated planning process that requires an understanding that stream modification will affect more than flood levels. All the significant hydrologic, geomorphic, ecologic, social and economic factors have to be considered, rather than approach the design as a plumbing problem. Therefore stream modifications are rarely single-purpose projects. They typically can include the following: flood damage reduction, protecting or restoring riparian ecosystems; providing recreational access; enhance property values along water corridor. (Otto B. McCormick K, Leccese M. 2004). Good example of this approach is Confluence Park, one of a string of parks that Denver, USA, has built since 1995 to combat flooding and promote wildlife habitat and recreational use on the South Platte River.(Figure 1b)

Qualities of Integral Urbanism in Confluence Park project: high levels of hybridity and connectivity are achieved by forming various and complex connections in place and with surrounding areas and wider context; porosity is achieved in almost all forms; authenticity gained through revealing latent qualities of space and integrating it into city life; vulnerability is important conceptual part of the project since it allows flooding and benefits from it in both aesthetic and ecological way.

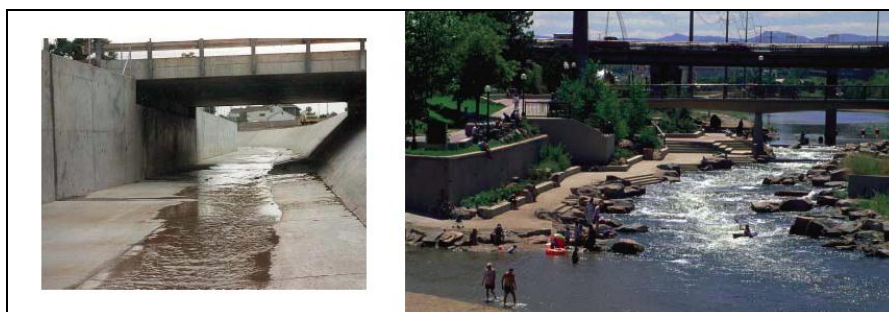


Figure 1. a) conventional, b) integral approach to flooding in open space design

Adaptation to overheating

Conventional approaches to overheating usually include choice of technical solutions (shades, greenery, bodies of water) focused primarily on an overheating problem as it affects human beings. Overheating is not treated as complex problem that has to be treated in systematical way and that can, besides reducing heating problems, also provide environmental and aesthetical benefits. (Figure 2a)

Integral approaches to overheating recognize overheating as a part of broader actions in enhancing living conditions in the city. Combating overheating should be approached simultaneously with improving water and air quality in the cities. For that reason – formation of connected, functionally attractive and accessible green and blue system is essential. Green streets of Portland is ASLA awarded project is good example of this approach. The network of green streets is planned and designed in order to a) improve urban climate, b) manage storm water runoff both at the source and the surface, c) use plants and soil to slow, filter, cleanse, and infiltrate runoff. d) Design facilities that aesthetically enhance the community. (Figure 2b).

Qualities of Integral Urbanism in Green streets of Portland project: hybridity and connectivity is achieved through creation of multifunctional spaces; porosity is mainly visual, administrative, spatial and ecological porosity; authenticity is achieved by creating unique solutions that are contextually dependent; quality of vulnerability is managed through design that embraces unpredictability of weather events.

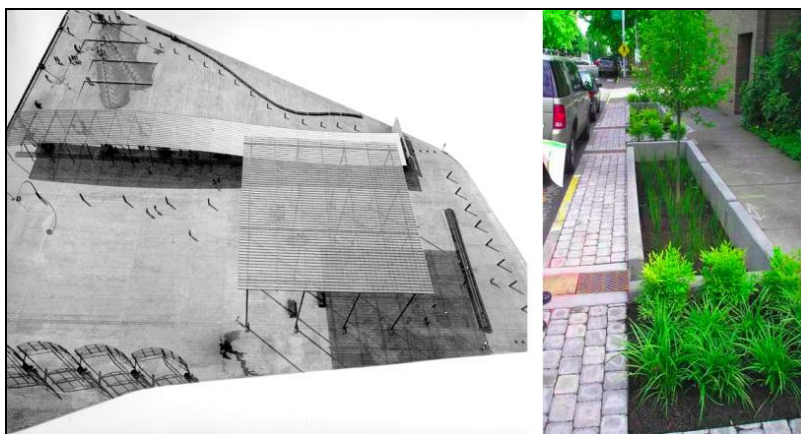


Figure 2. a) conventional, b) integral approach to overheating in open space design

Adaptation to droughts/water management

Conventional approaches to droughts/water management: Problem of polluted waters that can be re used in droughts period is conventionally treated by re-piping the polluted water to a remote wastewater treatment facility. This approach is expensive to realize, requires additional space and has high maintenance costs.(Figure 3a)

Integral approaches to droughts/water management: Integral approach starts with premise that it is possible to have affordable and low maintenance of polluted waters and conceptualize treatment system within the canal itself. It also suggests that it should be fully integrated in urban environment and urban life for to be appreciated and cared for. Good example of integrated approach is restoration project of Baima canal in Fuzhou, China. In 2002, John Todd Ecological Design collaborated with Ocean Arks In. to design a Canal Restorer using 12,000 plants composed of 20 native species. Constructed with a walkway down the center, the Restorer has met water quality goals and created a prized recreation area for the members of the community.(Figure 3b)

Qualities of Integral Urbanism in Baima canal project: hybridity and connectivity are achieved by forming a multifunctional place functionally and visually connected with surrounding areas, porosity

exists the most in visual, functional, ecological, administrative and symbolical way; authenticity is achieved through use of native species in creating ecologically, socially and aesthetically enhanced environment, vulnerability is achieved by a choice to act in situ, at a place where problem occurs.



Figure 3. a) conventional, b) integral approach to droughts/water management in open space design

DISCUSSION

Conceptual compatibility between Integral urbanism and problem of adapting cities to climate change.

Analysis of relations between basic goals, premises and principles of Integral urbanism and character and complexity of problem of adapting cities to climate change has shown that they are compatible. Climate adaptation, as a complex and multidimensional problem, relates to the main goal of Integral urbanism, that of restoring connections between human and nature, and among people. Therefore principles that emphasize relations - of hybridity, connectivity and porosity - are of fundamental importance in approaching complex problem of climate change. On the other hand, dynamism and vagueness of climate adaptation is compatible to deeper understanding of relations between human and non-human that brings ethics of taking care and relinquishing control to Integral urbanism. Finally, the emphasize of Integral design on optimizing numerous variables rather than trying to maximize one variable relates to the nature of climate change adaptation since climate adaptation can be seen as a part of overall sustainable development.

Applicability of Integral urbanism principles in climate-sensitive open space design in urban areas.

Case study analysis showed that though conventional approaches managed to (at least partially) to solve singular problems, integral projects managed to reach multidimensional goals and to contribute to different fields of climate adaptation action.

Analysis also confirmed that it is possible to apply Integral urbanism principles in climate-sensitive open space design in urban areas in all fields of action: flood, overheating, droughts/water management. Qualities of hybridity, connectivity and porosity turned to be essential to all aforementioned fields of action. They represented the need to improve relations between people and nature, thus contributing to sustainability by enhancing environmental, social and economic values of place in these integrated projects. Quality of vulnerability was of great importance in the field of combating flood and droughts/water management through open space design. It showed that conceptual shift in relinquishing control over water can induce new creativity and improve our relations with nature. Finally, it is important to mention that integral approaches to climate adaptation through open space design can reach high level of authenticity since there are based on recognition that both past, present and future of place is important. Authenticity of presented projects in turn, contributed to their sustainability through their better acceptance among local citizens and higher attraction to visitors.

CONCLUSIONS AND IMPLICATIONS

In recent years climate change has been recognized, in both scientific and political international community, as one of the most challenging and complex problems that calls for urgent action worldwide. Efforts to adapt to the impacts of inevitable climatic changes, while at the same time reducing greenhouse gas emissions, will require societies to adapt not only to the new biophysical conditions, but also to the new understandings of human-environment relationships. This requires a change in the way policies are formulated and cities designed, but also a much deeper philosophical transition involving the rethinking of the way human societies interact with wider physical environment at the local, regional and global scale.

Since open space planning and design is recognized as an important area of action in climate change adaptation policies, the main argument of this paper was that for open space design to be sustainable tool for adapting cities to climate change - an integral approach, based on strong theoretical foundations, is necessary. The capacity of Nan Elin's theory of Integral Urbanism was evaluated in relation to the complex role open space is supposed to play in adapting cities to climate change. It was done through conceptual analysis of relations between this theory and character of climate adaptation as developmental problem and through empirical comparative analysis of conventional and integral approach to open space design as a tool for climate adaptation in different fields of action.

Conceptual analysis of relations between basic goals, premises and principles of Integral urbanism and character and complexity of problem of adapting cities to climate change has shown that it is possible to relate them and that they are compatible. Complexity and multidimensionality of climate adaptation as a problem relates to the main goal of Integral urbanism that of restoring connections between human and nature, and among people. Therefore principles of hybridity, connectivity and porosity and of fundamental importance in approaching complex problem of climate change. Dynamism and vagueness of climate adaptation is compatible to ethics of taking care and relinquishing control of Integral urbanism, based on deeper understanding of relations between human and non-human. Finally, since climate adaptation can be seen as a part of overall sustainable development, emphasize of Integral design on optimizing numerous variables rather than trying to maximize one variable (through qualities of hybridity and connectivity) can be used as well.

Empirical analysis on applicability of Integral urbanism principles in climate-sensitive open space design in urban areas has shown that it is possible to apply these principles in all fields of action (flood, overheating, and droughts/water management). In all cases of integral approach that were analyzed, it was possible to identify qualities of hybridity, connectivity, porosity, authenticity and vulnerability. But they were realized in different forms and in different level of importance, according to a problem that initiated action.

This lead us to the general conclusion that complex problems, such as climate change adaptation, are not to be seen in isolation and approached only from its practical, technical side. Climate change is not simply an environmental problem, it is about human capacity of individuals and communities to respond to threats, it is closely related to how communities perceive themselves in the world, how humans both create and respond to change, how we sustain our development in balance with nature. Therefore dealing with adaptation to climate change through open space design requires a shift in mindset - from fragmentary and problem-solving way of thinking, towards an integral and proactive one. This research has shown that the theory of Integral urbanism can form the conceptual basis for this task.

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SPATIAL PLANNING AND GREENING IN URBAN AREAS

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**ORNAMENTAL PRUNUS TAXONS (*PRUNUS SERRULATA* LINDL.
AND *PRUNUS FRUTICOSA* PALL. 'GLOBOSA') ON NOVI SAD GREEN
AREAS**

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ABSTRACT

*Besides the use of cherries for obtaining edible fruits, there are genotypes that can be successfully used in the greening of urban areas. This paper examines two species, oriental cherry (*Prunus serrulata* Lindl.) and european dwarf cherry (*Prunus fruticosa* Pall. 'Globosa') which are introduced into green areas in broader downtown area of city Novi Sad. 74 trees at three locations were examined. Height of *Prunus serrulata* Lindl. species varied from 2.70 m on site Petrovaradin fortress up to 6.20 m in Petra Drapšina street. Chest height diameter ranged from 7.00 cm to 37.00 cm, while the width of the canopy varied from 0.80 m to 6.00 m. European dwarf cherry, with form 'Globosa' is present with 56 trees in the tree-lines in Vojvode Šupljikca street. Height of trees ranged from 2.35 m up to 3.50 m, while values of diameter at breast height varied from 8.00 cm to 16.00 cm. Crown width for this genotype had values from 0.90 m to 1.60 m. Both taxa showed high scores of vitality and decorativeness, indicating high level of adaptiveness to changing conditions of urban environment. Collection plot of six ornamental *Prunus* genotypes was established during spring 2011. and 2012. at nursery in Rimski Šančevi. Phenological occurrences and resistance to pests and diseases were observed with purpose of economical production and application of planting material in horticulture and landscape architecture.*

Key words: *Phenological observations, the bioecological basis, *Prunus serrulata* Lindl., *Prunus fruticosa* Pall. 'Globosa', collection plot.*

INTRODUCTION AND THEORY

City greenery is of vital significance for urban living. With its shape and life functions, plants represent irreplaceable natural elements. By the same token, trees improve the ecologically variable environment both by reducing the radiation temperature that results from heating the building and surrounding area, and reducing air temperature by evapotranspiration and wind speed reduction (Akbari et al., 2001). Green spaces improve living conditions, work and recreation, providing optimal bio-climatic, hygienic and aesthetic factors (Chen, 2004) and being basic structural and functional elements that make cities and urban regions suitable for life (Ninic-Todorovic et al., 2010).

The natural habitat of trees and shrubs are natural forests, where living conditions vary in many aspects from those in cities (Tomiczek, 2003). There are different environmental conditions in the city where plant communities are adapted to urban conditions (S. Zerbe et al., 2003). The greenery in urban areas, in addition to decoration, has an ecological function for it mitigates climate extremes. According Anastasijević (2011), its main functions are: sanitary-hygienic, engineering-technical, architectural and urbanistic, aesthetic, cultural, educational and psychological.

In addition to using sour cherry and cherry fruits as consume fruit, there are genotypes that can be successfully used in greening of urban areas. Oriental cherry (*Prunus serrulata* Lindl.) has more than 120 cultivars. It is characterized by rapid growth with a maximum height to 25 meters. Its decoration is best witnessed during flowering in April, and it can be used in many forms such as tree lines along roads, parking spaces, walking paths, meadows and many others.

Oriental cherry cultivar 'Kanzan' is very popular in landscape architecture (Maurer et al., 2000). The publication Forrest (2006) states that the cultivars 'Shirotae' and 'Taihaku' are to be used along walking paths, but also on locations such as shopping centers and hospitals. Oriental cherry tree is not native but cultivated species in Serbia. Authors Manic et al. (2011), state that it is suitable for planting on green urban areas. Oriental cherry is resistant to mild air and land pollution, while in case of inadequate care is prone to diseases caused by brown rot of stone fruits (*Monilia laxa* (Ehrenb.) Sacc.).

A form of steppe cherry (*Prunus fruticosa* Pall. 'Globosa') is a new taxon and therefore poorly represented. It is slow growing and can reach a height of 3 to 5 meters. If well drained, has no special maintenance requirement. It submits shady areas, but also successfully flourishes in sunlit places. It is most commonly used for tree lines on boulevards and promenades. According to the authors Kojić and Mratinić (1998) the main specie (*Prunus fruticosa* L.) in the Republic of Serbia grows at the edge of the forest area as a low shrub. On the eastern and southern slopes of Fruška gora there are two associations of steppe cherry (*Prunetum fruticosae* Korn. /1974/ and *Prunetum spinosae-fruticosae* Job. /1968/ cit. Tomić / 2004 /).

MATERIAL AND METHOD

The study included 74 trees at four sites in Novi Sad area. There are seventeen oriental cherry trees (*Prunus serrulata* Lindl) in Petra Drapšina street. The second site is Stevana Musića street where the oriental cherry tree of the significant age class is found. The same can be found on the third site, Petrovaradin fortress, and fourth site is Vojvode Šupljikca street where fifty-five specimens spherical shape steppe cherry (*Prunus fruticosa* Pall. 'Globosa') is recorded.

Parameters measured were development of trees, and estimation of the vitality of individuals and decoration. Measurement of height, height to the first branch and crown width were done using 360 Vertex IV instrument (Haglof Sweden AB), while chest height (1.30 m) diameter was measured by digital tree calliper Mantax MA95 (Haglof Sweden AB). Rating vitality and decoration is obtained by Anastasijević (2011) based on individual health status indicators (presence of diseases and pests, mechanical damage and visual assessment of the general layout).

During the year 2011 and 2012 collection of oriental cherry and European dwarf cherry taxon have been raised on the scientific field of Faculty of Agriculture in Novi Sad. During the spring of 2012 the phenological phenomena were observed in 25 individuals. Phenological phenomena are encoded using the BBCH scale. The extended BBCH-scale is a unique coding system of similar phenological growth stages of all mono - and dicotyledonous plant species. Decimal code, divided into primary and secondary phases of growth, is based on code developed for grains by Zadoks et al. (1974) with the purpose of unification with the well-known and widely used phenological key. Abbreviation BBCH derives from "*Biologische Bundesanstalt, Bundessortenamt and Chemical industry*".

The data were analysed using the statistical software package Statistica 10th (StatSoft Inc. Tulsa, USA)

RESULTS AND DISCUSSION

Taxons of oriental cherry are intensively grown on green areas on Far East, where cult of oriental cherry tree blooming cult is of great significance, especially in Japan, and this period is celebrated. Due to the flower decorative features of this taxon, it became very popular in green urban areas of Europe, and Serbia as well, while it has been planted in gardens from the very moment it was brought to Europe.

Due to the test results, the use of different *Prunus* taxon in dendoflora was justified. By measuring 19 oriental cherry trees (*Prunus serrulata* Lindl.), hierarchical classification based on six measured parameters was obtained. Four sub clusters have been isolated. The same principle was used for the

European dwarf cherry (*Prunus fruticosa* Pall. 'Globosa'). 55 trees were measured, and then divided into three subclusters. Mean values of selected subgroups are shown in Table 1.

Table 1: Mean values of selected subgroups

Cluster	Species	h (m)	ld (cm)	d (cm)	cw (m)	VIT	DEK
1	<i>P.serrulata</i>	3.12	1.31	11.12	1.31	4.75	4.62
2	<i>P.serrulata</i>	4.28	1.96	10.71	1.41	4.57	4.42
3	<i>P.serrulata</i>	6.05	2.26	34.00	5.40	5.00	5.00
4	<i>P.serrulata</i>	12.00	1.45	75.00	13.00	5.00	5.00
	x±Sx	6.36±1.97	1.74±0.22	32.70±15.11	5.28±2.74	4.83±0.10	4.76±0.14
	Cv (%)	62.03	25.36	92.40	103.93	4.33	0.06
	SD	3.94	0.44	30.22	5.48	0.2	0.29
1	<i>P.fruticosa</i> 'Globosa'	2.37	2.08	11.50	0.80	4.00	4.00
2	<i>P.fruticosa</i> 'Globosa'	3.06	2.11	13.00	1.12	4.38	4.38
3	<i>P.fruticosa</i> 'Globosa'	3.25	2.19	13.5	1.22	4.50	4.56
	x±Sx	2.89±0.26	2.12±0.03	12.66±0.6	1.04±0.12	4.37±0.10	4.41±0.09
	Cv (%)	16.00	2.67	8.21	20.96	17.78	16.04
	SD	0.46	0.05	1.04	0.21	0.77	0.70

Oriental cherry genotypes (*Prunus serrulata* Lindl.) of the first group had the lowest mean height value (h=3.12 m), height to the first branch of the tree (ld=1.31 m) and crown width (cw=1.31 m). The average height value of trees in the second sub cluster is 4.28 m, chest height diameter 10.71 cm, and crown width 1.41 m. The third and fourth sub clusters differ significantly in the mean values of those in the first and second sub clusters. In the fourth sub cluster the tree in Stevan Musić street imposed, with height of 12 m, chest height diameter of 23.88 cm and the crown width of 13 m.

Mean values for viability assessment of all specimens ranged from 4.57 to 5.00, while decorative features assessment was 4.62 to 5.00. High values indicate the adaptability of oriental cherry genotypes on green areas in Novi Sad.

Based on mean values, variation rate, standard deviation and error of the mean were calculated. Crown width was the parameter that varied the most, where variation rate was 103.93 %. Height and chest height diameter also varied with variation rate, 62.03% for height and 92.40% for chest height diameter. Vitality and decorative features assessments showed the less variations in oriental cherry genotypes examined

The examined individuals of European dwarf cherry (*Prunus fruticosa* Pall. 'Globosa'), was divided into three sub clusters, based on the average values of the parameters. Genotypes in the first group were characterized by the lowest values of height, height to first branch, diameter at chest height and crown width. The highest values were in the third sub cluster and stand at 3.25 m. The average value of the diameter at breast height in the sub clusters was 13.5 cm, and crown width 1.22 m.

Since the tree examination was unified by age, no high variability was observed. As the most variable feature crown width variation rate of 20.96% was pointed out. Lowest variation rate was observed for the height to the first branch (2.67%).

The correlation analysis was conducted in order to provide more thorough examination of growth parameters of oriental cherry and European dwarf cherry. This analysis includes relations between tree height, chest height diameter and crown width as growth parameters of these taxons in the city of Novi Sad conditions. All calculated correlations were positive and significant which approves

adaptation of examined *Prunus* taxons to city conditions, hence they can be successfully planted on different green area categories.

Charts 1 and 2 present correlation of oriental cherry tree height and chest height diameter (*Prunus serrulata* Lindl.). The uniformed individues group in tree line in Petra Drapšina street and two oriental cherry trees found in Stevana Musića street and Petrovaradin fortress point out in chart 1.

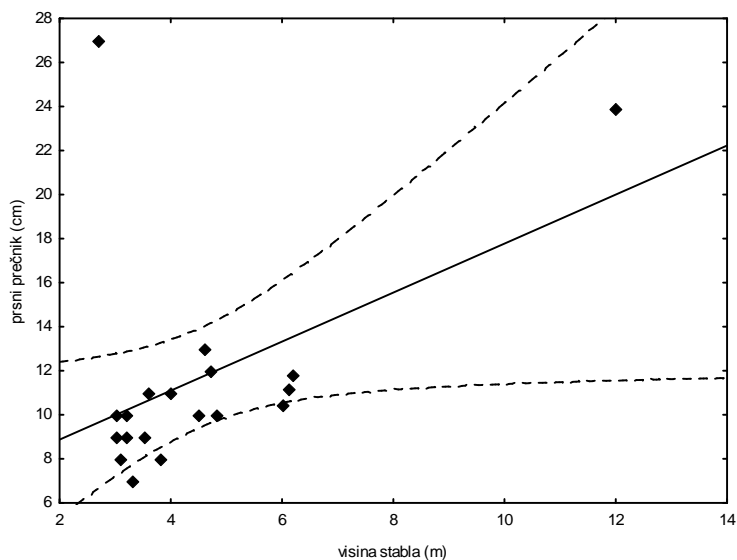


Chart 1. Correlation between tree height and chest height diameter of oriental cherry tree (*Prunus serrulata* Lindl.)

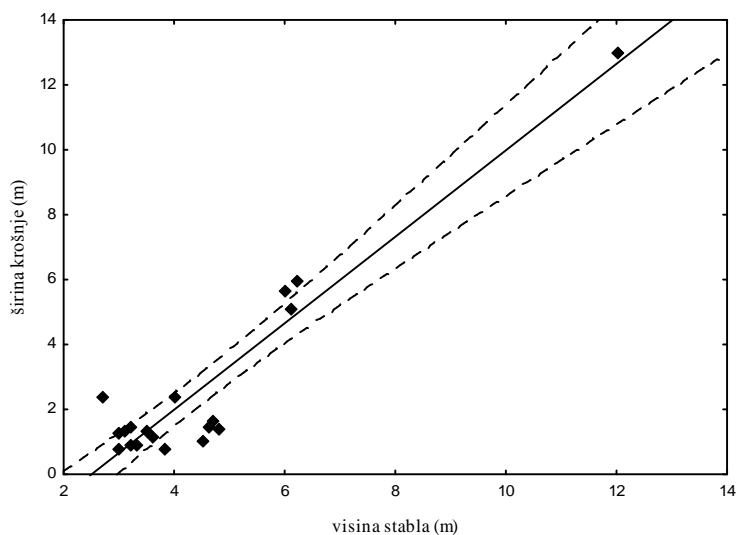


Chart 2. Correlation between tree height and crown width of oriental cherry tree (*Prunus serrulata* Lindl.)

Charts 3 and 4 present european dwarf cherry genotypes grouping. It is obvious that individuals are of uniform growth as for the tree height, chest height diameter and crown width, which indicates quality of seed material used while planting, according to standards set for tree plants.

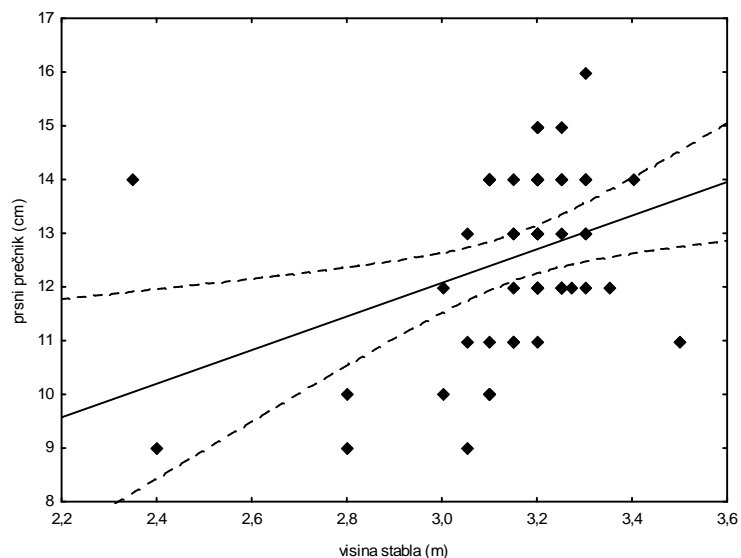


Chart 3. Correlation between tree height and chest height diameter of european dwarf cherry tree (*Prunus fruticosa* Pall.)

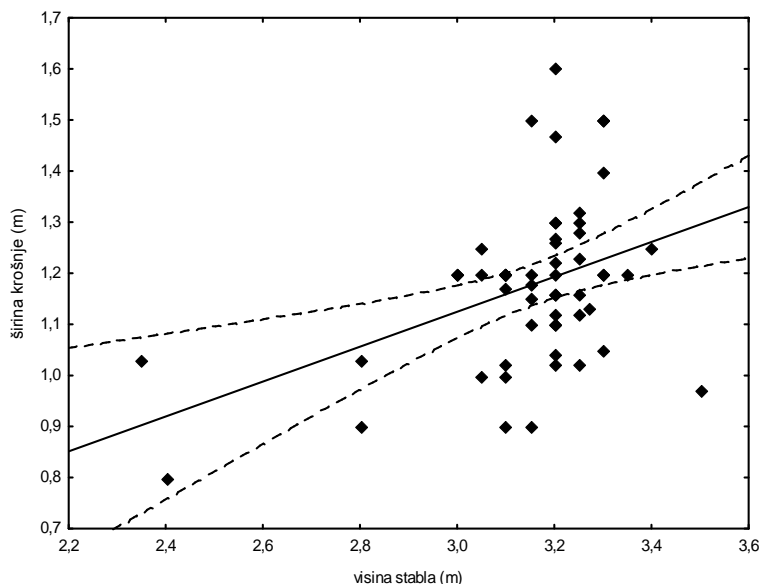


Chart 4. Correlation between tree height and crown width of european dwarf cherry tree (*Prunus fruticosa* Pall.)

Follow up of phenological phenomenon included species from collection plot of nursery in Rimski Šančevi during the spring of 2012 (Table 2). Phenological phases of vegetative and generative organs forming were followed according to BBCH identification key for stone fruit (Meier et al. 1994).

Table 2: Phenological growth stages and BBCH-identification keys of *Prunus* (Meier et al. 1994)

Species	<i>Prunus serrulata</i> 'Kanzan'	<i>Prunus serrulata</i> 'Amanogawa'	<i>Prunus serrulata</i> 'Kiku shidare'	<i>Prunus serrulata</i> 'Royal burgundy'	<i>Prunus fruticosa</i> 'Globosa'
Principal growth stage 1: Leaf development					
10	2.4.2012.	2.4.2012.	2.4.2012.	2.4.2012.	27.3.2012.
11	11.4.2012.	11.4.2012.	11.4.2012.	11.4.2012.	2.4.2012.
19	15.4.2012.	15.4.2012.	15.4.2012.	15.4.2012.	11.4.2012.
Principal growth stage 5: Inflorescence emergence					
51		2.4.2012.	27.3.2012.		
53					
54				2.4.2012.	
55	2.4.2012.				2.4.2012.
56					
57					
59		11.4.2012	2.4.2012.	11.4.2012	
Principal growth stage 6: Flowering					
60					11.4.2012
61	11.4.2012	15.4.2012		15.4.2012	
62					
63					15.4.2012
64					
65	15.4.2012.		11.4.2012		
67					

It was noted that there was a difference in leafing between species *P. serrulata* Lindl. and their cultivars and *P. fruticosa* 'Globosa' Pall., so that *P. fruticosa* 'Globosa' Pall. opens its first leaves a week earlier.

Between cultivars of *Prunus serrulata* Lindl., there is a difference in flowering time. The earliest flowering was noticed in 'Kiku Shidare' and the latest in cultivar 'Kanzan'. Cultivar of *Prunus fruticosa* Pall. 'Globosa' blooms simultaneously with the later cultivars *P. serrulata* Lindl.

Phenological phenomena of oriental cherry cultivars and european dwarf cherry cultivars took place in April. The identified differences in the early leafing and flowering of cultivars are particularly important for their use in urban green spaces. Flowering of cultivars provide succession and allows extension of this most attractive growth stage, from the point of cultivars visually aesthetic value.

CONCLUSION

There has been detected 19 oriental cherry trees (*Prunus serrulata* Lindl.) on Novi Sad territory, where 17 of them had been found in tree line in Petra Drapšina street, one in the garden in Stevana Musića street and solitary tree on Petrovaradin fortress. In tree line in Vojvide Šupljikca street 55 trees of globe shaped european dwarf cherry was detected (*Prunus fruticosa* 'Globosa' Pall.).

In order to monitor phenological phenomena, resistance to pests and diseases, resistance to abiotic stress, collection plot of ornamental *Prunus* taxon was raised during the year 2011 and 2012.

The ecological conditions of cultivation *Prunus* in study area shown that the optimum flowering was in mid-April. During this period, in this area there was no danger of late spring frosts, what contributed greatly to optimal flowering and decorative visual appearance of these taxon.

Previous researches found that the studied taxon has optimal vitality and decorative features in urban areas of Novi Sad.

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PLANTS AS DESIGN ELEMENTS OF URBAN SCENOGRAPHY

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ABSTRACT

Plants are an important element of urban scenography, which in combination with non-living elements of construction are a major component in organization and arrangement of space features. In the monotonous and cramped urban environment, plants represent a huge potential in designing of urban image, and superior spatial and formal elements to create a better and healthier living environment. Examples from the world's metropolis show how plants can be used in a different way to create an authentic picture of a space, in which it will be recognized. Vertical greening of Patrick Blanc, a topiary forms exhibited in honor of the Olympic Games in Beijing, the grass globe at Paris City Hall by Francois Abelanet, floating grass carpet of West 8 team at the archaeological site in Rome, are some of the examples of green sculptures that gives the seal and the uniqueness of the area. These examples can serve as models and inspiration for the design of public open space in Serbia, which lacks these elements that would certainly enhance the area and make it unique. Our society should pay more attention to landscaping cities, so that their design through the plant seemed more lively, more interesting and distinctly, similar to the urban scenography of world cities.

Key words: *green sculpture, urban scenography, urban design.*

INTRODUCTION

The identity of the space is a feature that makes it special, unique and distinctive - a place which people notice, in which often retain and which is easy to remember. The space includes two types of values: materialized – which could be measured and operationalized with precise criteria and non-material values as a result of the synthesis of natural, historical, cultural, economic, political, social and other developments in composition of urban space (Petovar, 2003). These values give the city its identity - the appropriate level of comfort and uniqueness, for example environmental values and environmental entities, the urban matrix, the memory of the city, the city symbol, the image of the city and others (Studija javnih prostora Beograda za potrebe urbanističkog planiranja, 2009). This paper explored how plants can be used in creating the identity and environmental values of the area, in order to show the vegetation as a basic element of spatial composition in the creation of an urban scenography.

THEORY

The greenery in the city and its environment has a significant importance. Plants, particularly trees and shrubs, their shape, material properties and environmental features, in urban areas are irreplaceable natural elements that contribute to the reclamation of the environment. Along with relief and buildings, plant material is a major component in the organization of a space and solving the basic functions of the free areas. It provides contact with the beauty of wildlife in the living environment, by using its characteristics such as: size, shape, color and texture. It should be noted that the plant material is alive, dynamic element, which is reflected in perpetual change of its characteristics with the change of seasons and growth. This dynamic makes it difficult to create a compositional solutions and achieving certain functions during the year. It gives form and proportion of the landscape, providing an artistic expression and creates a series of basic spatial composition of color in the green areas. Plant material also provides a sense of naturalness, particularly in urban areas, where provides a visual refreshment to a solid constructed buildings and spaces. Under such conditions, humane principles of

planning construction and arrangement of cities are set, in which all people will be more in touch with nature, while the city will provide a healthier and more comfortable living conditions and all other necessities of life and activity (Vujković, 2003).

As a visual element, the plant material can be used as a dominant point and visual connections depending on its product characteristics that have a major impact on their selection and use in spatial design: the appearance of habitus, shape and dimensions of trees, foliage and roots, foliage transparency, charming arrangement of branches, shape, color and mosaic of leaves, color of flowers and fruits, color and structure of the bark of trees, which determines their texture - visual roughness or smoothness whether the individual tree or group. As a structural element, the plant material is of great importance in the overall organization of the external environment and the arrangement of free space (Vujković at al., 2003). Visually incorporates other spatial elements (buildings, roads, infrastructure and other elements), directs the point of view and act on the directions of movement, blocking unsightly views, achieves the transition from closed to open spaces and vertical to horizontal surfaces, provides the foundation on which is better seen architectural and sculptural elements (pavilions, pergolas, statues, busts, monuments, etc.), frames mentioned elements and can be their additional decoration (Vujković at al., 2003).

However, the plants themselves can be a major element in the space - green sculptures, plant art, sculptural landscapes, land art, are some of the terms that show how plants can be used in a different way to create an authentic picture of a space (figure 1). This approach to greening the environment in a new and different way is shaping the space, by giving it a uniqueness and authenticity.



Figure 1. A. Green sculpture; B. Sculptural landscape at jupiter artland garden; C. Land art by laetitia carlotti

METHODS

In this paper, several methods have been applied depending of tasks of the research. In the first phase of work, all relevant professional international and national literature has been gathered and analyzed. Four objects of landscape architecture have been analyzed in this paper: Patrick Blanc's vertical gardens, Olympic Topiaries - Beijing Garden Sculptures, an exhibition of topiaries in honor of Olympic Games in Beijing, Francois Abelanet's 3d grass gloube at Paris City Hall and floating grass carpet of West 8 team at the archaeological site in Rome. In the second phase, the results were systematized and every object analyzed regarding to the space desing and arrangement. In the last phase, the results were systematized and conclusions were made.

FINDINGS AND DISCUSSION

Vertical Garden Sculptures by Patrick Blanc

French botanist Patrick Blanc for twenty five years investigates the behavior of plants and their adaptability to different environmental conditions. In developing his theory of vertical gardens, he created an entirely new concept of greening the cities. Looking at different types of plants, Blank is concluded that many of them in nature develop and grow without a soil, in a completely vertical

surfaces, rocks and tree bark. The only prerequisite for their growth is solid surface, the light and a constant source of water. That habit of plants was the basis for all of his experiments that would later follow. After careful selection of plants and materials that would be used in its construction, Patrik Blanc started the implementation of its first vertical garden. Since 1988. until today, he designed and performed nearly a hundred of these projects in interiors, exteriors of buildings and in various purpose (figure 2).



Figure 2. Patric Blanc's vertical gardens: A. Plaza de Espana, Santa Cruz de Tenerife; B. Siam Paragon Shopping Mall, Bangkok; C. Federation CFDT, Paris; D. Via Verde, Rio de Janeiro (project not realised) - <http://www.verticalgardenpatrickblanc.com/#/en/projects/geographical>

With the interesting character of scientist and artist at the same time, he managed to build a distinctive style, and opened the door to a whole new realm of design. His green walls fits into any environment and skillfully break the monotony and uniformity space. One green wall may have up to several thousands of different plant species. Artificial, non-degradable materials of the construction of the wall, allow to vertical gardens, along with regular maintenance, unlimited long lasting. Without land, the construction which bears the plant is very simple and can be mounted on any wall regardless of its size and structural properties.

His vertical garden projects are exceptional examples of the use of plant material in the formation of sculptural landscapes. In Figure 3 it can be seen the green facade of the building in Paris, where a completely ordinary and neglected area using plants got a whole new dimension. Also, vertical landscaping of bridge on the Cote d'Azur (figure 4) with green structures and water elements, removed the drab and uniformity of space.



Figure 3. Patric Blanc's vertical gardens: Rue d'Alsace, Paris (before and after)



Figure 4. Patric Blanc's vertical gardens: Pont Max Juvenal, Aix en Provence, Cote d'Azur; (before and after)

Olympic Topiaries - Beijing Garden Sculptures

In the 2008th year, China prepared a beautiful botanical display of artistic garden sculptures for the Beijing Olympics Games (figure 5). Topiary forms, like a green decor, represent masterful design and scrupulous landscaping. With an area of 60,000 square meters, the exhibition at Beijing Botanical Garden shows rarity flowers and trees of over 1,000 species from 205 countries and regions in the five continents (<http://www.ecofriend.com/entry/sculpted-green-flora-to-please-all-at-the-beijing-olympics/>). Olympic topiaries were displayed at the Science and Technology Park, the area which was specially chosen for its close proximity to other Beijing highlights including Tiananmen Square and the Central Olympic Zone. In keeping with Chinese botanical heritage, the topiaries depict images integral to the country's history. Giant Pandas, dragons and jumping dolphins join various water elements and images of Buddhism, Confucianism and Daoism to show the comprehensive culture of the Chinese people. In addition to these displays of national pride, plant sculptures of athletes

participating in various sports adorn the gardens, a testament to the 10,500 participants in the 29th Olympic Games (<http://ezinearticles.com/?Olympic-Topiaries---A-Symbol-of-Pride-to-Peoples-Republic-of-China&id=1584122>).



Figure 5. Olympic Topiaries - Beijing Garden Sculptures

3D Illusion - Grass Globe ‘Who to believe?’

François Abelanet is a French artist known for his anamorphic manipulations of landscapes. This versatile artist, in addition to land art is also engaged with photos, cinema, scenographie, industrial design. One of his wonderful 3D illusion is installed in front of the Paris’s city hall (figure 6). He created incredible 3-dimensional grass globe and called it ‘Who to believe?’. This was a temporary installation set in the summer 2011th year. This projection allows to create the illusion of three dimensions large sphere when viewed from the correct angle. Over 90 gardeners were engaged on this

project (http://www.paris.fr/accueil/accueil-paris-fr/une-anamorphose-vegetale-parvis-de-l-hotel-de-ville/rub_1_actu_102431_port_24329). It took over 5 days to complete the installation requiring 1200 square meters of lawn, 300 square meters of the coverplant sedum, and 650 cubic meters of sand and straw (<http://twistedstifter.com/2011/07/picture-of-the-day-the-craziest-illusion-in-paris/>). This contemporary garden represent the link between nature and city, plant and human worlds, at the intersection of architecture, decoration and land art.

In that occasion, Abelanet invited the viewer to feel and experience the fundamental place of nature: "We live in a world where we hear discussion ecologists, scientists, industrialists ... I just wanted to pose the problem of tree and invite people to consider the role that the tree, nature and the environment have for them. I wish that people ask the question to themselves and feel how the environment is fundamental" (http://www.paris.fr/accueil/accueil-paris-fr/une-anamorphose-vegetale-parvis-de-l-hotel-de-ville/rub_1_actu_102431_port_24329).



Figure 6. 3D illusion - Grass Globe 'Who to believe?'

Wonder Holland - Floating Grass Carpet, Rome

The project of revitalization of the ancient Mercati di Traiano in Rome was an extremely demanding and responsible, but also an extraordinary work for landscape architect. The idea was to create a green space with no contact with the archaeological remains of buildings, because as the Supervisor of the Roman Antiquities insists none of the ruins cannot be touched or damaged. The design response by West 8 team has corresponded to customer (the Royal Embassy of the Netherlands), although in a completely unconventional way. Their idea was to create "floating" green space among the Roman ruins (figure 7). The structure is basically quite simple and involves raised steel container planted with grass. Container structure is designed to have holes through which the remains of sites could be seen, a total of all, structures reminiscent of the type of cheese (with holes to allow for pieces of the ruins to protrude, visually linking and integrating the green carpet with the context, while also expressing its

proposed connection to Dutch culture). With red lights the illusion of grass flying carpet is emphasized. Maintenance of this area consists of watering and cutting the lawn (http://www.west8.nl/projects/installations/wonder_holland/).



Figure 7. Wonder Holland - Floating Grass Carpet, Rome

CONCLUSIONS AND IMPLICATIONS

From the results shown in this paper, it can be concluded that plants are inspiring element that can be used as a dominant point in space which gives the seal and the uniqueness of the area. Plants represent a huge potential in designing of urban image and authenticity of the space. In addition to make an influence to a better and healthier living environment, sculptural landscapes represent the space which people perceive, which often maintain, easier to remember. The presented examples can serve as models and inspiration for the design of public open space in Serbia, which lacks these elements that would certainly enhance the area and make it unique. Our society should pay more attention to landscaping cities, so that their design through the plant seemed more lively, more interesting and

distinctly, similar to the urban scenography of world cities. Implication of greening presented in this paper will contribute to creating a better and modern image of our cities.

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**POSSIBILITIES OF LEGISLATIVE AND METHODOLOGICAL
CONSOLIDATION BETWEEN PROCESSES OF DEVELOPMENT OF
SPATIAL PLANS AND SEA**

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ABSTRACT

Strategic environmental impact assessment (SEA) is a newer instrument of spatial planning. With the application of SEA it can be assessed whether the plans and policies are consolidated both, between themselves and with the goals of territorial sustainable development. With that in mind, a necessary prerequisite of SEA is its methodological, chronological and legislative consolidation with the processes of development and implementation of spatial plans. On the other hand, both the EU, and The Republic of Serbia do not have specially defined methodological frameworks that would facilitate simpler and standardized parallel development of these two documents. Although the EU and The Republic of Serbia provide exceptionally detailed legislative frameworks in the SEA and spatial planning domains, for now, there are no clearly defined correlative ties between these two fields. All of the above has, as a direct consequence, the fact that coordination between these documents is not in consideration until the late phases of planning, where SEA loses its role as a control and evaluation tool for the planned solutions, but only as practical validation. With this, plans gain in subjectivity of the planning bodies, and the significance of SEA is diminished. The paper will give detailed overview of the legislative inconsistencies of the Law, chronological and methodological non-consolidation in the development of these documents, and give recommendations for a more efficient harmonization.

Key words: *spatial planning, SEA, methodological approach, legislative non-coherency, Serbia.*

INTRODUCTION

Topics like environmental quality conditions, population life conditions and the importance of Strategic Environmental Impact Assessment (SEA) elaborating are present in all European countries, especially in developed countries. As a consequence of necessity for harmonization of social-economic interests and ecological principles of some territory, there is a need for integrated planning system defining. That is the way for inclusion basic principles of environmental protection and sustainable development in process of spatial and urban planning, at all hierarchical levels. As an important controlling and coordination instrument of planning process, SEA enables respect for the principles of sustainable development. SEA is the document which may affect the planned activities and processes that should be implemented. Planning solutions that involve activities in space are evaluated pursuant to goals defined by SEA. This provides an opportunity for planning solutions control in accordance with principles of environmental protection and sustainable development. Therefore, it is very important to harmonize the process of spatial and urban plan elaboration with the process of carrying out the SEA. This means that these processes should be methodological, chronological and legislative synchronized.

In practice, the main problem between these two processes is the fact that process of carrying out the SEA starts in late phases of planning process, when the planning solutions are already defined. This degrades the control role of SEA, because there is no possibility for planning solutions correction. The only thing that could be done in this planning phase is their confirmation or rejection of solutions, which procrastinates next phases of planning process.

SUSTAINABLE DEVELOPMENT PRINCIPLES AS A BASIS OF HARMONIZATION BETWEEN ENVIRONMENTAL PROTECTION AND SPATIAL PLANNING PROCESSES – LEGISLATIVE FRAMEWORK

Although the SEA represents relatively new instrument of spatial planning, principles that it complied with, were defined much earlier, and they are related to environmental protection and concept of sustainable development.

The idea about sustainable development was mentioned for the first time on United Nations Conference of the Human Environment, held in Stockholm (1972), when the representatives of more than one hundred countries were gathered because of problems of human environment on global level, whereby the United Nations Environment Programme was established. This conference was initiated international cooperation and legislative frameworks, on global level, which caused establishment of national ministries and agencies for environmental protection, as well as laws and regulations on national level, for members of the United Nations. Although some environmental conditions (reduce emissions of pollutants, waste management, waste water management) have been improved, results were not satisfactory, so it was necessary to approach the problem in some other ways.

In order to solve problems of environmental pollution and depletion of natural resources on one hand, and economic development problems on the other (particularly pronounced in poor countries), United Nations established World Commission on Environment and Development, in 1983. This Commission issued a report called “Our Common Future”, in 1987, which indicates problems incurred from relation between economy and environmental. These problems are related to global warming, destruction of the ozone layer, acidification, loss of forests and biological species, desertification, radioactive and other hazardous wastes. The term „sustainable development“ was used for the first time in this report.

Numerous international reports say that the concept of sustainable development on global level is possible to conduct only when three simultaneous processes are performed: poorness elimination, decrease in intensity of depletion of natural resources and waste producing in rich countries, and global cooperation in the field of environmental protection.

On the second United Nation conference (United Nations Conference on Environment and Development, Rio de Janeiro, 1992), the concept of sustainable development becomes a leading global concept, in form of protocols called „Agenda 21“, which was signed by 180 countries. In that way, the concept of sustainable development was proclaimed as the basic strategy of the future relationship between society, economy and ecology. The success of this concept lies in opportunities offered to different interest groups, which adjust them with their own needs.

Directive 2001/42/EC of the European Parliament and of the Council on the assessment of the effects of certain plans and programs on the environment was the basic document for defining of legal framework. This Directive enables environmental protection through a process of sustainable planning.

Following the experience of European Union and legislation on that level, the Parliament of the Republic of Serbia adopted a set of four laws:

1. The Law on Environmental Protection („Official Gazette of the Republic of Serbia”, No. 135/2004, 36/2009, 72/2009, 43/2011);
2. The Law on Strategic Environmental Impact („Official Gazette of the Republic of Serbia”, No. 135/2004, 88/2010);
3. The Law on Environmental Impact Assessment („Official Gazette of the Republic of Serbia”, No. 135/2004, 36/2009);
4. The Law on Integrated Environmental Pollution Prevention and Control („Official Gazette of the Republic of Serbia”, No. 135/2004).

This package of laws is the basis for sustainable management of natural resources, protection of environment and its conditions improvement, in coordination with the European standards.

As a very important component of sustainable development, environmental protection is included in National strategy for sustainable development („Official Gazette of the Republic of Serbia”, No. 57/08), which aims to achieve balance between this one, and two more components of sustainable management – economic growth and social development.

In the process of the European integration and harmonization with European legislative framework, the Parliament of the Republic of Serbia adopted in 2009. set of 16 laws, called „Green Package“, which includes legislation on the protection and preservation of all environmental segments, considering everything that could undamaged human health, and adversely affect flora and fauna.

The „Green Package“ includes the following laws:

1. The Law on Environmental Protection („Official Gazette of the Republic of Serbia”, No. 135/2004, 36/2009, 72/2009, 43/2011);
2. The Law on Environmental Impact Assessment („Official Gazette of the Republic of Serbia”, No. 135/2004, 36/2009);
3. The Law on the Protection of Nature („Official Gazette of the Republic of Serbia”, No. 36/2009);
4. The Law on Protection against Ionizing Radiation and Nuclear Safety („Official Gazette of the Republic of Serbia”, No.46/96);
5. The Law on Non-Ionizing Radiation Protection („Official Gazette of the Republic of Serbia”, No. 36/09);
6. The Law on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction („Official Gazette of the Republic of Serbia”, No. 36/09);
7. The Law on Waste Management („Official Gazette of the Republic of Serbia”, No. 36/2009);
8. The Law on Packaging and Packaging Waste („Official Gazette of the Republic of Serbia”, No. 36/2009);
9. The Law on Air Protection („Official Gazette of the Republic of Serbia”, No. 36/09);
10. The Law on Chemicals („Official Gazette of the Republic of Serbia”, No. 36/09)
11. The Law on Biocide Products („Official Gazette of the Republic of Serbia”, No. 36/09);
12. The Law on the Protection of the noise in environment („Official Gazette of the Republic of Serbia”, No. 36/09);
13. The Law on the Protection and Sustainable Use of fish resources („Official Gazette of the Republic of Serbia”, No. 36/09);
14. The Law on the Ratification of the amendment on Annex B of the Kyoto Protocol with United Nations Framework Convention on Climate Change („Official Gazette of the Republic of Serbia – International Agreements”, No. 38/09);
15. The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade („Official Gazette of the Republic of Serbia – International Agreements”, No. 38/09); and
16. The UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters („Official Gazette of the Republic of Serbia – International Agreements”, No. 38/09).

Adoption of this set of laws enables an opportunity to create a new ecological policy, that would indicate the importance of environmental problems. Ecological policy requires new environmental standards nomination, which could improve relation between economic development and environmental protection. In some way, “Green package” contributes to local community development, because some liabilities are switched to that level, with defined budget that must be used only for that purpose.

In all European Union countries, the system of spatial planning is in coordination with principles of sustainable development during the last decades, which means that issues like environment and quality of life are included in strategic documents. In Serbia, the spatial planning process is regulated by Law

on Spatial Planning and Construction („Official Gazette of the Republic of Serbia”, No. 72/2009) and by Law on Spatial Plan of the Republic of Serbia from 2010 to 2020 („Official Gazette of the Republic of Serbia“, No. 88/2010). Principles of sustainable development are general principles in both documents, at all vertical and horizontal levels.

Spatial Plan of the Republic of Serbia describes the sustainable spatial development as process with: improved environmental role in the politics of local development; spatial and sectoral plans; implementation of EIA (Environmental Impact Assessment), SEA (Strategic Environmental Impact Assessment) and IPPC (Integrated Environmental Pollution Prevention and Control), made for development plans, programs and projects; public participation in decision-making; eliminated negative effects of development projects on environment; preserved nature, environment and cultural heritage.

The Law on Environmental Protection established an integral system of environmental protection, as well as measures and instruments for sustainable management and protection of nature resources and heritage. The law stipulates that the Spatial Plan of the Republic of Serbia and the National Strategy for Sustainable Use of Natural Resources and Goods represent legal bases for sustainable use and protection of natural Resources and Heritage, whereas spatial planning represents planning basis for integrated protection of the environment, resources and goods. The law on strategic impact assessment provides for use of this environmental tool for plans, programs and bases in the domain of spatial and sectoral planning of transport, energetics, agriculture, forestry, fishery, hunting, industry, waste management, water management, telecommunications, tourism etc. with the aim of avoiding or limiting negative impact of planned decisions on the environment. The problem is that in practice it is applied only in the domain of spatial and urban planning (Maksin-Mićić *et al.*, 2009).

Harmonization of aforementioned laws in the domains of spatial planning and environmental protection creates opportunities to neutralize the negative impact of development processes on the environment. In that sense, SEA elaboration is the very important process, referring to possibly environmentally harmful impacts, that would be the consequence of some strategic solutions implementation, defined in strategic guidelines documents, such as spatial and urban plans, programs, projects and development strategies. That is the reason for necessary harmonization of this two documents, on methodological, chronological and legislative ways.

CONSOLIDATION BETWEEN PROCESSES OF DEVELOPMENT OF SPATIAL PLANS AND SEA

Spatial planning practices of all developed European countries, as well as of developing countries, show there is a growing need for integrated approach to planning, which accepts the space as a system with interconnected components – social, economic, spatial and environmental. Considering the synergistic effects of these components, it is possible to plan the future development of space, as unique system.

In order to define appropriate planning solutions, that involve environmental protection and preservation of human health processes, there is a need for coordination of spatial planning process with carrying out the SEA. Simultaneous development of these two strategic planning processes and documents, with defined guidelines for development processes and SEA implementation, could create the conditions for horizontal and vertical harmonization of two important control instruments, with the dominant guiding role. This approach is a prerequisite for the development of the overall planning, at all hierarchical levels. The primary purpose of SEA is to recognize the potential negative impacts on environment, which would result from the implementation of planning solutions, and to assess their possible intensity and spread directions, using for this multi-criteria analysis. Also, SEA proposes measures that would neutralize the negative impacts or limit them, while the positive impacts enlarge. During the SEA elaboration it is possible to recognize specifically problems of some territory, and according to them define planning solutions that are ecological feasible.

The SEA implementation, as a process integrated into the planning system, is a document that determines whether the plans and policies coordinated among themselves and with the objectives of sustainable development (Nenković-Riznić, Milijić, 2010).

Integration of SEA, as a strategic instrument, in the process of developing spatial plans, creates a binding framework for the protection, which is defined by SEA guidelines, and implemented through appropriate plans of lower level, programs and projects.

The SEA goals depend on the level of planning and on the specific characteristics of the territory. Evaluation of planning solutions for different planning sectors (environmental protection, tourism, infrastructure, economy and others) shows what would be the level of environmental degradation if planning solutions would be implemented. That is the way for some solutions to be discarded, and some other favor, which depends on negative impact intensity on environment, people's health, cultural heritage and quality of life.

The relation between processes of spatial planning and environmental protection is based on effective implementation of sustainable development principles. In developed European countries with significant planning experience, that relation is based on adequate legislation in one hand, and important effects of implementation, on the other. Experience in European countries has shown that the level of harmonization of spatial planning and environmental protection processes, realized through SEA elaborating, is at high-level.

In Serbia, on the contrary, the situation is much different. Although the Law on Environmental Impact Assessment is available for nearly a decade, the level of harmonization with the laws and regulations in domain of spatial planning is not satisfactory. This is corroborated by the fact that the legal basis in Serbia is extremely extensive and uncodified. The problematic of managing space, protecting the environment, resources and heritage, and sustainable development are directly or indirectly regulated by more than 40 laws (Maksin-Mičić *et al.*, 2009). In this way, the spatial development is not primarily regulated by the Law on Planning and Construction, but by number of sectoral laws, relating to different fields – traffic, energy, agriculture, forestry, industry, water management, waste management, tourism and others.

The relation between processes of spatial planning and SEA elaboration is characterized by number of problems. This condition is a direct consequence of disparity in phases of implementation, adopting and approving plans and SEAs, but also of lack of multi-criteria analysis results inclusion in spatial and urban plans.

The Law on Spatial Planning and Construction clearly defined plans in relation to their strategic applicability (from national, through regional plans and local government, to the level of urban development plans and projects), without clearly defining their mutual alignment with sectoral analyzes and studies, especially in the environmental protection. The law provides a parallel development of strategic environmental impact assessment of the environmental plans and spatial plans themselves, but without an obligation to implement measures, realized by multiple-criteria analysis, done for strategic assessment needs. Also, there are no legal mechanisms and procedures for the integration and coordination of these two documents, defined by this Law.

Although the Law on Planning and Construction defines SEA as an integral part of the plan, there is a lack of systematization in the coordination of laws, which caused disparities in the processes of creating these documents. Mostly, the role of SEA is only declarative, and process of its elaboration starts at the late phases of planning, after the concept phase, when planning solutions are already defined. Thus degrades the control and guiding role of SEA, as a strategic document, because the evaluation of planning solutions was not made at the right time. The only possibility in this phase is rejection of some planning solutions, or reformulation of some others. This slows down the next phases of planning process, and finally adoption of the plan.

Non-consolidation between processes of plans elaborating and carrying out of SEA is a consequence of fact that none of the laws pertaining to these strategic documents did not clearly defined obligation to conform the process of planning, utilization and protection of the environment and space

In addition to inconsistency with the process of strategic documents to which they relate, SEA is characterized by some other problems. One of them is the lack of a uniform methodology in the SEA preparation. For this reason, problems can occur both within the multicriteria analysis, and later, in the representation of results and defining measures and monitoring system (Stojanović, Maričić, 2008). The practice of SEA making in Serbia has shown that obtaining reliable results need to combine more evaluating methods of planning solutions¹, and different activities defined in space. All methods used to SEA elaborating are with same objectives - the protection of the environment and respect for the principles of sustainable development. Using more than one method provides the possibility of checking and updating the criteria for evaluation of planning solutions. Based on that, some planning solutions are eliminated from the plan, in next phases of SEA elaborating.

A common problem is a lack of relevant data on environmental parameter's conditions. In that case, SEA presents the environment conditions as an assessment, based on potential contaminant sources and their possible impact on the environment.

Lack of qualified personnel, which would adequately check solutions resulting from the implementation of multi-criteria analysis during the SEA development, is also a considerable problem. Despite the fact that there are problems in development processes of spatial planning and carrying out of SEA, defining of integral planning system, which includes all development components – spatial, social, economic and environmental, the good basis for evaluation of different planning solutions were made. SEA offers a possibility for development directing, by defined guidelines, which might contribute to such a spatial organization that involves improving the quality of environment and quality of life.

Sectoral approach to planning brings problems in terms of the presence of sectoral interests, which are generally at collision with the sustainable territorial development. In order to overcome this problem and to ensure the sustainability of planning solutions at this level, it is necessary to carry out the legal obligations of SEA, as well as sectoral plans and programs, and thus to add them environmental component of development, besides the already present components (economic, social and spatial).

The integration of strategic impact assessment in spatial planning process can be summarized schematically as in Figure 1.

¹ Experts within Institute of architecture and urban and spatial planning of Serbia use combination of the two methods of evaluation of planning solutions. The first one is "basic method", developed within the scientific project "Method for Strategic Environmental Assessment in Planning the Spatial Development of Lignite Basins" (Project Manager B.Stojanović, PhD), and the second is SOTAVENTO method

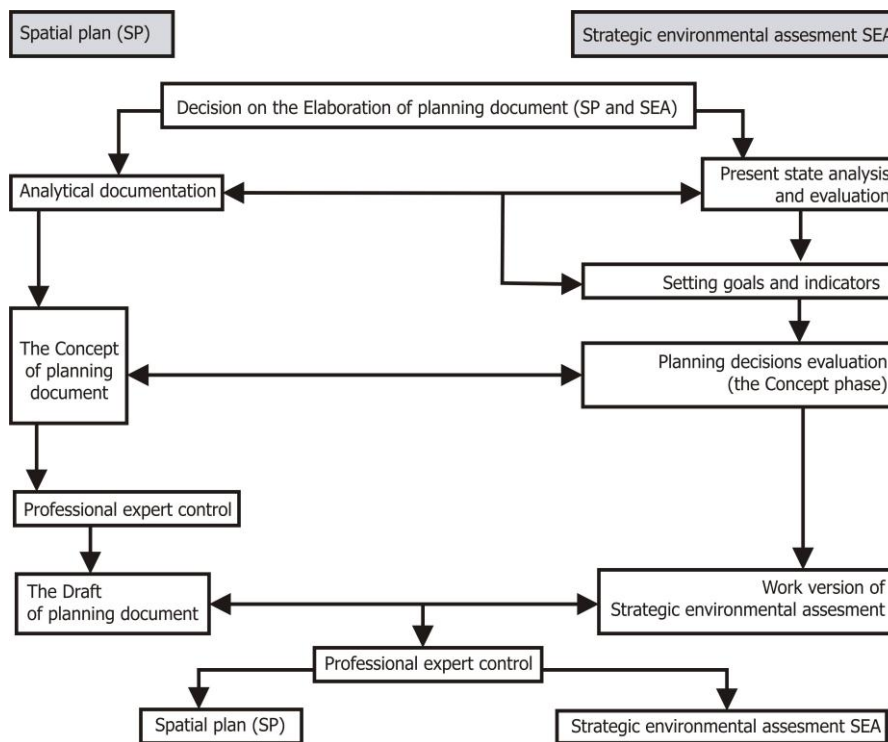


Figure 1. Process of spatial plan elaboration and the SEA process in Serbia

Public participation in the SEA decision-making process is on much higher level in European countries than in Serbia. Public participation implies that the processes of planning, both spatial as well as environmental, include planners, local governments, investors, citizens, NGOs, and other interest groups that influence their involvement in decisions affecting the environment. In Serbia, the right of citizens to be informed is regulate by the ratification of the Aarhus Convention (2009), and partly by the Law on Environmental Protection of the Republic of Serbia, which stipulates that there is an obligation of public inspection on SEA. That is the way for public to inform and to participate in the consideration of the report of SEA.

The main precondition for overcoming problems of non-consolidation between processes of development of spatial plans and SEA in Serbia is the reform of the legal basis, which means defining such spatial planning system that insists on: horizontal and vertical cooperation and coordination between sectors and levels of governance; participation of residents and other participants in the decision-making process; responsibility for checking environmental and territorial impacts of planned development; greater flexibility of planning process and planning tools; etc. (Maksin-Mićić *et al.*, 2009).

Legislative reform in the domains of planning and environment would create the possibility of harmonizing two strategically important processes, where one relates to the strategic planning of the territory, and the other on strategic integration of sustainable development principles into the planning process.

The lack of a unique methodological framework, which could facilitate the implementation of these two parallel processes, would also be overcome by redefining the legislation, which would bring their coordination to a higher level, with an unchanged essence.

Overcoming of current lacks in the relation between the development processes of spatial planning and carrying out of SEA would solve the problem of inappropriate planning solutions definition. Then, the process of developing a strategic assessment would be in line with early phases of planning process,

which significantly facilitates the creation of guidelines for making planning decisions, so as to recognize and eliminate their potential negative impact on the environment.

CONCLUSIONS

An integrated approach to spatial planning introduces an increasingly important component of development - environmental protection, in the planning process. That is the way that allows integration spatial and strategic planning objectives with principles of sustainable development.

Process of carrying out of SEA, as an instrument that is included in the legal system of the Republic of Serbia by adopting of the Law on Strategic Environmental Impact, created opportunities for environmental conditions influence. Process that includes discussion and evaluation of the solutions defined in plan (applying multi-criteria analysis) indicate how the development processes, provided by the plan, are in accordance with the principles of sustainable development. Solutions that could cause environmental degradation are rejected as unacceptable, and development is directed by guidelines defined in SEA document, in way that is ecologically justified

Experience in planning practice Serbia has shown that the level of coordination between processes in spatial development and SEA is unsatisfactory.

Development of SEA begins when the spatial or urban planning development is in its later phases, and planning solutions are already defined. In this way, the role of the strategic assessment is the verification of these solutions, which reduces the importance of this strategic document.

Reform of legislative frameworks in the field of urban planning and protection (which includes the protection of the environment, nature, people, heritage, etc.) could create an obligation of harmonization of development of spatial planning and SEA processes, as well as define specific methodologies, whose implementation could provide the adequate level of coordination of mentioned processes. In that way, evaluation of planning solutions would be related to earlier phases of spatial plan elaboration, so some solutions could be dismissed or reformulated in phase that precedes the concept of spatial plan.

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DEVELOPMENT OF URBAN ECOLOGY THROUGH EDUCATIVE AND INFORMATION ACTIVITIES

**II International Conference
“ECOLOGY OF URBAN AREAS” 2012**

**WAYS OF PROMOTING EDUCATION AND RAISING PUBLIC
AWARENESS ABOUT SUSTAINABLE DEVELOPMENT ON THE
TERRITORY OF THE MUNICIPALITY OF LUCANI**

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ABSTRACT

The paper explores the practical possibilities of planning and implementation of informative and educational ecological materials at the level of local self-government of the municipality of Lucani, with the aim of raising people's ecological awareness. Reduction of waste generation and its management is an absolute necessity which is impossible to achieve without the public awareness, education and training as key components of society's path to sustainability. Such an approach opens up possibilities of development as well as creation and implementation of new strategic frameworks, acceptable approaches and objectives of local units of self-government.

Key words: *sustainable development, strategic planning, education, globalization.*

INTRODUCTION

The model of development in industrialized countries was based on the market economic model, which was a basically ecophobic (from the Greek: *phobos*, meaning “fear”) orientation. In other words, in the process of economic development (transition from the 18th century into the 19th century) and subsequent economic growth (especially in the second half of the 20th century), developed countries had a primarily consumerist approach, both towards the natural environment (biosphere) and the social environment.

The economic growth was made possible through large-scale exploitation of natural and man-made resources. Up to the end of the 20th century, developed countries followed the lucrative practice of “transfer of waste” to less developed countries. However, this approach has lost its former momentum due to the fact that developing countries have become increasingly aware of ecological hazards and the fact that developed countries have come to realize that “transfer of waste” offers no solution to the problem. In order to survive ecologically, developed countries had to raise their “level of ecophilia” (from the Greek: *philia*, meaning “love”) and make strides towards creating a more eco-friendly market.

The 1990s witnessed an emergence of several branches of ecologization of development and social activities. Environmental aspects begin to loom large in market relations. A system of economic levers which enables combining of economic growth and certain environmental restrictions is being actively administered. Thus the term ‘environmentalism’ becomes essentially subsumed under the term “economism”. Furthermore, ecologically-oriented sustainable market economy is clearly backed by the legal system. The process of raising social awareness of individuals and society as a whole is also underway. The man of the future is environmentally educated and plays an active role in solving ecological problems. The conditions for raising the level of “ecophilia” entail the integration of the social and economic system into the ecosystem in the course of decision making. The need for

sustainable development has sprung from the necessity of reducing the pressure exerted on the environment which, in the foreseeable future, could result in an environmental disaster.

The application of sustainable development as a planetary concept requires strategic planning on the part of all members of society, both at the local and regional level, but at the global level as well. The concept of sustainable development is reflected in the need for creating a „harmonized system of technological, economic and social activities, where natural and man-made resources are utilized economically, and the aim of which is the preservation and protection of the environment for the sake of present and future generations, including natural habitats and biodiversity.” Due to the gravity of the situation and the fact Serbia is lagging behind other countries in overcoming its environmental problems, it is of paramount importance that certain measures be taken to raise the educational and cultural level of citizens about the issues related to the protection of the environment and attainment of sustainable development.

Bearing in mind the fact that there are marked discrepancies in economic, technological and developmental potential among local units of self-government, each municipality should create an acceptable model and adopt a way of educating its citizenry in accordance with The National Sustainable Development Strategy (NSDS). In The National Sustainable Development Strategy of the Republic of Serbia one of the principles of sustainable development is: *Knowledge as the carrier of development* (this entails promotion of a prosperous, innovative, competitive and ecologically efficient knowledge-based economy which ensures a high living standard and full high-quality employment; promotion of education and raising people’s awareness about sustainable development). This indicates a need to find a suitable way of action and a practical method of achieving balanced and integral solutions based on sustainable development.

A significant potential for waste reduction and providing a solution to environmental issues is reflected in sustainability education and participation of wider public at all relevant levels of decision making of a local self-government unit, which also entails the right to all information concerning the preservation of the environment, health and application of sustainable development policy. Environmental education does not merely entail providing solutions to existing problems, but also the application of the precautionary principle in all the activities connected with the environment. According to a number of experts (Varsavsky, Kleiner), the process of globalization can be divided into two phases: “*informational civilization*” and “*knowledge civilization*”. The first phase – “*informational civilization*” – is the phase that the civilization has not yet gone through and only a small number of countries have taken part in it. At the same time, many technologically advanced countries and world’s largest economies are already in the course of application of technological innovations of the second phase – the age of “*knowledge civilization*”. The goals and objectives for restructuring the field of education have been defined on the basis of the assumption that new information and knowledge figure more and more prominently in socio-economic processes.

Tidbury D. also highlights the seminal role of new knowledge: „Education is an essential tool for achieving sustainability. People around the world recognize that current economic development trends are not sustainable and that public awareness, education and training are key to moving society toward sustainability. Beyond that there is little agreement. People argue about the term sustainable development and whether or not it is attainable. They have different visions of what sustainable societies will look like or be. These same people wonder why educators have not developed education for sustainability programmes. Yet, with little agreement about sustainability itself, it is no mystery why education for sustainability (EfS) has experienced difficulty moving forward...”¹

„The years between 2005 and 2014 have been declared as a worldwide Decade of Education for Sustainable Development (DESD) by the United Nations. DESD's intended purpose is to promote and

¹ Daniella Tilbury, Robert B. Stevenson, John Fien, Danie Schreuder, Education and Sustainability Responding to the Global Challenge, IUCN

more thoroughly focus education as a crucial tool preparing young people to be responsible future citizens, so that our future generations can shape society in a sustainable manner. All educational levels and domains are to be involved in contributing to ESD.²

Bearing in mind substantial discrepancies in environmental literacy of the citizenry of Serbia in relation to the citizenry of the US, EU and other developed countries in which the concept of sustainable development is already underway, it is essential to point out that, according to some authors, the knowledge about the protection of the environment in Serbia was carried out in two phases:

- Traditional – which implies a limited ecological approach
- Modern – based on taking measures to protect the environment where the ecological component is functionally separated (with minimal costs)

The phase based on the so-called “precautionary approach”, which was introduced in European and other developed countries and which is based on the principles of sustainable development, precaution, and making investment decisions with the aim of preserving the environment, would constitute the next logical stage of development. Based on the example of the waste management model on the territory of the municipality of Lucani, this paper aims to pinpoint the possibilities of integrating education, information, and communication into the process of environmental surveillance and to maximize successful implementation of the given model.

The need for incorporating sustainable development into the process of education has been appreciated and adopted by the representatives of 350 universities from 40 countries through a declaration signed at the international conference of the Association of University Leaders for a Sustainable Future in Talloires, France (*The Talloires Declaration*). The adopted goals entailed raising public awareness about ecologically sustainable development, creating an institutional sustainability plan, educating environmentally-conscious citizens, improving environmental literacy, including all interested parties, i.e. individuals, groups, organizations or institutions which have been or can be affected by any organized action in this field, etc. The recycling and environmental education program, which has been organized in primary school “Milan Blagojevic” as a pilot project for the last two years and which has given good results, was modeled on the views of developed countries about the need for incorporating Education for Sustainability into the curriculum.

ONE STEP OF PROPOSAL OF A NEW MODEL OF WASTE MANAGEMENT AT THE LEVEL OF LOCAL SELF-MANAGEMENT

The Municipality of Lucani covers the region of western Serbia by an area of 454 km². Having a population of 23750 inhabitants. Taking into consideration the fact that the quantity of mass of accumulated municipal waste amounts to 0,80 kg per citizen at an annual level³, a figure reached is that in this municipality 6,935t of waste is accumulated at an annual level. In 2011, a new model of waste management at the level of local self-government was proposed in order to minimize the amount of waste, boost recycling, and introduce sustainability on the territory of the municipality of Lucani. This model shows a necessary requirement for development and cooperation of the local self-management unit processors and the population. In that manner cooperation and participation of a greater number of inhabitants in the recycling process would be motivated, the development and introduction of new processing technologies would be motivated and the possibility would be opened for expansion of the recycle raw materials market and cooperation between the municipalities. The Municipality of Lucani is participating in the construction of the regional dump “Duboko“ with another eight municipalities. This shall upgrade the recycling process significantly because separation and preparation for further processing of secondary raw materials shall take place at the dump but the access of the inhabitants towards waste shall remain the same. That is why it is necessary to affect waste separation at its very source as with the inhabitants also in the industrial sector of the

² <http://pubs.rsc.org/en/Content/ArticleLanding/2012/RP/c1rp90060a>

³ www.ekoforum.org.yu

municipality. Practice shows that actions can not be realized successfully if every participant in the chain does not see his benefit. Thus, an awarding system should be introduced for those that do perform separating, but also penalties for those who do not do so, since the local self-management is enabled by the Law on waste management to organize and collect payment in the field of municipal waste management on its territory. The waste management model at the level of the Lucani local self-management unit would have as an objective the realization of a pilot project with the objective of creating an ecologic municipality and it would understand the applying of the following steps the benefit and dynamics of which are illustrated on Figure 1 – Strategic gap fulfillment plan.

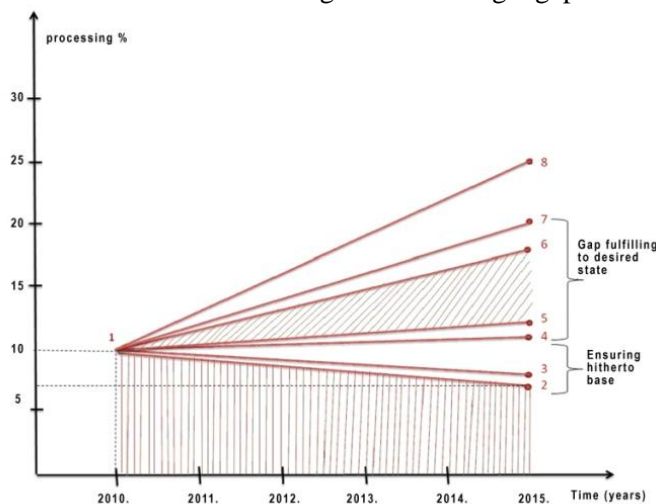


Figure 1. Waste management strategic gap fulfillment plan on the territory of the Lucani local self-management unit as a transition towards sustainable development

The numbers in the diagram indicate steps within the scope of the proposed waste management model:

- 1 – hitherto separation and processing
- 2-3 – waste collection and processing gap that is fulfilled by actions of waste minimization
- 3-4 – waste collection and processing gap that is fulfilled by actions of at-source waste selection
- 4-5 – waste collection and processing gap that is fulfilled by encouraging cleaner production
- 5-6 – waste collection and processing gap that is fulfilled by introduction of new waste recycling technologies and formation of Public Private Partnerships for waste collection and recycling
- 6-7 – gap that is fulfilled by development of an own market at municipality level for recycling, production and sale of specific products made from recycled raw materials
- 7-8 – gap that is fulfilled by construction of a transfer station and operation of the regional dump “Duboko” where separation and recycling of a significant quantity of waste shall take place taking into consideration that during a five year period the effects of construction of this dump will already be partially seen.

Based on performed analysis it is noticeable that by application of the plan for fulfillment of two gaps (2-4) the current state is maintained in the future. Namely, the forecast is that if nothing changes in the field of waste collection and recycling on this territory, the quantity of waste shall be increasing, due to which these two types of actions have a maintainable objective. Bearing in mind the fact that the development of urban ecology cannot be achieved without educational and informative activities, in the first step of the proposed model the emphasis is laid on raising people’s ecological awareness.

Minimizing waste creating

In the illustration that follows particular first step of the proposed model shall be explained in greater detail:

Waste management understands “collecting, sorting, transporting and treatment of waste, its storing and disposal above or under ground, circulation, as well as the treatment operations necessary for its

reuse, recycling and regeneration”⁴. The basic objective of waste management is actually its minimization. Despite Serbia’s inapprehension to apply New Zealand’s practice and their “Zero Waste” strategies, it is inevitable to introduce urgent measures that shall in any way influence minimizing of waste creating. The conditions in Serbia prescribe initial steps that will influence the creating of ecological culture of the population and their educating in that direction. At the level of the Lucani Municipality from the aspect of actual possibilities that would understand the following steps:

- Making a Plan of activities for a “pilot project” for the needs of informing and educating of the population with the objective of upgrading the ecological culture by engaging a PR service that would permanently work on increasing the awareness of the population and on emphasizing to the producers the necessity of waste reduction, the power efficiency and benefit of waste selection and recycling as well as organizing of workshops for preschool and school children on waste and recycling along with a tour of the recycling stations and familiarizing with waste treatment and the new raw materials that are obtained from waste.
- Organizing an expert team that shall work on upgrading of the internal relations of all participants in ecological activities in the Lucani Municipality, as well as developing of quality external relations between the Lucani Municipality and the relevant factors that can in any way exert influence on the realization of the foreseen plan (e.g. partner municipalities, competent ministries, investors, banks, non-government sectors, media and other) in order for it to be properly implemented.
- Establishing a system for controlling implementation and evaluation of planned activities.

In May 2011 and 2012, a pilot project was conducted in primary school “Milan Blagojevic”, Lucani. It was part of an urgent need to start educating children of school age in both ecology and recycling, as it was assumed that they are not well-versed in these fields of knowledge. Four classes of eighth-graders filled in a questionnaire on ecology and recycling.

The following chart presents the views of 86 pupils who completed the questionnaire and their future attitudes towards waste.

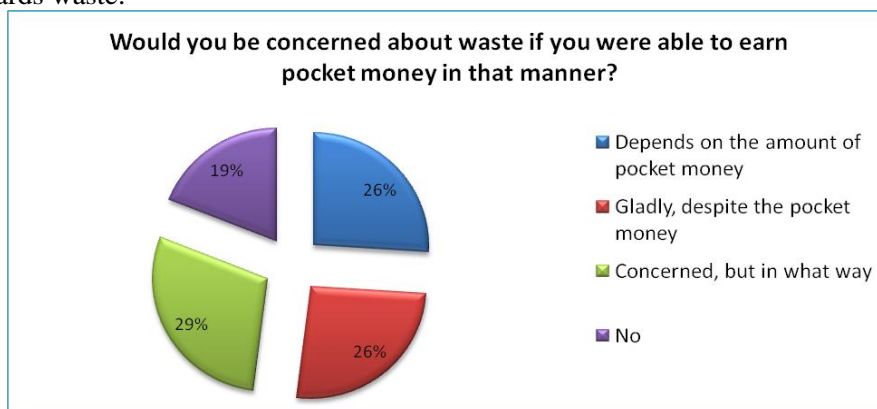


Figure 2. Opinion poll of pupils regarding the future attitude towards recycling

The fact that 29% of pupils would take care of waste, but do not know how, is a very significant piece of data. 26% of pupils would take care of waste irrespective of the allowance, which leads to the conclusion that at least half of the pupils would willingly take part in education and development of recycling technology. For 19% of pupils, not even the money would provide an incentive strong enough for them to take care of waste, whereas for 26% of pupils the amount of allowance would be a decisive factor. The results of the questionnaire are well beyond expectations. Bearing in mind the fact that the pupils who took part in the survey have been part of the educational process for almost a decade and have access to the Internet, the question arises as to whether and to what extent recycling and ecology are present in the education of children in Serbia, especially in small communities. As a

⁴ Republic of Serbia waste management strategy for the period from 2010-2019, (Official Gazette of the Republic of Serbia”, No. 29/10)

way of contributing to their practical education, all the surveyed pupils were taken on a tour of the recycling plant in Lucani, where they got familiarized with the process of recycling and its products. The pupils actively participated the separation and sorting of recyclable materials and learned about their characteristics. They also expressed great interest in learning about these processes and found this experience far more rewarding and useful than the traditional learning methods. The process of shaping and reinforcing their attitude toward the environment, sustainability and ecophilia is possible to achieve by dint of a proactive and lifelong influence.

In order to reach this objective, the following steps have been defined in order to facilitate the implantation of planned educational materials in citizens of local units of self-government:

- Promotion of sustainable development through formal and informal ways of learning
- Diffusion of innovations and knowledge (integration of innovations, education, training, research and development, and provision of relevant materials for imparting knowledge)
- Teacher training programs on sustainable development
- Provision of adequate resources and educational materials on sustainable development
- Provision of adequate practical experience through workshops and guided tours of recycling plants
- Provision of regular educational radio and television programs at local level
- Aid from a local unit of self-government in pursuing research in the field of Education for Sustainable Development and establishing innovation centres, as a form of cooperation with institutions of higher education and scientific research institutes, etc.

CONCLUSION

From the aspect of planning of integral and sustainable development, educational ecological materials should become part of the compulsory curriculum in the implementation of the sustainable development strategy. The introduction of additional educational materials about sustainable development, though the realization of the pilot project on the territory of the municipality of Lucani, attests to the fact that these processes have been instigated, but also that there is an evident need to expand research in this field.

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**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

**CREATING AN INTERNATIONAL NETWORK OF WATER
RESOURCES SPECIALISTS THROUGH A DISTANCE LEARNING
PROGRAMME**

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ABSTRACT

The EDUCATEn! Postgraduate Study Programme in Water Resources and Environmental Management is an international postgraduate programme organised by four leading Universities in the South-Eastern European region: the University of Belgrade - Faculty of Civil Engineering, the National Technical University of Athens, the Technical University of Civil Engineering of Bucharest and the University of Ljubljana. Successful completion of the entire postgraduate programme leads to certificate of specialist degree and the accompanying academic title of Academic Specialist in Environmental Engineering from the University of Belgrade - Faculty of Civil Engineering. The main innovative element of the programme relates to its e-learning component. The modules are delivered to the students through a set of easy-to-use, flexible e-learning support tools, integrated in a web-based platform. These tools aim to promote exchange of knowledge and ideas on environmental issues between teaching staff and students. Four generations of students have graduated from the programme and two generations are currently enrolled. The programme presents a success story and has formed an international network of students and graduates who are able to share experiences and work together in the future, as well as apply their knowledge in the field.

Key words: *distance learning, water resources, environmental management, specialist academic studies.*

INTRODUCTION AND BACKGROUND

In today's world, continuing education and lifelong learning is becoming a necessity in ever more so challenging work environments. Engineers work in multidisciplinary teams where, sometimes, they need to acquire knowledge that was not taught during their bachelor or master degree programs. Different jobs demand that engineering professionals, especially young professionals, have a host of knowledge based skills that need to be acquired efficiently and this sometimes cannot be done solely through practical experience at the workplace. The broadened knowledge and skills are also valued "resume builders", as young professionals today often seek new employment opportunities, due to the desire for personal and professional growth and better working conditions, or due to the economic crisis and loss of current employment.

When choosing a postgraduate educational program, students look for a specialized program that will offer them the right set of skills. Also, there is a growing number of students who cannot afford, professionally nor financially, to leave their jobs and pursue continuing education opportunities as a sole occupation, especially in a country outside the students' place of residence. These students look for ever more popular distance-learning programmes, especially if they offer the flexibility of personal time management, i.e. where the students can plan their study time around their work commitments. Also, distance-learning programmes offer the opportunity for professors from different universities and countries to create a programme where each will teach a module (course) in the area of their expertise and the students will have the benefit of learning from the top professors in the chosen study area from their own home. The added benefit of such a programme is the creation of a network of

professionals that can be used to create cross-country projects and various new job opportunities, as well as the opportunity to meet professors who you may serve as mentors for doctoral study programs.

The idea to create a specialist study programme in the area of water resources and environmental management was born through a vision of professors from the leading Universities in the South-Eastern European region: University of Belgrade - Faculty of Civil Engineering, the National Technical University of Athens, the Technical University of Civil Engineering of Bucharest and the University of Ljubljana. The thinking behind the idea and the motivation for creating a continuing education program can be highlighted through the following realities:

- The environment of SE Europe and Western Balkans has been subjected to pressures over the years, requiring enormous effort to remedy the situation;
- The capacity of the region to undertake this work is limited by the lack of trained professional with knowledge and transnational perspectives;
- Much of the EU funded research in the area seems to be addressing institutional capacity needs, however long term human resources needs are not properly addressed.

The goal of the new postgraduate programme would be to:

- Reverse the flow of trained professionals leaving the region;
- Increase the region's participation in project development (rather than relying exclusively on outside expertise);
- Change the attitude and increase the capacity to deal with integrated water resources management.

The programme was initiated within and supported through UNESCO's Reconstruction of Scientific Cooperation in SEE Programme and realized in 2007 as part of an INTERREG III B CADSES project. The first generation of students received stipends for the two-year programme. After the first launch year, the programme has been self-sustainable and is attracting students from all over the world.

A key component of the postgraduate course is an educational web portal which serves two closely related needs:

- Collaboration and exchange of knowledge between students and teaching staff (web collaboration area)
- Support of asynchronous and synchronous e-learning activities (e-learning platform)

The design and development of the educational portal is in line with the international character of the postgraduate course. It allows the cross-cultural exchange of views and ideas both between academics and students and directly supports the broader objectives of promoting cooperation within the Balkan region.

PROGRAMME ORGANISATION

Aims

The programme aims to enhance and broaden students' academic competencies in the field of: urban water systems (including the analysis, design, modelling and management of all their aspects), catchment management issues related to both surface water and groundwater systems and their associated processes (specific capacities are developed for analysis, modelling through a variety of hydroinformatics tools and management of all of key aspects of catchment and integrated water management systems), water and environmental policy and legislation (with an emphasis on EU legislation and the Water Framework Directive), policy making and social processes and the role of public participation in the decision making process.

Admission

The EDUCATE! programme invites applications from an international audience and is targeting recent university graduates and professionals from the public or private sector seeking specialisation in the field of Water Resources and Environmental Management. Successful candidates must have a good first degree from a recognized university with at least 240 European Credit Transfer System (ECTS) credits or equivalent in Engineering. Candidates should also show commitment to water resources and environmental management issues, usually through schooling, work or research experience.

Programme Structure and Modules

The postgraduate course in Water Resources and Environmental Management is a flexible, distance learning programme based on e-learning. Lectures and tutorials are given in English. Students can follow the entire postgraduate course (11 modules, 2 years) or alternatively they can select specific course elements, such as Thematic Areas and/or Modules according to their needs. Upon successful admission, a weekend-long Introductory Session is organised for all students at the beginning of the programme, during which the students meet their professors and fellow students, as well as get familiar with the EDUCATE web portal interface.

The postgraduate programme is a two-year course. It consists of four taught semesters and the preparation of a thesis. The successful completion of a minimum of 11 modules is required for the final qualification. Each module consists of lectures taught through the e-learning platform, quizzes/exercises, assignments and an examination held at the end each semester/ Thematic Area. The attendance of all e-learning lectures and the submission of exercises and assignments are mandatory for all students. Each module is equivalent to 8 ECTS credits; a minimum of 11 modules must be completed in total, and a minimum of 88 ECTS credits are awarded for successfully completed modules at the end of the course.

Modules are distributed in 4 Thematic Areas. Thematic Area 1 provides the basic scientific background in order to bring all students at a common level. Thematic Area 2 deals with the elements of urban water management in an integrative approach within a sustainable make-space for-water management context. Thematic Area 3 tackles catchment management issues by utilising hydroinformatics tools, including distributed hydrologic models, geographic information systems (GIS), advanced optimisation and geostatistics. Finally Thematic Area 4 focuses on environmental management including policy and legislation issues with an emphasis on the Water Framework Directive (WFD), environmental assessment and other advanced topics.

Written examinations are held at the end of each Thematic Area and require the physical presence of the students. Examinations are held at the University of Belgrade – Faculty of Civil Engineering. The student must also complete a research project, practical work and write a thesis. The research work and practice and the thesis are valued at 32 ECTS. The entire programme is valued at 120 ECTS.

The overall course structure can be seen in Figure 1, while the further breakdown into modules and lessons can be seen in Figure 2 and Figure 3, respectively (Katsiri et al., 2008; Makropoulos et al., 2009). Typical lesson components include:

- a. Topics in the form of hypertext (lecture notes, case studies) or animated presentations (video, animations, graphics)
- b. Quiz (Knowledge stabilization units/Formative Assessment) (not to be evaluated), solved problems, questions and answers, multiple choices
- c. Exercises (to be evaluate/Summative Assessment), reports, software applications (GIS, models, commercial software)
- d. Bibliographical material: digital library (papers, studies, books, manuals), theses catalogue, links to URLs, dictionary of terms

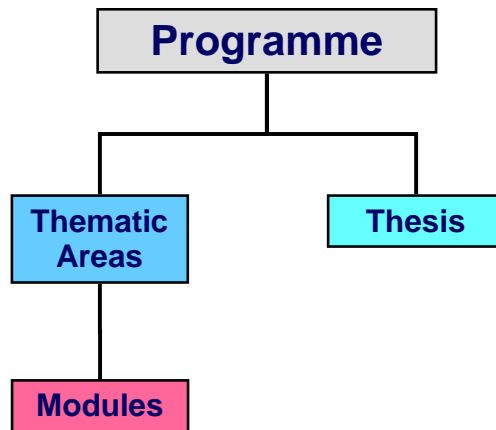


Figure 1. The EDUCATE! programme structure

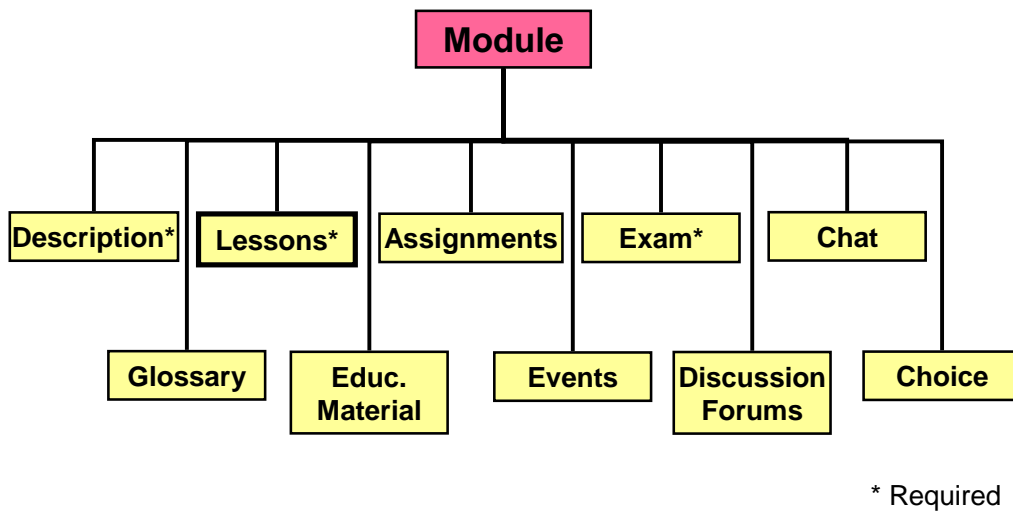


Figure 2. Module components

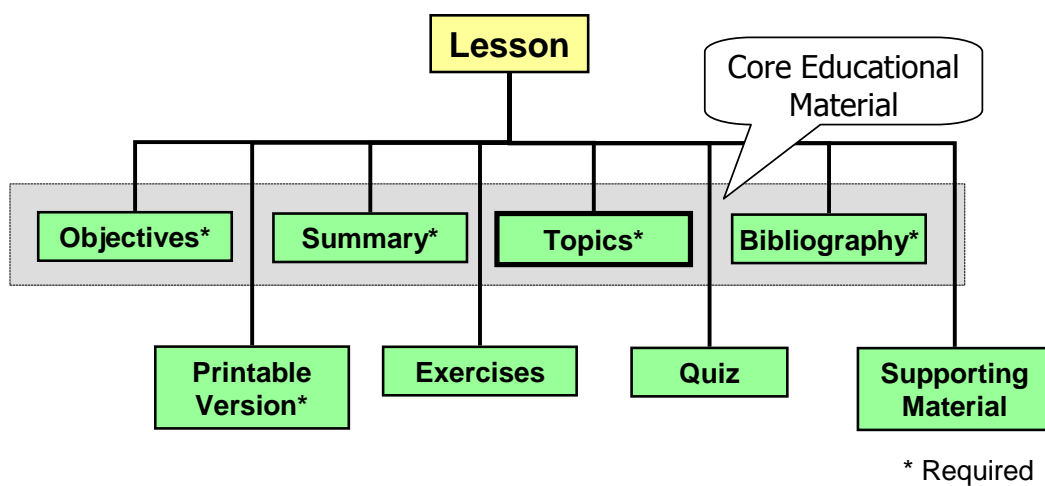


Figure 3. Lesson components

Current modules on offer within the e-learning course include:

Thematic areas 1 & 2

- Hydraulics and Hydrology
- Ecology, Chemistry & Microbiology
- Data Analysis Tools (GIS & Statistics)
- Water Supply and Distribution Management
- Wastewater Collection and Treatment
- Stormwater Management

Thematic areas 3 & 4

- Integrated Flood Risk Management
- Groundwater
- Integrated Water Resources Management
- Policy and Legislation
- Environmental Assessment
- Coastal Erosion Management

Learning Outcomes

The learning outcomes of the EDUCATE programme include knowledge and understanding of a range of water resources and environmental management topics as well as development of intellectual, practical and transferable skills and competencies, as detailed below.

- After developing specific competencies for understanding the basic processes related to the fields of hydrology, hydraulics, ecology, chemistry and microbiology in Thematic Area 1, the students are able to follow more specialised topics. The students start to acquire an ability to function in multi-national teams and the community of the postgraduate course is strengthened.
- Thematic Area 2 develops specific competencies for understanding urban water systems and of their associated processes, as well as for the analysis, design, modelling and management of all their aspects. Students learn how to critically assess research results and acquire an understanding of the impact of engineering solutions within a physical and societal context. IT literacy, reporting and presentation skills are further improved and an ability to function in multi-national teams is acquired.
- Thematic Area 3 develops specific competencies for understanding catchment management issues. Specific capacities are developed for analysis, modelling through a variety of hydroinformatics tools and management of all of key aspects of catchment and integrated water management systems. IT, data analysis, reporting and presentation skills are further improved, as well as the necessary skills for independent learning.
- Thematic Area 4 provides specific competencies for understanding water and environmental policy and legislation, with an emphasis on EU legislation and the Water Framework Directive (WFD), policy making and social processes and the role of public participation in the decision making process. Furthermore it develops an understanding of environmental assessment, its components, the different techniques widely used and how they can contribute to sustainable development.
- The development of a thesis gives the students the opportunity to focus in a specific field of their interest related to water resources and environmental management. The process enables students to become independent self-critical learners, critically assessing as well as interpreting and synthesizing research results and thus developing a problem solving ability. Due to the international character of the Educate programme the theses are focusing, to the extent possible, on transnational integrated water resources management issues. Hence an understanding of cross-boundary water resource problems will be developed, as well as the ability to develop cross boundary solutions to such problems.

Accreditation and Degree Awarded

The EDUCATE! programme is accredited by the Serbian National Council of Higher Education Commission for Accreditation and Quality Assurance.

Successful completion of the entire postgraduate course (2 years) leads to the award of the Specialist Degree Diploma and the accompanying academic title of Academic Specialist in Environmental Engineering from the University of Belgrade - Faculty of Civil Engineering. In case that only specific modules are selected students receive a certificate that includes the corresponding ECTS credits obtained upon successful completion of the selected modules.

CURRENT STUDIES AND STUDENTS

At its beginnings, the educate program was attended by students from the countries of the founding universities (Serbia, Greece, Romania and Slovenia) and from the region (Bosnia and Herzegovina, Montenegro). Today, the programme had attracted a broader international audience and can boast to have students from Ireland, Jamaica and Libya. This truly international audience was captivated by the uniqueness of the EDUCATE program and the desire to meet contemporaries from other parts of the world and establish links and a network. Four generations of students have graduated from the programme and two generations are currently enrolled. The EDUCATE alumni group has 36 members and there are currently 19 students enrolled in the programme.

The programme presents a success story and has formed an international network of students and graduates who are able to share experiences and work together in the future, as well as apply their knowledge in the field. An example of this is the construction of a multi-barrier water disinfection system, consisting of a physical and chemical disinfectant (ultraviolet (UV) radiation and chlorine dioxide), in City of Kraljevo in Serbia. The City's water supply provides water for 50,000 inhabitants. Improvements to the water disinfection system were a result of the EDUCATE specialist thesis "Source Water Quality and Disinfection Methods: Finding the Right Match" written by Marija Joksimović. Ms. Joksimović is an engineer employed by the Kraljevo Water Utility Company and following her successful completion of the EDUCATE! programme, she initiated the new disinfection system project that will contribute to the health and wellbeing of her fellow citizens.

Other notable specialist theses topics include:

- "Climate Change and Sea Level Rise"
- "Sustainable management of biomass residues for energy production in a closed energy system"
- "Coastal Erosion and Sea Level Rise"
- "Flow measurement and flow control in open channels"
- "Mathematical Modelling of the effect of global climate change on aquatic ecosystems - A critical review"
- "Methodology for determination of damage functions"
- "Delineation of Flooded area and Flood Risk Management. Case study - Lilas River (Euboea, Greece)"
- "Developing Roadmaps and Options for New Urban Water Cycle Services"
- "Desertification of Pinios river"
- "Sensitivity analysis of evaporation estimation methods"
- "Concept of the Ship Waste Management on the Danube Case Study - Serbia"
- "Cost Recovery Analysis for Water Supply and Sewerage in Serbia"
- "Pollutants Analysis on Paved Surfaces in an Experimental Catchment"

Figure 4 below shows the graduation class of 2010 and student Ana Novković is shown while presenting her thesis titled "Sensitivity analysis of evaporation estimation methods" in 2011 in Figure 5.



Figure 4. The graduating class of 2010 with their professors and friends

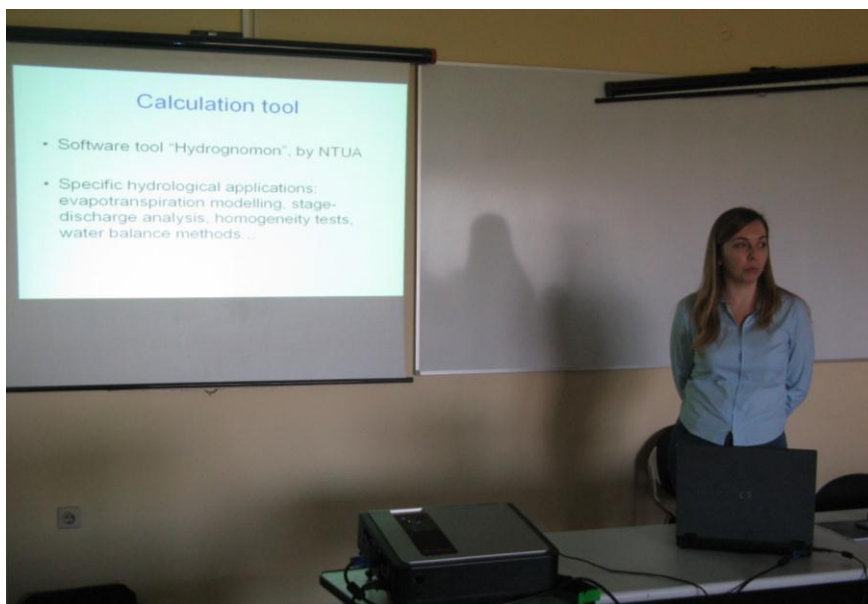


Figure 5. Student Ana Novković presenting her thesis titled "Sensitivity analysis of evaporation estimation methods" in 2011

CONCLUSION

Four generations of students have graduated from the programme and two generations are currently enrolled. The programme presents a success story and has formed an international network of students and graduates who are able to share experiences and work together in the future, as well as apply their knowledge in the field.

ACKNOWLEDGEMENT

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**II International Conference
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**ENVIRONMENTAL AWARENESS AMONG CHILDREN UNDER 7
YEARS**

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ABSTRACT

With every our activity we directly affect the Planet's resources, which we become aware only when the usage of these resources increase beyond its regenerative capacity. Developing environmental awareness in children early age is one of the main tasks of their image and behavior in the environment. During the Festival of the Science, 2012th year in the city of Novi Sad, in the workshop called "Wherever you find a suitable place, plant a tree", it was conducted a survey among the children aged under 7 years. For this purpose, it was composed a questionnaire of 10 questions adjusted for their age. The questions were divided into two groups: ecology and ecological behavior in the environment. Data analysis was elaborated by using standard statistical procedures, and the results showed positive outcomes. Children highlighted their understanding about the ecology and its laws, but also their behavior in nature was rated at a high level. We should be faced with the fact that the Earth will still remain to our children and that the children, with such early formed environmental awareness, for sure will be much better to the Planet than we are till now.

Key words: children aged under 7 years, environment, children's environmental awareness and behavior.

INTRODUCTION

Ecology studies the relationships of living beings and their environment. Ecology is primarily a way of life. Environmental awareness is starting to create from the moment when the child begins to understand and analyze the world around it. The influence of surroundings at developing the attitudes and personality of individuals is inevitable. Only healthy and ecologically educated environment can provide healthy survival for future generations.

The attitude of children towards the environment is being built at an early age, and the crucial role in that has the family. Children in pre-school growth do not have that knowledge about the environment like adults, but in that period they form their attitudes on the basis of the experiences that their parents and adults are transferred to them.

Topic of this paper is to analyze the state of environmental awareness among children up to 7 years. How close the term of ecology is to them and whether their behavior in the environment is ecological, are just some of the questions that this work is dealing with. The survey was conducted as a part of the fourth Festival of Science (Figure 1), which was held in Novi Sad 2012th, in the scope of the section "Climate change", and as part of the workshop ("Wherever you find a suitable place, plant a tree") and the directions of the Faculty of Agriculture and Departments for Horticulture and Landscape Architecture.

THEORY

With the rapid growth of cities worldwide, there is a need to better understand factors contributing to life satisfaction in urban environments (Vemuri, 2011) and ecological factors as integral parts of it. The term ecology was first used and introduced into science by E. Haeckel, German biologist. It is derived from a greek word "oikos" (house, habitat) and the word "logia" (knowledge, learning, science). This relates that the study of the ecology is the habitat of living beings. Haeckel defined

ecology as a science of relationship between living beings and their environment, living and inanimate environment. Later, the term of ecology is expanded, and refers to their relationship and relationship between man and living and inanimate environment (Cvejić, 1999).

Interest in ecology is primarily expressed through interest and concern for the environment, and in recent years was associated exclusively with the fear of the consequences of excessive or irreversible contamination of the environment in which we are living. How Vratuša (2005) emphasizes, ecology deals with the complex, systematic and deliberate introduction of the overall relationship of living organisms, humans and all other living beings, and the environment in which life exists, their complex studying and resolving problems and assignments that result from them.

In her research, Wilkinson (2012), emphasized that planning theorists are calling for more attention to matters of substance alongside matters of process, social-ecological resilience provides a timely contribution, particularly given the minimal attention in planning theory scholarship to environmental and ecological considerations as a driving concern.

The relationship between urbanization and the natural environment has never been the focus of an environmental sociological study (Clement, 2010). This article is an initial attempt to address that gap, also to emphasize that the most important thing is education about the relationship between man and nature, and understanding the importance of this relationship and its promotion conducted by children of their earliest childhood. Nearly, every regulation, pertaining to public preschool programs, emphasizes the importance of creating a high-quality preschool environment, which maximizes children's opportunities to learn (Mashburn, Pianta, 2010).

The one of the key, characteristic of the environmental education is action, because environmental education has to promote civic responsibility, to encourage learners to use their knowledge, personal skills, and assessments of environmental problems and issues, as a basic environmental problem solving and action (Petrović i sar., 2011).



Figure 1. Illustrations from IV Festival of Science, section "Climate change – Wherever you find a suitable place plant a tree."

METHODS

The survey was conducted in May 2012th year in the scope of Festival of Science in the city of Novi Sad. The object was to get information about environmental awareness among children aged under 7. The purpose of this research, as the main method of data collection, was used a method of interviews. A questionnaire was composed of 6 questions, which were directly referred to the assessment of respondents' knowledge about ecology and its laws, also to their ecological behavior in the environment. The content of the questionnaire was therefore divided into two groups of questions, questions that were related to ecology and questions related to the ecological behavior in the environment. Each group had the 3 questions. Total sample compounded 100 respondents.

For the conducted survey it is given the photo-analyze (photographic presentation of the current situation in space). With systematization of the study results and comparative analysis with previous researches with similar issues, conclusions have been made and the idea further was developed. In order to organize obtained data, their interpretation and the relevant evaluation, data were analyzed by using statistical estimation by Excel program, MS Office.

In the last phase with a systematization of obtained results and with comparative analysis, the findings of the paper were derived.

FINDINGS

The survey was conducted on a sample of 100 respondents, namely the group of children up to 7 years. The age of the respondents was evaluated in two categories, children up to 4 years and children aged between 4 to 7 years. The questionnaire was made up of 6 questions, of which 3 were aimed at testing children's knowledge about the ecology, and the other three questions were aimed at determining the extent of their ecological behavior in the environment. Questions were adapted to their age and the pattern was based on the concepts and terms that are familiar to them.

In a sample of 100 respondents, 45 were female and 55 were male. Of these, 15% were children under the age of 4 years, while 85% were children aged 4 to 7 years. The children showed great interest to answering questions. More freedom, i.e. independence in the responses was emphasized between children aged 4 to 7 years, while the younger children before their final answer almost always awaited confirmation from their parents.

The first question (Figure 2) was related to the children's closest environment, and to understanding the existence of basic environmental elements in their street. Of all respondents 76% said that the most important role of trees in their street is a creation of the shade, 12% responded that the reason is noise reduction, 6% of respondents that is perfect to have the trees in the street because of climbing on them, and 6% of them respondents did not know the answer.

On the second question (Figure 3), 70% of respondents said that the smoke from a factory makes planet dirtier than it is, after it, there is a trash with 17% and cars with 9%. The third and final question in ecology group (Figure 4), was related to the nature conservation and who are its main protagonist. Most answers were given under park ranger (89%), followed by Mom and Dad (7%), and the bus driver (3%). Only 1% of respondents said they do not know the answer to this question.

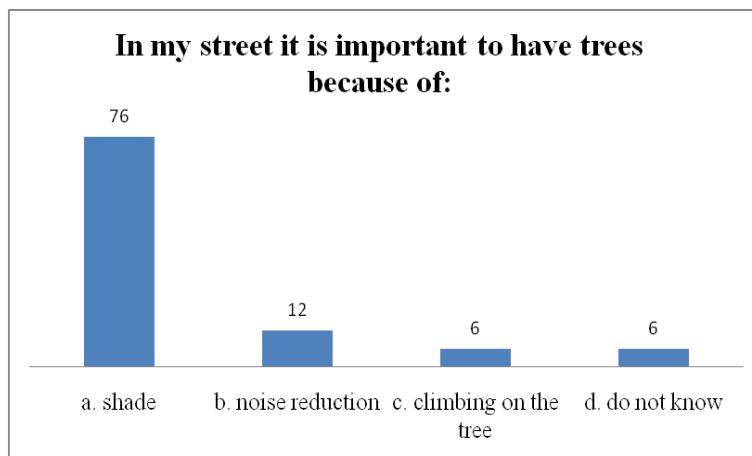


Figure 2. The results obtained from the first question of conducted Questionnaire

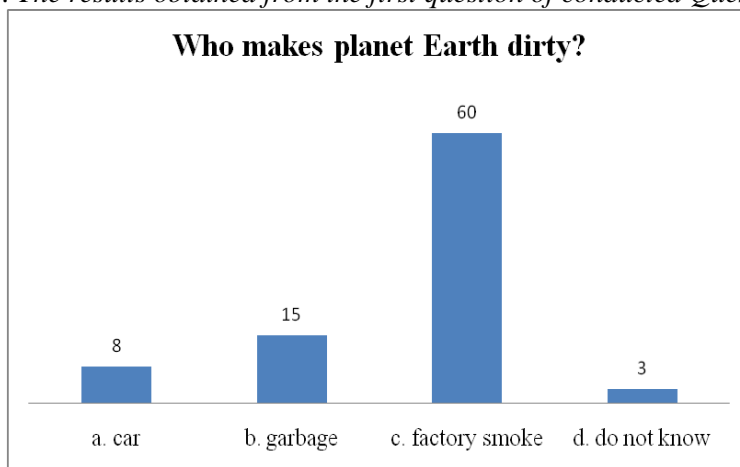


Figure 3. The results obtained from the second question of conducted Questionnaire

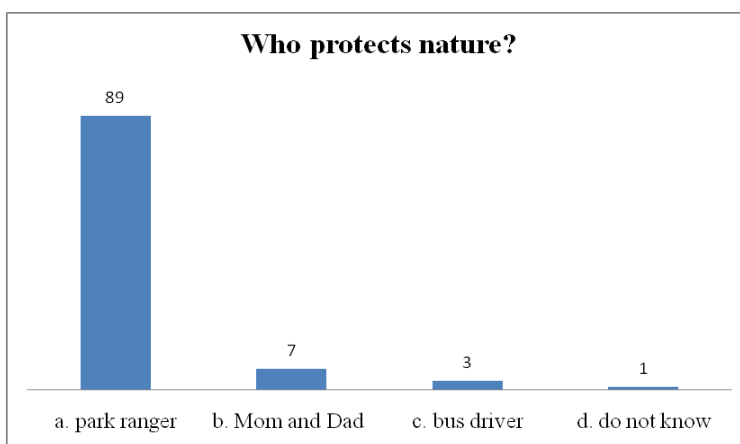


Figure 4. The results obtained from the third question of conducted Questionnaire

The next group of questions focused on examining the ecological behavior of children in the nature. When they were asked where the garbage is dumped (Figure 5), 99% of respondents said that they are throwing garbage into a trash bin, and only 1% of that would be in the neighbor's yard. On the statement that the stepping on the grass is not allowed, 90% of children responded positively, while 10% of them were opposite of this fact (Figure 6). Also a high percentage of children (99%) said that plants need to be watered, and only 1% said it was not necessary (Figure 7).

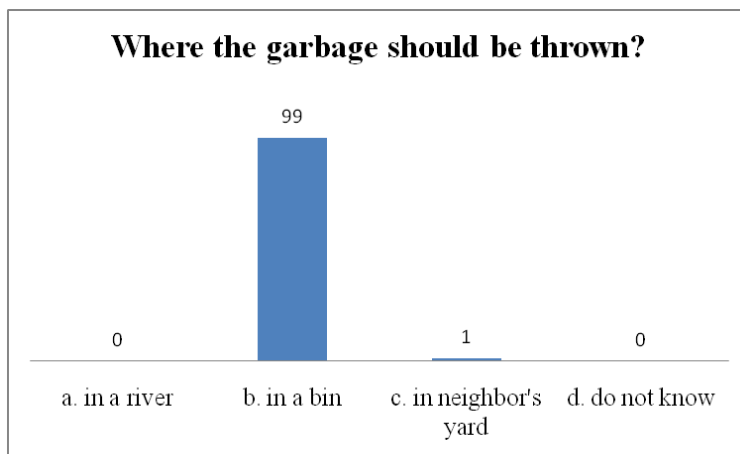


Figure 5. The results obtained from the fourth question of conducted Questionnaire

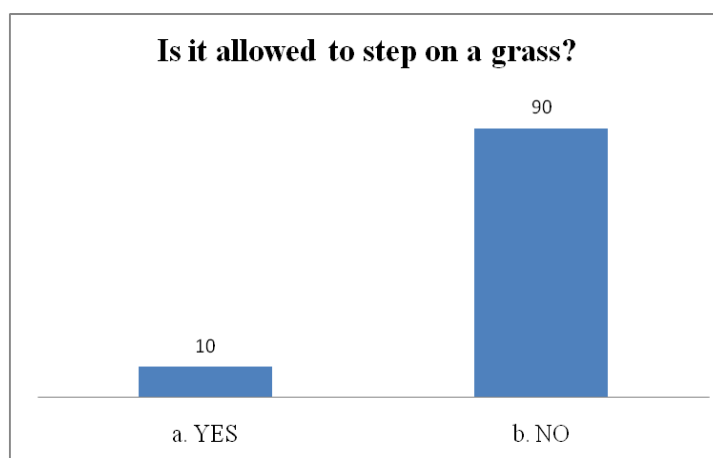


Figure 6. The results obtained from the fifth question of conducted Questionnaire

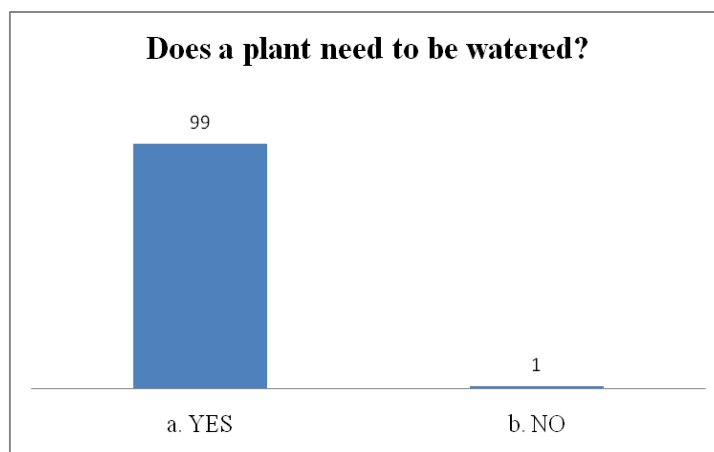


Figure 7. The results obtained from the sixth question of conducted Questionnaire

DISCUSSIONS

Certain preschool institutions implement environmental programs and activities through all the content in the kindergartens. Habits acquired in that period, remain for whole life. It is particularly important for children to know the reasons, because if they understand the causal relationship between man and nature in earliest period of their life, they are on the good way to develop themselves into active and nature responsible persons when they become adults.

Nursery-governesses (educators) are trying to make a connection between children and the environment. In kindergartens children are planting flowers, trees, vegetables. These are activities in which children follow the development process of a plant, what they need for its growing and developing. Children take care of those plants, from seed to fruit. Certain content, educators are trying to bring closer to children a plant and animal world, as well as natural phenomena and how they affect the living world. Some of the covered topics include: why is water, air and soil important for us, and how to preserve them. Exactly, and this study has shown that the results of such work are positive, because the environmental awareness and behavior of children aged up to 7 years was rated at a very high level.

It was also shown that these questionnaires are very tricky for younger children and that cannot be one hundred percent considered relevant, because the children's scale and scale of adults, in observing the environment, are significantly different. For example, if the first question is interpreted, trees are important both for the shade and for reducing a noise. If there is no shade, that they provide, it would be more warming in the street and therefore greater exposure to thermal hazards; on the other side, their primary task is to reduce a noise. An example of this is second question (Who makes the planet Earth dirty the most?). Will it be a garbage or a smoke from the factory - probably both, but viewed from the perspective of children, smoke is somewhere high in the air, and do not see how it could make the planet dirty, while the garbage is something tangible and visible for them and to the eye of the extent of contamination all around us.

CONCLUSIONS AND IMPLICATIONS

Environmental awareness, as a manifestation of global understanding of the relationship between man and nature, on the individual level, is an essential element of broader social and political activities, in order to preserve the environment. Without knowledge of the existence of environmental problems, ecological values and environmentally responsible behavior at the level of individuals, each global effort in this direction remained unsuccessful.

Formal ecological education of children and youth, takes place through the education system, still stiff and theoretically, without the possibility of experiential learning. Nature, its beauty, mystery and the need for its preservation cannot and must not be a theory, but a way of life, with the clear responsibility of every young man. Currently the environmental education in primary and high schools is present in subject of biology and usually it isn't paid on it enough attention. Primary education of young people has to have as an essential segment also to include environmental education, which will both have theoretical approaches and build awareness of the need to preserve and protect the environment.

The active participation of young people in creating a healthy and unpolluted environment is a primary goal. Investment in environmental education and education of young highly-skilled environmental staff would create a resolute public opinion which respects, understands and protects environment and natural resources. This attitude is confirmed by the fact that the awakening of environmental consciousness, first arose among youth who were in the eighties of the last century, through various forms of association and action, begun to affect the entire population and its relationship to the environment.

The current state of the environment indicates the need for priority to solving pressing problems. If the plan is not to take radical steps, the consequences can be fatal. Legacy for future generations will remain completely depleted wildlife. Degraded forest areas will be converted to low-grade woody plantations of certain species, and protected areas (national parks, nature reserves, etc.) will be ruined. The end result of these processes is completely natural balance disruption and threat to the survival of the human population. In order to enable further progress of the human population, it is necessary to adopt and implement a sustainable development. The basic idea of sustainable development is to meet the needs of present generations without compromising the possibilities of future generations to meet their own needs.

It is well known that children learn best throughout play. Through active participation, numerous workshops, theater performances, creative games, children will learn about ecological terms such as recycling, treatment, composting, biodiversity, and so on. Since the acquisition of awareness of any issues intensively in the period of childhood, it is a good time to get acquainted with the importance of addressing environmental concerns.

Each generation is responsible for transferring lessons about the future of the world and the preservation of the planet to the next generation. Like Petrović et al. (2011) pointed out environmental education can be defined as learning to protect and improve environment in a systematic, planned and knowledge-based way during the whole human lifecycle in order to spread awareness about basic characteristics of environment, its structure and relationships that tends to make a human protect and improve environment in a way that will ensure humans' existences now as well as in the future.

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**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

IMPORTANCE OF SCHOOL FOR ECOLOGICAL EDUCATION

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ABSTRACT

Environmental education must not be at the level of information and reproduce knowledge. The formation of ecological thinking should start from an early age, the young generation to be involved in solving problems related to environmental protection. Only in this way will develop environmental awareness among children. It is our wish that this work, no matter how much or not, the subjects concerning ecology represented in the curriculum, point out that the study of this subject has. We believe that some of the proposals formed the basis of some of our experiences gained in the maintenance of environmental workshops for children ages preschool to high school, as well as seminars for professional development of educators, will come to schools life in Serbia.

Key words: *environmental education, environmental awareness, environmental protection.*

INTRODUCTION

The Assembly of the United Nations General the period 2005-2015. years. proclaimed as "the Decade of Education for Sustainable Development" (OECD, 1990). Then the Law on Basic Education (Law 72/2009), the Law on Environmental Protection (Law 36/2009) and the National Sustainable Development Strategy (National Strategy for Sustainable Development, 2008), says just about the importance of education in the field of environmental protection. Reforming the educational system and the introduction of new subjects, much improved attitude towards environmental education.

IMPORTANCE OF SCHOOL FOR ENVIRONMENTAL EDUCATION

The importance of the school in education. It provides the greatest opportunity to build environmental awareness of children, from the earliest times. How the school provides knowledge, so should work on the development of environmental awareness among children and young people. Often, in practice, to complete knowledge, no educational moment, is not enough. There must not forget the family, whose upbringing and behavior models are of great importance for the subsequent development of the child.

Teachers should give more importance to environmental amenities within the existing curriculum. Often only individual preferences and knowledge of teachers depends correlation (horizontal or vertical), in the teaching process. It is of great importance for the development of environmental awareness and introduce children have different activities related to the observed problems, such extracurricular activities at the school.

It is necessary and required by law to teachers and associates, professional training. The catalog of professional development for the period 2012/2013 and 2013/2014 there are seventeen of topics related to environmental issues (Catalogue, 2012), among others, our third year in a row accredited seminar "Packaging, waste and recycling." From this year the program is enhanced with a one-day in-day. We must notice that the interest of teachers with higher grades higher than the lower grades.

New trends, technologies and innovations available to every teacher, educators and experts. It is important to emphasize that definitely high structure of our educational system, take into account the need for constant availability of the freshest and the most important information and content related to the topic of ecology and environmental protection. In this way, teachers have the opportunity to convey to children the latest knowledge and developments in these fields. In the area of environmental protection, but also in other areas, it is necessary to apply different, new, interactive teaching and learning methods. These steps lead to the modernization of teaching, which will result in the formation and development of critical thinking in students, through their direct involvement and active participation in discussions. In addition comes to analysis, synthesis and subsequently processed content, as well as clear and unambiguous putting forward views. At the end is the adoption of appropriate conclusions, and its application in life, almost guaranteed.

EDUCATION ON ECOLOGY IN OUR COUNTRY

Ecology in kindergartens and preschools

Ecological way of thinking, and thus behavior, is formed through the individual's relationship to the natural and social environment. Children of preschool age are practically ideal to start accepting and nurturing environmental culture. Eco content and activities, as well as providing information on the need to protect and improve the environment, regardless of the initial difficulties in their adoption, to be implemented in educational work with preschool children, in order to enable the integration of ecological and moral education (Trifunovic and Curcic, 2010). It is important that children are in preschool children learn to properly assess and timely insights into the dangers and consequences of inappropriate behavior toward nature, to be ready to engage in the protection and enhancement of the environment (Kopas-Vukasinović and Budimir-Ninkovic, 2009). Ongoing monitoring of the legality of a change in the nature, and the behavior and activities of children and young people, contributing to the formation of their environmental awareness and the development of a kind of ecological culture. Education influences the formation of a positive attitude towards the environment, and phenomena in nature. In addition to encouraging appropriate behavior and attitude towards the natural beauty, so that environmental education should be one of the key segments of the general education within the family and the educational system. Through the preschool program on children and interesting for them, definitely most susceptible ways, ie through the game, learn about their immediate environment and the continuing need to protect the environment. Of the Regulation on basic principles of preschool program (Ordinance, 2006), is defined by one of the General Plans preschool program that reads inter alia: **Understanding the natural and social environment (environmental).**

Before the Environmental Education sets the task of the research model human behavior toward the environment, based the restoration of the lost and broken ties with nature in perception, cognition and action (Andevski, 2006). In practice, the goals and objectives of environmental education, often come down to a level of insight into the issues related to environmental protection. However, it should be just the first steps in the system operation between adults - children and youth. There is no education in the field of environmental protection, or the formation of environmental awareness and environmental culture, with no direct experience of environmental values. Stated one of the reasons why educational activities with children of preschool and school-age children, often implemented as planned and outdoor activities. Through their own experiences children acquire knowledge, develop their environmental culture and environmental awareness of the form (Budimir-Ninkovic, 2005).

Environmental education in primary and secondary schools

Looking at the modern education system, there is a need for environmental education of children and youth, as well as develop their awareness of the environment and of man's obligations lifestyle. It is therefore necessary to harmonize all economic activity with environmental opportunities and natural laws. Thus arises the need to build a new system of values, within which is dominated progress of man with one hand and environmental protection on the other hand (Markovic, 2005). Analysis of the

curriculum of the first cycle of primary education, we conclude that the subject of The World about us taught in first and second grade. In the third and fourth grade that item replaces nature and society. Second cycle of primary education belong grades five through eight. Available in ecology are represented by the following subjects: biology, technology and computer education, chemistry, physics, civics. For the purpose of clarity in Table 1 are presented in which objects are from 1 to 8 years of studying environmental issues.

Table 1: Courses for which grades are taught ecology

Classes are taught in which topics related to ecology	Courses
1	The world around us
2	The world around us
3	Nature and Society
4	Nature and Society
5	Biology
5	Geography
5	Technical and computer education
6	Biology
6	Geography
6	Physics
6	Chemistry
7	Biology
7	Geography
7	Physics
7	Chemistry
8	Geography
8	Physics
8	Chemistry
8	Technical and computer education

The presented table 1 shows that the activities related to environmental issues, process, but the question is to what extent and whether it is enough. Mandatory addition, there are optional courses that deal with the above problems, so that in the first cycle to the subject conservationists, with one lesson per week. Important to note that in schools, facilities which topics are closely related to the concept of environmental protection, further implemented through a range of different leisure activities such as clubs, classes in nature, ecology, community service and maintenance of school premises and yard decorating classrooms, offices, landscaping and cleaning the school yard and the immediate environment of the school building, collecting waste paper, plastic bottles, cans and the like. Regarding the situation at the level of secondary education, ecology emerges as compulsory subject in some professional schools (eco-sanitary technician, a technician for the environment), and for the first time as an independent, separate subject. As in primary education, the environment is taught through other subjects of natural sciences. It is necessary to separate high schools, as well as a separate category because of their ecology has the status of a special case. However, this type of content is taught through: chemistry, biology, physics and geography during all four years of schooling and lasts. civic education subject which is represented as an elective subject in all secondary schools within their facilities, among others, and includes topics in the field of environmental protection.

Environmental education at the university

In accordance with the Bologna Declaration has been reformed higher education in Serbia. Reformed, as the state (total of 7), and the family (total of 9) Universities and colleges in the country. After a thorough review of plans and programs of basic and specialized studies in all the faculties of the University of Serbia, and the remaining private colleges which have a total of 6, it was found that at

the university level, the environment is studied at four Universities in Serbia founded The Republic of Serbia and in Belgrade, Novi Sad, Nis and Kragujevac (Jasin et al., 2011; Jasin, 2011) as well as at universities in Zrenjanin (Faculty of Engineering, Mihajlo Pupin), Bor (Technical University), and Kosovska Mitrovica (Faculty of Engineering).

SUGGESTIONS FOR INTRODUCING ENVIRONMENTAL ISSUES IN TEACHING

We want to emphasize the possibility of introducing content-related environmental issues through various activities in the school. Students are far more interesting learning in nature, where they have the feeling they are doing something good for our environment. Our schools are opting for the classroom or office, in which students acquire knowledge, despite the fact that most of the information if we adopt practically do, through an experiment, what we learn. In addition to the above is the fact that a number of experiential learning as the author points out the most important in the educational process (Knowles, 1980, Norman, 2003, Vygotsky, 2005; Lalovic, 2009; Bognar, 2010). Teacher teaching some topics can be implemented more effectively outside the classroom. Students may also in interesting ways to acquire knowledge of the ecology on the Internet, visits to museums and exhibitions, being in nature and the other, a number of activities. Extracurricular activities are a great value when Upitanju environment. Students are more relaxed when they leave the classroom, and then, more positive and more open to embracing new content. It is important to experience the environment and not formally known. Based on their past experiences (Jasiin et al, 2011) suggest the introduction of the following activities in schools to make learning more interesting and enduring acquired knowledge:

1. Marking on the environmental calendar at the school level. For example.: Earth Day. Thematic planning teams at school, at the level of its proposed asset correlation case.
2. The introduction of correlation at the school level, grades, classes with the theme of ecology. The correlation can serve as horizontal or vertical.
3. Working Saturdays used for ecological excursions, visits to museums, exhibitions, school facilities and equipment yard
4. The promotion of community service, can be a school, daycare assistance, arranging park in the city and others.
5. Popularization of volunteerism, as more and more young people like to engage in these activities
6. Involved in projects within the department, school, and community
7. Forming Eco- patrols at the school level, in order to detect critical ecological points around the school

CONCLUSION

Based on the above, one can observe that there is no ecology as a separate subject in the compulsory education system of the Republic of Serbia. However, it is obvious that the continuity of the educational work in the field of environmental issues and the content of preschool and day, to doctoral studies. Quantity and quality of organic content in the electoral framework, free, and optional activities depended directly correlated with the interest of, and often enthusiastic teachers themselves, although there are situations in which the involvement of schools in general are very strong. Improving education for the protection of the environment in the present, and future time must be a priority and it must be designed so that the individual becomes responsible towards the environment (in my town, village, street).

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**II International Conference
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**ENVIRONMENTAL AWARENESS OF YOUTH IN THE
MUNICIPALITY ZRENJANIN**

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ABSTRACT

Given that the state policy of Serbia supports the European values, which imply a high level of environmental awareness, and the fact that they are in Zrenjanin, in the past ten years, taken appropriate measures regarding the development of environmental awareness of young people, we have examined, in order to find guidelines for the improvement of its quality, collecting and analyzing data on the current level of its three segments: environmental knowledge, environmental attitudes and ecological agency. Next, we investigated the independent variables of which depends on the willingness of young people in recruitment, as well as the relationship of knowledge about ecology and environmental readiness for action, and which factors most affect the acquisition of knowledge about environmental issues and what is the opinion of young people about the best ways to solve environmental problem. The sample consisted of 412 pupils from 15 to 19 years, the youngest subjects of which 257 eighth graders and 155 high school pupils. i.e., 206 pupils from urban areas, 135 from rural and 68 from suburban areas. The survey was conducted by written survey. Instrument was used as a questionnaire consisting of 31 questions. The results show that the level of knowledge of pupils is relatively low, the statements are true, a moderate effect. In addition, the results show that girls and children from the countryside are willing to engage in environmental activities. Pupils' involvement in extracurricular sports activities is not statistically significant variable for participation in such activities. The students showed a very low knowledge when I needed to list the ways they can contribute to environmental protection. We believe that the most important result of our research concluded that there is proportionality between knowledge and engaging students in environmental action.

Key words: ecology, awareness, youth, Zrenjanin city, LEAP.

INTRODUCTION

The problem that is particularly developed in the documents on environmental protection of the European Union, is the enlargement of the EU, i.e. accepting new members. In the process of joining the EU, candidate countries will have to harmonize their legislation in this area with the EU, but also to adopt the current principles, and an appropriate view of the world. The current action plan for protection of the environment provided that the candidate countries need to: establish sustainable economic development, coordinate public transport, urban planning and development work on raising environmental awareness among citizens. "Activities in the direction of raising environmental awareness cannot leave out the young, which may represent a force for positive environmental change in the future." [1] At the Ministerial Conference "Environment of Europe", held in Lucerne in 1993, signed the "Environmental Action Programme for Central and Eastern Europe," EAR. In most countries of Central and Eastern Europe during the process of establishing National Environmental Action Plans (NEAP - National Environmental Action Plan) and those at the local level, so the Zrenjanin city has adopted Local Environmental Action Plan as well. Besides many others, one of the most important goals of LEAP in Zrenjanin is to promote public awareness and responsibility for

¹ Ana Pajvančić PDF file: Ekološka svest kao univerzalna evropska vrednost , Internet, retrieved on 02/27/2012, <http://www.natef.net/downloads/AnaPajvancic.pdf>

environmental issues and raising the level of public participation in the design and implementation of action strategies and investments, as well as improving understanding of environmental problems at the local level. One of the reasons for its implementation and increasing is the awareness and knowledge about environmental problems. LEAP includes the search for ideas, thoughts and opinions of citizens, ensuring that priorities and solutions reflecting what are considered community as a whole, in our youth.[2] One of the stages of LEAP (Phase 5) is a monitoring and evaluation of its implementation.

The subject of our research is attitudes, actions and knowledge of young people in environmental issues in the municipality of Zrenjanin. The goal of our research is to find guidelines for improving the quality of environmental awareness among young people, collecting and analyzing data on the current level of environmental awareness. The tasks of our study was to define pupils' knowledge of environmental issues, pupils' attitudes towards environmental issues and the willingness of pupils to engage in environmental activities. We examined the interdependence of all three segments of environmental awareness, as well as the influence of different factors that influence the environmental awareness of young people: schools, families, peer groups, the media, in order to point out potential mistakes, and to discover the best channels for informing young people about ecology, to find ways to actively involve young people in solving problems. We have examined the attitudes of young people about how to solve environmental problems. We provide two hypotheses, general and special, as follows: The general hypothesis - There is a correlation between segments of environmental awareness. It is assumed that students with greater knowledge of ecology, more willing to engage in environmental activities; Specific hypothesis - Children from rural areas have more developed environmental awareness. When you start implementing the plan, it is important to monitor and evaluate the results, which are often neglected. Our study we tried to find out what the current state of environmental awareness among young people, given that the LEAP in Zrenjanin applied ten years, and to devise guidelines for its improvement. Also, we learned what the opinion of young people about environmental problems and ways to address them. The study of environmental awareness of young people in Zrenjanin, have not been done, until now.

METHODOLOGY

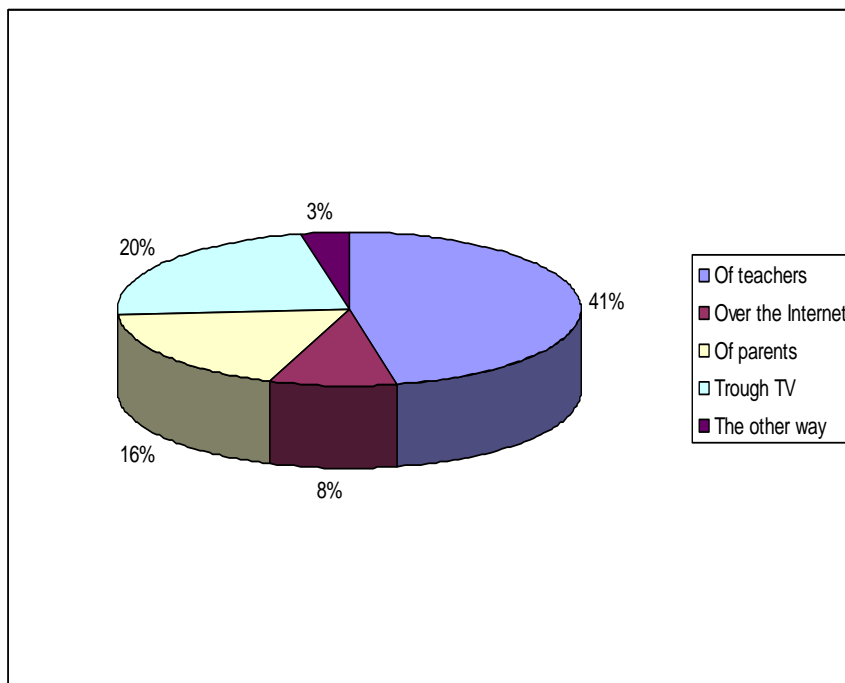
For the data we used the method of content analysis and a written examination, with the questionnaire used as an instrument composed of five groups of questions. Within the three groups of questions was examined by one segment of environmental awareness, and the other two were collected general information and opinions. The study was conducted in elementary and secondary schools in the municipality of Zrenjanin in the period from September till December 2011. The sample consisted of 412 pupils from the city, with rural and suburban areas. We examined the youth who attend primary school, technical school and high school. Methods for processing data that we used are: statistical, comparative and descriptive methods. Statistical analysis was performed using Microsoft Excel for editing.

RESEARCH RESULTS

When asked "Do you actively participate in the work of a section / workshops at the school or where you live?", A total of 405 subjects who responded, 87 of them, and 21% responded that they participate, with only 8 subjects participating in work of some of the environmental sections (approximately 2%). While 77% of respondents, or 310 of them, the respondents did not participate in the work of any one section. We wanted also to find out whether the respondent engaged in environmental work in the school section, if it is established, and we obtained the following results: "Yes" responded 94 pupils, with "no" answer is 103 pupils, and as many as 205 pupils responded to the work involved in the environmental section, if it included some of his friends. Ten pupils did not answer the question. It is interesting to note that most pupils who are not involved in the work of environmental sections, the main reason cited lack of time, while some of them claim that they do not

² LEAP Internet, retrieved on 02/29/2012 Zrenjanin: <http://www.zrenjanin.rs/userfiles/file/LEAPZrenjanin.pdf>

interest them and to them is a "burden". Some of the respondents who said they would like to participate in such sections in the school as the main reasons cited love of nature and desire to contribute to its preservation. Pupils' knowledge of environmental conditions, we studied in the third group of questions. When asked about the biggest polluters and largest environmental problems in the world, respondents answered descriptive, and we classified them according to their knowledge ranging on a scale from 1 to 5 (1 given to all who knew nothing). Average pupils' knowledge about these two issues is quite low. The majority, about 63%, listed only the two of the biggest polluters of the two environmental problems on the planet, while very small percentage, about 2%, listed 4 or 5 of pollutants and environmental concerns. Any pollutant not known to be enumerated of approximately 9% of respondents, and no environmental problem were not known to be specified as many as 31% of respondents. About 22% of respondents knew the three pollutants, and about 11% of them are aware of three environmental problems. At the same time we must note that most respondents as the biggest polluters led industry, transport and man, as a major environmental problems of global warming and the ozone hole, two concepts that are often mentioned in the media. Only one respondent said plastic bags as pollutants of the environment. The greatest knowledge about both issues showed high school pupils, "Uros Predic," who have the educational department for environmental protection, and the worst knowledge showed grammar school students. We asked them also to answer whether that is a chemical element in the main polluter of water in Zrenjanin, 59% could not answer this question, while individuals from the remaining 41% who said they know, as a major pollutant cited elements not a major polluter of water in Zrenjanin, such as. ammonia, aluminum, iron, selenium, chlorine, lead. So the percentage of those who do not know that arsenic (arsenium, As) is the main pollutant of drinking water in the municipality of Zrenjanin is greater than the above 59%. When asked how they think they can contribute to environmental protection, 32% responded that they do not know or can not contribute, 8% that can contribute to recycling, saving, no pollution, 52% that can not contribute to littering; 6% said afforestation, 12% for different actions. When asked from whom they learned the most about the environment, respondents were as follows: 41% - of teachers, 8% - over the Internet, 16% - of parents, 20% - through TV and the 3% - the other way, where the mostly cited various combinations of the three preceding responses (Figure 1).



Picture 1. Sources of information on environmental protection

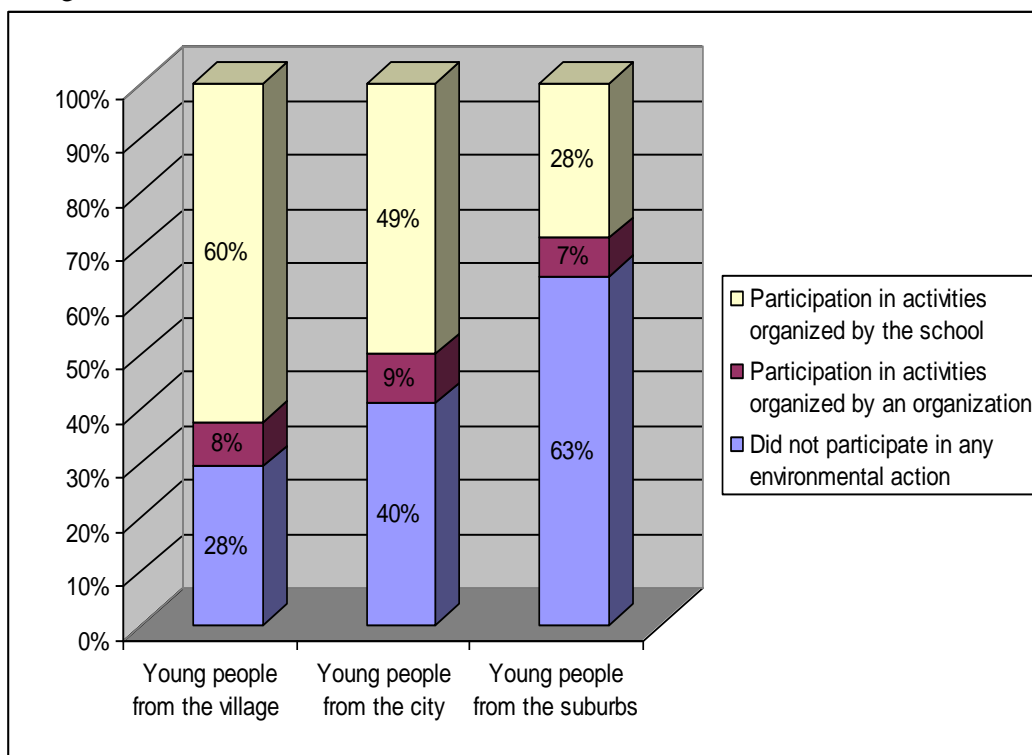
When we examined the environmental attitudes of students, one of the most important issues for us was "Do you think it is necessary that we all care about wildlife and to protect it?" Which we tried to find out was whether the pupils themselves are responsible for what is happening in the environment.

It turned out that 90% of respondents believe that everyone should take care, while 5% felt that the state should take care, while 3% thought that local management should take care. Only 1% thought that someone else should take care, while 1% of pupils did not answer this question. This confirms that a significant majority of young people have the right attitude in this matter. When asked "Do you take part in an organized collection of recyclable waste?", 63% of the respondents answered "yes" and 9% "yes, if not too complicated", while 23% of students would not have supported such an action. We investigated and how the students participated in the action for the environment, and their interest in specific actions, and what their habits that contribute to environmental protection. When asked "Which of the following activities do you think are the most interesting?", Young people in the highest percentage (38%) responded to the reforestation and planting of plants, while their equally interested in landscaping around the school and cleaning the park or forest (19%), less interesting to them is to clean the river (10%) and collecting paper, glass and other recyclable materials (9%). Questions under "something else" were answered by combining the previous answers, but to a greater extent, they attributed them to any of the above is interesting (4%). What specific actions are concerned, 27% of respondents often self-regulate the area around their home, 48% of it is edited the times, 11% and 15% even once. When you leave the room 46% regularly turn off TV and lights, 28% sometimes, 14% rarely and 12% never. When asked "Do you throw trash out of containers and waste baskets?" 45% of respondents answered 'no, never, 28% yes, when there is no waste basket, 22% yes, sometimes and 5% yes, often. When asked "Have you participated in environmental activities?", Respondents answered the following : 50% - yes, in those organized by the school, 9% - that, in those organized by someone else: 41% - no. It is interesting to note that the organizers of environmental action organized by someone other than school, and in which young people were involved, referred to action, "Good tree" (1%), "Clean up Serbia" (1%) and those organized by the local community (1%) and only one student said the action organized by "Cekom" and "Pannonian dawn" while several students indicated that they own or any of their relatives organized some of the actions. Other environmental groups - which Zrenjanin city has got 10 - are not mentioned at all. It was interesting to find out what young people think that the best way to solve environmental problems. So 11% of them thought it would be to achieve better education, 22% think that the problems are solved better home school education, learn about the importance of caring for others and nature, 30% believe that to achieve this by introducing stricter penalties for environmental violations to individuals and businesses, and these only 4% think that they should pay more attention to better information. About 25% of respondents considered it necessary to provide better infrastructure (better facilities for waste disposal, pest treatment and recycling of waste gases), 7% said that environmental problems are solved training and hiring experts. Several pupils mentioned that they would choose to combine several of these measures and these are generally cited a combination of stricter penalties and better infrastructure. The objections were mainly pupils mentioned that it takes a lot more waste baskets around town, it is necessary to organize more actions, build more sports fields surrounded by greenery and control the operation of factories. Also cited the need to introduce a regular class on nature conservation, the need to educate more people, and that the government should do more to take care of nature conservation. Several have expressed skepticism about the purpose of this type of research because they think that their opinions anyway no one is listening, nor can it take into account, for which blame the whole system in which we live, where everyone thinks only of oneself, and noted that "possible solutions to real implemented." "As long as we live in a system that was created by the disease called man, out of nothing," reads the opinion of one of the respondents. Some propose concrete actions for cleaning, planting flowers around the city, the use of electric cars, investing more money in the animal shelter, organizing trips to places with a preserved nature and a diverse culture of living in the community, and et cetera.

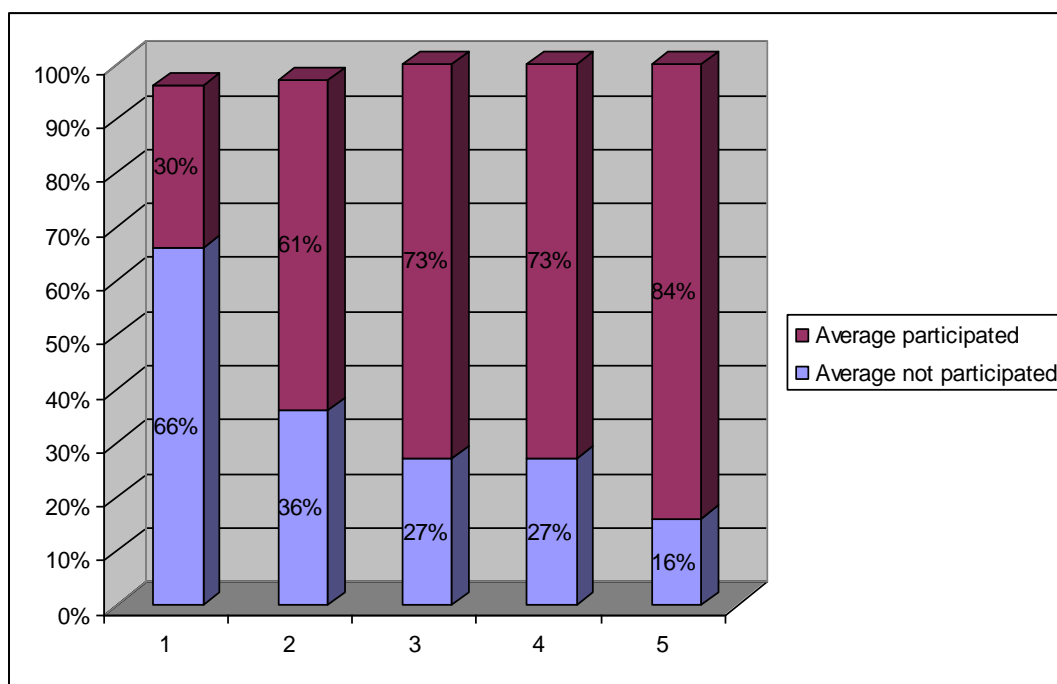
The crossing of the results with independent variables

At the intersection of the results of the independent variables in terms of involvement in environmental activities, knowledge and attitudes of accuracy, the girls are at an advantage relative to boys. High school pupils showed slightly better knowledge of and involvement of eighth graders, while their views as correct. Figure 2 shows that young people from rural areas are most involved in environmental action, and then the youth of the city, a minimum of involvement on this issue have

shown young people from suburban areas, while their knowledge and attitudes is on the same level. There was also a correlation between the level of knowledge and level of engagement. Pupils with greater knowledge have proven to be more active in environmental actions. Participation of students in environmental activities in relation to the average of knowledge shown by the two major issues is shown in Figure 3.



Picture 2. Youth participation in Zrenjanin in the environmental action



Picture 3. Engaging students in the environmental section of the level of knowledge

Some additional crossings we found that pupils who spend enough time outdoors, for about 10 to 20% are more motivated to participate in environmental action. When we wanted to examine whether children who train some sport, are more involved in environmental activities, we got exactly the same percentage of those who participate and those who do not participate in such actions, 50% -50%.

DISCUSSION

This study shows that young people from the municipality of Zrenjanin, aged 15 to 19 years, with average knowledge rated as satisfactory (on scale 1 to 5, rated 2), correct environmental attitudes and actions deemed mediocre. We cannot conclude whether it is in the past ten years that an increase has seen in environmental awareness of young people, because previous studies on this subject do not exist. However, we can conclude that the current state of environmental awareness is not high, but there is great potential in the form of readiness for action. With the general hypothesis we wanted to prove a connection between segments of environmental awareness. We believe that youth with higher levels of knowledge about the ecology are ready for environmental action; we have proved our study (Figure 3). While 83% of pupils, whose level of knowledge in the field of ecology rated at 5, took part in some of the environmental actions, the point is only 31% of those who were judged to have 1, participated in activities organized by the school, which in addition, presumably is required. Special hypotheses, that we wanted to prove, is that children from rural areas have more developed environmental awareness. The average knowledge score for children from rural areas was 2.025, and 2.065 of the children from city areas, while their positions are identical. The exception is the participation and willingness to environmental actions, where the children are from villages in the benefits (Figure 2) to ten percent. With this we conclude that children from rural areas are slightly more developed consciousness, which is reflected in the willingness to take action. The school is the most important factor in raising environmental awareness, given that the largest percentage of young people (41%) said that the most knowledge on this subject received from the teacher. However, these skills are, how we are rated at moderate or low. As one of the reasons we might state to the teaching of environmental protection is not well organized, nor are deeper methodological searched for solutions to environmental education and education of students. As for their proper development and cultural relationship to the objects of nature, which is one of the aims of education, we can say that the goal is half achieved, since about half of the respondents demonstrated through concrete personal action for the conservation of nature (not to throw rubbish out baskets, fire lights, landscaping around the house), that has a cultured attitude towards it. It is interesting to note that the subjects showed very low when the knowledge needed to list the ways they can contribute to the preservation of nature, so their answers on the culture of behavior, should be interpreted with caution. However, the school more than any other organization has managed to mobilize and engage young people to engage in environmental activities. Although 41% of young people not involved in any environmental activities, those who participated, it seems you are, overwhelmingly, the organization of schools. The influence of media on young people is evident and no one can deny.[3] We noted that in response to major environmental problems most young people on the planet mentions global warming and the ozone hole, two concepts that we hear most often in the media. The empirical findings show that the means of mass media have a remarkable ability to affect the ecological culture and to contribute to environmental awareness and adequate environmental behavior of people. Thus, we concluded in our study to the data that is TV for young people in a significant percentage (20%) source of knowledge on environmental issues, and we consider it important that their superficial reporting on ecology get more serious, deeper and more professional approach. Commitment to improving ways to utilize the mass media in the development of ecological culture among the citizens, is rooted in the fact that the environmental awareness of adults, as shown by previous studies, the level is low. And parents can teach children what they themselves do not know. Peer groups in our study proved to be an important motivator for taking environmental action. So that as many as 51% of respondents replied that would be included in the environmental section of the work if it included some of the friends and 44% of them would be involved in the cleanup river if that part was taken by their friends. First, law enforcement and improvement of infrastructure and better education, young people see as the solution of environmental

³ The publication of "Mladi i mediji", HCA, 2005, www.hcabl.org

problems. Comparison of our results and those obtained from the research conducted in 2003, among the respondents of all ages in the Zrenjanin LEAP was obtained that the youth agree with the rest of their fellow citizens who have the problem of drinking water cited as the most with what they have a similar importance to both pollution air, and other rivers and beaches. In the said research indicated that with a grain of looking at the activities and actions of local governments and NGOs, which, even in our study did not justify its existence. The skepticism that has been identified in the survey of citizens of Zrenjanin in 2003, in the Zrenjanin and youth is expressed in the comments of our questionnaire, where some also indicated they believe that their opinion no one is listening and that therefore any poll is meaningless. In a study from 2009, conducted by Jelena Stanisic, the sample of respondents consisted of 284 eighth grade pupils of elementary school.[4] When the results of their participation in environmental action of the youngest subjects compared with the results from our midst, we see that the results are similar in terms of readiness for engagement, which in both cases is high, and the most interesting activities where they are most receptive as specified organization and maintenance of green spaces around schools, reforestation and planting of plants.

CONCLUSION

To raise the environmental awareness of young people in Zrenjanin, which is in the work judged not to be on a high level, it is necessary to first of all systematically coordinate their actions, frequently organized, with accompanying lectures, and align with their interests, which will, through practical engagement, to achieve a double benefit - gaining knowledge and solving the concrete of an environmental problem. Also, it is necessary to improve the level of knowledge through the education system was reorganized to protect the environment, where in the world as much attention by deliberately and purposefully is directed in engagement of mass media in the development of ecological culture in general, and therefore the pupils.

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**II International Conference
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**ENVIRONMENTAL PROTECTION IN ELEMENTARY SCHOOL
EDUCATION**

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ABSTRACT

The education in the field of environmental protection is taught in the elementary school education, starting from the first and second grade through the subject The World Around us. In the third and fourth grade environmental protection is learnt within the subject The Nature and Society. In further elementary education the environmental protection is learnt at the classes of biology, chemistry, geography and physics. The paper describes the thematic units learnt during the natural sciences classes in the elementary school in the republic of Serbia.

Key words: *environmental protection, elementary education.*

INTRODUCTION

The environmental protection education plays an important role in elementary school curriculum. The environmental protection education represents the synthesis of knowledge of natural and social sciences. The environmental protection curriculum tends to develop knowledge on the human environment in order to develop awareness of the basic characteristics of the human environment and the relations in it. The education in the field of environmental protection should provide knowledge on basic issues of the contemporary society, increasing danger of nature destruction and emphasize the necessity of rational use of natural resources.

METHODOLOGY

The subject of interest was to determine the status of environmental protection in elementary school education in the Republic of Serbia. This paper analyzes the natural sciences educational programs that are implemented in elementary schools' curriculum. The analysis was made on the perception method.

THEMATIC UNITS ON THE ENVIRONMENTAL EDUCATION IN THE ELEMENTARY SCHOOL EDUCATION

In the first and second grade of the elementary school education environmental protection is studied within the subject The World Around Us (Official Gazette of the Republic of Serbia, no. 10/2004). The objectives of the subject The World Around Us is to develop the basic concepts of natural and social sciences, encourage the research skills in pupils, to make the observations on the changes around us and identify the causal and consequential relationships within the natural phenomena. In the third and fourth grade of the elementary school education environmental protection is studied within the framework of The Nature and Society (Official Gazette of the Republic of Serbia-Educational Gazette no. 6/2006). The aim of the subject The Nature and Society is to introduce to pupils the world around them and develop skills for responsible life in it. The subject - The Nature and Society is a continuing education to the subject The World Around Us and a beginning to the pupils for the basic scientific literacy, the basic observations of natural phenomena and processes. The elements

that characterise scientific discipline should develop in pupils capability to find the argumentation using empirical evidence and methods, find the link to the technology and find the scientific explanation of phenomena around them. The first element that characterise scientific discipline is empirical evidence. This method is as old as the rocks. The empirical evidence to support a hypothesis is one of the approaches. The next element is to find the link between science and technology, environmental protection and technology, with the positive or negative implamentation on the environment. One can notice that technological innovations are not always coupled to scientific advances, the advances in the environmental protection. The next element is knowledge, pupils have accepted during the lessons, to explain on the scientific ground the phenomena around them.

The environmental protection is taught within the classes of biology, chemistry, geography and physics in the elementary school. The paper describes activities that are studied under mentioned subjects. In biology, the environmental protection is incorporated in the courses in the fifth, sixth and seventh grade (Official Gazette of the Republic of Serbia-Educational Gazette no. 6/2006). In the fifth grade studied is the plant life on Earth, with an annual fund of 72 hours. During the sixth grade studied is the animal life on Earth with a fund of 72 hours. In the seventh grade studied is the ecology with the fund of 72 hours. Through these thematic units the material on the environmental protection is taught during the classes of biology. The recommended objectives of the biology courses are: that pupils gain responsibility on the environment protection, to understand the degree of vulnerability of the environment and develop awareness in order to preserve the environment.

Chemistry is a subject in the elementary school education taught in the seventh and eighth grade. In the seventh grade taught are the basic concepts of general chemistry classes with a fund of 72 hours. In the eighth grade learnt is the inorganic and organic chemistry with a fund of 68 hours (Official Gazette of the Republic of Serbia-Educational Gazette no. 9/2006). One of the objectives of teaching chemistry is to develop awareness on the importance of the responsible and rational use and disposal of various substances in everyday life.

Through the teaching of chemistry, pupils should gain the basic chemical literacy which should enable them to understand the environment. In the chemistry textbook for the eighth grade of primary education, there is a chapter on the Environmental Chemistry. Chapter describes the pollutants of air, water and soil and the protection measures. It is alleged that a man has a right to a healthy environment, clean water, food and air. Man, as a conscious being, has the obligation to preserve the nature. The textbook lists, the main polluters of the air and begins from the oxides of carbon, sulfur and nitrogen. Sources of the carbon oxides are products of combustion of fuel in furnaces and engines. Sulfur (IV) oxide is a product of burning coal that contains the sulfur compounds. The oxides of nitrogen are formed in the reaction of nitrogen and oxygen uniting under the influence of the electrical discharge (Mandic et al., 2010). The textbook states that measures to the reduction of carbon (IV) oxide in the air, is planting and maintaining of forests. Plants in the process of photosynthesis take carbon (IV) oxide and produce pure oxygen. In the textbook further is described the pollution of water. It is written that water pollutants are: natural contaminants (soil washing, dissolution of organic matter), waste water from the houses and industrial waste waters. Described in the textbook is that the solution to prevent the pollution of water is incorporation of the devices for the wastewater treatment and cleaning. It is outlined that the major polluters of the land are direct soil pollutants - pesticides and insecticides. Then, the land is polluted from the air by absorbing and dissolving the sulfur (IV) oxide and carbon (IV) oxide.

It is concluded that water, air and soil pollutants, are inorganic and organic substances. Within the additional texts in the chemistry textbook is the issue on packaging and polymers where it is stated that polymer materials can be recycled. One of the themes within these texts is on the soil fertilizers. The dissolution of the nitrate fertilizers is a main source of water pollution. To pupils is explained that the major nitrogen fertilizers are needed for the growth processes of plants, but excessive use of nitrogen fertilizer is the source of water pollution. The following topics within these texts is eutrophication, where it is explained to pupils that the eutrophication process is over-enrichment of the surface waters with nitrogen and phosphorus, which causes the huge development of the aquatic

vegetation. The consequences of eutrophication have been numerous. The prevention of eutrophication is the removal of phosphate from municipal waste.

The geography courses are taught from the fifth to the eighth grade. The environmental protection is mostly studied in the fifth grade through the thematic unit of the physical geography (Official Gazette of the Republic of Serbia-Educational Gazette no. 9/2006). It is recommended to explain to the pupils the need to protect the Earth's sphere and the complex geographical environment in which men live. During this course pupils get the geography knowledge on the importance of all the geospheres, which are the basis of the life on Earth and during this course pupils develop the responsibility towards the protection of the environment.

Physics is taught in the elementary school in the sixth, seventh and eighth grade (Official Gazette of the Republic of Serbia-Educational Gazette no. 6/2006). Through the teaching of physics pupils learn about the basic physical laws and phenomena that exist in nature. Through the acquisition of knowledge about natural laws and forces, types of energies pupils are directed to understand the renewable types of energies and the importance of the economical use of the natural resources.

In the elementary school natural sciences curriculum pupils acquire the basic knowledge on the environmental protection. For the elementary school education is important to transmit the ideas of reasoning with evidence, testing hypothesis, suggesting alternative ideas and creativity to solve problems of everyday life.

Through the classes of science pupils acquire basic knowledge about the environment through the thematic units that are described in textbooks and implemented in the teaching process. The classes include the following sessions: within the biology classes the disappearance of various plant and animal species is taught, through the chemistry classes the pollution of air, water and soil is taught, through the geography course the climate change caused by greenhouse gases is learnt and renewable sources of energy are learnt during the lessons of physics.

CONCLUSION

The education and learning in the field of environmental protection is necessary during the elementary school to develop pupils' awareness about the environment. An integral part of the awareness on THE environmental protection is willingness to engage pupils in the protection and preservation of the environment. Pupil gets the impression that the nature and sources of life have to be preserved. To achieve this, pupil should try not to disturb the natural balance and diversity. Environmental protection is a cost-effective management of natural resources, rational use of natural resources, recycling, biodiversity, etc. Teaching science in elementary school educates pupils to understand the basic principles on the environmental protection.

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**GENERAL CHARACTERISTICS OF ANIMALS RIGHTS
PROTECTION IN CONTINENTAL AND ANGLO-SAXON LEGAL
SYSTEMS**

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ABSTRACT

Protection of animal right has begun very late in many countries, but it assumes changes. Changes in moral attitude among the greatest number of people in relation to animal world reflected on protection of rights and welfare of animals in some countries. Namely, gradually they left extremely anthropocentric conception, and moved towards bio-centric ethics. The authors of this paper analyze general characteristics of legal systems in which, in the last few decades, very significant legislation steps have been made, when protection of animals and their welfare is in question. These legal systems have made a great progress in building and giving relevant legal protection of animals and they should serve as examples to other countries which are the beginning of this process. Firstly, Anglo-Saxon legal system is described, but since in the last several decades European countries lead in protecting animal rights and welfare, we paid special attention to continental system, with reference to good examples from German, Swiss and Swedish laws. New regulations in these countries anticipate completely new position of animals in legal relationship. In this way, legislations of European countries have improved in greatest extent towards the concept of protection of “animal rights”, so in this context we can talk about animals as passive subjects of law, but, first of all, we have in mind certain kinds of animals. Animal as “sensitive being” becomes a holder of rights and because of violation of these rights an offender should take responsibility for his deeds.

Key words: *protection of animal rights, welfare of animals, anthropocentric conception, biocentrism, law.*

INTRODUCTION

The protection of animal rights was initiated very late in many countries. However, in a great number of countries that protection hasn't even begun or hasn't moved so far. The change in a moral position of large number of people concerning the animal world reflected the protection of animal rights and welfare in certain countries. This phenomenon is particularly obvious in European Union countries. Namely, they gradually rejected the principle of anthropocentrism, according to which legal protection must be given only to humans from damages made by animals. It has been comprehended that legal protection must be given to animals from damages, both from killing and abuse, made by humans. That is why, in our theory, this change towards bio-centric ethics is confirmed by the following statement “anyway, bio-centric ethics directs us towards something because of survival of nature and complete flora and fauna, including humans” (Paunovic, 2004). Animal rights can be approached pragmatically, “by respecting the fact of deterioration of their life conditions and total biotical ecumene conditions” (Cifric, 2006). It is estimated that in the world about 40 % of all animal species are endangered. That is why, in theory, the statement that “that if the state weren't alarming, we wouldn't talk about natural rights and animal protection” is made.

Based on the critics of anthropocentrism, especially its practice and animal jeopardy, a wide movement for animal protection and their rights, which has its theoretical stronghold, has been developed (Tom Regan, 1983, Peter Singer, 1998, Desjardins, 2003.:121–137), “and which is, in the context of ecological ethics, nominated as “individualism” (Armstrong; Botzler, 1993.:318–368).(Cifric,2006).

An empiric research was published in Croatia and the results of the empirical research of animal species' rights to life which was carried out in 2005, on the sample of students from five faculties at the University of Zagreb (N=492). Techniques of univariate, bivariate and multivariate statistics were used in the interpretation of the results (component analysis by GK criterion). Respondents were asked to give their opinion about three concepts: biological egalitarianism – equal rights for all living beings, anthropological exemption – human kind has bigger rights than animals and Darwinian concept – species' rights gained in the fight for living space. The analysis showed that none of the views was greatly predominant: 58.1% of respondents accepted equal rights for human kind and animal species, 32.5% considered human rights superior to animals' and 20.6% chose Darwinian theory. Correlation analyses have shown a connection between those views and the results of survey about “responsibility for life”, “biocentrism”, “socio- ecological orientation” and “religious beliefs”. Biological egalitarianism (equal rights for all living beings) is largely accepted by respondents who favour man's “responsibility for all life”, “respect for life”, “eco-centrism” and “cosmic religion”, the left-oriented, students of science, mechanical engineering and the Faculty of Philosophy. Anthropological exemption (man's rights are bigger) is embraced by respondents close to “anthropocentrism” and “Christian beliefs”, male respondents, the right-oriented and students of Catholic Theological Faculty. Darwinian theory (species' rights gained in the fight for living space) is mostly acceptable to respondents who are inclined to the ideas of man's “responsibility for mankind only” and “anthropocentrism” and examinees from the Faculty of Medicine, Philosophy and Mechanical engineering (Cifric, 2007)

Several years later, based on the survey research carried out in Novi Sad, at the Faculty of Law, on animal rights and some other issues concerning ecological, biological and legal ethics, in the paper whose title was “On animal rights- attitudes of Faculty of Law students from Novi Sad who attended the course from Legal Ethics”, were analyzed and only the results related to animal rights were reported (N= 125) (Marjanovic, 2008). The analyses showed that 53,6% of respondents accept the opinion that, from the legal point of view, it cannot be spoken on animal rights. Variations, which were not so big, according to gender, average mark, political and religious orientations were explained. The statement that the God determines that humans control all animal and plant species accepted only 25.6 % of examinees and that protection of the environment is concern about God's creatures accepted even 63.2 % of them. From the previously mentioned research conducted at Zagreb University (2005) three claims were taken and the comparative results are the following: the statement that every animal species has the right to life like humans accepts 58.1% of examinees in Zagreb but in Novi Sad even 71.2%; the second statement that human rights are superior to animal ones (32.5%: 37.6%) and the statement that every species has as many rights as it manages to fight for comparing to other species (Darwinian conception) (20.6%:44.0%). It can be concluded that the attitudes of surveyed students from Novi Sad are dominantly “between moderate anthropocentric and bio-centric ethics but that a strange mixture of theological and Darwinian understanding exists.” (Marjanovic,2008). In the final part of the paper, the author discusses some theoretical questions about animal rights from the perspective of anthropocentric and bio-centric ethics in their radical and moderate variants. According to this, the main conclusion is that in legal theory and practice moderate anthropocentric comprehension is still dominant but that the arguments of bio-centric ethics are becoming more versatile, coherent and convincing.(Marjanovic, 2008)

Therefore, the researches confirm the statement that in the countries in which changes in moral attitude of people in relation to animals exist, and that these changes of attitude are moving from exceptional anthropocentrism towards bio-centric ethics, first of all, when it is about animal rights to life, this creates the necessity for animal rights protection. It needs to be examined how it reflects on norming of protection of rights and wellbeing of animals in certain countries.

In many contries, including ours, where the attitude towards extreme bio-centric ethics hasn't been changed yet, legal protection of animals and their wellbeing is very delayed. Such delayed legal protection of animal wellbeing, which has small results in practice, is followed by unequal protection

for different animal species. If this trend continues, there won't be any significant progress in animal rights protection, and specific attitude to this issue will still be present.

However, certain countries have made great progress in processes of building their legal systems for animal protection. In this paper we will mention only general characteristics of that protection, and the examples of some good solutions related to animal protection in countries which represent great legal systems, and according to our opinion, should serve as examples concerning this issue. These countries belong to Anglo-Saxon legal system, which will be first presented, and then the countries of continental legal system. Between these two systems, in spite of their differences, there is interaction, too². In these legal systems it can be even spoken about animal rights. Due to complex issues and the volume of the material, we cannot process every norm which exists in these countries, but we shall give only a review of general characteristics and the most significant solutions from both systems. The impact of international law is also significant, because of its great influence on the field of legal protection and wellbeing of animals.³

PROTECTION OF ANIMAL RIGHTS IN ANGLO-SAXON AND CONTINENTAL LEGAL SYSTEMS

Modern movement for animal rights protection has been developed since 80s, first in West-European countries and in the USA. The activities of this movement are based on critical relation which represents dominant pattern of behaviour towards animals (specism). Only with nonanthropocentric extension of traditional ethics and recognition of moral dignity to creatures who are different from humans, bases for developing moral obligations, empathy and feeling of duty and responsibility is created in order to correct the injustice made to animals (Zarden, 2006).

Not only in Western Europe and the USA, but all over the world, in the last few decades the number of organizations which deal with animal rights protection has been increasing. However, there are significant differences concerning the volume and types of their activities.⁴ In a certain extent, the level of movement development follows the level of economic development, so in economic developed countries these organizations are more numerous and active. Still, significantly smaller number of these activities in Asia (even in rich Japan), shows that a society's relation towards animals varies not only depending on economic, but also on cultural conditions. (Finsen and Finnsen, 1994)

British and American laws in the field of animal protection were, until the middle of 20th century, among leaders in some aspects of animal species protection. However, we would agree with certain authors that today's law can be evaluated in two ways (Paunovic, 2004), because it can be said that they still have relatively high position comparing to the rest of the world, especially in comparison

¹ The term "*specism*" (derived from engl. "species") denotes any form of human discrimination against animals as members of an inferior biological species. (Visković, 2004). In the theory it is distinguished that the term "specism" is denoted as kind of discrimination, in other words, unequal (moral, legal, etc.) treatment based on (non) possession of certain characteristics, in this case, belonging to human race (Zarden, 2007). Specism represents belief that all non-human species are inferior in comparison to a man and, as such, they can be used for satisfying human needs, no matter how much they suffer (Vukelic, 2012).

² Legal systems of Great Britain and the USA, which rely on case law and statute law differ from law in European countries, or in continental legal system in which the acts derive from the law.

³ Declaration on Animal Rights (Paris, 1978 Geneva, 1990) in fourteen points declared that animals are equal by birth and that they have equal rights to life, to be respected, that they must not be subjected to harassment, abandonment, experiments that cause suffering, etc., that they have the right to live in natural environment, as well as normal conditions in that environment, etc. In developed societies, acts on animal protection were passed. The first act on animal protection in Europe was adopted in England in 1822.

⁴ For example, recently, two acts, whose aim is to protect animals used in experiments, were adopted by means of associations for animal rights protection who were lobbying for this cause. Authorization Act is permanently established by Interagency Coordinating Committee on the Validation of Alternative Methods (ICCVAM). This Committee considers alternatives to testing on animals and recommends changes in testing procedures to relevant federal agencies. In addition, organizations for animal rights have managed to mobilize their members in order to adopt Act on health improvement and protection of chimps (CHIMP Act), which determines the system of safe places for chimps in state possession, and which were used in the experiments financed by federal state.

with economically less developed countries. Still, that advantage in relation to too slow approach of humanity to altruistic and bio-centric ethics, today shows delay when compared to the state of law in modern European countries. It can be concluded that continental systems by abandoning anthropocentrism take over a primate in animal protection and use of modern solutions in this field.

Protection of Animal Rights in Anglo-Saxon Legal System

Back in the nineteenth century, in Great Britain and the USA, as representatives of case law, organized efforts in order to confirm that human behavior towards animals had begun. In fact, in these countries, close relationship between man and animals could be observed many centuries ago. The first organized attempts to protect rights and wellbeing of animals can be traced back at the beginning of the nineteenth century in England. The act that prevents abuse of animals was passed in 1822, and two years later The Society for the prevention of cruelty to animals (which, from 1844, carries the name Royal Society for Prevention of Cruelty to Animals, RSPCA) was founded⁵. Not long after, similar initiatives came to life in America, when American society for the prevention of cruelty to animals (1866) was founded. Afterwards, a few hundreds of similar societies began their work across the country.

Although England is the homeland of the movement of anti vivisectionists, no legal prohibition/ban of scientific experiments on animals existed. Only when appropriate European convention was approved in 1985 and implementation of the European union directive in 1986 began, this matter started to stand out from general regulations on animal protection and is more fully regulated from 1986 with Act about animals (methods in science). This Act introduces a number of new provisions which protect animals being used for experiments or other scientific purposes.⁶

In the USA, at the federal level, different acts, which aim is to reduce animal suffering, especially domestic animals intensively bred on farms⁷ and animals which are used for experiments, have been only recently passed. ⁸In the 60s two laws, Act on Welfare of Animals and Act on Humane Slaughter (of animals), that have been subject of amendment for years, were passed.⁹ Unlike the Great Britain,

⁵ Public politics concerning the movement for welfare of animals in Great Britain started legally by passing one act in 1835 which consolidated and supplemented several previous sporadic acts related to cruel and indecent behaviour towards animals and it was finished in 1911 when the Parliament of this country adopted Protection of Animals Law which is still valid with some amendments. This law prohibits and punishes cruel behaviour towards animals and also causing unnecessary suffering of domestic and wild animals. All kinds of cruelty and other forms of unhuman behaviour towards animals are explicitly forbidden. This act regulates transport of animals in the way which could not cause their unnecessary suffering. Some forms of surgery related to animal which were not humans are also regulated. In other words, while people still have power and can subjugate animals the law only prohibits them to cause them unnecessary suffering. Although Protection of Animal Act was progressive for the time it was passed it is basically still anthropocentric. Theory explains this issue by the fact that it was only "concern for man who started feeling uneasy conscience because he causes unnecessary suffering to these beings" (Paunovic, 2004).

⁶ With Act about animals from 1986 laboratory testing of domestic and wild animals is legalized. However, this Act sets certain requirements (specifically for vertebrates) in terms of licenses for scientific institutions and individuals, for animal breeding and keeping, experiments, rules about anesthesia, euthanasia, keeping records and more strict state and non-state monitoring of these processes. This supervision is under the authority of Home Secretary and Animal procedures committee. With the adoption of Act about animals this, very important issue of animal protection, is compiled with European standards. That is why it can be concluded that this issue is much better regulated in England than in the USA.

⁷ The first regulation which is adopted in 1960, under the name Federal act on humane slaughter, demanded a humane practice from American Slaughtering Industry. In the attempt to strengthen legislation from 1960, in 1978 a new Federal act on humane slaughter was introduced, which aim was to ensure additional application of existing law in practice

⁸ In the USA an appropriate act concerning the treatment of animals which are being used in experiments was passed only in 1985. Although all federal states passed some kind of regulations against cruel treatment of animals, some of them excluded the issue of experiments on animals. In the meantime, two acts, which aim is to protect animals used in experiments, were passed, Authorization Act and CHIMP Act. Federal Animal Welfare Act (7 U.S.C. §§2131-2159) (Jasper, Appendix 3: str. 123-14) contains primary (basic) legislation adopted so far, and which considers usage of animals in biomedical experiments – practice known as "vivisection". The most important amendments to this act were in the form of legal act: Act on improved standards for laboratory animals, adopted in 1985.

⁹ In the USA, the state of New York, within its legislature, adopted its first Act against cruelty to animals in 1828. By the year 1921, all the other USA member-states adopted their regulations against cruelty to animals. However, it is still a problem, because in the USA, basically, protective legislation is under the supervision of federal units. Although, according

in the USA protective legislation concerning animals is mainly at the level of member-states of American federation. Although there is a difference between English, centralized and the law in the USA, which is federally established,¹⁰ from the above mentioned it can be concluded that they have in common that their first goals were preventing cruelty against animals and opposing to experiments on animals.

Nowadays, in these countries legal systems which protect animals have high level of standards. The question is in what extent are these standards respected in practice. Namely, there is certain resistance in implementation of adopted regulations. In theory it is explained by the opinion that " profit and economic development are in these countries, especially in the USA, the greatest in the world and numerous companies, when their profit is endangered, are trying to find ways to avoid the regulations." (Paunovic, 2004)

In the USA and in Great Britain, earlier than in all other countries, different movements for animal rights protection and welfare have been organized and are still active.¹¹ However, apart from previously mentioned legal activity and various activities of referent organizations and movements, animals in Great Britain and the USA are still not recognized as legal subjects or beings who are recognized by the law. In these countries animals are still only legal objects with a tendency that certain animals (pets and endangered wild animals) in certain legal relations " these beings start being treated as valuable and sensitive beings which impose to people not only economic interests but also certain obligations and duties"¹² (Paunovic, 2004).

Animal Rights Protection in Continental Legal System

Continental legal system is slowly, at least normatively, leaving anthropocentrism. In European countries, in the last few decades, there has been significant legislative progress concerning protection of animals and their welfare. Namely, continental system is based on the principle of legality, which is characteristic for European countries, which have lately passed separate acts on protection or welfare of animals or they supplemented and changed already existing acts within different legal branches. It resulted in new regulations which anticipated completely new position of animals in legal relations. That is why it is generally accepted attitude that legal systems of European countries came closer to the concept of protection of "animal rights", so in this context, we can speak, with great caution, about animals as passive subjects of law. However, legal systems of these countries still treat animals as objects of law. If we speak about animals as passive subjects of law, we speak about certain animal species.

We cannot even notice progressive movements in this field in legal systems of European countries. This legal position of animals, in most European countries, has been influenced by regional European conventions as well as recommendations, or resolutions, adopted within European Committee, but also

to those acts, appropriate sentences which varied were determined, terms such as "pain" or "suffering" of animals are rarely mentioned, which clearly indicates their anthropocentric character. (Viskovic, 465)

¹⁰ This fact isn't insignificant, because animal protection in the USA is much more uneven, depending on observed federal unit. In all 50 states in the USA there are valid regulations which protect animals from cruelty, which is a lot of regulations. All these regulations solidly forbid cruel treatment. Some authors believe that by these statutes and acts certain rights of animals are protected, so they mention following protected animal rights: 1. Right to food and adequate conditions of life, 2. Right to protection from abandonment, 3. Right to protection from poisoning, 4. Right to have humane transport. The problem is implementation of these regulations, because prosecution according to those regulations is rare and the penalties are relatively small, which reduces prevention of these offences commission.

¹¹ The first society for preventing cruelty against animals was founded in London in 1824. It was called Royal society for prevention of cruelty against animals. The goal of this society was to prevent cruelty against animals and improves treatment of animals, that is, treatment of animals as sensitive creatures and to involve as many people as possible in this kind of movement.

¹² Back in eighteenth century many jurists in Great Britain and in the USA began to discuss if animals feel pain and suffering, vivisection (cruel surgeries performed on live animals during experiments), cruel behaviour against animals produced only for food and religious teaching that humane behaviour must be directed towards humans and animals as well. (Guither, 1998).

different resolutions of EU bodies.¹³ Legal standardization of legislature in European countries, represents international, or regional character.

A good example, which can explain these attitudes in developed European countries represents protection of domestic animals, especially pets. Under strong influence of European convention on protection of pets, from 1987 which was recently rectified by our Parliament, the protection of cats and dogs, as most wide-spread pets, has been especially distinguished. Other animals, which are also kept in houses are not left without protection, even of criminal law. It is especially referred to different endangered wild animals, which are the subject of universal protection. Legal position of dogs and cats has improved significantly and along with them of many other pets, at least in EU countries. In criminal legal codes of these countries new chapters related to delicts against, are being introduced.¹⁴ The one who abandons and throws out on the street dogs, cats or any other pet will be criminally liable. Prison sentences are predicted for those who abuse or kill animals.¹⁵

Unlike previous legislation and practice when the laws protected only animal owners – so when someone tortured or killed pets they could sue and demand a sentence, that is an indemnification, for personal suffering – according to new laws, the animal itself as “a sensitive being” becomes the holder of rights and when these rights are affected the torturer has responsibility to animals. We can say that dog, at last, in most European countries, have gained appropriate legal protection. The owner no longer can throw his dog out on the street, nor torture him, and especially he cannot use dogs for dog fights.

Although in European countries these new regulations are generally approved by altruistic publicity,¹⁶ there is awareness that their implementation in practice is difficult. Unfortunately, implementation of law, concerning the animal protection, is different in real life. Verdicts that punish violators of these laws are still rare. This condition is burdened by deeply rooted man-animal relations. Great problem lies in process failures. Although animals are treated as alive and sensitive being, animals as victims cannot by themselves participate in the process or to report a crime. A man should point on those problems and, in the same time, provide undeniable proofs to the court, which is very difficult in the practice.

As we have mentioned in the introduction, our aim is to process general characteristics of protection, but we shall list the examples of some good solutions of animal protection in the countries which, according to our opinion, should serve as an example for animal protection in modern times.

As for the animal protection, in legislation activities, Germany leads in Europe. Namely, the example of Germany is very important because it became the first European country which decided to

¹³ As an example, we emphasize that, in Germany from 1976, the whole field of protection of animals bred on agricultural farms has been regulated by special orders based on European convention on protection of animals bred on agricultural farms

¹⁴ For example, in the Criminal Act of Austria, a chapter is introduced with only one member that refers to torturing of animals. It is chapter 11 under the title “Torturing of animals”: Those who treat animals with cruelty or cause unnecessary suffering to them will be sent to prison for a year or will pay fee of 360 daily fines. Even those who act negligently will be punished too, because they avoided to feed or to water animals, or to torture them in longer period of time. Forrger - Sereni, StGB - Strafgesetzbuch, 6. Auflage, Manc-tezxtauslagen, 1982. From 23 May 1949. (BGB1.S.1), with last changes from 26 June 2002. (BGB1.IS.2863).

¹⁵ Criminal provisions of Act on animal protection Tierschutzgesetzes from 1986. are especially important, and they determine great financial as well as prison sentences for everybody who violates the provisions of this act. For example, in the member ¹⁷ of this act it is anticipated that criminal act which is punished with two years of prison to those who: 1. Kill vertebrates without reasonable reason or 2. To vertebrate a. Causes significant pain and suffering or b. Inflicts longer or serial pain or suffering.

¹⁶ The following example shows how new regulations in European countries get general approval of publicity. In Switzerland, Federal Court of Switzerland in 1989 recognized animals as “alive and sensitive beings, as close creatures (beings) (...) that should be respected and which serve as moral precondition for humans who are only thanks to their intellect superior”. (Ruling of Federal Court BGE 115 IV 254). This opinion on „dignity of creatures (beings)“ was broadly accepted in public in the struggle against genetic engineering. Referendum was held so that this opinion can find its way to Federal Constitution of Switzerland. At the referendum held on 17 May 1992 in the member 120, paragraph 2 of the new Federal Constitution this opinion was adopted through special provision.

guarantee by its Constitution protection and right of animals. The main law in Germany,¹⁷ the Constitution, by its separate provision, adopted during the latest changes of this act, obliges the state on this protection.¹⁸ On the base of this provision,¹⁹ German Constitutional Court will have to balance animal rights in comparison to other rights, such as right to scientific research or the right to perform religious ceremonies (whose subjects are animals). From the stand point of legal technique in Germany is norming of animal protection has been performed which much more details and more completely than in other European countries. It has been done, first of all, by general regulations which are related to protection of the environment, ²⁰which protects endangered wild animals, and by general regulations which are related to prohibition of cruelty against domestic animals, in other words only all vertebrates, or by a great number of regulations in different legal branches in which some animals are protected in different legal relations (civil law, criminal law, sanitary law, administrative law, customs law, etc.). There is a great number of regulations in Germany related to protection and welfare of animals but the most significant one is The Act on Animal Protection (Tierschutzgesetz) from 1986,²¹ which according to many solutions leads in European countries and many other countries, for example Switzerland, Sweden, Netherlands have taken it over. The provisions of this Act represent inspiration for legislators in many countries.

Member 1 of the Tierschutzgesetz from 1986, shows that in Germany we can speak about modern regulations which leave anthropocentrism and follow the newest moral beliefs related to animals because they treat them in greatest extent as beings with their own interests and values.²² In this member of the act we see that there is responsibility of man towards animals as co-beings, by protecting their health and life and that nobody must, without any reasonable reason cause pain, suffering or injuries to animals. This provision indicates several new things that will direct modern legislation. All animals ²³ are no longer observed as objects which are completely at man's disposal, but as man's co-beings to whom humans mustn't cause pain or suffering. Many authors in this provision find a compromise with traditional approach which is still present in the words "that we mustn't do that without "reasonable reasons"", because it can be understood differently, like in citation "but traditional relations towards animals is in legal relations seriously damaged" ²⁴Paunović, 2004). In German law the institution of Trustee for animals which is a step forward to recognition of passive subjectivity of animals. ²⁵A significant feature of this act is pretty broad legal protection of different kinds of domestic and wild animals found in all severe conditions in which they can be found due to

¹⁷ General Act of Germany from 23 May 1949 (BGB1.S.1), with the latest changes from 26 June 2002. . (BGB1.IS 2863).

¹⁸ The member 20 of General Act of Germany says: „ Taking into account self-responsibility and responsibility towards future generations the state protects natural basis of life and animals, withing constitutional order, via legislative, and based on law and legislation, via executive and judicial power.“

¹⁹ In the theory an opinion is stated that the member 20a of General act of Germany „ is not well fitted in the system of general act“ (II chapter of General act, titled Federal state and countries, but not in the first chapter titled General rights, where this provision should be placed) (Paunovic, 2004)

²⁰ The Act on Nature Protection from 1976 with changes from 1986, That Orderth Bundeses Tenschtzverordnung from 1986, with a list of permanently protected species including those protected by The Order of European Community Commission no. 3626/82 which adopted CITES Convention (Gunter, 1998)

²¹ The Act on Animal Protection in German version from 18 August 1986 (Federal official paper I 132', the translation of this act (A. Bužančić) published in *Zbornik pravnog fakulteta u Splitu* p. 101-119)

²² The member 1 of *Tierschutzgesetz* in 1986 „ The purpose of this act is to protect animals and their health because of man's responsibility for animals as co-beings. No one must cause pain, suffering and injuries to animals without reasonable reason“.

²³ At least principally (from invertebrates to primates), because later, many provisions are dedicated to vertebrates

²⁴ These changes have caused changes in many branches of law. So, the Civil Act in Germany was renovated in 1990, with special chapter 2 with a title "Objects and animals", in which a paragraph 90 was added, and which says: "Animals are not objects. They are protected by special acts. Relevant regulations which are meant for objects are used for them as well, if nothing else is not especially predicted" (BGB) Bürgerliches Gesetzbuch, 2002. Animals and their injuries are still subject to criminal punishment (par. 242, par. 303) Palandt, Heinrius, Bürgerliches Gesetzbuch, 61. Auflage, München, 2002, par. 90 a, n.l.

²⁵ Although the role of trustee is limited to „to performing experiments on vertebrates“, his duty is to humanize such experiments in accordance to member 7 of the act which determines the conditions under which these experiment on animals can be performed.

modern industrial society. In addition, the act protects vertebrates as beings which are scientifically proved to endure different feelings, including pain and suffering.

In continental legal system, Switzerland is a country which in terms of animal protection and welfare stands out because it has broad constitutional provisions, that give a basis for animal protection (Federal constitution of Swiss Confederation from 18. April 1999-state 3. March 2002). The great autonomy of Swiss cantons made it possible to some of them, for example Zurich canton, to make brave steps in the field of animal protection by introducing a completely new legal institution such as “the right of the association to complain against administrative act” and “the lawyer for welfare of animals in criminal affairs for Zurich canton”. However, we consider that the institution of a lawyer for welfare of animals is of great importance. He is nominated by Canton Government to initiate law-suits based on criminal responsibility of those who broke this law from 1991, and he receives reports of organizations for animal welfare, if there were any animal rights and their interests violation. The lawyer for welfare of animals has the right to be present at investigations of certain cases, when the act is violated, he has the right to question the accused persons, witnesses or experts as well as the right to complain at first instance decisions to federal bodies. In Switzerland, on the grounds of constitutional changes the adopted legislature is especially significant in the fields related to experiments on animals, passed in accordance to modern understanding of bio-centrism.²⁶

Very important example is Sweden which has appropriately, with its legal system, protected animals in accordance with European and universal standards. Beside the series of regulations which are related to protection of nature where many endangered wild animals species are under protection, Sweden has particularly made progress in the field of protection of domestic animals which are exploited in agriculture. By the Act on Animal Protection from 1986 it was completely consolidated previously adopted legislation concerning animal welfare in unique legal act.²⁷ That is why it is distinguished in theory that these regulations serve as examples for other countries because they show how to organize the field of animal breeding on farms, “suffering of these animals will be reduced, as long as economical conditions show that it cannot be abolished for the time being”. (Visković, 1986)

CONCLUSION

The protection of animal rights was initiated very late in many countries. However, in a great number of countries that protection hasn't even begun or hasn't moved so far. The change in a moral position of large number of people concerning the animal world reflected the protection of animal rights and welfare in certain countries. Namely, they gradually rejected the principle of anthropocentrism, according to which legal protection must be given only to humans from damages made by animals. It has been comprehended that legal protection must be given to animals from damages, both from killing and abuse, made by humans.

Based on the critics of anthropocentrism, especially its practice and animal jeopardy, a wide movement for animal protection and their rights.

²⁶ In accordance to the Act on Animal Welfare in Switzerland from 1981, these beings do not have real rights, but they have protected interests which include to be free from pain, protection of physical and mental integrity and the value of life.

The fact that animals are much more than objects with certain interests was first established in federal court in Switzerland when in 1989 the animals were recognized as „alive and sensitive beings“ that should be respected and which represent moral precondition for men who is only thanks to his intellect superior. This opinion about animals as “dignified beings” is widely accepted in public and after referendum it was introduced in new federal Constitution as constitutional provision 28. This provision in a certain way overcomes animal protection in the field of genetic engineering and experiments on animals. It has also come into the very essence of man-animal relations because the use of the term referred to “dignity of beings” has certainly changed the relations of man to animal welfare (and probably to animal right) in different fields, for example in breeding animals, relations towards pets, etc.

²⁷ In what extent the Act on Animal Protection in Sweden influenced breeding of some kinds of animals on farms show regulations which followed. Based on the member 4 of The Act on Animal Protection a provision on protection of domestic animals was adopted in 1988, which protects animals on farms and previously mentioned European convention.

The researches confirm the statement that in the countries in which changes in moral attitude of people in relation to animals exist, and that these changes of attitude are moving from exceptional anthropocentrism towards bio-centric ethics, first of all, when it is about animal rights to life, this creates the necessity for animal rights protection.

In many countries, including ours, where the attitude towards extreme bio-centric ethics hasn't been changed yet, legal protection of animals and their wellbeing is very delayed. Such delayed legal protection of animal wellbeing, which has small results in practice, is followed by unequal protection for different animal species. If this trend continues, there won't be any significant progress in animal rights protection, and specific attitude to this issue will still be present. However, certain countries have made great progress in processes of building their legal systems for animal protection. The impact of international law is also significant, because of its great influence on the field of legal protection and wellbeing of animals.

British and American laws in the field of animal protection were, until the middle of 20th century, among leaders in some aspects of animal species protection. They still have relatively high position comparing to the rest of the world, especially in comparison with economically less developed countries. Still, that advantage in relation to too slow approach of humanity to altruistic and bio-centric ethics, today shows delay when compared to the state of law in modern European countries. It can be concluded that continental systems by abandoning anthropocentrism take over a primate in animal protection and use of modern solutions in this field.

Continental legal system is slowly, at least normatively, leaving anthropocentrism. In European countries, in the last few decades, there has been significant legislative progress concerning protection of animals and their welfare. It resulted in new regulations which anticipated completely new position of animals in legal relations. That is why it is generally accepted attitude that legal systems of European countries came closer to the concept of protection of "animal rights", so in this context, we can speak, with great caution, about animals as passive subjects of law. However, legal systems of these countries still treat animals as objects of law. If we speak about animals as passive subjects of law, we speak about certain animal species.

We cannot even notice progressive movements in this field in legal systems of European countries. This legal position of animals, in most European countries, has been influenced by regional European conventions as well as recommendations, or resolutions, adopted within European Committee, but also different resolutions of EU bodies. In criminal legal codes of these countries new chapters related to delicts against, are being introduced.

Unlike previous legislation and practice when the laws protected only animal owners, according to new laws, the animal itself as "a sensitive being" becomes the holder of rights and when these rights are affected the torturer has responsibility to animals.

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**ENVIRONMENTAL PROTECTION IN ELEMENTARY SCHOOL
TEXTBOOKS OF BIOLOGY AND CHEMISTRY**

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ABSTRACT

Abstract. Thematic units on the environmental protection present in the elementary school textbooks of biology and chemistry in the Republic of Serbia and Republic of Montenegro is described. On the market there are several publishers of textbooks and school teachers are able to choose the one of the textbooks offered. This paper describes the thematic units taught in the textbooks for the fifth grade biology curriculum and the chemistry for the eighth grade curriculum in the Republic of Serbia. From the 2004/2005 school year, the Republic of Montenegro has introduced the elementary school education of nine years. The paper describes the chapter on the protection of the environment found in the textbook for the sixth grade biology curriculum and the chemistry curriculum in the ninth grade in the Republic of Montenegro.

Key words: elementary school, textbook, biology, chemistry, environmental protection.

INTRODUCTION

In the elementary school education in the Republic of Serbia, biology is taught in the fifth, sixth, seventh and eighth grade. Biological topics are learnt from the first grade of the elementary education through the course The World Around Us and in the third and fourth grade through courses of the subject Nature and Society (Official Gazette of the Republic of Serbia, no. 10/2004 and Official Gazette of the Republic of Serbia-Educational Gazette no. 6/2006.). From 2004/2005 school year, the Republic of Montenegro has switched from the elementary school education of eight years to elementary school education of nine years. (Informator o devetogodisnjoj osnovnoj skoli, 2004). Elementary school in the Republic of Montenegro is compulsory and free for all children and private elementary schools do not exist (Montenegro in the XXI century – in the era of competitiveness, 2010). By moving to the nine-year elementary school curricula have changed. Changes of curricula, printing of textbooks and equipping the schools with the teaching materials are the conditions to be complied in order to achieve the successful ongoing educational reform.

MATERIALS AND METHODS

The study was the analysis of the thematic unit distribution of the environmental protection in the elementary school textbooks of biology and chemistry. The survey aims to describe the thematic representation of the environmental protection units within the elementary school teaching of biology and chemistry.

ENVIRONMENTAL PROTECTION IN BIOLOGY TEXTBOOKS

Pupils during the elementary education should get the knowledge on the living world, natural phenomena and laws that govern it. By learning biology pupils develop basic scientific literacy, logical reasoning, develop critical thinking, develop the respect for the nature and the duty to preserve and protect it (Biology curriculum, Official Gazette of the Republic of Serbia-Educational Gazette no. 6/2006.).

In the biology textbook for the fifth grade of the elementary education described is the disappearance of plants and fungi and their protection. The policy framework of this thematic unit describes the use of gentian plant, whose bitter root is used as a medicine (Jancic et al., 2007). Strong demand for gentian root has led to the plant disappearance from the meadows. In order to prevent the disappearance of plant species laws on the protection. On the mountain Tara is prohibited the logging, collection of medicinal plants and making fire in order to preserve the plant life. The textbook further presents four national parks: the Djerdap, Fruška gora, Kopaonik and Tara, and these are the areas where the plants and animals are protected from the devastating effects of irresponsible people. At the end of the textbook, to pupils is explained the concept of biodiversity and the importance of nature conservation. Every day a man pollutes rivers, air, meadows and forests. The attention is drawn to the need for a rational use of natural resources.

In the biology textbook for the seventh grade elementary school in the Republic of Montenegro, there is a chapter on Human being and the biosphere within which to pupils is describe the following units: Balance is important, Clean air and drinkable water, Waste and what to do with it, Biodiversity and its protection and National parks (Božič Krstic et al., 2010). To pupils is systematically introduced and explained the basic concepts in the enviromental protection. It begins with a description of the disturbances in the biosphere, which the human beings have caused changing natural communities. Excessive cutting of forests, conversion of meadows into the fertile land, excessive hunting and fishing and uncontrolled desepearance of herbs are some of the main damage to the nature. A concrete example of how human beings have destroyed the natural balance is the example of the introduction of one carp variety in the lake Skadar which has reduced the population of the carp variety. To pupils is explained which human activities have led to the negative changes in environmental quality. It is described, the accumulation of substances which do not decompose naturally: plastics, rubber, glass and heavy metals. Next, the negative environmental change is the introduction of toxins that accumulate in plants and through the food chain come to the human beings. The concept of monitoring is introduced-tracking and analyzing the composition and quality of water, air and land. Next topic in this chapter is on clean air and drinkable water. To pupils is explained that clean air and drinking water, everywhere on Earth, has become very precious. The question is: What pollutes the air? It is alleged that the air polluting gases are a result of the fossil fuels combustion. The coal, oil and gas after oxidation give sulfur oxides. Due to the high temperatures in car engines, nitrogen oxides are formed. The methods for the measurement of air quality are described. The method can be instrumental analytical or a natural one, the indicator can be the lichens. When on the tree are lichens, there is no sulfur dioxide in the air. The formation of acid rains is explained and that the increased amounts of carbon dioxide in the air induce the greenhouse effect. The sources of drinking water and the way it is polluted is written. The thematic units under this chapter, Wastes and what to do with it, explain to pupils the possibility of recycling the waste. The products that can be recycled are: paper, glass, plastic, etc.. In the thematic unit Biodiversity and its protection explained is what is biodiversity, how to protect flora and fauna and the Red Book, in which endemic, rare and endangered plant and animal species are noted. It is alleged that the rare and protected plants in Montenegro are: *Taxus baccata*, *Quercus robur* and *Wulfenia bleicii*. Rare and protected animals in Montenegro are: *Triturus alpestris*, *Lucanus cervus* and *Salmothymus obtusirostris*. The National Parks are: Durmitor, Biogradska gora, Lovćen and Lake Skadar.

ENVIROMENTAL PROTECTION IN CHEMISTRY TEXTBOOKS

Chemistry is a subject in elementary school education in the Republic of Serbia taught in the seventh and eighth grade. In the seventh grade are taught the basic concepts of general chemistry, and in eighth grade learnt is the inorganic and organic chemistry (Chemistry curriculum, Official Gazette of the Republic of Serbia-Educational Gazette no. 9/2006.). One of the objectives of teaching chemistry is to develop awareness on responsible and rational use and disposal of various substances in everyday life. Through the teaching of chemistry, pupils gain basic chemical knowledge which should enable them to understand the environment. In the chemistry textbook for the eighth grade of the elementary education, there is a chapter on Environmental Chemistry. Chapter describes the pollutants of air, water and soil and the protection measures. It is alleged that a man has a right to a healthy

environment, clean water, food and air. Man, as a conscious being, has the obligation to preserve the nature. The textbook lists, the main polluters of air and starts from the oxides of carbon, sulfur and nitrogen. Source of carbon oxides are products of combustion of fuel in furnaces and engines. Sulfur (IV) oxide is a product of burning coal containing sulfur. Oxides of nitrogen are formed in the reaction of nitrogen and oxygen uniting under the influence of electrical discharge (Mandic, Korolija, Danilovic). The textbook states that the measures to reduce carbon (IV) oxide in the air is planting and maintaining the forests. Plants in the process of photosynthesis take carbon (IV) oxide and produce pure oxygen. The textbook is further describing water pollutants. It is said that water pollutants are: natural contaminants (soil washing, dissolution of organic matter), waste water from the household and industrial waste waters. The major polluters of the land are direct soil pollutants - pesticides and insecticides. Then, the land is polluted from the air by absorbing and dissolving sulfur (IV) oxide and carbon (IV) oxide. It is concluded that water pollutants, air and soil ones are inorganic and organic substances. Within the text for the curious pupils is a text on the packagings and polymers, which states that the polymers are recycled materials. One of the themes within the text for the curious pupils is, on the dissolution of nitrate fertilizers which are a source of water pollution. To the pupils is explained that the major nitrogen fertilizers are needed for the growth process of plants, but excessive use of nitrogen fertilizer is the source of water pollution. The following topic within the textbook for the curious pupils is Eutrophication, where the eutrophication process is described as an over-enrichment of surface waters with nitrogen and phosphorus, which causes the development of aquatic vegetation. The consequences of eutrophication have been numerous. The prevention of eutrophication is the removal of phosphate from municipal waste.

In the Republic of Montenegro, chemistry is taught in the eighth and ninth grade of the elementary school. In the eighth grade taught are the basic concepts of general chemistry and inorganic chemistry. In the ninth grade learnt is the organic chemistry. Within the thematic unit Petroleum hydrocarbons, environmental pollutants of air are described (Trivic et al., 2010). Described is that the biggest air polluters are oxides of carbon, sulfur and nitrogen. Describes the formation of acid rains. The possibility to prevent the air pollution is the application of filtration, chemical treatment or catalytic decomposition before the polluted air reaches the atmosphere. In the chapter on Polymers described is the physical properties of polymers, properties of some polymers, the use of polymers and the polymers and the environment. Within the thematic unit of polymers and the environment mentioned is the increasing use of polymers. Polymers are stable and chemically inert, what causes concern about the possibility of recycling it. The solution is the use of biodegradable polymers and polymer recycling.

CONCLUSION

Contents on environmental protection is found in textbooks of biology and chemistry in elementary school. These concepts are interesting for pupils and pupils can gain knowledge on the environment. Last editions of the textbooks tend to describe the thematic units, that are taught in the elementary school, more diverse, more comprehensive, more interesting and attractive to pupils. The main goal is to achieve the knowledge that will be useful in everyday life. Printing of textbooks and teaching materials for schools are the conditions to be fulfilled in order to improve the education in the field of environmental protection.

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ICT IN THE ECOLOGY OF URBAN AREAS

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GREEN IT INITIATIVE IN SCHOOLS

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ABSTRACT

Information technology presents one of most important infrastructure elements of organizations. Organizations go green in many working areas, motivated mostly by regulations. In recent years, green IT initiative is widespread in organizations. Most of the organizations that applied green IT practices are production and service organizations. Special types of organizations are educational institutions, where green IT initiative should also be applied. In this paper it has been presented how green IT initiative could be applied in schools. A model of application of Green IT is proposed. Application of the model presents a basis for defining and conducting improvement projects in schools.

Key words: *green IT, school management, ecology education.*

INTRODUCTION

Environmental protection has been introduced many years ago at state and government level throughout policies and laws and regulations. These regulations state requirements of human behavior regarding environmental protection, as well it requires certain organizational process and technologies to adapt to the needs of environmental protection. Organization infrastructure, business processes and human behavior should be changed in aim to be dedicated to minimize environmental impact. Usually, ecology movement that is focused on environmental protection is simply called “going green”, or in organizations: “corporate social responsibility”, sustainability etc. (Martinez, Bahloul 2008).

“Green IT” is another short name for efforts in the field of information technology construction and usage in aim to minimize their impact to environment (www.greenit.net). There are several approaches in Green IT activities organization. One of them is called “cleaning IT”, which means that existing information technology should be used with less power and material resources, improving technical performances of existing hardware equipment. Others are directed towards better construction of equipment. Third is focused on “cleaning business by using IT”, which means that information technologies are used to improve business processes effectiveness, and therefore improve their impact to environment

In this paper generally is presented Green IT as movement- goals, directions and activities in this field. Particularly, focus is made on how Green IT is used in organizations, especially educational institutions. Educational institutions are non-profit organizations and goals of “going green” are much different comparing to business organizations. In this paper we propose a model of green IT initiative process that could lead to implementing green IT efforts in schools. We propose set of projects that could be applied in schools, according to the proposed model.

THEORETICAL BACKGROUND

Green IT is broader term that is related to whole information technology products lifecycle, from production, using, reuse and recycling. “This includes the goals of controlling and reducing a product’s environmental footprint by minimizing the use of hazardous materials, energy, water, and other scarce resources, as well as minimizing waste from manufacturing and throughout the supply chain. Green computing goals extend to the product’s use over its lifecycle, and the recycling, reuse, and biodegradability of obsolete products.” (Harmon and Auseklis, 2009).

In the phase of using, Green IT is called green computing and is mostly related to improvement (related to environmental impact) of information technology application. Green computing is “the practice of maximizing the efficient use of computing resources to minimize environmental impact” (Harmon and Auseklis, 2009). “Green computing is the study and practice of using computing resources efficiently and that the main objective is to minimize the pollutions of environment. Green computing is considered as a major contributing factor to green environment. Green computing has a significant impact in green environment because modern societies dependent on IT for works and operations, and that the production and disposal of computer wastes would directly poison our green environment. There is no easy solution to green computing because it is complicated mix of people, IT hardware, and production.” (Chow and Chen 2009). “We define sustainable IT services in broader terms to include the impact of IT service strategies on the firm’s and customers’ societal bottom line to include economic, environmental, and social responsibility criteria for defining organizational success.” (Harmon and Auseklis, 2009)

Factors that influence environment and are related to IT are called Green IT impact factors. In research (Laszewski and Wang 2009) the model that present relationship of categories of green computing factors is presented. The proposed model presents four categories: Hardware (processors and other computer units, consumption of energy and producing heat), Software (n-tier layers software, software as service, efficiency of using hardware resources, speed of algorithms), Working environment for hardware (design of buildings, heat, ventilation and air conditioning (HVAC), computers rack) and Behavior (definition of metrics for green impact, people behavior directed by education and policies).

RELATED WORK

Green computing history is divided in two phases (Harmon and Auseklis, 2009). First phase is called “green computing” and is related to: factors driving the adoption of green computing (rapid growth of Internet, increasing equipment power density, increasing cooling requirements, increasing energy costs, restrictions on energy supply and access, low server utilization rates, growing awareness of IT's impact on environment), implementing green computing strategies: data center infrastructure, power and workload management, thermal load management, product design, virtualization, cloud computing and cloud services) and development of green computing metrics (energy efficiency, environmental impact). Second phase is called “sustainable IT services” and is related to: moving from software programs to software as service, developing sustainable IT services according to criteria (service sustainability, temporal sustainability, cost sustainability, organizational sustainability and environmental sustainability), moving goals from business value to customer value to societal value, developing sustainable IT strategy and introducing environmental regulations.

In recent years, there are several studies conducted with IT professionals and IT companies related to green IT and green computing motivators and sources of green direction forces. Green IT application main motivators for IT professionals study (Tebbutt et al. 2009) shows that most frequent reason for introducing green IT are regulations and cost savings, while PR image, customers requirements, genuine concern and shareholder pressure is less frequent. Another survey is conducted with European large IT companies directors (Martinez, Bahloul 2008) and it shows that great majority of number of IT companies that have already green IT strategy for IT infrastructure are from Germany and UK, less from Nordics and France, while the least are from Italy, Spain and Netherlands. Green IT initiative

driving forces for these IT companies are mostly: cost reduction/savings, regulatory compliance, reaching sustainable level of energy consumption, while recycling and corporate social responsibility are less present. Finally, the least present are chief executives forcing, transparency to company carbon footprint, brand image, customer expectation, employers choice and employees initiatives.

Green IT initiatives present activities that are moving forward in implementing environmental protection goals in the field of IT production and implementation. These activities could be categorized according to previously presented four categories of impact factors (Laszewski and Wang 2009).

In the field of behavior category, there are several types of activities. At international level, corporate sustainability index is defined as a standard metrics system for measuring application of environmental initiatives in organizations (Chakraborty, 2009). Company level is related to introducing policies and procedures for implementation of green IT, established internal recycling programmes, conducting energy audits in the workplace (Adamson et al. 2005), encouraging remote working and teleconferencing as a travel replacement (Martinez and Bahloul 2008). Education level is related to introducing Green IT seminars, Green IT graduate diplomas and professional certificates for IT professionals (www.greenit.net), research on educational impact (Katz 2010) and role of green IT in computer science curriculum (Talebi and Way 2009). Personal level include activities such as using fewer IT resources such as printing paper and read only DVD/CD, power off computer when not using it, dimming the PC brightness etc. (Chow and Chen 2009).

Hardware and working environment for hardware include green IT initiatives and activities such as: investing in technology such as hardware and software virtualization to increase datacenter efficiency (Martinez and Bahloul 2008), more efficient processors, flat monitors, smaller hard disks use less energy (Roy and Bag), consolidation of storage (Katz 2010), devices are designed to have idle/sleep mode (Tebbutt et al. 2009), remote shut down of computers (Katz 2010); networks - centralization of printer devices, database and processors with thin clients, mobile devices - mobile phones, PDA, laptops - less time of charging, recycling; reusing heat from air-conditioners, while travelling / using satellite/communications devices and software for navigation and shortest travelling routes, using sensors that could remotely measure and control devices, substitution of physical process to digital (Tebbutt et al. 2009).

Some of green IT initiatives in software aspect include: scheduling algorithms (Laszewski and Wang 2009), creating autonomous software controllers of quality of service and energy management (De Palma et al. 2010), having software monitor state of usage of hardware devices and optimize its usage (Tebbutt et al. 2009), defining metrics for distributed software project management environmental impact (Kazi et al. 2011).

APPLYING GREEN IT INITIATIVES IN SCHOOLS – A MODEL AND SET OF PROJECTS

Data that is used in the model of applying green IT initiatives in schools is presented at Table 1. This model is created as integration of theoretical approaches in this field that were previously presented.

Table 1: Data of the model of applying green IT initiatives in schools

GREEN IT initiatives: 1. Cleaning IT 2. Cleaning business by using IT		
TARGETS:		
PROCESS (Behavior aspect)	OBJECTS	ACTORS (Behavior aspect)
Basic business process: education	Teaching materials and documents	Teaching staff Pupils/Students Parents
Supporting processes: infrastructure, equipment and materials supply and maintenance, administrative work, human resources work	Infrastructure (including working environment for hardware) Equipment (including: Hardware, Software) Materials	Administrative staff
Management processes related to: basic business process and related to supporting processes.	Regulations, laws, procedures	Management staff

In separate section there are two major types of green IT initiatives that we called: cleaning IT and cleaning business by using IT. These initiatives are targeted to processes, objects and actors in schools. A model of applying green IT initiatives is actually a three dimensional cube (Figure 1):

- One side of cube has *targets*,
- Other side of cube has *green IT activities*
- Third side of cube is *time*, since efforts of applying green IT activities are performed during time, with results that occur in certain period of time.

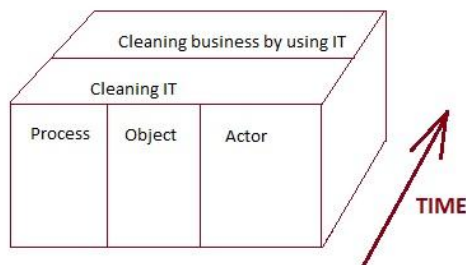


Figure 1. A three dimensional cube – a model of applying green IT initiatives in schools

This model could be a directive for implementation of Green IT approach in schools. Application could be performed in the way that for each of targets both cleaning IT and cleaning business by using IT is performed. Efforts to implement these activities are performed during time, and usually need set of projects to be conducted for each targeting problem or area.

Proposed set of some projects (based on proposed model), that could be implemented in schools for improvement of existing Green IT state is presented at Table 2.

Table 2: Proposed set of projects

TARGET	Cleaning IT	Cleaning business by using IT
PROCESS (Behavior aspect)		
Basic business process: education	Paperless communication	Using educational software for educational process improvement
Supporting processes: infrastructure, equipment and materials supply and maintenance, administrative work, human resources work	Supply and maintain infrastructure, equipment and materials that are green IT certified	Using Internet for communication with suppliers (email) and parents (web site of school), creating software for administrative work support (increasing paperless communication)
Management processes related to: basic business process and related to supporting processes.	Paperless communication with other staff	Creating management support software, such as data warehouse and business intelligence systems Encouraging green IT behavior by special grants to teaching and administrative staff Encouraging pupils/students for green IT behavior by competitions and grants
OBJECTS		
Teaching materials and documents	Paperless communication and teaching material	Educational content at school website, on-line learning by e-learning systems at school web site
Infrastructure (including working environment for hardware) Equipment (including: Hardware, Software) Materials	Buying green IT certified equipment to enable teaching staff and administrative staff to use computers in their work	Creating efficient software for administrative work, in aim to support minimize power consumption
Regulations, laws, procedures	Procedures for using IT equipment in green IT manner	Establishing support for e-learning accreditation
ACTORS (Behavior aspect)		
Teaching staff Pupils/Students Parents	Education to use existing IT equipment in green IT manner	Education in IT application
Administrative staff		
Management staff		

CONCLUSION

Green IT is one of human working areas that present effort to minimize impact of IT to environment. This area covers all phases of information technology production, using, reusing and recycling. Especially in the field of using, it is called green computing.

There are many factors that influence Green IT. Categories of factors are hardware, software, working environment and behavior. Qualitative characteristics of these groups of factors influence current state of green IT in organizations. Several studies show that most motivators for green IT application for IT professionals and IT organizations are regulations and cost and energy savings. There are many green IT initiatives that are implemented at hardware and software level, as well as at human behavior level.

In this paper a model for applying green IT is presented. The proposed model presents a three dimensional cube – one side are targets (process, objects, actors), second are initiatives (cleaning IT, cleaning business by using IT), while third is time, since efforts and results are created within time. The proposed model is basis for set of projects, that could be implemented in schools and therefore improve existing state of green IT in these organizations. The set of projects is proposed in aim to illustrate the proposed model possible implementation.

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II International Conference
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DATABASE MODELING IN ECOLOGY

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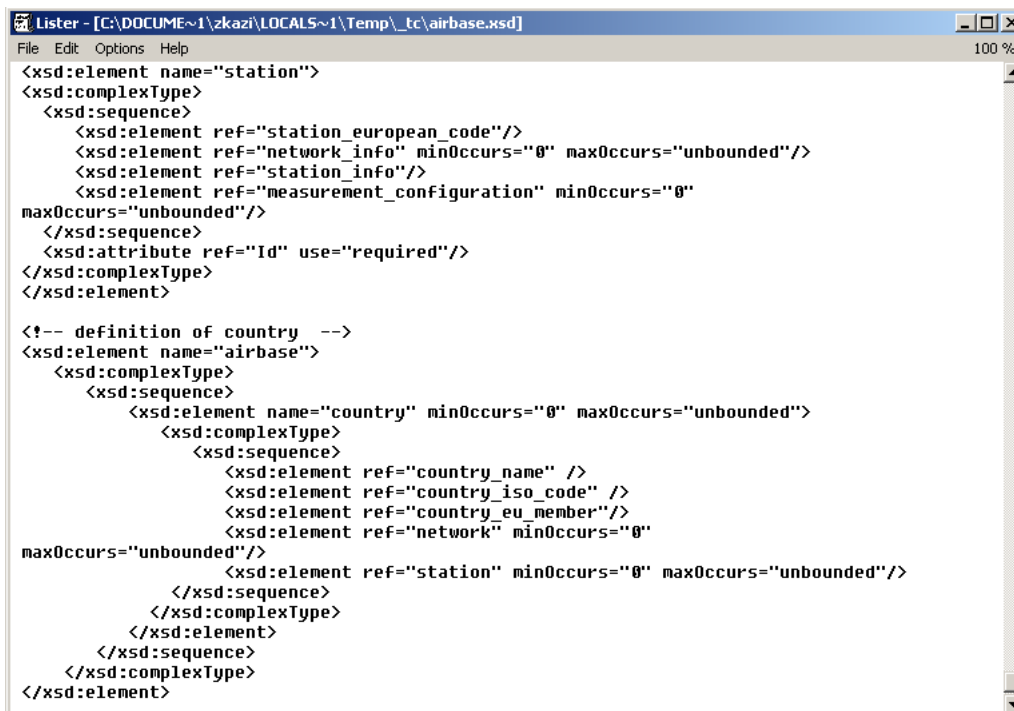
ABSTRACT

This paper presents a process of database design in ecology area from structured data that was found on Internet. We described basic terms in area of data models and databases. Conceptual and Physical data models are presented, as well as implemented models in Relational database management system.

Key words: *database, ecology, model, schema.*

INTRODUCTION

The structure of this database database is designed according to data structures used in XML source files from European air quality database (see Figure 1). AirBase is the air quality information system maintained by the EEA through the European topic centre on Air and Climate Change (European air quality database). Also, at the web site of Provincial Secretariat for Protection of Environment and Sustainable Development of Vojvodina region we found data that present measurements from seven measurement stations accross Vojvodina. Each station's measurements are presented with PDF files, where each file presents data for each month (in year 2008) or each day (from 2009). Combing this structured data files from Internet, database in area of ecology is projected in Sybase Power Designer tool and implemented in Microsoft Access database management system.



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Listner - [C:\DOCUME~1\zkazi\LOCALS~1\Temp\_tc\airbase.xsd]
File Edit Options Help 100 %
<xsd:element name="station">
  <xsd:complexType>
    <xsd:sequence>
      <xsd:element ref="station_european_code"/>
      <xsd:element ref="network_info" minOccurs="0" maxOccurs="unbounded"/>
      <xsd:element ref="station_info"/>
      <xsd:element ref="measurement_configuration" minOccurs="0"
maxOccurs="unbounded"/>
    </xsd:sequence>
    <xsd:attribute ref="Id" use="required"/>
  </xsd:complexType>
</xsd:element>

<!-- definition of country -->
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  <xsd:complexType>
    <xsd:sequence>
      <xsd:element name="country" minOccurs="0" maxOccurs="unbounded">
        <xsd:complexType>
          <xsd:sequence>
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            <xsd:element ref="country_iso_code" />
            <xsd:element ref="country_eu_member"/>
            <xsd:element ref="network" minOccurs="0"
maxOccurs="unbounded"/>
          </xsd:sequence>
        </xsd:complexType>
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</xsd:element>
</xsd:sequence>
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</xsd:element>

```

Figure 1. XML file with ecological data

DATABASE MODELING

Data models are usually created in the process of information systems development by using CASE tools that integrate business process modeling results to data modeling. Data models are specific theoretically based specifications that are used for creation of real databases of information systems (Elmasri & Navathe, 2007). Data model is a formal abstraction through which the real world is mapped in the database (Ullman et al., 2002).

Data model enables representation of a real world system through a set of data entities and their connections. They can be represented in various ways:

- Diagram (schema) – graphical representation, using specific set of symbols with methodology based meanings,
- Data dictionary representation – where elements of data model are listed and textually described in non-structural or semi/structural way,
- Formal languages representation, such as predicate logic calculus.

A data model is a representation of the information consumed and produced by a system. Data modeling involves analyzing the data objects present in a system and the relationships between them. Power Designer tool provides conceptual, logical, and physical data models to allow you to analyze and model your system at all levels of abstraction.

One of the fundamental principles of the database approach is that a database allows unified representation of all data managed in an organization. This is achieved only when methodologies are available to support integration across organizational and application boundaries. Methodologies for database design usually perform the design activity by separately producing several schemas, representing parts of the application, which are subsequently merged. Database schema integration is the activity of integrating the schemas of existing or proposed databases into a global, unified schema. The aim of this research is to provide first a unifying framework for the problem of schema integration, then a comparative review of the work done thus far in this area. Such a framework, with the associated analysis of the existing approaches, provides a basis for identifying strengths and weaknesses of individual methodologies, as well as general guidelines for future improvements and extensions. (Batini et al., 1986)

CONCEPTUAL DATA MODELING

A Conceptual data model represents the structure of future database, independent of any software or data storage structure. It describes entities (things of significance to a organization) and their identifiers and other attributes, along with the relationships and inheritances that connect them. An entity represents an object about which you want to store information.

Attributes are data items attached to an entity, association, or inheritance. An identifier is one or many entity attributes, whose values uniquely identify each occurrence of the entity. Each entity must have at least one identifier. If an entity has only one identifier, it is designated by default as the primary identifier.

A relationship is a link between entities. An occurrence of a relationship corresponds to one instance of each of the two entities involved in the relationship. An inheritance allows you to define an entity as a special case of a more general entity. The general, or supertype (or parent) entity contains all of the common characteristics, and the subtype (or child) entity contains only the particular characteristics.

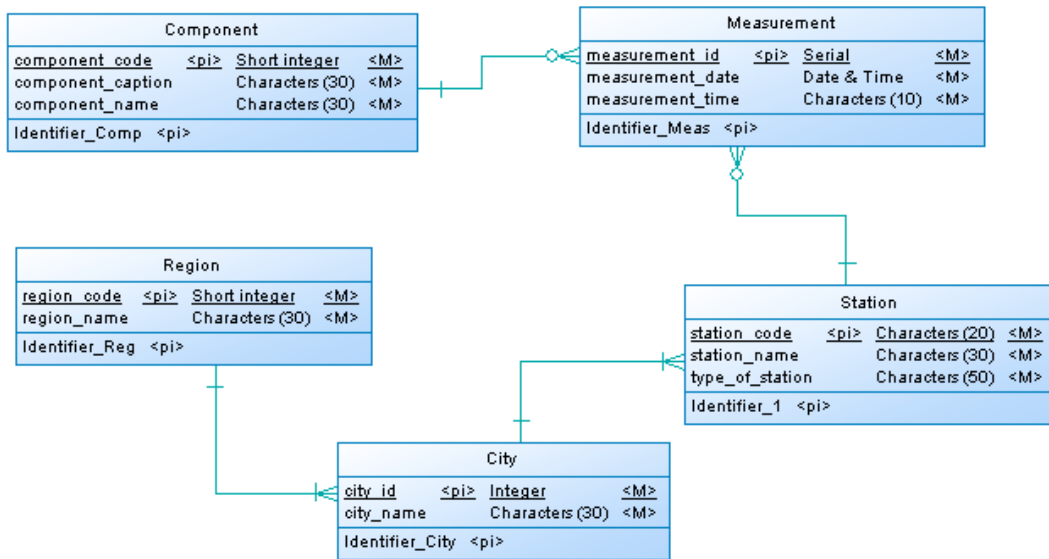


Figure 2. Conceptual data model schema

In Conceptual data model we defined:

- Entities,
- Attributes (data items) of entities,
- Identifiers of entities,
- Relationships between entities (see Figure 3).

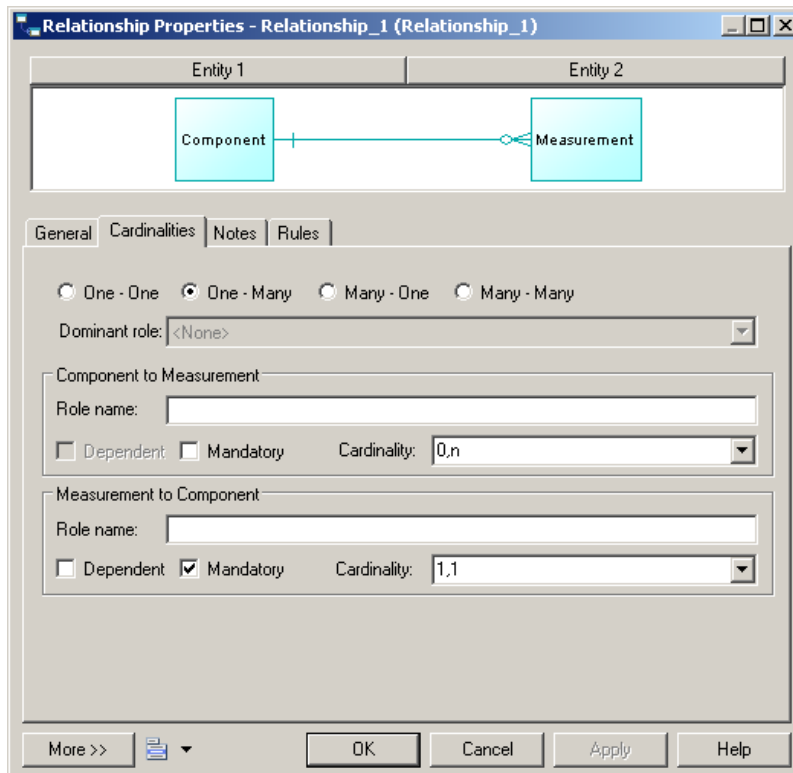


Figure 3. Relationship properties

After creating Entity Relationship data model (Conceptual data model in our example, Figure 2), CASE tool enable automatic transformation to logical or relational data models, following well-defined rules.

PHYSICAL DATA MODELING

A physical diagram (see Figure 4) allows you to define a database structure from the physical implementation point of view. It takes into account the physical resources: database management system, data storage structures and software, to describe the structure of the database. You build a physical diagram at the end of the data analysis process, before you start the software programming. The physical diagram allows you to define how data from conceptual model are implemented in the database. A table represents a collection of data arranged in columns and rows. Tables may contain any of the following objects:

- Columns are named properties of a table that describe its characteristics.
- Indexes are data structures associated with a table that are logically ordered by key values.
- Keys are columns, or combinations of columns, that uniquely identify rows in a table. Each key can generate a unique index or a unique constraint in a target database.
- Triggers are segments of SQL code associated with tables, and stored in a database. They are invoked automatically whenever there is an attempt to modify data in associated tables.

A column contains an individual data item within a row. It is the model equivalent of a database column. A column is always defined for a table. When you create a column, it must be assigned a name and code. You can also select a data type for the column. This can be done directly from a list of available data types, or by attaching the column to a domain. Key is a column, or a combination of columns, that uniquely identifies a row in a table. Each key can generate a unique index or a unique constraint in a target database.

The physical diagram supports the following types of keys:

- Primary - Column or combination of columns whose values uniquely identify every row in a table. A table can have only one primary key.
- Alternate - Column or combination of columns (not the same column or combination of columns as for a primary key) whose values uniquely identify every row in a table.
- Foreign - Column or combination of columns whose values are required to match a primary key, or alternate key, in some other table.

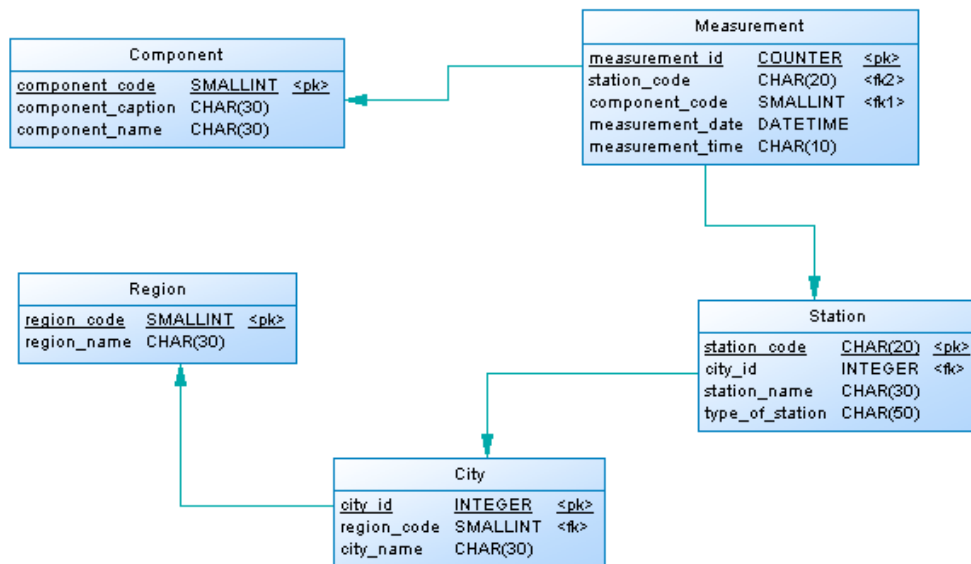


Figure 4. Relational data model schema

A database management system is a software package with computer programs that control the creation, maintenance, and use of a database. It allows organizations to conveniently develop databases for various applications by database administrators and other specialists. A database is an integrated collection of data records, files, and other objects. A database management system allows different user application programs to concurrently access the same database.

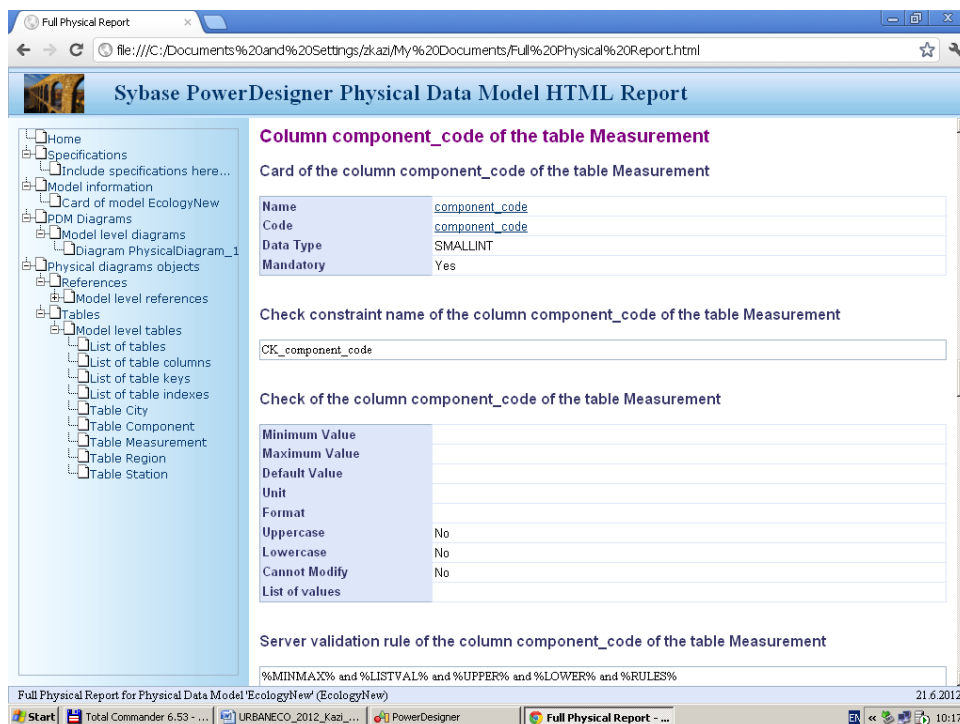


Figure 5. Data dictionary report

Data dictionary representation – where elements of data model are listed and textually described in non-structural or semi/structural way,

Power Designer tool can generate a database creation script that you can run in your database management system environment or generate a database structure directly to a live database connection. After executing script the process of database creation is completed and finished.

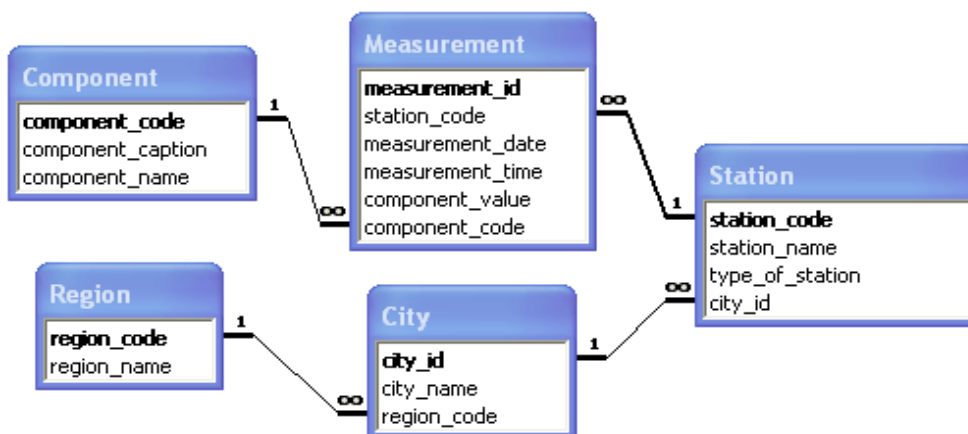


Figure 6. Created database schema

DATA ACQUISITION

Collected data about air pollution that has been measured by automated monitoring stations across the Vojvodina province in Serbia. For each hour a day, automatic stations are designed to monitor pollution levels of values of following components: ozone (O₃), oxides of nitrogen - nitrogen monoxide, nitrogen dioxide (NO, NO₂, NO_x), sulphur dioxide (SO₂), carbon monoxide (CO), particulate matter (PM₁₀, PM_{2.5}), hydrogen sulfide (H₂S), benzene, toluene, m.p-Xylene, o-Xylene and ethylbenzene. Monitoring data were stored and published as Adobe Acrobat file format (PDF) at Internet portal of Provincial Secretariat for Protection of Environment and Sustainable Development

of Vojvodina region, Serbia. We use public access of these data from <http://www.eko.vojvodina.gov.rs>. These measurements acquired data for each day (date) and appropriate time (hour, minute), having measurements each hour a day. These measurement data are concentrations of CO, SO₂, NO, NO₂, NO_x, O₃, H₂S, PM₁₀ (Particulate Matter 10), Benzene, Toluene, m.p-Xylene, o-Xylene and Ethylbenzene, with other relevant data such as: air temperature, atmospheric pressure, wind speed and wind direction. All the measurement units of air pollutant values are [$\mu\text{g}/\text{m}^3$] except for wind speed [m/s] and air temperature [$^{\circ}\text{C}$]. We converted data from PDF format to simple ASCII text format using Adobe Acrobat Reader tool (Save as text option). This ASCII file is imported by Microsoft Excel tool to be transformed to Microsoft Excel table. Within MS Access tool we imported MS Excel file data and they are transformed it to rows to fill projected relational database tables. (Kazi et al., 2011)

component_code	component_caption	component_name
1	SO2	Sulphur dioxide
2	H2S	Hydrogen sulfide
3	WS	Wind speed
4	CH3	Toluene
5	PM	Particulate matter
6	C6H6	Benzene
7	O3	Ozone
8	NO2	Nitrogen dioxide
9	NO	Nitrogen monoxide
10	CO	Carbon monoxide
11	T	Temperature

Figure 7. Ecological data in relational database table

CONCLUSION

Projecting database from structured XML and PDF data of air pollution monitoring and European air quality database requires specific knowledge in area of information technologies and database design, software tools and transaction processing data. But, the final result is database that can improve the work of researchers in ecology area, who can create analysis of these data from the database. This kind of implemented database also can be used as a support for making strategic decisions. Managers, researchers or others can make their own analysis by creating queries, charts or datawarehouses.

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ACCIDENTS IN URBAN AREAS

**II International Conference
„ECOLOGY OF URBAN AREAS“ 2012**

**LIQUEFIED PETROLEUM GAS (LPG) ACCIDENTS, ECOLOGY AND
FORENSICS**

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ABSTRACT

Liquefied petroleum gas (LPG), better known as auto-gas, is very representative fuel for motor vehicles, ecologically the cleanest (it is a mixture of propane and butane which combustion product is watervapor), economically the most affordable and, from the aspect of security, the safest fuel exploited at present. It is used in 15 million cars across the world. Japan, Italy, Netherlands, South Korea, Australia are countries with the most cars using LPG and in Europe it is most common in Vienna, Moscow, Kiev and Prague. The security of auto-gas system is on much higher level than one using petrol (higher thickness of reservoir wall, attest is done under pressure of 60 bars, safety valve reacts on pressure of 30 bars and has three valves, contrary to petrol reservoir which has one or no valves at all). Now days there is expansion concerning usage of LPG system, competition is strong and quality is suspicious therefore there is an increase in improvisations in the process of installation (non-adequate components are being used with lack of skill, while known trademarks are falsified). In this paper one example of forensic case study connected with explosion of gas reservoir is presented.

Key words: *Liquefied Petroleum Gas, Ecology, Accidents, Forensics.*

INTRODUCTION

The usage of liquefied petroleum gas (LPG) started in 19th century. By the end of the century, the production rate was over 30000 engines using gas. The transport of LPG in that time wasn't solved technically, so the gasoline replaced gas. Again, gas became popular in the beginning of 20th century during the Great economic crisis. Today, around 14,6 million vehicles use gas: Japan (taxi), Italy, Netherlands, South Korea, Australia are the countries in the world that have the highest number of vehicles using gas, while in the Europe this type of fuel is most popular in Vienna, Moscow, Kiev and Prague. LPG is mixture of Propane and Butane (ecological fuel), which ratio varies depending on country. For example, in England and Ireland just propane is used. In Denmark, Belgium and Netherlands that ratio is 50:50, in Greece 20:80, in Spain 30:70. Italy has vehicles that use 50% of gas and 50% gasoline (mostly public transfer vehicles).

INSTALLATIONS FOR LPG AND TYPES OF DEVICES

Figures 1 and 2 finely describe the types of built-in LPG devices.

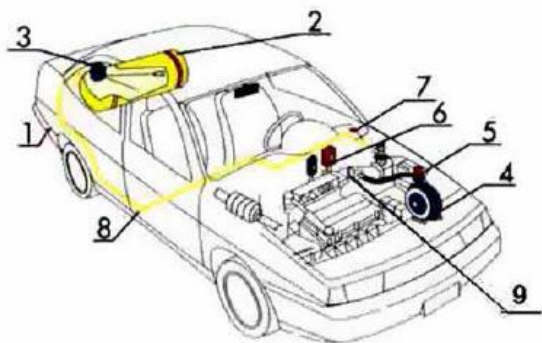


Figure 1. Connection supply, reservoir, evaporator, mixer

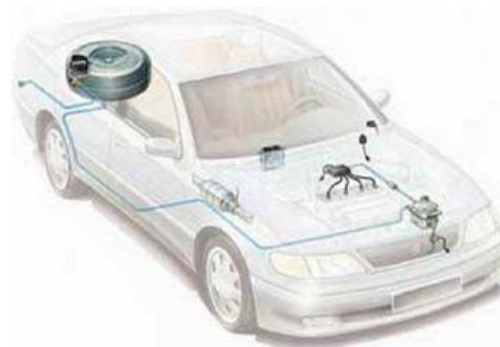


Figure 2. Toroid reservoir and built-in system

Work system for both types of built-in is the same. Difference is only in the type of tank showed in figures 3 and 4.



Figure 3. Cylindrical reservoir ($V=45-100\text{ dm}^3$)



Figure 4. Toroid reservoir ($V=33-59\text{ dm}^3$)

All reservoirs are tested for the pressure of 3 MPa (30 bars) as well as for the breaking pressure (min. 6,75 MPa (67,5 bars)). Authorized services on the territory of Novi Sad and Belgrade are providing 10-year warranty for the built-in reservoirs.

SAFETY OF AUTO GAS DEVICES

Safety of LPG devices is far higher than of gasoline installation: tank thickness is 3-4 mm, attest is done for the pressure value of 60 bars, while the valve is reacting on the pressure value of 30 bars. On the tank valve, there are two more safety valves and a valve that disables filling above 80% of tank volume (because of the dilatation of gas on higher temperatures). Evaporator is constructed in such way to disable gas flow when the engine is turned off (regardless of contact), and the tank is filled from outside and the valve box eject the excess of gas. For example, gasoline tanks have one and some have neither one valve, while modern gasoline tanks are plastic.

EXAMPLES OF ACCIDENTS

Statistics of Ministry of Internal Affairs of Republic of Serbia indicates increased number of accidents due to the great expansion of installations of gas systems, great competition, suspicious quality and the increase of improvisation level, as well as because of falsification of some trademarks (Lovato is being hoaxed instead of BRC).

From the work of Ministry of Internal Affairs of Republic of Serbia, we separate two accidents connected with LPG installations.

Example of accident 1: Passenger vehicle of mark Zastava type 128, near Novi Sad on the open road completely burned out with the driver. During the investigation, a non-exploded boiler tank was noticed as well as abruption of supplying pipe for gas, and is a consequence, as it was determined latter, of work performed in nonauthorized service.

Example of accident 2: Passenger vehicle of mark Zastava type Yugo 55, in tenement area of Novi Sad (faculty campus), exploded! Driver parked the vehicle and after just a few seconds tremendous explosion happened. During the investigation, parts of vehicle were found even on the distance of 100 meters from the place of event while the tank was found 30 meters from vehicle.

On the several photographs, investigated vehicle is shown as well as some parts of vehicle.



Figure 5. Place of accident



Figure 6. Investigated vehicle



Figure 7. Back side of the vehicle



Figure 8. Lateral side of vehicle



Figure 9. Front side of vehicle



Figure 10. Part inside the trunk



Figure 11. Part of shed metal from trunk



Figure 12. Reservoir-tank, 30 meters from vehicle



Figure 13. Deformed reservoir



Figure 14. Closer look of tank with manometer

After commenced analyses and obtained results it was determined that the tank was overfilled due to the unprofessional method of filling – decantation from the household tanks. In addition, air temperature was extremely high on that day, over 40°C.

CONCLUSION

All obtained statistical data of Ministry of Internal Affairs of Republic of Serbia concerning accidents related with vehicles with built-in gas system indicate that these accidents happened due to the unprofessional handling during the installations of gas systems, low-quality parts (obtained from primitive production) or during the exploitation.

Forensic approach to the mentioned accidents turned out to be algorithmically correct, as well as interpretation of obtained results and their connection with the legal event, leading to the explanation of accident.

Liquid petrol gas or commonly named in Serbia-“gas”, represents ecological fuel, economically costeffective and with high level of security comparing with other systems (gasoline, diesel).

ACKNOWLEDGMENT

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ENVIRONMENTAL ASPECTS OF TRAFFIC IN URBAN AREAS

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**POTENTIALS FOR DEPOLLUTION END-OF-LIFE VEHICLES AND
THEIR IMPORTANCE FOR ENVIRONMENTAL QUALITY IN SERBIA**

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ABSTRACT

Using a large number of motor vehicles has caused many negative impacts on the environmental quality during the last decades. These influences are expressed not only during the operation of the vehicles, but also at the end of their life cycles. This paper provides an overview of hazardous components in the vehicle at the end of the life cycle and the side effects which may occur due to their uncontrolled waste into the environment. These harmful substances cause that an end-of-life vehicle (ELV) is considered as a hazardous waste. Proper depollution and using of the specialized equipment can minimize the negative impacts on the environment. There is no precise statistics on the number of recycled vehicles in Serbia. Thus, the amount of the properly treated pollutants is unknown. This paper presents how the potential environmental impacts differ on the various percentage of recycled cars in Serbia.

Key words: *depollution, end-of-live vehicle, hazardous components.*

INTRODUCTION

The development and widespread use of motor vehicles during the last century have made transportation of both the goods and people easier. The latter two have created better conditions for economic and business development. That's why, people almost didn't pay any attention to the negative sides of the use of motor vehicles, particularly to their negative impacts on the environment, until recently. With the idea of the sustainable development came the question about vehicle's negative influences to the environmental quality. It turned out that they make a very significant source of pollution, starting with the manufacturing process and ending with the end of their life cycle. This paper is restricted only to removing the hazardous components from the vehicle at the end of its life cycle, the process known as depollution. Large amounts of the end-of-life vehicles create a serious problem in almost every country. Serbia also faces this problem. Furthermore, it is very difficult to make a good estimate of the amount of discarded motor vehicles in Serbia, especially recycled ones. Nevertheless the vague statistics for end-of-life cars and small vans (ELVs) which are to be scrapped exists. That's why this paper is restricted to them. Motor vehicles were collected only so that their metal parts could be recycled, until recently. From the environmental aspects this is not the best possible solution. It is true that it had reduced landfill of old cars, but the fact is that their most dangerous waste hadn't been treated properly. It had caused the environmental pollution. Proper separation of hazardous materials is a prerequisite for minimizing the negative impacts of the ELVs to the environmental quality. The easiest way to accomplish this is by using specialized equipment for the depollution of vehicles, especially for removing fluids from the vehicle. It prevents leakage into the environment and fluid mixing. In order to recycle the liquid it is necessary to organize separate collection and storage of different fluids. This can be achieved by using a single tank for each liquid type. Fluids are contained in the interior of the ELV, in appropriate housings, tanks or devices. That's why fluids are usually hard to come by, which is another reason to use the specialized depollution equipment. Using this equipment facilitates the manipulation of the vehicle during the depollution process, a vehicle is placed in the most advantageous position, fluid is taken out and the vehicle is sent

for further treatment. Vehicle’s depollution, done with the specialized equipment reduces to a minimum the negative impacts on the environment and the health of employees.

THE QUANTITIES AND TYPES OF HAZARDOUS COMPONENTS FROM THE ELVs IN SERBIA

Depolluting process includes removal of all potentially hazardous components: battery, wheels, lead balance weights, LPG tank, potentially explosive materials, all liquids in the ELV (fuel, motor oil, transmission oil, gearbox oil, hydraulic oil, cooling liquids, antifreeze, brake fluid, air con fluids, windscreen wash), oil filters, components containing mercury (i.e. some switches), catalyst, fluid from the shock absorbers or the shock absorbers themselves. This paper is primarily oriented toward the proper treatment of fluids from the ELVs. In order to determine the amount of hazardous components it is necessary to know the number of motor vehicles which are discarded per year. It is estimated that this number ranges from 4% to 6.7% of the number of registered vehicles (Arsovski and Pavlović, 2009). An estimation of the number of ELVs in Serbia is given in Table 1. It is based on the number of registered cars in Serbia (SORS, 2012). The results shown in Table 1 are only an estimation of the total number of ELVs. Due to the impact of the economic crisis, this number could be significantly lower.

Table 1: The estimated number of the ELVs in Serbia per year

Year	Number of registered cars	Min. number of the ELVs	Max. number of the ELVs
2011	1677510	67100	112393
2010	1565550	62622	104892
2009	1637002	65480	109679
2008	1486608	59464	99603
2007	1476642	59066	98935
2006	1511837	60473	101293
2005	1481498	59260	99260
2004	1449843	57994	97139
2003	1388109	55524	93003
2002	1343658	53746	90025
2001	1382396	55296	92621

Almost a third of all vehicles in Serbia are domestic (Pavlovic, 2009), primarily the vehicle type Zastava (31%). It is followed by Opel (18%), Volkswagen (16%), Kia, Fiat and Renault (7%). Based on these data and the previously mentioned that the number of ELVs may be less than estimated as a referenced vehicle is taken Yugo Koral 1.1. The Yugo has the least amount of hazardous components, and the real number of ELVs is probably lower than estimated. Thus, the adoption of Yugo as a reference vehicle reduces the error of the estimate of amounts of hazardous components. The reference vehicle has 15.69 liters of liquids, without fuel („Tehničko uputstvo“, 2005). Figure 1 shows the volume ratios of different liquids. It is difficult to estimate how much fuel is in an ELV. The fuel reserve is 5l („Tehničko uputstvo“, 2005), but there may be less than this when ELV is brought on recycling. It is obvious that the cooling liquids have the highest volume ratio, then, the engine oil and the transmission oil. There is only 2% of the brake fluid, but it should be given a special attention because of its toxicity. It can not be ignored despite the small quantities in which it is present.

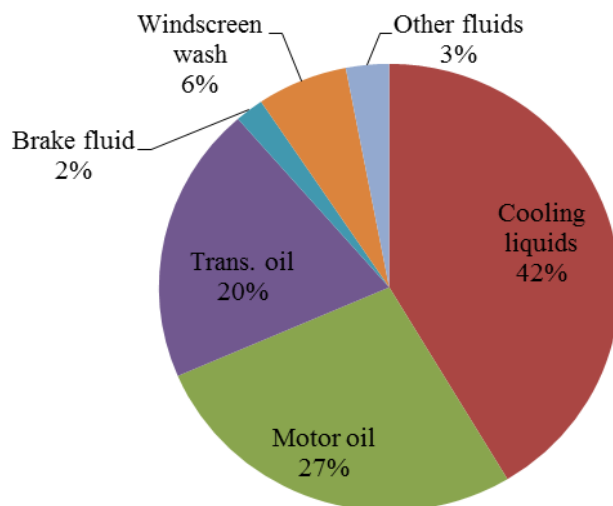


Figure 1. Volume ratios of different fluids in the automobile Yugo Koral 1.1

Estimated amounts of the hazardous liquids which have been taken out from the ELVs during the last ten years in Serbia are classified by type in Tables 2 and 3. The estimation was conducted based on the values given in Table 1, the referenced vehicle and the volume ratios from the Figure 1. Estimated minimum volumes of liquids are given in Table 2, while Table 3 shows the estimated maximum amounts of fluids. Average annual volumes of hazardous liquids are determined by getting the average values of the data from Tables 2 and 3. According to this Serbia faces between 935,732 liters and 1,567,351 liters of hazardous liquids every year.

Table 2: Estimated minimum volumes of hazardous liquids per year

Year	Cooling liquids, dm ³	Motor oil, dm ³	Transmission oil, dm ³	Brake fluid, dm ³	Windscreen wash, dm ³	Other fluids, dm ³
2011	436153	352277	211366	21137	67100	31873
2010	407043	328766	197259	19726	62622	29745
2009	425621	343770	206262	20626	65480	31103
2008	386518	312188	187313	18731	59464	28246
2007	383927	310095	186057	18606	59066	28056
2006	393078	317486	190491	19049	60473	28725
2005	385189	311115	186669	18667	59260	28148
2004	376959	304467	182680	18268	57994	27547
2003	360908	291503	174902	17490	55524	26374
2002	349351	282168	169301	16930	53746	25530
2001	359423	290303	174182	17418	55296	26266

Table 3: Estimated maximum volumes of hazardous liquids per year

Year	Cooling liquids, dm ³	Motor oil, dm ³	Transmission oil, dm ³	Brake fluid, dm ³	Windscreen wash, dm ³	Other fluids, dm ³
2011	730556	477671	354038	35404	112393	53387
2010	681797	445790	330409	33041	104892	49824
2009	712914	466136	345489	34549	109679	52098
2008	647418	423312	313749	31375	99603	47311
2007	643078	420474	311645	31165	98935	46994
2006	658405	430496	319073	31907	101293	48114
2005	645192	421857	312670	31267	99260	47149
2004	631407	412843	305989	30599	97139	46141
2003	604521	395264	292960	29296	93003	44177
2002	585163	382607	283579	28358	90025	42762
2001	602033	393637	291755	29175	92621	43995

LEGISLATION

The relevant pieces of legislation are:

1. „Pravilnik o načinu i postupku upravljanja otpadnim vozilima“ (*Sl. glasnik RS*, br. 98/2010). This piece of legislation sets forth the manners and processes of the ELVs management. It is in accordance with the EU-Directive 2000/53/EC;
2. „Pravilnik o načinu i postupku upravljanja istrošenim baterijama i akumulatorima“ (*Sl. glasnik RS*, br. 86/2010). This regulation sets forth the content and appearance of marks on the batteries, button batteries and vehicle accumulators, which show the content of hazardous substances. It also introduces the manners and procedures for management and handling of waste batteries and accumulators, as well as devices with built-in rechargeable batteries and accumulators;
3. „Pravilnik o uslovima, načinu i postupku upravljanja otpadnim uljima“ (*Sl. glasnik RS*, br. 71/2010). This regulation specifies the conditions, manners and procedures of the used oils management.

ELV's DEPOLLUTION METHODS AND EQUIPMENT

It is recommended that depollution activities are conducted using the equipment which has been specifically designed for carrying out the required depollution operations. The use of such equipment ensures that a high level of depollution (removal of over 98% of fluids contained in the ELV) can be achieved in a relatively short time-frame (20-30 minutes per ELV). The simpler, alternative methods can be used, but it is necessary to achieve the same level of depollution (over 98% removal of fluids). Even though alternative methods are used both, the health and safety requirements must not be compromised. The majority of commercially available equipment is usually operated pneumatically (Zameri et al., 2006). Consequently, the compressor used to power this equipment must have sufficient capacity to ensure that the equipment can operate satisfactorily.

The complete depollution of the ELVs consists of several stages. First, it is necessary to take so-called preliminary activities (Hiroyuki et al., 2001). The second stage is removal of all the liquids from a vehicle. After that comes the removal or deployment of air bags and finally the last stage. In the last stage ELV is classified as a non-hazardous waste. This paper is primarily oriented toward the second stage.

Figure 2 shows a specially designed equipment for carrying out the removal of liquids from the ELVs. It consists of the following subsystems:

1. Air compressor with tank;
2. Steel containment bund;
3. Car girder with hydraulic power unit;
4. Funnels;
5. Fluid reservoirs;
6. Pneumatic drill;
7. Needle for outpouring the cooling liquids;
8. Pneumatic subsystem;
9. Subsystems for filtration of waste fuels;
10. Hose system for draining waste liquids.

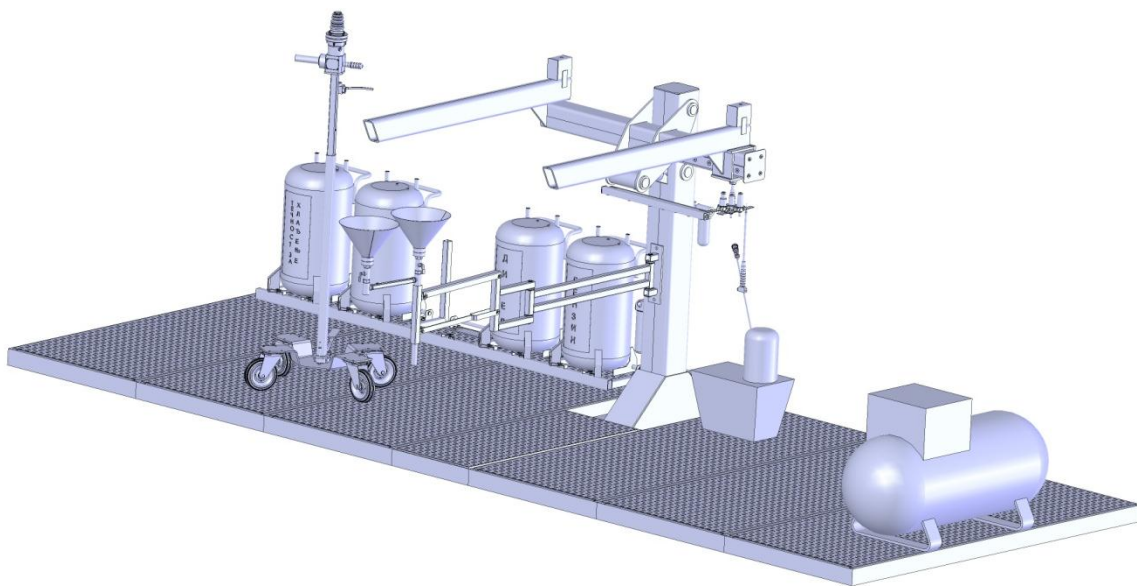


Figure 2. The equipment specially designed for carrying out the removal of fluids from the ELVs

A vehicle is set on the car girder using an industrial forklift. The upper part of the girder can be rotated for 6° so liquids could be easily discharged. Compressed air flows through the Venturi ejectors, due to which air is drawn from the reception tank, creating a vacuum in the collector tank. Discharge of fluids from the vehicle is done using a system of hoses and vacuum in the system. The pneumatic drill is used to drill a hole in the fuel tank, so the fuel can be easily removed. To remove motor oil from the vehicle it is necessary to unscrew the bolt on the crankcase. Then oil starts to leak from the crankcase, first into the funnel and then through a hose into the reservoir. Something similar is done for draining oil from the gearbox and differential. In order to increase the efficiency of draining liquids from brakes and cooling system it is necessary to obtain the overpressure in those systems. It prevents fluid retention in the brakes and the vehicle cooling systems. Under the wheel cylinder a funnel should be placed. It receives the brake liquid, which later flows through a hose into the reservoir. Discharge of fluid from the cooling system is done using the special needle, which is hollow in its center. The needle pierces the hose which leads from the radiator to the engine block. The fluid starts to flow through the hole in the needle, and find its path through the system of hoses into the reservoir.

SCENARIOS OF POSSIBLE NEGATIVE INFLUENCES ON THE ENVIRONMENTAL QUALITY IN SERBIA

In order to protect the environment it is necessary to prevent the uncontrolled disposal of hazardous components. Batteries contain sulfuric acid, lead and other harmful materials. Their bad treatment may cause acid leakage in the land and waterways. Special attention should be given to precautions in the process of battery recycling. It should be done in order to prevent recyclers injuries. Battery has dangerous chemicals which may cause skin burns, choking and poisoning. When airbags aren't treated professionally sodium azide (NaN_3) may be released into the environment. It is highly soluble in water, so it can easily reach and pollute a large amounts of water. Antifreeze is toxic if swallowed (affects the central nervous system), its sweet taste may attract children or animals. Despite it is biodegradable, used antifreeze can be contaminated with heavy metals, benzene and anticorrosion additives, which makes it a hazardous waste. The brake fluid should not be treated just as the used oil because of its toxicity. It becomes very dangerous when comes in contact with chlorinated solvents from sprays which are used to clean the brakes. Switches which may contain mercury aren't dangerous during the vehicle's lifetime. They have to be removed at the end of a life cycle, otherwise mercury can be released into the environment, during the shredding process. The waste motor oil contains a high percentage of highly toxic and carcinogenic substances. This makes of waste motor oil a hazardous waste. It is very important that motor oil is treated professionally, because it can, as a liquid, easily penetrate the soil and water. Windscreen wash is made of alcohol, detergent, water and a small amount of antifreeze. It can easily pollute soil, water and air. On one hand it can leak into the soil and create a mixture with water. On the other hand it evaporates easily, so it can also pollute the air. Proper waste disposal and its recycling are prerequisites for minimizing their impacts on the environment. However, there are no precise figures on the number of recycled cars in Serbia. Thus the amount of hazardous materials, which are properly treated is unknown.

An estimate of the minimum volume of fluids which are not properly treated is done based on the equation:

$$V_{np,min} = V_{year,min} \cdot \left(1 - \frac{k \cdot a}{100}\right). \quad (1)$$

An estimate of the maximum volume of fluids which are not properly treated is done based on the equation:

$$V_{np,max} = V_{year,max} \cdot \left(1 - \frac{k \cdot a}{100}\right). \quad (2)$$

Symbols used in (1) and (2) are:

- $V_{np,min} \left[\frac{dm^3}{year} \right]$ – minimum volume of fluids which are not properly treated;
- $V_{np,max} \left[\frac{dm^3}{year} \right]$ – maximum volume of fluids which are not properly treated;
- $V_{year,min} \left[\frac{dm^3}{god} \right]$ – minimum volume of the hazardous liquids per year;
- $V_{year,max} \left[\frac{dm^3}{god} \right]$ – maximum volume of the hazardous liquids per year;
- $k \geq 0,98$ [/] – efficiency coefficient of the specialized equipment;
- a [%] – percentage of the recycled ELVs per year.

The estimated volumes of hazardous fluids which may not been properly treated are shown in Table 4. The volume varies with percentage of recycled cars. For the calculation of average volume values of hazardous liquids per year data were taken from Tables 2 and 3.

Table 4: Estimated minimum and maximum volumes of hazardous fluids which are not properly treated per year

a, %	$V_{np,min} \left[\frac{dm^3}{god} \right]$	$V_{np,max} \left[\frac{dm^3}{god} \right]$
5	889881	1490551
10	844030	1413751
20	752329	1260150
30	660627	1106550
40	568925	952949
50	477223	799349
60	385522	645749
70	293820	492148
80	202118	338548
90	110416	184947
95	64566	108147
100	18715	31347

Figure 2 gives a graphical illustration of the results given in Table 4. Minimum estimated values are painted in red, while maximum are painted in blue.

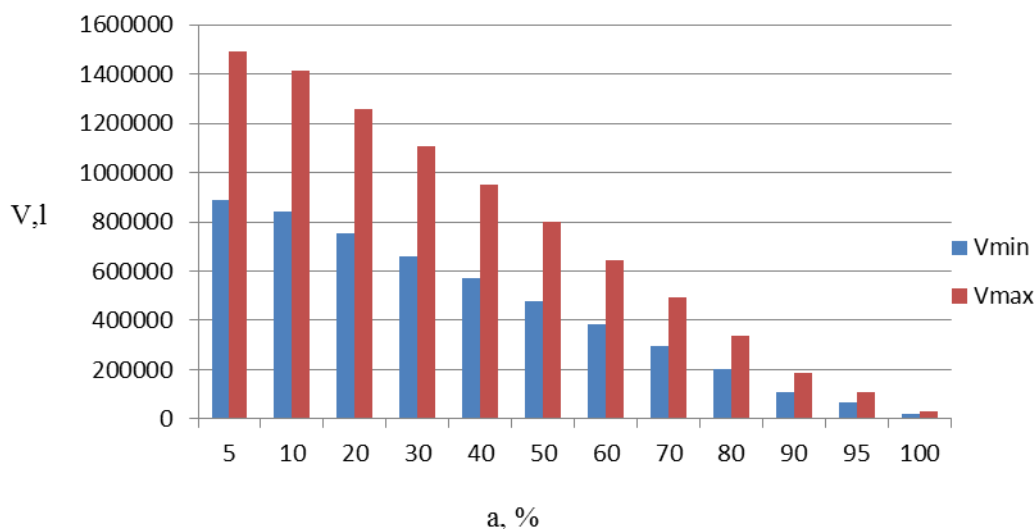


Figure 3. Estimated minimum and maximum volumes of hazardous fluids which are not properly treated per year

The increase in a number of recycled ELVs causes decrease in amounts of hazardous waste, which may harm the environment. However, not even the recycling of all ELVs can warranty the full environment protection. Due to equipment's efficiency of 98%, not all hazardous components can be removed from a vehicle.

CONCLUSION

Serbia faces a problem of large amounts of the hazardous materials every year. Some of them come from the ELVs. The problem are not only their amounts, it is also the way they are treated. Large amounts of hazardous materials aren't properly treated. Due to the lack of real data, it is not possible to determine the exact amounts of these hazardous materials. Thus, their potential negative impact on the environment is unknown. This paper gives a rough estimate of the amounts of different fluids which may occur due to depollution of the ELVs. Both the freons and air bags are not considered in this paper because of the age structure of the most of current ELVs in Serbia. Most of them doesn't have neither freons nor air bags. Because of the quite developed recycling market of the old vehicle accumulators they aren't considered in this paper. A review of types of hazardous liquids and an estimation of their quantities are given, as well as an example of the modern depollution equipment. Only an estimation is given, but the real problem is unknown, because of the unknown number of the recycled ELVs.

ACKNOWLEDGEMENT

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IMPACT OF AGRICULTURAL ACTIVITIES TO URBAN AREA

**II International Conference
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**ECOLOGY AND THE USE OF CHEMICAL AGENTS IN
AGRICULTURE**

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ABSTRACT

The constant deterioration of nature and the increasing number of pollutants distributed through atmosphere, soil and water due to the enormous development of industry, agriculture and motor vehicle traffic, and the extended use of fossil fuels, like coal and natural gas, put the world in front of serious problems in the near future. This paper deals with the use, maintenance and protection of humans and the environment from chemical agents used in agriculture.

Key words: *ecology, agriculture, chemical agents, protection.*

INTRODUCTION

Modern agricultural production is characterized by high yields which are impossible without the use of chemical agents. They are used to feed the crops (mineral fertilizer) and for the protection of crops from various diseases and insects (pesticides). The increased use of chemical agents increases the possibility of health damage and immeasurable pollution of soil and water and air. Therefore, efficient protection measures for people and environment during the use of chemical agents are of highest importance. Therefore modern agricultural production must be based on knowledge from the fields of biology, physics, chemistry and ecology (Merfield, 2010) (*Figure:1*).

Pollution occurs when hazardous substances come into the environment in such concentrations that they pose a risk for people, animals, plants and their habitats. Pollution control is the biggest problem the world is confronted with today. Vast areas can become uninhabitable in a short time, many species of plants and animals can vanish forever. The public puts pressure on governments and industries to fight pollution.

Efficient protection from negative influence of chemical agents used in agriculture is primarily based on the knowledge about their effects on crops, people and environments, the application of protection agents, strict compliance to the instructions for their use, storage and the training of workers.

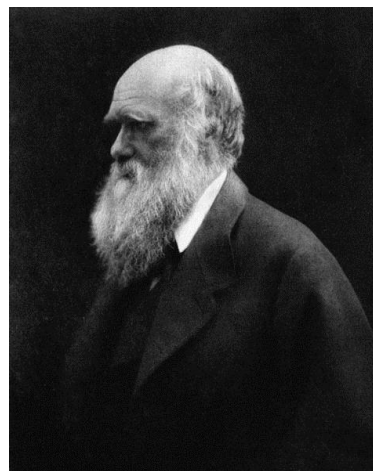
ECOLOGY

The word ecology comes from Greek words (oikos) and logos (logos). The founder of ecology is Charles Darwin (*table:1*), who in 1859 in his book mentioned many details of ecology, not defining the term ecology itself. The term itself was first used by scientist and biologist Ernest Haeckel in 1868. Ernest Haeckel (*table:2*) writes: "Ecology is the summary knowledge which refers to the economy of nature: it studies the complete relationship between the world of beings and the environment that surrounds them, organic and inorganic, friendly and unfriendly relationship with animals and plants with which they contact directly or indirectly. In one word: ecology is the science of all interactive relations, which Darwin calls conditions and the battle for survival."

Table 1: Charles Darwin



Charles Darwin 1854



Charles Darwin 1868

Darwin was born in Shrewsbury, Shropshire, on February 12th, 1809 as the fifth child of a well-situated English family. His maternal great grandfather was the famous manufacturer Josiah Wedgwood, and his paternal great grandfather was the famous 18th-century psychologist and scientist, Erasmus Darwin.

In 1825, after finishing an elite school in Shrewsbury, the young Darwin began to study medicine at the University of Edinburgh. In 1827, he had to leave the study of medicine and went to the university of Cambridge in order to become an Anglican priest. There he met geologist Adam Sedgwick and naturalist John Henslow. Henslow not only helped Darwin in gaining self-confidence, but he taught his student how to become a careful observer of natural phenomena and the species of living beings.

Darwin's work was recognized by his fellow scientists and so he was admitted to the Royal Society in 1839 and to the French Academy of Sciences (1878). He was buried in Westminster Abbey with all honors, following his death on April, 19th 1882 in Down, Kent.

CHEMICAL AGENTS IN AGRICULTURE

From seeding to harvesting the plants are exposed to many kinds of damages. To help the plants develop without problems it is necessary to protect the plants from various damaging influences. The task of plant protection should be to ensure that there are no harmful effects on plants and environment, and to also be economically acceptable. Plant protection (Ercegović, 1987) can be:

- mechanical (drilling, rolling, etc.),
- physical (irrigation, anti-hail protection, etc.),
- chemical (fertilizing, application of various chemical agents).

Chemical maintenance of plants should besides applying additional mineral fertilizer, also ensure protection against plant diseases and attacking vermin during their growth. This type of maintenance of plants includes:

- the maintenance of plants by using various pesticides and
- feeding of plants.

Table 2: Ernest Haeckel

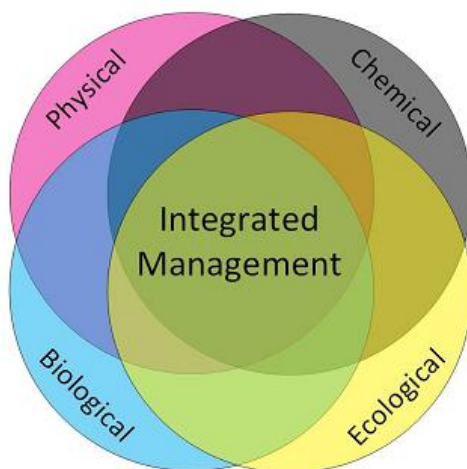
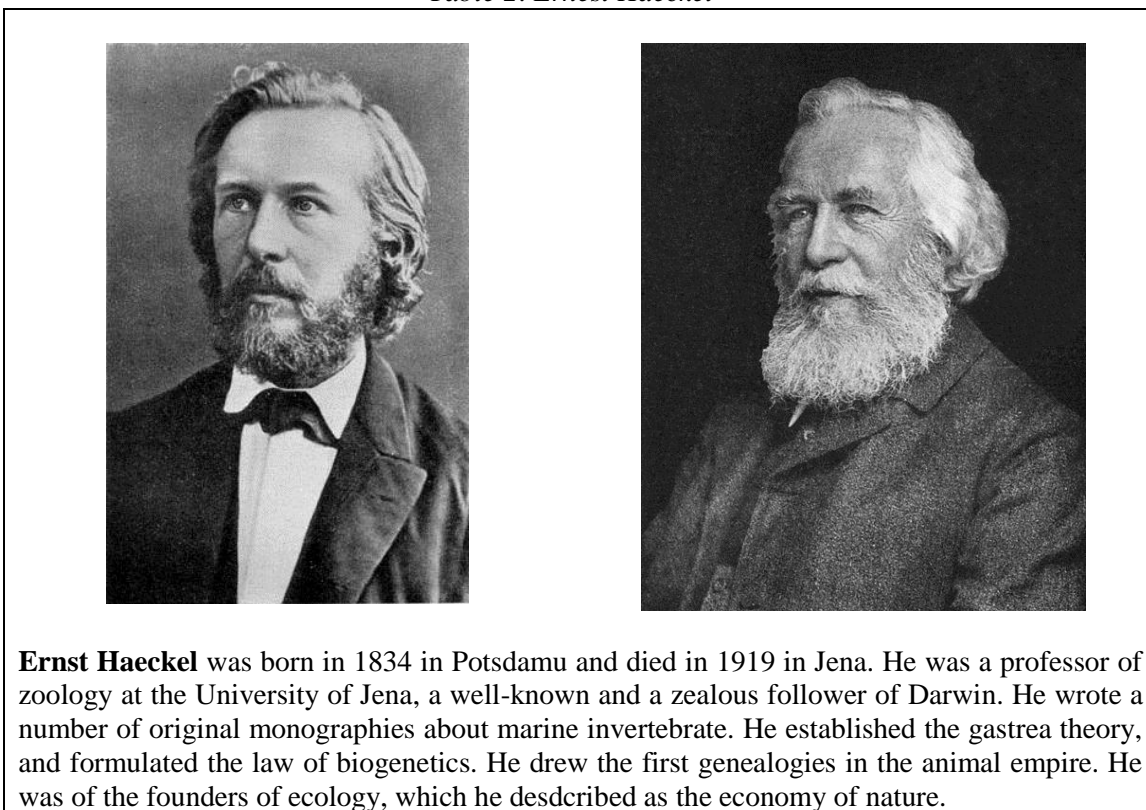


Figure 1. The four “fundamental” science that when used toether create integrated managements in agriculture

Chemical agents that are used to fight plant diseases, insects and weed, are known under the common name of pesticides (latinski *pestis*-contagious; *caedo*-kill). Pesticides can be used for protection of seed, soil, parts of plants above the ground, to combat weed, insects (in the fields, warehouses and homes) and other damaging species (birds, rodents, snails etc.) (figure 2), (figure 3) and (figure4), (Arnold L: 2000)

PESTICIDES

Pesticides are more or less toxic for humans, domestic and wild animals, fish, and often bees too. Pesticides can be encountered in various states (Butorac,1999), (Milojić and Milošević, (2000) :

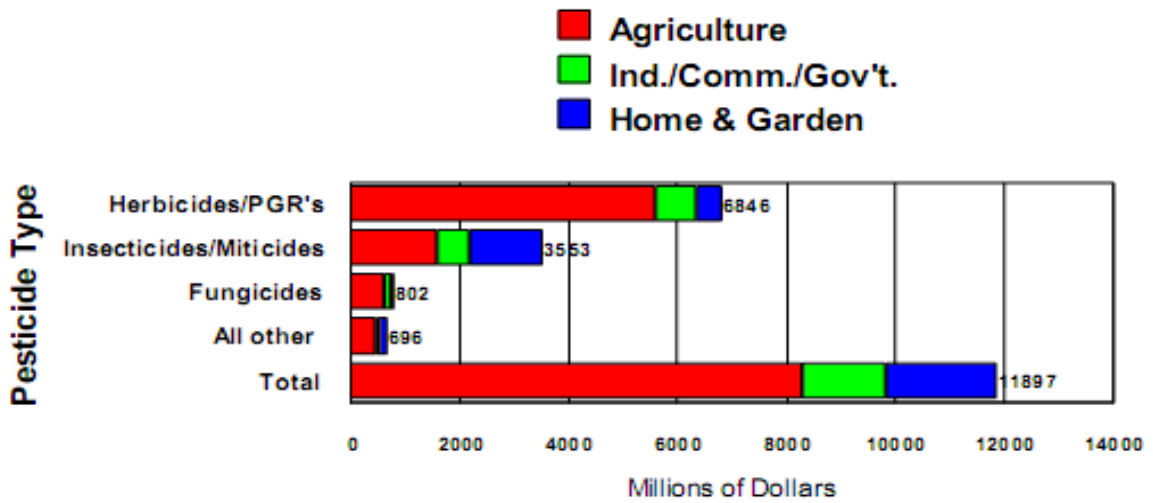
- liquid (concentrated or solutions),
- solid (powder, granules, pills, etc.) and
- gaseous (smoke, mist, gas, etc.).

Pesticides are rarely used in pure condition. Some pesticides have to be diluted before use. The amount of water depends on the surface area to be treated. Today pesticides are mainly produced in the following forms (Živković, 2005):

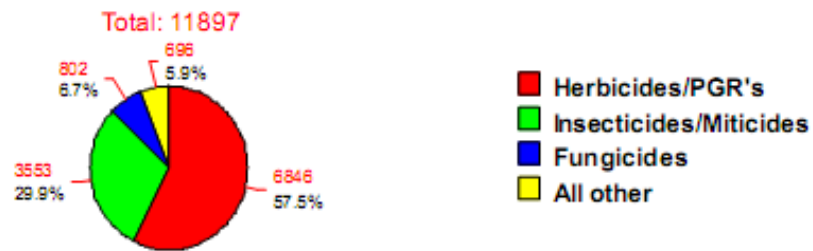
- **Pesticides in powder form**, containing up to 10% of active matter, which is applied by spraying.
- **Pesticides in the form of concentrates for suspension** are fine ground active substances, containing from 20-90% of active substances which are applied by sprinlers and automatizers.
- **Pesticides in the form of granulas**, which contain from 5-10% of active substances.
- **Pesticides for misting** are in liquid form, where active substance has been diluted in the solvent (no dilution in water) and are applied by misting devices or special airborne devices.
- **Pesticides in the form of concentrates for emulsion** are liquids containing from 10-60% of active substance diluted in solvent with the addition of emulsifier or a wetter. Before use, a pesticide of this form is diluted in water to a certain concentration.

The following aspects have to be taken into account during the maintenance of plants using chemical agents-pesticides:

- The chemical agent has to be distributed evenly on the whole surface it is applied to. When determining this surface area it is necessary to take into account that the chemical agent that is applied on the surface of the plant, is much larger than the surface of land where the plant is located. The surface of the part of plant above ground (stem, branches and leaves) is from 2,5 to 5 times bigger than the surface of the soil it is located on. With trees this is much higher.
- The protection of plants against various insects and diseases has to be profound and it has to be fast and efficient. It has to be carried out in a very short time, from 2 to 4 days.
- It is necessary to ensure that the protection agent reaches all parts of the plants. If this is difficult to achieve, then it is considered that a coverage of 40 to 50% of the plant surface is satisfying. If plant maintenance targets mainly its protection against diseases, then the surface covered by plant protection agent should be larger than when it is protected against insects.
- Plant protection agent should be in a form that allows efficient and uniform coverage of the whole area where the plants are located. It is important that the plant protection agent be disintegrated into fine droplets in order to avoid insufficient or unequal coverage of the plant, and to prevent too large concentrations of chemical agent which could damage the part of the plant it would fall onto.
- In applying the agent on the plant mechanical or chemical damages should be avoided,
- Mechanical spreading equipment for plant protection agent should be protected against their erosive - corrosive properties.
- Mechanical spreading equipment for plant protection agent should be highly effective, so that plant maintenance could be carried out as fast as possible.



	Herbicides/PGR's	Insecticides/Miticides	Fungicides	All other	Total
■ Agriculture	5610	1599	632	462	8303
■ Ind./Comm./Gov't	743	576	144	70	1533
■ Home & Garden	493	1378	26	164	2061
	6846	3553	802	696	11897



Millions of Dollars

Figure 2. Dependence pesticide type of millions of dollars

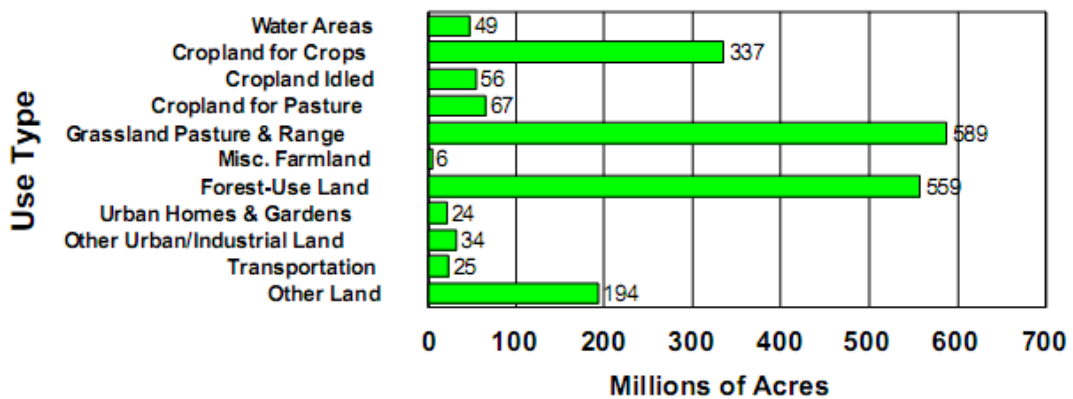
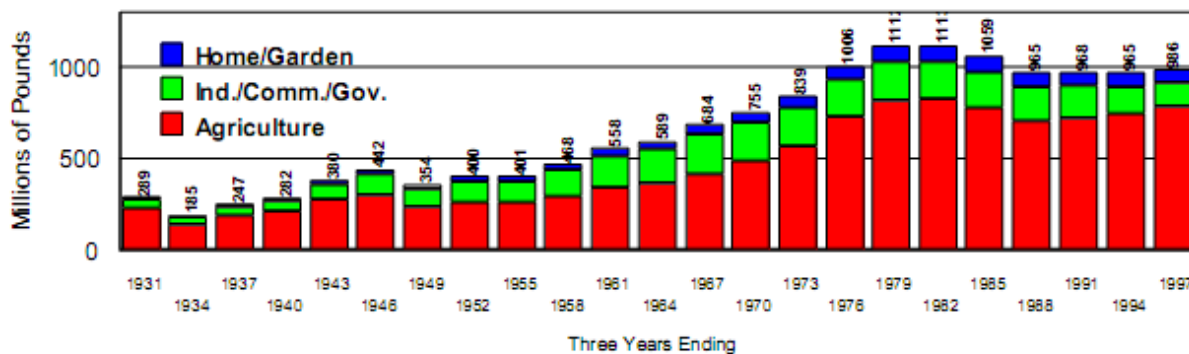


Figure 3. U.S. Land area, acreage by type of Land Use, circa 1990.



■ Agriculture	230	140	188	208	270	297	230	282	258	292	341	382	413	482	570	723	817	821	777	704	722	742	782
■ Ind./Comm./Gov.	47	36	47	59	88	115	100	111	117	140	173	182	219	217	208	209	212	207	198	182	189	148	128
■ Home/Garden	13	9	12	15	24	30	24	27	28	35	44	45	52	58	62	73	83	86	84	79	77	74	75
Total	289	185	247	282	380	442	354	400	401	468	558	599	684	755	839	1006	1112	1113	1059	965	968	965	986

Figure 4. Volume of conventional pesticide active ingredient usage in U.S.

Depending on the form of pesticides (powder, granulae, diluted in water), the form of its application also varies. Basic types of plant maintenance, depending on the size of the droplets and particles of the plant protection agent (Živković and Veljić, 2011) are as follows:

- sprinkling (Figure:5) (plant protection agent is in the form of a solution, the average size of droplets is 150 μm),
- dewing (Figure:6) (plant protection agent is in the form of a solution, the average size of droplets is from 50-150 μm),
- misting (plant protection agent is in the form of a solution, the average size of droplets is up to 50 μm) and
- spraying (plant protection agent is in the form of a solution, the average size of droplets is from 3-50 μm,).



Figure 5. Wide-angle sprinkler “Evrard” tank capacity from 3000 to 4500 litres

The number of droplets deposited on the surface of application and their uniform distribution is an indicator of the plant maintenance quality. From a quality viewpoint it is the same if one cm³ of plant protection agent is converted into 10 or 1.000 droplets, because the surface covered by 10 droplets will be smaller than the surface covered by 1.000 droplets (table:3). Bigger droplets concentrate on the

ends of the leaves, so that most of the agent does not stay on the surface of the plant, but drains down to the lower parts of the plant and into the soil. That increases the concentration of the agent on the lower parts of the plant, which can lead to burns and damages on the plant.

Table 3: Size of the droplets of pesticides and consumption (Živković, 2005)

	Droplet size	Farming	Fruit	Viticulture
	(μm)	(t/ha)	(t/ha)	(t/ha)
Sprinkling	250	200-800	600-3000	600-3000
Derwing	50-250	25-300	100-800	100-800
Fine dewing	25-125	6-30	10-150	10-150
Misting	50	3-10	3-25	3-15

STORING OF PESTICIDES

Incompetent storing of plant protection agents represents a direct threat to workers in the storage facility, and for all who come in contact with them. These chemical agents are mainly stored in unsuitable facilities which do not fulfill the minimum requirements. A big danger exists for workers who receive substances returned from the field. The storage facility workers have to conduct checks and they should be informed about dangers for them and their co-workers.

Work protection Codes in agriculture contain measures which have to be applied in chemical agent storage facilities.

Chemical agent storage facilities have to be far away from residential objects, the waste gas and dust concentration in the storage facility must not exceed the maximum allowed concentrations determined by existing standards. The door to the facility has to be locked when the worker is not around. It is also forbidden to drink, eat, smoke or sleep there. All these restrictions have to be visible on a plate. Chemical agents have to be kept in their original package which has to contain a declaration containing relevant data.

Without that declaration, the chemical agent must not be put into operation until its content is checked. If this is not possible it has to be destroyed. Handing out of pesticides is possible only upon the instruction of an expert person which is in charge of these operations.

PROTECTION AGAINST HARMFUL EFFECTS OF CHEMICAL AGENTS ON THE ENVIRONMENT

Before using chemical plant protection agents, the user should study the following (Živković, 2003):

- chemical agent manufacturer's instructions for safe work,
- type of application of plant protection agent,
- toxicity of the chemical plant protection agent,
- protection measures on the work place with devices for spreading chemical plant protection agents,
- first aid steps in case of intoxication,
- personal hygiene during work,
- how to use personal protection equipment when chemical plant protection agents are used.

Personal protection equipment is necessary when handling pesticides. Depending on the type of pesticide, its method of application, weather conditions and other conditions, the type of protection device is determined. Individuals handling chemical protection agents, and pesticides have to use the following personal protection equipment:

- when opening the chemical agent packaging a respirator is necessary when they are diluted or poured and also necessary are rubber gloves, rubber boots, working suit with a rubber overall,

- when preparing chemical agents in glasshouses a respirator, rubber gloves, rubber boots, impregnable coat with a cape is necessary,
- when preparing chemical agents-aerosols in closed facilities a respirator, rubber gloves, rubber boots, impregnable working suit with a rubber overall is necessary,
- when applying chemical plant protection agents, a respirator, goggles, rubber gloves, rubber boots, and an impregnable coat with a cape is necessary.

When rubber gloves are used, its ends have to be pulled over the sleeves of the working suit. The legs of the working suit should be pushed into the rubber boots. After the application of pesticides all body parts which have been in direct contact with the pesticide have to be washed thoroughly. During work with chemical agents, workers must not eat, drink or smoke. Empty packages of the plant protection agent should be destroyed.



Figure 6: Pulled dewing device „Tifone” capacity up to 2000 litres

CONCLUSION

The ever worsening condition of nature, the increasing number of substances that are carried through atmosphere, soil and water, which is the consequence of agricultural development puts mankind in front of big problems in the near future. One of the best known messages of environmentalists is "think globally, act locally". That means it is not enough to know what the threat is, but we must know how to protect ourselves against these threats, and also how to prevent them.

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**IMPACTS OF AGRICULTURAL ACTIVITIES
ON SPATIAL DEVELOPMENT OF PERI-URBAN AREAS IN SERBIA¹**

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ABSTRACT

Starting from the fact that the city as a whole cannot be considered independently of its rural environment, which eventually became its periurban zone, the paper discusses the impacts of agricultural activities on the spatial development of periurban areas. Urbanization initially leads to the degradation of natural resources in the periurban areas due to increased pressure on land resources. For agriculture in periurban areas there is a need for monitoring and evaluation of the increasing competition between land use for agricultural and non-agricultural purposes, water and other resources. All this affects to the use of natural resources, production systems and food supply, as well as social stability. Changes in the agricultural sector due to constantly and irreversibly reduction of arable land have repercussions on the conservation of natural resources, and quality of life of people in the city, too. Therefore, in this paper an attempt is made to point to this trend at the example of periurban areas of selected cities (Belgrade, Valjevo).

Key words: periurban areas, agricultural activities, Serbia.

INTRODUCTION

Any growth of the cities, especially large cities, necessarily leads to the oncoming of the closest villages. Many villages were the nucleus of the settlement development, which eventually became suburbs, fringe and peri-urban settlements, which had combined and interconnected impacts of the countryside and the city. Urban settlements, especially larger ones with more functions are centers around which is concentrated the life of much wider territory. At a certain stage of development of the city's function is transferred to the environment, but in most cases means the occupation of the highest quality, agricultural land.

The importance of agriculture in sustainable development of peri-urban zones

Steady but uneven process of urbanization that is taking place especially in the peri-urban areas of the cities, generally is associated with land speculation or it is its product. Since the price of agricultural land, for instance, is more than ten times lower than the price of land intended for urban purposes, there must be legislative measures to prevent speculation in agricultural land (Ђорђевић, 1995), because “instability in the land use includes a variety of land speculation which often changes its purpose” (Матијевић, 2005) . If the planning documents do not exist or routes of city expansion are not determined, it is possible that land will not change its use, but the owner-farmer will not invest in increasing of productivity on that land, but will often change the way of using the land in the search of a quick earnings. In this way, peri-urban zone is no longer a ring around the city with intensive agriculture, “but a dynamic area in the immediate metropolitan environment with agriculture that gets weaker as the land is used for it is closer to the growing city” (Ђорђевић, 1995). In Poland, for example, between the 2004 and 2006 the price of agricultural land has increased by 40% by the quite

¹ The paper was prepared within the scientific projects “Sustainable spatial development of Danube region in Serbia” (TR 36036) and “The role and implementation of the National spatial plan and regional development documents in renewal of strategic research, thinking and governance in Serbia” (III 47014) financed by the Republic of Serbia Ministry of Education and Science in the period 2011-2014.

clear motivation of landowners -selling agricultural land for the construction of residential buildings and others provides to themselves significant financial benefits (EEA, 2006).

In many cases, urbanization has dramatic effects on the peri-urban zones; above all, it initially leads to resource degradation in the peri-urban zones due to increased pressure on land resources. For agriculture in peri-urban zones there is a need to monitor and assess the growing competition between land use for agricultural and non-agricultural uses, water and other resources and how this competition and associated changes in the price of resources affect the use of resources, production systems, food supply and social stability (EESC, 2004).

In the case of the expansion of settlements, occupation and use of the land must be carefully considered. Land resources cannot be increased, so the use of land for urban development must be defined according to specific criteria.

EU documents determine agriculture as a multifunctional, which aims to accomplish the sustainable development in providing of food and other “non-market” functions, such as rural development, high living standard and environmental protection. In recent years, multifunctional agriculture, multifunctional landscape and multifunctional land use are a common subject of scientific research (Silber, Wyrzens, 2005, Van Huylenbroeck et al, 2007; Wiggering et al, 2006; Wilson, 2007, Wilson, 2008, Wilson, 2009, etc). In most cases, researchers are focusing on developing strategies concerning the preservation of multifunctional urban agriculture and diversification activities on multifunctional farms but less on impacts of multifunctional use of agricultural land.

A study conducted for Linz / Urfahr region in Upper Austria, supports the idea of multifunctionality of agriculture in intensively used urban regions. It is considered that agriculture is one of multifunctional landscapes (Silber, Wyrzens, 2005). Silber and Wyrzens distinguished 6 main functions of urban agriculture, following the concept of sustainability; production, employment, regeneration and protection, ecosystem, spatial and cultural function (Figure 1).

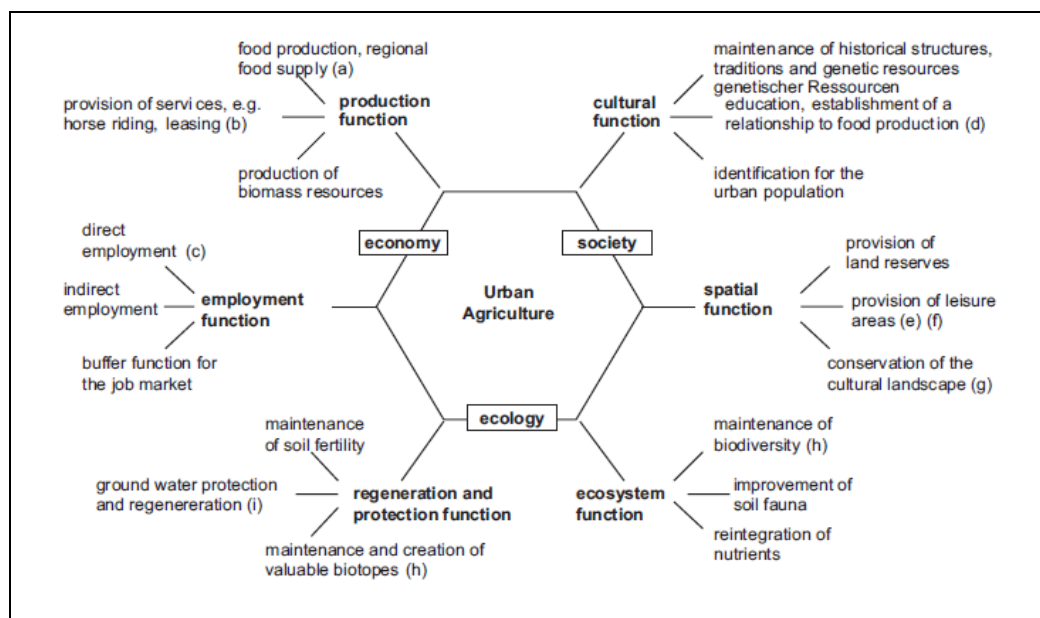


Figure 1. Multifunctionality of urban agriculture (Source: Silber, Wyrzens, 2005)

In ex-Yugoslavia, socialist republic government favored intensive industrialization, which caused the rapid urbanization in the 60's and 70's of the twentieth century. The wars in the former Yugoslavia in 1990s, causing major internal and cross-border relocation of residents, contributed to the migration from rural to urban areas. Many peri-urban areas are developed illegally, without the urban

infrastructure and services, especially in areas with high economic potential and development in the areas of potential for tourism. As a result, some of the nature and landscape values that represent an important competitive advantage of the region are endangered, and the quality of life in urban areas decreases due to crowded neighborhoods and a lack of infrastructure and other facilities.

After the several nationalization of different scope and character, as well as the translation of construction land into the mode of city construction land, with all the controversial aspects of the decades-long use, or misuse thereof, agricultural land, so that to the surface maximum land has not changed ownership, but it changed the owner in order to new owner will use it for non-agricultural purposes. On the other hand, the concept of demetropolization, which is not supported by legal and market mechanisms, and misconceptions about the urban standards of so-called satellite settlements, undermines authentic advantages of periurbanog areas.

Traffic problems in urban areas also increased. Urban areas are suffering from the increased volume of generated waste, air pollution, changes in land use etc.

At the same time the process of over-urbanization without adequate planning and migration, caused a large decline of the agricultural sector. The best agricultural land is lost because of urban development, while the land in the mountains is abandoned when the population went to the cities (UNDP, 2007).

A restrictive policy towards private initiative and individual construction in the socialist period of Serbia - urbocentric policy - caused extensive illegal housing in response on housing and urban policy (Petovar, 2003), which is even intensified in the last fifteen years. Rigid urbanistic regulations and undeveloped estate market caused extensive illegal construction, resulting in expansion and fragmentation of the urban fabric and the conversion of fertile agricultural land in rural areas (Стојановић, 2006).

By the mid 1980s, illegal construction in most cities of the former Yugoslavia was localized in the peripheral zone of the city, outside the built continuous urban area. The buildings are constructed out of the building regions, on the parceled agricultural land, which were sold by the owners as construction parcels, because that was more profitable than the use of agricultural land for agricultural production. The law did not allowed for such transactions, but authorities did not punish the owners because of the illegal conversion of agricultural land into construction (Milić et al., 2004).

Last twenty years in Serbia, as a consequence of tragic scenes in Balkan region, many refugees from Croatia, Bosnia and Kosovo, as domestic dwellers with unsolved residences, tried to reach their own “roof above head” by illegal building of houses on agricultural soil in peri-urban area of Belgrade. This is a consequence, above all, of negligence of the competent managing and planning agency. Unfortunately, for such situation of illegal constructions, only that people pay and are sanctioned, though they are not the only one to blame (Živanović Miljković, 2008; Живановић Миљковић, 2009).

Spatial and urban planning has not been able to deal with these processes. In the past, urban plans were more technical documents that have responded to the initiative of investors, than instruments of dynamic development management. To deal with this problem, the government adopted a new law on planning and construction. These laws provide opportunities of legalization of existing structures on the one hand, while, on the other hand, trying to make the planning system more efficient.

Spatial development of peri-urban zones in Serbia – examples

In post-war planning documents (Master -general plan from 1953), part of the suburban area of Belgrade on the left bank of the Danube remained undefined, shown as a green belt and agriculture. Since 1957 all construction throughout this area was directed and controlled. At that time, the Directorate for construction and development of the left bank of the Danube were established, and

when it was canceled, the urban planning of this territory was shifted to the Urban Institute of Belgrade.

According to the Master Plan for Belgrade from 1972 the immediate metropolitan area (continuous built-up area) comprising the 69 537 ha with about 1,116,310 inhabitants, while the other area, a number of “semi-urban” settlements in a ring around a continuous built-up area, included 262 648 ha and about 254 890 population. The specificity of this approach to the planning organization of this area is comprised of concentric expansion of the town, with the breaking of the compact urban mass into smaller urban units and the creation of so-called “archipelago settlements in the green”. Master Plan from 1972 predicted the gradual assimilation of the surrounding urbanized settlements by Belgrade. Also, it was considered whether and to what extent should Belgrade “steps” on the Danube left bank (the idea of the so-called Danube-town²), but the idea were abandoned because of the limitations of the area for housing and work, with the exception of agricultural production and for specific forms of agriculture and recreation. The design of these settlements was planned, but it was limited in scope. However, during the implementation of housing construction in the settlements, there were a common connection to the city’s network infrastructure, resulting in increased and accelerated construction of which is far beyond the idea of the Master Plan, but closer to the realization of the already rejected the idea of the Danube-town (Живановић Миљковић, 2009).

According to the Master Plan for Belgrade 2021 (Official Gazette of the City of Belgrade 27/03), peri-urban zones include the settlements: Crvenka, Borča, Ovča and settlements of economic zone Pančevački Rit on the left bank of the Danube. On the territory covered by this plan, most presented purpose in 2001 was agricultural purpose. A projection for 2021 is decreasing of agricultural area by 36 % (Živanović Miljković, 2008). The biggest growth area is going to happen in the green sector, mainly forests, then the housing and the economy, i.e. that area will be transformed into forest land, and partly built. As a result, farmland is reduced by 16 400 ha.

Also, in this plan rural settlements are treated integrally, as a group consisting of rural settlement and agricultural area, but the two subgroup observed independently of each other, ignoring their functional and spatial dependencies.

Data on obtained urbanization of the Belgrade suburbs, the original villages in the surrounding area, are not complete, nor always correct, because urbanization processes is constant (Стојановић, 2000). It is evident, however, that in the last few decades, extensive construction occurred out of control. It should be noted that the situation in Belgrade, on the ground, is much different from the situation that was planned. Since the plans (and the Cadastre) show only legalized land use change, there are indications that a significant part of the land, which is officially still agricultural, is largely transformed into construction. Specifically, where there is agricultural land planned, there are newly built residential areas. So we can talk about the so-called “quasi-agricultural land” (Ђорђевић, 1999), which is a consequence of the process of urbanization in rural areas, and particular types of uses are residential, office, houses for vacation and other forms of land use characteristic of the relatively short distance from the city agglomeration, increased value and frequency of buying and selling land, as well as socio-economic and cultural changes in the system of values of the owners. The emergence of quasi-agricultural land is particularly characteristic of the suburban areas of major cities, and the intensity decreases with increasing distance from the city center.

These statements and other observed trends are applicable for Valjevo, the urban agglomeration that is also the subject of this analysis. Specifics may be contained in the primary reasons that lead to the reduction of agricultural land in peri-urban area. While, in the case of Belgrade, agricultural land disappear entirely under the pressures of urbanization and metropolization, pressure on the peri-urban area of Valjevo is from housing needs and for establishing infrastructure corridors.

² Urban plan for commercial zone of Danube-town, (Institute of Urbanism Belgrade, 1969)

Town of Valjevo has the features of a multifunctional center of national importance, with a sphere of influence which includes the settlements in the municipalities of Valjevo, Mionica and some settlements of the municipality of Lajkovac, Osečina and Kosjerić.

According to data contained in Analytical documentation of the Spatial plan of the municipality of Valjevo, Sectoral Annex: Agriculture and agricultural land, fringe zone of Valjevo (peri-urban area) and its suburbs are characterized by extremely fragmented structure of land ownership (62% of households have less than 1 ha of arable land, and only 3.0% have more than 5 ha), a high share of non-agricultural and low share of agricultural and mixed income sources (respectively 93%, 1% and 1.1% of total households), above-average representation of households with no income, and a small number of active farmers who are already elderly (Table 1). Agricultural production is based mainly on the additional/occasional work outside the farm employees, or those who are on the rolls of the unemployed. The priority is the protection of arable land from non-agricultural purposes, parallel to the implementation of urban planning of settlements and complex arrangement of rural districts (land management, hydraulic and biological land improvement, landscaping of field roads and landscapes, etc.).

Table 1: Review of the land resource usage in the urban and peri-urban area of Valjevo, 2005-2022

Area / District	Year	Agricultural land	Forests	Wastelands	The total area
Recap of the planned changes of land use in ha					
METROPOLITAN AREA OF VALJEVO	2005	57.786	27.227	5.337	90.350
	2022	53.067	31.407	5.876	90.350
	In total	-4.719	4.180	539	0
II. A. Valjevo and suburbs	2005	3.730	1.192	1.462	6.385
	2022	3.698	1.192	1.494	6.385
	In total	-32	0	32	0
Proportion of districts in the appropriate category of the total land resources – in %					
II. The hilly area	2005	59.6	46.9	62.3	55.9
	2022	64.6	40.8	59.2	55.9
II. A. Valjevo and suburbs	2005	6.5	4.4	27.4	7.1
	2022	7.0	3.8	25.4	7.1
II. B. Other / villages	2005	53.1	42.5	34.9	48.9
	2022	57.6	37.0	33.8	48.9
The structure of agricultural and total area per rural regions – in %					
METROPOLITAN AREA OF VALJEVO	2005	64.0	30.1	5.9	100.0
	2022	58.7	34.8	6.5	100.0
II. The hilly area	2005	68.1	25.3	6.6	100.0
	2022	67.8	25.3	6.9	100.0
II. A. Valjevo and suburbs	2005	58.4	18.7	22.9	100.0
	2022	57.9	18.7	23.4	100.0
II. B. Other / villages	2005	69.5	26.2	4.2	100.0
	2022	69.2	26.3	4.5	100.0

Source: Spatial plan of Town Valjevo-draft version

Planning baselines in the Draft of the spatial plan of Valjevo are (IAUS, 2012):

- strengthening, adding and improving the quality of urban functions of national importance of Valjevo;
- it is not realistic to expect that it is possible to significantly divert the long-term trend of depopulation of rural areas and the concentration of people and activities in and around the urban center, and
- development of the settlement network is based on a model of community settlements established on the principles of territorial and functional networking and provides a three-level hierarchy of centers in the network of settlements of Valjevo: (1) urban center of national importance Valjevo

with sub-center in the peri-zone (Popučke); (2) subcentar - Divci, and (3) six rural community centers.

Model of concentrated decentralization/dispersion of development in the area are planned, in line with the principles of sustainable development of the area. Concentrated development of certain functions and activities in Valjevo and its peri-urban zone, zone along the main traffic lines in and out of the urban center and the other centers in the network of settlements means increasing density of housing and building control and land use, to protect the remaining quality agricultural land and other resources.

In addition to the areas intended for reforestation in the planning area, it is necessary to remove from the agricultural usage additional 540 ha intended for development water and transport infrastructure. Regarding the peri-urban areas the formation of ring road transit is of great importance. Transit bypass of Valjevo urban center DP IB -23 (no. 4) and DP IB -23 (No. 21) will be formed by already built southeast and planned north section. The southwest ring road section will not be completed in the time frame included in this plan (until 2022). The basic plan solution for determining the position of the northern ring road corridor is to avoid already built parts of the settlements Popučke, Iverak, Valjevo and Rađevo selo. The spatial plan is proposing, as a better solution, a variant of corridor by relocation of the state road through the valley. After the completion of the route relocated section DP IB -23 (no. 4), the existing state road section Lajkovac-Valjevo would be re-categorized as a lower category and, possibly, on the part of the section in the Gorić and Popučke re-categorized as main city road. This would enable the construction of bike paths adjacent to the existing roads.

Valjevo urban plan (2012) includes a town of Valjevo with suburbs west of Valjevo valley and in the lower parts of the river Obnica and Jablanica valley. Total of 89,432 residents are living on 2630 ha. Planned solutions define: optimal gross living area of 1.5 to 2 residents per ha, 40-50m² as average gross apartment size per inhabitant and 4046 residents as the optimal number of users.

CONCLUSIONS

There is a special situation in urban regions due to the fact that they are characterized by overlapping of different land uses as a result of competing interests. As urban areas sometimes have problems to maintain sustainable multifunctional use of agricultural land as desired by population, it is necessary to know how to approach, how to preserve and how to support the aspects of multi-functionality of agriculture and landscape

The basic direction of the changes occurring in the peri-urban areas of all large cities refers to the land which is used or has been used for agriculture. The only tendency for that land is reversing into urban purposes. Agriculture in peri-urban areas is faced with disadvantages (e.g. increased competition for land) as well as the benefits (e.g. greater market) formed as a product of urbanization.

Reduction of agricultural land due to the conversion into non-agricultural purposes is a consequence of economic development, which is inevitable, but with the permanent institutionalized control, especially in terms of size and speed of reverting (substitution) to other purposes for which there are suitable regulatory and implementation mechanisms of spatial and urban planning. On the other hand, the peri-urban agriculture also helps in maintaining of green areas, so it is important element of spatial planning in controlling of urban growth.

Since the agricultural sector is becoming increasingly faced with the pressures of population, environmental policies or with spatial planning, agriculture in peri-urban areas still has its undoubtedly role in the preservation of the landscape, in the local socio-economic improvement of quality of life, completing the ecological functions etc. In order to maintain this role, it is necessary for the agriculture in urban areas to be sustainable (these kinds of statements have found a place in the starting points of the study developed in Belgium (SPSD II, 2005)).

Agriculture in peri-urban areas is facing with more difficulties than it is the case with “rural” agriculture, due to which, in general, sustainability is becoming less noticeable. Therefore, farmers in peri-urban areas have to deal with the opportunities and limitations that urbanization brings, for which a good basis is provided by various forms of associations, including the co-operative organization.

In the city municipalities, conflicts in the land use - which are the result of the opposite interests – as a consequence often have various problems in preserving of sustainable multifunctional use of agricultural land because of a variety of desires / interests of residents. This is also the case with the aspect of the already happened, unformalized, spontaneous expansion of urban housing, as so as illegal construction or construction in the process of legalization. If municipalities want to have a multifunctional agriculture and authentic peri-urban landscapes they must also to have concepts on how to approach, how to preserve and how to support these aspects. Positive in the analyzed case studies is that all municipalities have local environmental action plan-LEAP. Belgrade beside this also has a strategy of agricultural development.

Local policies must be actively used to increasing the sustainability of agriculture in urbanized regions, and part of those policies should be shifted to the local level (as proposed in the LEADER program). Well-targeted policies related to agriculture in peri-urban areas, which are based on the perspective that agriculture may offer in order to achieve sustainability of the urbanized areas, must be developed and researched.

While the area of agricultural zone is decreased due to urban development, the pressure is growing on the rest of the non-agricultural areas (as it is evidenced by the number of request for the legalization in the analyzed areas). Of course, the illegal occupation of agricultural land cannot be the exclusive limiting factor in the process of legalization, but legalization of these objects should be supported by technical, administrative and constructional measures in order to be incorporated in the ambient and functional features of these areas.

Agricultural land in the city is developing from the production area to the area for consumers. Thus, the development converts the agricultural land in (peri-) urban regions to the meeting points of interest many stakeholders such as farmers, those involved in the conservation of nature and the environment, residents, consumers, planners. Republic government should encourage the initiatives that are shortening the food supply chain as it is evident that reduction of transport costs complements the economic dimension of sustainability.

The contribution of spatial planning in this area would be that, instead of creating rigid spatial planning solutions, especially for areas around the cities, it provides flexible instruments that favor multifunctional agricultural purposes and the preservation of an attractive rural area in a fringe around the city.

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DEGRADATION OF PESTICIDES IN SOIL

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ABSTRACT

Soil is a medium where pesticides accumulate so it serves as a reservoir of particularly persistent pesticides until they are translocated through the root system into plants, become adopted by other members of ecosystem and transported into the air or water. The future of pesticides in soil is determined by action of various physical, chemical and biological processes which cause degradation and movement of chemicals. Pesticide degradation depends on chemical properties, initial concentration, solubility in water, temperature, moisture and PH of soil, content of humus, ability to bond pesticides with colloid particles of mineral and organic substances, and if the pesticide was used once for the first time, or more times over many years. The paper will show products of degradation of insecticide imidacloprid which has different effects if compared to other insecticides.

Key words: *Pesticides, soil, insecticides, imidacloprid.*

INTRODUCTION

Soil, along with microorganisms which live in it, is a universal biological environment and neutralizer of diverse organic compounds where waste, being a result of man's activity, is broken down.

Soil is also an environment where pesticides are accumulated, but it also serves as a reservoir particularly of persistent pesticides until they are translocated into plants via root system and become adopted by other members of ecosystems and finally enter the air or water.

Pesticides enter the soil directly or indirectly; directly, as a result of controlled use for protection against rodents, soil insects, nematodes, weeds. The activity of pesticides is determined by effects of different physical-chemical and biological processes which cause deterioration and movement of chemicals. These processes can transform a pesticide from its basic compound into a series of degrading products (of lower or higher toxicity than the basic compound) and thus define its behavior in soil.

Degradation of pesticides depends on chemical properties, initial concentration, size of particles, its solubility in water, temperature, humidity and PH of soil, humus content, pesticide ability to bond with colloid particles of mineral and organic substances and on whether a pesticide is used on a one-time basis and for the first time, or for multiple uses over a period of several years.

Pesticides degradation processes in soil are various and they comprise dehalogenation, dealkylation, reduction, oxidation, hydrolysis, hydroxylation, decarboxylation, etc.

The paper will show products of insecticide imidacloprid degradation which has different effects in comparison with other insecticides.

PESTICIDES

Pesticides are a common name for all chemical agents used in agronomy, forestry, animal husbandry, food industry and communal hygiene for protection against insects, microorganisms, maggots, rodents, slugs, birds, weeds and other biological agents.

According to the type of harmful biological agents (pests) which are destroyed or whose occurrence is prevented, pesticides may be classified as

- Insecticides - they control and kill insects, the most numerous and dangerous type of pest
- Fungicides - they control and kill parasite, phytopathogenic fungi and bacteria
- Herbicides - they control and kill weeds and other parasite plants
- Acaricides - they control and kill maggots
- Nematicides - they control and kill nematodes
- Limacides - they control and kill slugs and snails
- Bird repellents - they repel birds
- Rodenticides - they control and kill rodents as direct pests
- Repellents - they repel birds and rodents.

Chemical classification of pesticides

According to their chemical composition pesticides may be divided into five groups:

- Pesticides halogen derivatives of hydrocarbon (DDT insecticides and homologues, cyclohexane compounds derivatives of lindane and polychlorocamphene)
- Homologues and benzene derivatives (insecticides, fungicides, bactericides and herbicides)
- Phosphorous compounds (inorganic Zn_3P_2 , organic insecticides, acaricides, nematicides, fungicides, herbicides)
- Carbamide (fungicides, insecticides, herbicides)
- Triazine preparations (herbicides)

PESTICIDES DEGRADATION

Depending on chemical and physical properties of pesticides and soil, climate conditions, biogenesis of soil, the fate of pesticides in soil may be very different. Pesticides may create a bond with various compounds in soil, they may be adsorbed to soil particles, they may vaporize, leached into deeper layers of soil, plants may absorb them via their root system while the representatives of the fauna ingest them. Besides, degradation of pesticides which may be microbiological, chemical and photochemical may occur.

Degradation of pesticides depends on chemical properties, initial concentration, size of particles, its solubility in water, temperature, humidity and PH of soil, humus content, pesticide ability to bond with colloid particles of mineral and organic substances and on whether a pesticide is used on a one-time basis and for the first time, or for multiple uses over a period of several years.

From the ecological point of view, persistence of the preparation itself and degradation products, which may be more or less toxic than the basic compound, is very important.

Pesticides in soil should remain stable as long as possible so that the desirable objective could be achieved and then to decompose as soon as possible into compounds with no harmful impact on living organisms.

According to their persistence (stability) in soil, pesticides may be divided into several groups. Pesticides of low persistence are those which remain in soil i.e. maintain their effects up to 30 days, pesticides of medium persistence from 30 up to 60 days and persistent pesticides from 6 months up to one year, while highly-persistent pesticides remain in soil for more than two years.

Persistence of pesticides depends on chemical property of a compound, type of soil, ecological conditions, soil cultivation, plant coverage, etc.

The insecticide IMIDACLOPRID is a chemical patented by Bayer and is sold under other names: Kohinor, Gaucho, Prothor, Condifor. It is used for pests control, seed treatment, termite control and as a systemic insecticide.

The chemical works by interfering with the transmission of stimuli in the insect nervous system.

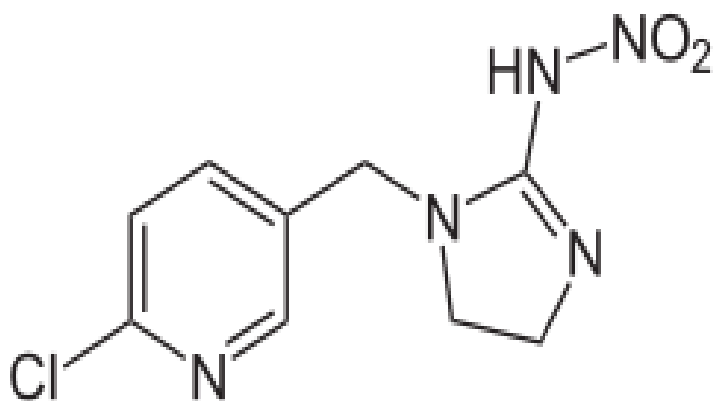


Figure 1. Structural formula of imidacloprid

Toxicity of imidacloprid – toxicity index is 18919, while the waiting period is 28 days.

Toxicity may be:

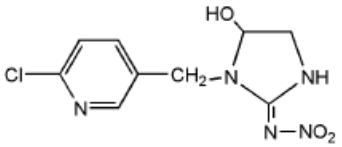
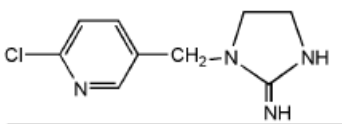
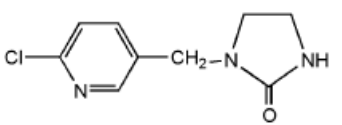
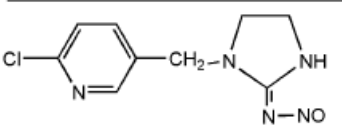
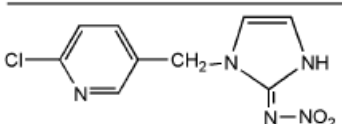
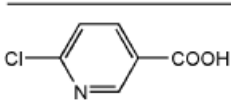
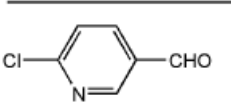
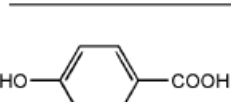
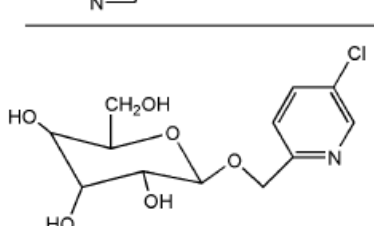
- Acute (caused by one ingestion)
- Subacute (ingestion over several weeks)
- Subchronic (up to two year of ingestion)
- Chronic toxicity (caused by ingestion over several years).

Imidacloprid exhibits no genotoxic or mutagenic potential and has no primary reproductive toxicity.

IMIDACLOPRID DEGRADATION PRODUCTS

Nine types of products are results of Imidacloprid degradation and their structure is shown in Table 1.

Table 1: Structural formulae of Imidacloprid degradation products

	1 monohydroxy-imidacloprid
	2 Imidacloprid guanidine: 1-(6-chloropyridin-3-ylmethyl)imidazolidin-2-ylideneamine
	3 Imidacloprid urea: 1-(6-chloro-3-pyridimethyl)-imidazolin-2-one
	4 Imidacloprid nitrosimine
	5 Imidacloprid olefin: 1-(6-chloropyridin-3-ylmethyl)-N-nitroimidazolin-2-ylideneamine
	6 6-chloronicotinic acid
	7 6-chloronicotinic aldehyde
	8 6-hydroxynicotinic acid
	9 monoglucoside of 6-chloropicolyl alcohol

Degradation pesticides in soil

Reduction of pesticide concentration is carried out either on the soil surface by vaporization, codistillation and phytodegradation, or in the soil by chemical and enzymatic (microbiological) degradation, adsorption and leach. Pesticides degradation processes in soil vary and they comprise dehalogenation, dealkylation, reduction, oxidation, hydrolysis, decarboxylation, hydroxylation, etc.

Chemicals which have high vapor pressure are subjected to photochemical degradation faster on the soil surface; the higher the temperature, the faster the vaporization, while pesticide concentration on soil surface is reduced. After they penetrate the soil, pesticides and their degradation products bond with organic substances mainly with humin fractions or humin/clay or mineral fractions of clay. Being in such a bond, the pesticide is hard to extract and determine its quantity, so it is considered to have lost its biological activity. It has been established that all pesticides, to a larger or smaller extent, constitute bound residues with various compounds and the soil affects the ability to adsorbability. Processes which limit bonding are metabolic processes – chemical, photochemical, enzymatic and

processes of metabolism on grown plants or weeds before the substance goes into the soil as well as chemical and microbiological degradation in soil itself. There are two mechanisms involved in bonded residues occurrence: surface adsorption and covalent bond formation. In spite of their high persistence, bonded residues slowly degrade under the influence of microorganisms.

CONCLUSION

Soil is a medium where pesticides are accumulated. The fate of pesticides in soil is defined by effects of various physical-chemical and biological processes which cause degradation and movement of chemicals.

Degradation of imidacloprid results in nine products. The main degradation products in soil are:

- Imidacloprid urea,
- 6-hydroxynicotinic acid and
- 6-chloronicotinic acid

Degradation products may be of higher or lower toxicity than the basic compound. Reduction of pesticide concentration in soil is carried out through chemical and enzymatic degradation. Pesticide degradation depends on chemical properties, initial concentration, solubility in water, quality of soil, kinds of pesticide application, humidity and PH of soil, pesticide ability to bond (adsorption) with colloid particles of mineral and organic substances. Soils vary in their adsorption ability. Processes which limit bonding are metabolic processes in plants and chemical and microbiological degradation in soil.

Persistence, i.e. ability to remain in the soil, i.e. the rate at which they disappear from the soil is important from the ecological point of view.

The moisture content affects pesticide persistence, i.e. their solubility in water, temperature of soil, and susceptibility to hydrolytic degradation.

Regardless of their high persistence, bonded residues are slowly broken down under effects of microorganisms. Pesticides which form biologically inactive residues with long half-life of degradation may have weaker effects on soil organisms than pesticides which plants or soil microorganisms more easily uptake.

The problems in connection with pesticides residues in soil comprise:

- Translocation of pesticides into future crops with the possibility to accumulate or cause phytotoxicity,
- Effect on soil macroorganisms and microorganisms,
- Their transfer to aquatic systems, leaching and reaching underground waters used as drinking water sources, and
- Long-term unfavorable effects on soil fertility and quality

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PUBLIC HEALTH AND THE ECOLOGY OF URBAN AREAS

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**CONTAMINATION OF SOIL WITH HEAVY METALS AND THEIR
GEOCHEMICAL AN INVESTIGATION**

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ABSTRACT

The production of sufficient quantities of good quality and healthy food is becoming increasingly complex task of world agriculture, because it achieves all the smaller areas. The intensive cultivation of crops involves the application of fertilizer and pesticides as an essential measure to achieve high and stable yield, which can lead to unwanted contamination agro ecosystems. The soil has many ecology functions which are essential for the environment, for sustainable development in the agriculture but also for the economy and the development of the society in whole.

Key words: *contamination, environment, soil, food.*

INTRODUCTION

Soil contamination with heavy metals represents a chemical degradation. In nature there are soils that are literate rocks such as basic and ultra basic that contain significant amounts of heavy metals with this possible contamination with heavy metals has litogenics origin and usually occurs in the solid phase soil in the form of various minerals that are insoluble in water. Significantly dangerous anthropogenic degradation in which heavy metals come in different forms and participate in various processes in the soil, similar biogenic elements.

Contaminated soils with heavy metals is a serious environmental problem, human and animal health and therefore preventing soil degradation represents a major challenge. This is achieved by specific policy measures for the protection and management of soils in which the measures for removing or reducing the contamination are complex, and the manner of their application will depend on the manifolds of harmful substances in the soil. It is important to emphasize that this precious resource is irreplaceable and course destroy means should be kept and future generations who come to the village over in better condition. Some heavy metals represent important biogenic elements which, in small quantities, are necessary to plants (Zn, Mn, Ni and Fe) while others are not essential biogenic elements (Pb, Cd, Cr, As, Hg). At increased levels, both essential and non essential metals are toxic (Karenlampi, et al., 2000). The world research results show that there are areas with expressed deficits and surpluses of many of the plants' essential elements (Bertić et al, 1985; Filipović et al. 1993; Čuvarđić et al. 1993; Mitkova, 2005; Andreevski, 2009).

RESULTS AND DISCUSSION

Heavy metals in soils come from the parent substratum where they are formed in the course of soil genesis or they are produced antropogenic (industry, traffic, agriculture etc.)

In this research will be reviewed two Asked heavy metal contamination of the soil and its consequences in the territories of the Republic of Macedonia

Anthropogenic soil degradation is very intensive occur very quickly depending on the proximity of the source of pollution, or by repeating with larger disasters. Huge of heavy metals of anthropogenic origin comes in solid phase of the soil directly into insoluble form or can past soluble form in the soil solution, insoluble form in the solid soil phase

Some of these elements in minimal quantity are of biogenic importance for wildlife. Plant it: Co, Cu, Fe, Mn, Mo, Zn, and animals: Cr, Ni, Sn. Contamination in our soils is the biggest and most common with lead, zinc and cadmium, and rare with copper, chromium, nickel arsenic, mercury and manganese. These heavy metals in larger quantities can reduce soil fertility or lead to sterilization of the same.

Heavy metals have different phytotoxicity in the same concentration. Plants adopt these hard metals same way as adopt makronutrients. Adoption of most heavy metals increases, with acidification of the soil solution, Assist is decreases influenced alkaline take alkaline elements kalcization.

Different limit values for heavy metals are often given by various authors, or the same vary between countries and regions deepening on the manner of use of the soils, the contents of clay, organic matter, pH of the soil solution etc. (Hinsenveld, 1991; Ubavić et al, 1993; Visser, 1993; Kabata - Pndias, et al 1995; Kastori, 1990,1997; Kàdàr, 2001).

When chemical analysis of soil is important to know natural content of heavy metals inherited from the parent material, and the maximum content is determined on the basis of toxicity technical metals on living organisms.

Contamination affecting the area under pasture and under various crops, and is extremely dangerous. Heavy metals plant clients adopt entering the food chain and thus act harmful to humans and animals. Especially toxic: Pb, Cd, Hg and As.

In the Republic of Macedonia greatest heavy metal soil contaminants exploitation of mines coal, zinc and copper lead and zinc smelter in Veles, large industrial complexes Feni Industry REK Bitola, Zelezara - Skopje Okta oil and refinery Skopje. etc No.1 rounded main sources of soil pollution by heavy metals.

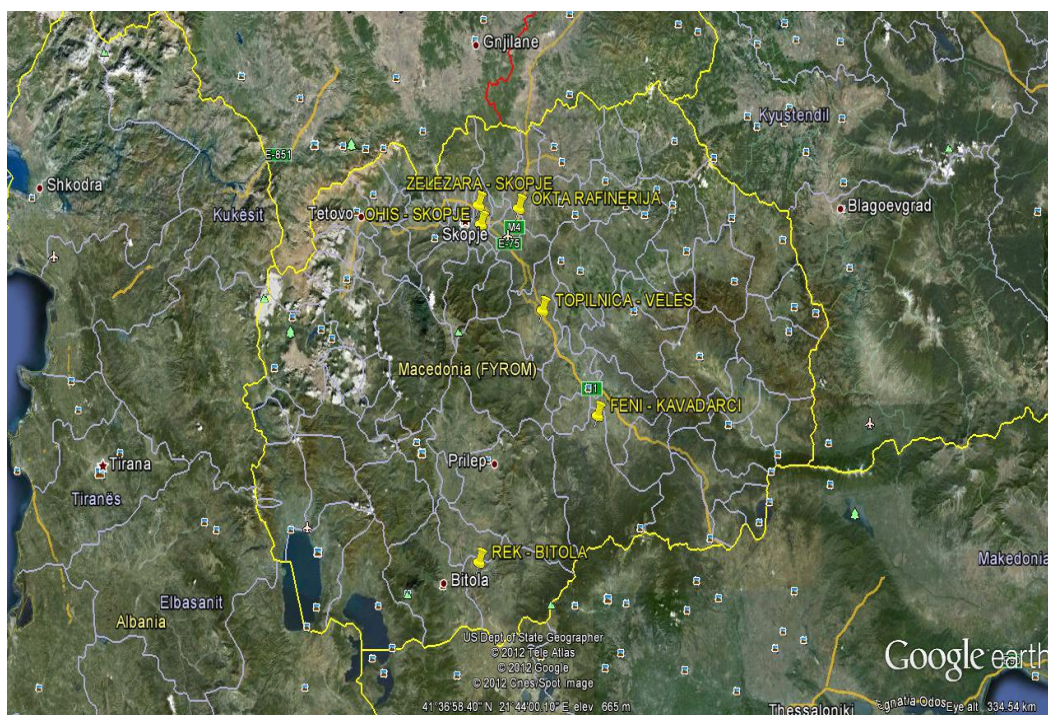


Figure 1.

To get a better representation of soil contamination with heavy metals on figure 2. given some basic indicators for 10 heavy metals in the territory of the Republic Macedonia.

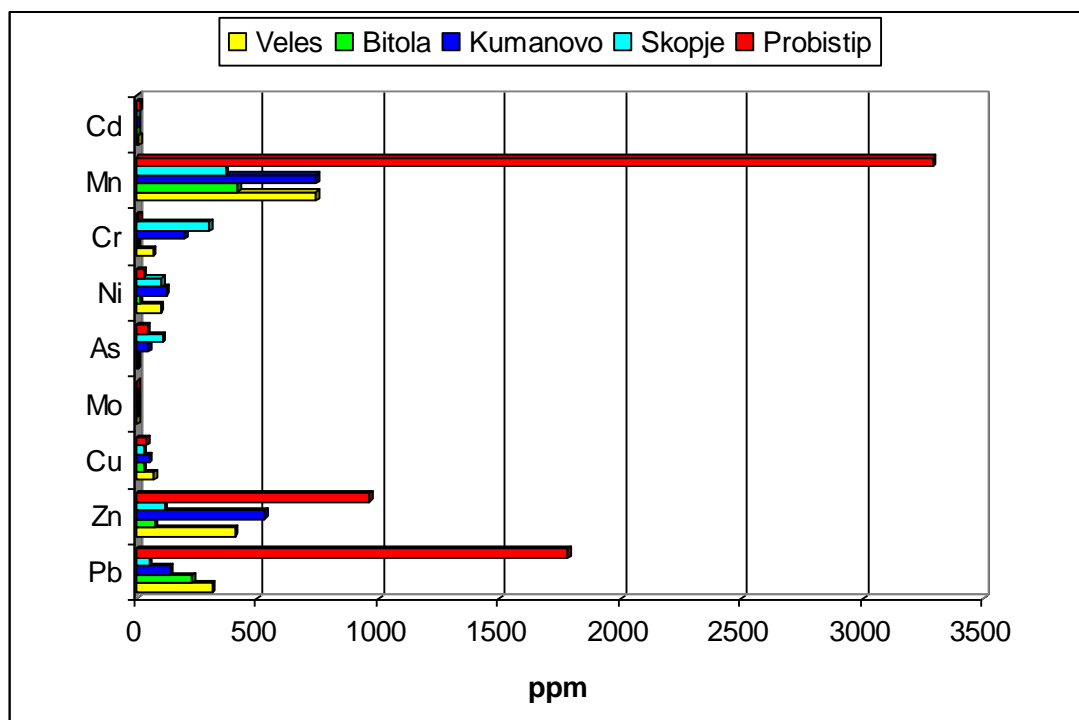


Figure 2.

Highest values of heavy metals especially Pb, Cd and Zn has Probistip, where in 2003 there was a spill of tailings from the lead and zinc mine in Zletovo - adjacent Probistip.

As the most characteristic example of soil contamination with heavy metals will take soil in and around the lead and zinc smelter in Veles. Smelter does not work, but as a result of three decades of work. The total amount of lead in the soil layer of 0-20 sm is above the maximum concentration in the vicinity of the smelter and in fields adjacent smelter has 3 one more lead than allowed, with 200m before smelter 67.2 times lead than allowed. The average content of lead mobility is much smaller than that of the total and in percentage was 1.1 to 54%. The accumulation of zinc is lower but it is above the maximum limits (1.7 o 5.8 times). Similarly, lead and zinc is the most abundant on the surface of the soil, and as it goes down its amount decreases. Cadmium is present in amounts above the maximum permissible concentration (1.4 to 3.6 times more arable land around the smelter, while 2.2 to 5.5 times in unworkable areas around the smelter, while 2.2 to 5.5 times in unworkable areas near the smelter) Local Agenda 21 for the Municipality of Veles, 2005).

CONCLUSION

Heavy metal contaminated soils Environmental serious problem for human and animal health and thus prevent soil degradation represents a challenge. Ova achieved by specific policy measures for the protection and management of soils in the measures for the elimination or reduction contamination are complex, and the manner of their application will depend on the type of harmful substances in the soil.

Accumulated heavy metals in the soil are incorruptible, can not be removed by natural processes, purification and also can not be fully removed from the plants. In raw soil heavy metals accumulate on the surface or very shallow of several cm, while in agricultural soils in ploughed field.

In R. Macedonia identified 16 sites with soil contamination, characterized as hot spots. But unfortunately there is still no strategy and national policy for the management of contaminated sites.

Great task to decontaminate polluted soils with heavy metals when you need to perform zoning contaminated surfaces, to make recommendations on cultivation crops that have lower capacity absorption power to allow the diversion of agricultural production and depending on the financial capacity to implement the remediation of polluted soils.

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**POSSIBILITY OF RECYCLING MEDICAL WASTE IN THE REGION
BIJELJINA IN THE FUNCTION OF ENVIRONMENTAL
PROTECTION**

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ABSTRACT

In this paper is data collected the quantity and category of medical waste generated in health care facilities in the area of Bijeljina region in order to investigate the possibility of establishing and implementing the recycling process. Set up a system of recycling medical waste in health care facilities may be subject to certain conditions that positive economic and financial results, keep material national resources, create the basis for new knowledge and jobs, and improve business and aesthetic living conditions. The paper explores the possibilities of economic evaluation of selected components recyclables from medical waste to reduce the level of environmental pollution, using the recycling of non-hazardous medical waste offenses.

Keywords: *Medical waste, recycling activities, secondary raw materials, economic and financial analysis.*

INTRODUCTION

Result of continuous and dynamic growth of the degree of urbanization, economic wealth and population growth in the developed countries but also in developing countries, generating an increasing amount of medical waste. Between 75% and 90% of medical waste generated in the health sector, can be compared to municipal solid waste (non-hazardous waste), and the remaining 10% to 25% of the total waste is considered potentially dangerous.

In the region of Bijeljina numerous health facilities, currently implemented less effort in managing medical waste in accordance with the recommendations of the World Health Organization (WHO) and EU Directives. Hospitals as a source of medical waste generated in practice are not made of waste segregation at source and in most cases, the waste is collected along with SWM and ends without processing the dump, which poses a serious threat to environmental quality and public health. The main problems related to the lack of separation operations hazardous and non-hazardous medical waste, lack of educational training for medical waste management in health institutions and the lack of monitoring of the quantity generated. (Stankovic, A.et. al. 2008.).

The World Health Organization has classified medical waste to hazardous and non-hazardous medical waste. Based on WHO statistics average structure of medical waste generated in a health facility is shown in Figure 1 Non-hazardous waste (general waste) takes up about 80% and hazardous waste about 20% (pathological and infectious waste 5%, chemical and pharmaceutical waste 3%, blades 1% and special hazardous waste 1%). (Chaerul M. et. Al .2007).

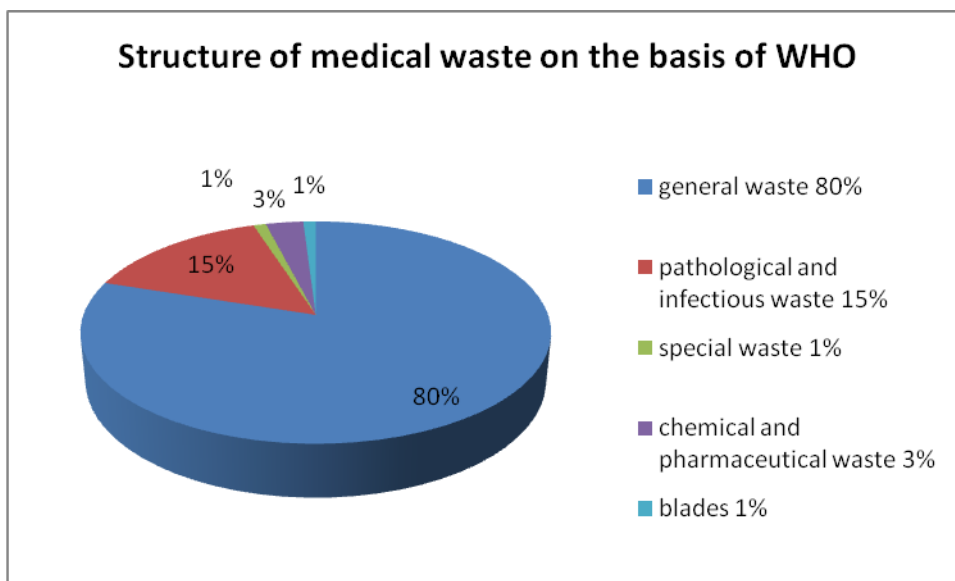


Figure 1. The structure of medical waste according to WHO

In order to establish a system of recycling and use of secondary raw materials from medical waste, it is necessary to determine the amount and category of medical waste generated in efficiency and the possibility of recyclable components.

RESEARCH METHODOLOGY

The research is based on data collected through surveys in the territory Bijeljina region, where about 450,000 people are concentrated and 42 health facilities (taken into account the greater generating sources), which are arranged on the primary and secondary levels of health care.

From a technical point of view surveys related to the total amount and the volume of medical waste generated in health care facilities.

Analysis of possible isolated amounts of recyclable components from non-hazardous medical waste, reducing the volume of waste to be deposited, on the other hand come to the financial gains from the sale of recyclable materials in the market.

The research area

The Republic of Srpska was created by the Dayton Peace Accords in 1995. The atypical shape and has the country's territory, which is elongated in the north part of the west-east, and the eastern part of the north-south direction. The total area is 24 617 km² and inhabited by a population of 1,439,673.

The study was conducted in the cities of Bijeljina, Ugljevik, Lopare, Brcko and Zvornik. (Figure 2)

Sudden urbanization and large-scale migrations of population, especially in urban areas, caused by the conflict, mainly due to the increase in the number and structure of medical facilities. Holders and organizers of most of the health services research field hospitals, dialysis centers, health centers, clinics, dispensaries and pharmacies.

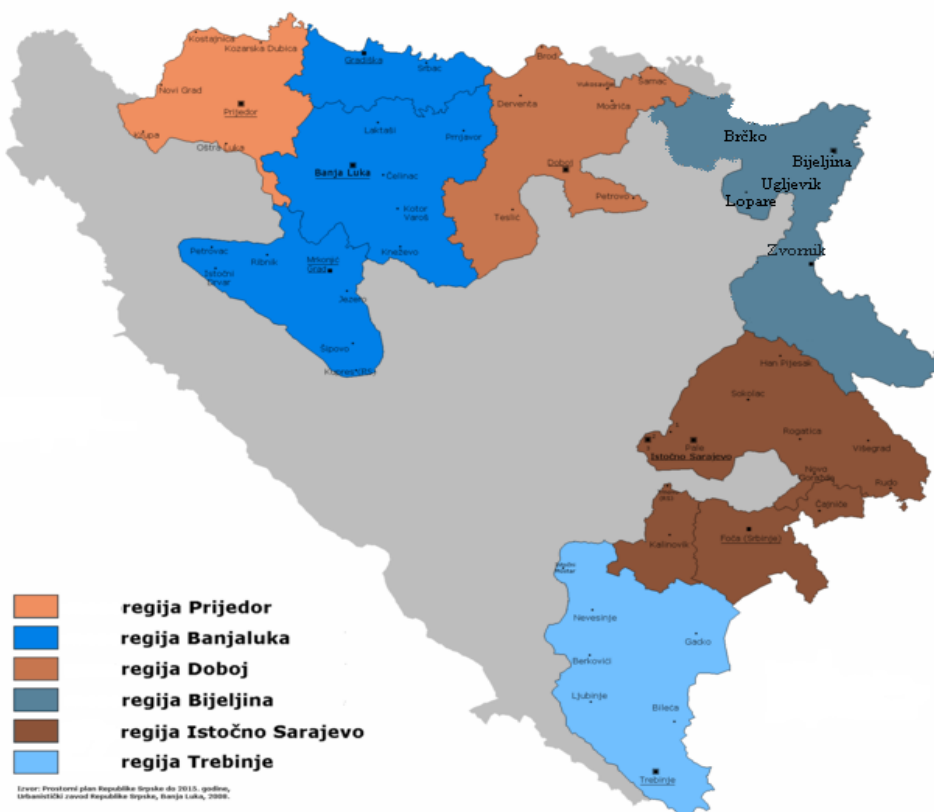


Figure 2. Regional map showing the The Republic of Srpska areas of research

RESULTS

The current practice of irresponsible depositing medical waste without sorting and detoxification, leads to the loss of natural resources, and the rapid spread of infectious diseases, transmission of microorganisms through water, soil and air, as well as through rodents, insects and birds. Good practice in the treatment of medical waste includes its classification at source of hazardous and non-hazardous (general) medical waste, with opportunities created by the application of specialized treatment procedures for hazardous waste and non-hazardous waste from recyclable components stand out. In this way, shortening time to waste re-use, with subsequent cost savings and increase the quality sorting of recyclable materials.

Results of the survey of health facilities in the region Bijeljina

The result of the survey of health facilities in the region Bijeljina, generisanjog shows the approximate amount of medical waste. Thus, the weekly survey on a monthly basis for estimation of the total amount of medical waste generated in each department in each building 42 major medical institutions. The absence of a system for monitoring the amount of waste generation leads to some inaccuracy of data, so they should be taken with some reserve. Some data obtained estimates are statistically reduced in these municipalities in order to improve the precision of estimates, as well as quality impacts to the prediction of the amount of waste generated.

Category, volume and quantity of medical waste generated varies depending on the type of health care facilities. It is notable that the medical waste is generated in the diagnosis, treatment and immunization of patients. Identified the following types of hazardous waste: pathological and infectious waste, sharps, pharmaceutical products, pressure vessels, chemical waste and inert (general) waste. Table 1 summarizes the average total quantity of medical waste per month, which is generated by the various medical facilities.

Table 1: Review estimates the average amount of medical waste generated gathered by surveying the territory of the region Bijeljina

Type of health facility	Estimated total amount of medical waste (t / month)
Health care centers	56,9
Dialysis Centers	71,4
Polyclinics	132,1
Hospitals	155,1
Ambulance	24,5
Total:	440,0

According to the World Health Organization (WHO), we can assume that the total amount of medical waste generated by 440 tons per month, reduce it to 80% inert (non-hazardous) waste and 20% of hazardous waste, which in our study was 352 tons and 88 tons of non-hazardous of hazardous waste per month. Figure 3.

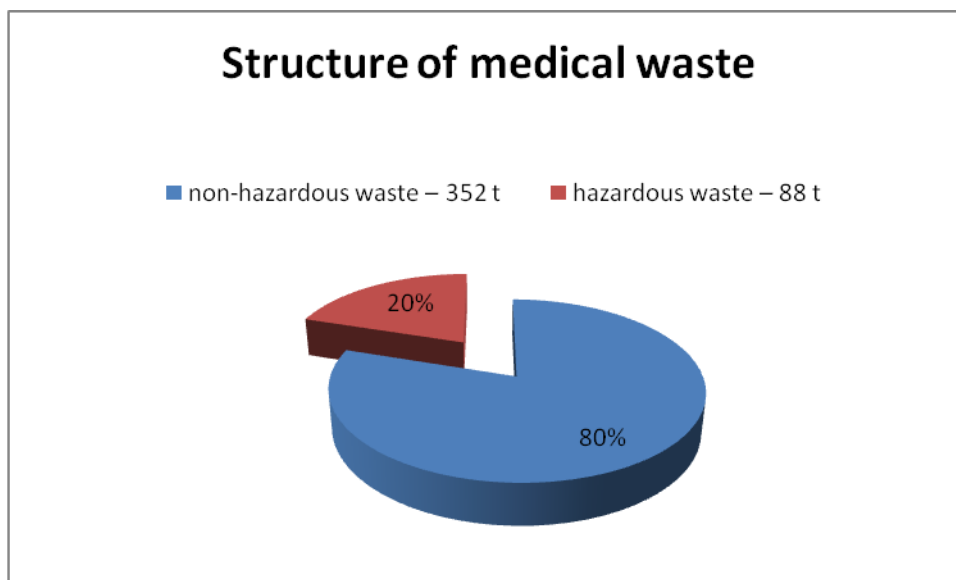


Figure 3. Percentage composition of the total amount of medical waste generated in Bijeljina region

Based on WHO data, we can compare the average structure of non-hazardous medical waste and recyclables down to the weight and volume percentage: paper, plastic, organic waste, diapers, metal, glass, and other yard waste. (Table 2.)

Table 2: The share of raw materials in the structure of non-hazardous medical waste

Secondary raw materials	Weighted participation	Volume participation
Paper	53	20
Glass	2	2
Plastic	14	35
Metals	3	2
Diapers	4	1
Organic waste	17	36
Yard (plant) waste	2	2
Others	5	2
Total	100%	100%

Table 3. shows the structure of the bulk and volume of non-hazardous medical waste generated in the region of Bijeljina on a monthly basis, where it clearly shows the quantities of raw materials to establishing recycling activities.

Table 3: The amount and volume of secondary raw materials

Secondary raw materials	Quantity (tons)	Volume (m ³)
Paper	187	2671
Glass	7	21,5
Plastic	50	357
Metals	11	16
Diapers	14	80
Organic waste	60	150
Yard (plant) waste	7	17,5
Others	16	32
Total	352	3.345

Many factors are involved in the generation of medical waste, often are connected to each other and require a comprehensive analysis.

Reducing the total volume of non-hazardous medical waste for disposal

For the estimated quantities of non-hazardous medical waste have been adopted by the medium density of waste types. Medium Density adopted the recommended literature consulted, although the value of density generally depends on several influencing factors. In Table 4. provides an overview of the adopted medium density recyclable components for some of the non-hazardous medical waste.

Table 4: Medium density recyclable individual components

Recyclable component	Medium density (t/m ³)
Paper	0,070
Glass	0,330
Plastic	0,140
Rubber	0,195
Textiles	0,175
Metal	0,700
Organic waste	0,400
Other	0,500

The separation of recyclable components from non-hazardous medical waste, which are easily available in practice reduces the volume of waste to be disposed.

The initial volume of non-hazardous medical waste per month to 352 tons, or an average of 3345.0 m³ is reduced to about 2364.0 m³ of waste per month, after the separation, as shown in Table 5.

Table 5: Possible reduction in volume on a monthly basis

Raw material	Capacity share (%)	Monthly volume (m ³)	Coefficient of utilization	After separation (m ³)
Paper	20	2671	0,3	801,5
Glass	2	21,5	0,3	6,5
Plastic - unclassified	35	357	0,3	107,0
Metal	2	16	0,8	15,0
Organic waste	36	167,5	0.3	51,0
Total:				981,0

If it is assumed, that one part of waste that can theoretically be extracted, remain mixed with the rest of the waste for final disposal, it is obvious that by decreasing the volume of waste by 30%, making the useful life of the existing landfill effectively extends and significantly slows the depletion of natural resources, raw materials, and reducing emissions from landfills.

Economic and financial analysis

Analyzing the possible financial gain (Table 6) of the separated recyclable components, we arrive at a monthly income of around 2,491.50 €, and the annual income is 29,900.00 €.

Table 6: Possible financial monthly effects

Raw material	Weighted participation (%)	Monthly quantity (t)	Possibly extract (t)	Sale price (€ / t)	Revenues (€ / month)
Paper	14	187	56,1	25,0	1.402,00
Glass	2	7	2,1	15,0	31,50
Plastic - unclassified	12	50	15	50,0	750,00
Metal	2	11	8,8	35,0	308,00
Total:		255	82		2.491,50

Funds received by selling secondary raw materials in the market, health care institutions in the region could settle utility bills and purchase supplies. Investment funds in the present, to the revenues and benefits over the years in the future, thereby reducing the high level of uncertainty and have the expected socio-economic performance of these investments.

DISCUSSION

Traditional financial analysis examines cash flows of the investment project, without considering the costs and benefits that the project brings to society as a whole. Economic analysis is an upgrade of the financial analysis and takes into account the wider effects of investment projects on society and the environment. In comparison to standard financial analysis, economic analysis includes a social dimension (in which the company is de facto investor).

Termination degradation of water, air and soil, represents a significant step forward in preserving the environmental quality of the region Bijeljina, improves the level of culture and improving living conditions for future generations.

Separation of the total amount of medical waste generated at the site is the most environmentally friendly solution and would be used as a pretreatment, followed by a non-hazardous medical waste can be transported, recycled and disposed of the remainder of the landfill complex. Certainly, this proposal represents an interim solution, which fits well into the future final solution - the construction of plants for the incineration or purchase of equipment for the destruction of hazardous medical waste.

CONCLUSION

On the basis of this research, it can be concluded that there is a possibility of increase in medical waste generated in Bijeljina region, due to the absence of recycling activities. It is essential that the management of health care institutions and decision approaches of education of staff in order to increase the degree of separation and selection of medical waste at the source. Proportion of potentially hazardous medical waste, which represents 2% of the total amount of medical waste, can be further reduced by 1-5% with the use of the appropriate procedure of separation at the source.

Separation of recyclable solid waste components still remains a part of waste that must be landfilled. The total amount of solid waste prior to depositing reciklažom decreases and thus extends the life of the landfill complex. In the future, shall be deposited only those wastes which can not be utilized.

Since the general hospital is one of the biggest sources of medical waste generated in Bijeljina region, it is essential that the personnel make a serious effort to reduce the bulk and increase the degree of

separation and segregation of medical waste, reducing the use of natural resources and energy as a function sustainable development and European integration.

Applying recycling activities reduces the average amount of waste disposal by 30%, which represents a significant saving on the level of the exploitation of landfill complex. By reducing the volume load dump body for about 12000.0 m³/god extends the life of the landfill complex operation, and marketing of secondary raw materials can bring about an annual income of € 29,900.00 and job creation.

Based on the data presented in this work in this field in accordance with the needs and opportunities of sustainable development of the municipality of Bijeljina, this work opens up new avenues of research waste management in the Republic of Serbian, based on the principles of sustainable development and the demands of European integration.

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**LOW DOSES EFFECTS OF EMERGING SUBSTANCES,
PSEUDOPERSISTENCY AND HAZARD CONSEQUENCES TO
AQUATIC ENVIRONMENT AND PUBLIC HEALTH**

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ABSTRACT

An increasing number of chemicals cause hazardous pressure on the environment, public health and biosphere. Emerging substances (EmS), low doses and pseudo-persistence effect are recognized as a powerful chemical and eco stressors and a strong pressure on total biosphere with the little understanding of toxicology implication. Low doses effect is observed in the picomolar to nanomolar range. Emerging substances can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programs at EU level and whose fate, behavior and (eco) toxicological effects are not understood. EmS are mostly present in waste and receiving waters, in a very low concentration level. The results of our research group indicate the presence of more than 150 different EmS mostly polar compounds, and from the group of pharmaceuticals, personal care products, and anticorrosive agents, flame retardants, endocrine disruptors and others, in the surface water of the river Danube near Novi Sad. The research and detection of EmS within the International Project for Peace and Safety was conducted for the first time in the Danube water samples taken from waste water (municipal and industrial) and surface water in the vicinity of Novi Sad.

Key words: *emerging substances, low doses effect, pseudo - persistence, surface water of Danube River, Novi Sad.*

INTRODUCTION

Emerging substances, physical and chemical characteristics

Emerging substances (EmS) are contaminants/pollutants, that occur in the environment as the result of natural, industrial and human activities and are not included in the routine monitoring programmes but must be candidates for future regulation, depending on their (eco) toxicity, potential health effects, public perception and on monitoring data regarding their occurrence in the various environmental compartments. A wide range of man-made chemicals, designed for use in industry, agriculture, pharmacy, veterinary and as a consumer goods are of extraordinary environmental concern belong to the family of emerging contaminants.

NORMAN (network laboratories monitoring of emerging pollutants) has identified a list of the currently most frequently discussed emerging substances and emerging pollutants today. Examples of EmS on this list are surfactants, pharmaceuticals and personal care products, methyl tert-butyl ether (MTBE) and other related petrol additives and their degradation products, polar pesticides and their degradation products and various proven or suspected endocrine disrupting compounds (EDCs). Another example of emerging pollutants are nanoparticles which behave aerodynamically like gas molecules and have a large surface area per unit mass. NORMAN is open and dynamic list of pollutants which last update has been approved in March of 2011. It consists of 25 different classes of pollutants with more than 750 individual substances with CAS (Chemical Abstracts Service). These classes of substances/pollutants are: Algal toxins, Anticorrosives, Antifoaming agents, Antifouling compounds, Antioxidants, Biocides, Bio-terrorism / sabotage agents, Complexing agents, Detergents,

Disinfection by-products (drinking water), Drugs of abuse, Flame retardants, Food additives, Fragrances, Gasoline additives, Industrial chemicals, Nanoparticles, Perfluoroalkylated substances and their transformation products, Personal care products, Pesticides, Pharmaceuticals, Plasticisers, Trace metals and their compounds, Wood preservatives.

In recent years, EmS, have motivated and provoked increasing concern, particularly as no legal requirements has been set for discharge of these ubiquitous, persistent and biologically active substances into surface water bodies. These arrays of emerging pollutants act as emerging stressors, they are occupational hazard with long existence period, and are produced constantly by myriads of human and industrial activities.

In this paper we would like to emphasize the new phenomena of EmS low doses, pseudo -persistency and the new approaches to their negative effects. The two case studies based on the literature references of occurrence of emerging substances in the river Danube and Somes river will be described and presented, as well as the first original preliminary screening results of the occurrence of EmS in the river Danube in the vicinity of Novi Sad, obtained by our research activities.

Physicochemical characteristic of EmS

The dominant physicochemical characteristics particularly specific for EmS are: low doses occurrence and effects, pseudo - persistency / persistency, steady and constant structure, low/non degradability, hydrophilicity and lipophilicity ($\text{Log } K_{ow}$ in the range of 0.6 – 6.2), bioconcentration/bioaccumulation in aquatic organisms, toxicity with hazardous effects with acute, but rather chronic effect, endocrine disruption, suspected teratogenic and carcinogenic consequence in low and sublow doses, volatile, non - or semivolatile compounds, water soluble molecules, but could be lipid soluble, polar molecules, and others. Emerging compounds can be neutral, acidic, basic, and ionic or zwitter ionic.

Their main physical and chemical properties are characterized by following constants of: protonation ($\text{Log } pK_a$) which lie in the range of 9.6 – 2.5, octanol–water partition coefficient ($\text{Log } K_{ow}$) which lie in range 0.35 – 6.02 and solubility (S_w) which lie in range from $1 * 10^6$ mg/l to 0.02 mg/l.

The sorption removal of EmS are quite low (<20%). According to a simple rule, compounds with $K_d > 500$ L/kg ($\text{Log } K_d > 2.7$) potentially tend to adsorb onto sludge and particles. According to the literature references, $\text{Log } K_d$ values for most of selected EmS substances are less than 2.7 confirming their low tendency to adsorb. The value of EmS/pharmaceuticals molecular charge at pH 7 provides information about its potential to create electrostatic interactions with the negatively charged soil/sediment surface. Sorption of EmS compounds is in general pH dependent.

Attempts to correlate biodegradation removal of EmS to its molecular structure demonstrate that a large set of emerging organic chemicals including type of esters, nitril and aromatic alcohols may increase biodegradability while aromatic amines, iodide, nitro- and azo- groups increase the persistency of the compound. The long and highly branched side chains (i.e. ranitidine) could provide EmS compounds more persistent as well as complicated aromatic ring structure (i.e. diazepam) and halogen group.

Chemical and physical properties of EmS (solubility, volatility/semivolatility, adsorbability, absorbability, biodegradability, polarity, stability, persistency) vary greatly depending on different molecular structures and number of asymmetric C atoms, which have great repercussions on biosystems, environment and human health. EmS belong to the old chemical classes which are newly recognized as well as the new chemical classes, new types of use, new effects, not well known mechanism of action, source or (way of introduction) pathway of exposure.

For most EmS, there is currently little information about their potential toxicological significance in ecosystems, particularly from long - term low - level environmental exposure.

The fate and the transport of EmS in natural aquatic media are practically unknown, especially in context of water/soil/sediment distribution and partitioning processes.

Low - dose effect and non monotonic dose response

At the beginning of 21 century, a "low dose" effect was proposed based on studies which showed that hormonally active environmental emerging agents were causing a variety of adverse effects, mainly reproductive and developmental, at "low doses." One of main physicochemical characteristics of EmS in surface and waste water is very low and sublow doses in the range of nano- and pico- molar concentration. There are two major characteristics of endocrine disrupting chemicals (EDCs), low dose exposures and non monotonic dose response curves (NMDRCs). Natural hormones act at extremely low serum concentrations. Many studies showed that EDCs can act in nanomolar to micromolar range, which is the same concentration level in which active EmS were found in surface and wastewaters, and potentially in drinking water. Low doses include a dose below the lowest dose at which a biological change for a specific chemical could be measured. Any dose below the lowest observed effect level or lowest observed adverse effect level (LOAEL) is considered a low dose.

NMDRCs present an important challenge to traditional approaches in regulatory toxicology, which assume that the dose response curve is monotonic. There is now substantial evidence that low doses of EDCs have adverse effects on human health as well as on wildlife, including nonmammalian species.

The traditional thinking in toxicology studies are not adequate to assess adverse effects from these hormonally active EmS because they do not recognize the effects occurring at "low doses." It is claimed that "low dose" effects are occurring at levels comparable to those to which humans are being exposed.

“Low dose” effects could be defined as specific phenomena that occur in the range of human exposures or effects observed at doses below concentration level that are used for traditional toxicological studies. Non-monotonic dose response curves, defined as a nonlinear relationship between dose and effect were the slope of the curve changes sign somewhere within the range of doses examined.

Table 1: Low-dose definitions and cutoff doses: Bisphenol - A , BPA

Chemical	Estimated range of human exposures	Doses below the NOAEL	Doses below the LOAEL	Administered doses (to animals) that produce blood levels in typical humans
BPA	0.4 – 5 g/kg d (679)	No NOAEL was ever established in toxicological studies	50 mg/kg d (38)	400 g/kg d to rodents and nonhuman primates

NOAEL - No observed adverse effect level

LOAEL - Lowest observed adverse effect level

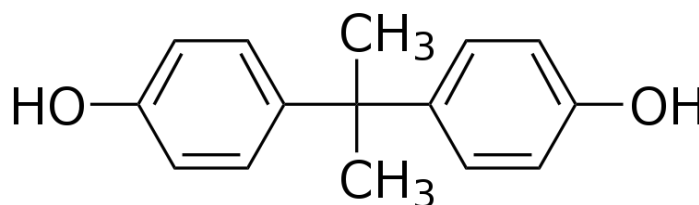


Figure 1. Bisphenol A, Solubility in water 120–300 ppm (21.5 °C)

Biological hormone concentrations in human organism are in the range of micro, nano- and picomolar level, i.e., in the same range of occurrence of EmS in the environment, particularly in waste-, surface-, and groundwater. Higher concentrations of chemicals, are characterized by the properties of aggregation, association and, clustering with the number of molecules from $N=2$ to infinity. Substances present in higher concentrations (high doses) are found as bimolecule system to polymolecule system. Cluster, aggregation and association form, reduces the effective concentration of chemical substances, slowing chemical reaction rate, reactivity, mobility and the effect on other systems.

Molecules of EmS in aquatic solutions in very low molar concentrations are free in the sense of activity, rate and effects, i.e. exist in the state of mono molecules. Free mono molecules have open shape with openly exposed, protruding, active centers which provide mono-molecules with high reactivity and high mobility. Mono-molecules of EmS “attack” different hormone systems in the body. Active concentrations of EmS in solution are effective concentrations with factor of activity concentration $f=1$. Mono molecule, as individual chemical species, can easily “attack” susceptible hormone molecules within living organisms, potentially causing adverse effect. These adverse and hazardous effects of EmS are primarily a result of low concentration levels (nano-, pico-, or even lower). The number of active molecules in picomolar and nanomolar concentrations is in the ranges from 6.02310^{11} to 6.02310^{14} numbers of molecules in picomolar and nanomolar concentrations, respectively. These concentrations of EmS are equal and correspond to the biological concentration of hormones.

Persistence and Pseudo-persistence

Persistence in abiotic matrices (soil, water, sediment), as a physicochemical characteristic, is determined by the rates of the chemical removal by physical, biological and chemical processes. Chemical processes of removal include abiotic degradation processes like hydrolysis, direct/indirect photolysis and oxidation/reduction reactions. Microbial degradation is basic and the most important process of biotic degradation. Standardized test methods are available for most but not all degradation processes. One of the friendly oriented physicochemical test methods is quantitative structure-activity relationships (QSARs), and the methods of pathway prediction system (UM-PPS).

All the persistent chemicals have observed or predicted half-lives with guideline limits for various media. Long life of “overall persistence” (Pov) is based on chemical fate modeling.

In general persistent and bioaccumulative pollutants have the following half-lives in days: water 182 days, sediment 365 days and soil 182 days.

Pseudo-persistence

Emerging chemicals – contaminants/pollutants which are continually released to aquatic environment are attributed as pseudo – persistent even if their half-lives are short.

Pseudo – persistence is the consequences of the constant supply of emerging contaminants/pollutants which are continually replenished in environment, especially in aquatic media, i.e. receiving water or open aquatic bodies.

Toxic effects of EmS in very low doses and the phenomena of pseudo-persistence are particularly important for continual, multigenerational exposure of aquatic organisms.

Thermodynamic kinetic equilibrium processes within domain of pseudo persistence phenomena could be presented by mathematical relation in which the rate of input of EmS (V_i) is considerably higher than the rate of observed EmS output (V_{au}).

$$V_{input} > V_{output}$$

That means that the rate of input (release, emission, generation) of EmS into receiving water is much higher than the rate of output, namely, the kinetic rate of different physicochemical and biological degradation processes, transformation and mineralization processes of EmS.

EmS/pharmaceuticals with short half live, $t_{1/2}$, may be able to cause the same exposure potential and effect as persistent pollutants, i.e. pseudo persistent, since their high transformation and removal rates can be compensated by their continues input into environment/receiving water.

Most Ems/ pharmaceutical substances are by nature, biologically active and hydrophilic, and the human body can take them up easily. Due to structure stability and pseudo - persistency, EmS avoid degradation before they have a curing or toxic effect. EmS/pharmaceuticals could be excreted as a mixture of metabolites, as unchanged substance, or as complex compound. When they enter a wastewater-treatment plant, emerging xenobiotics are either partially retained in the sludge or metabolized to a more hydrophilic chemical species but still persistent form and, therefore, pass through the wastewater-treatment plant (WWTP) and end up in the receiving waters. Their removal in WWTPs is variable and depends on the properties of the emerging substance and process conditions, e.g. sludge retention time (SRT), hydraulic retention time (HRT), temperature and other parameters and types of treatment. Although the concentration levels of EmS are very low, they are detectable in WWTP by sophisticated analytical equipment UPLC tandem double MS, effluents. The presence of pharmaceuticals in surface, drinking, and wastewaters is well documented in the literature. Although present at low concentrations in the environment, emerging drugs can have adverse effects on aquatic organisms. These effects are chronic rather than acute toxic, and depend on exposure and bioavailability, susceptibility to the EmS, stability, lipophilicity/hydrophilicity, water solubility, polarity and degradability.

Recent investigations documented that pharmaceuticals production and administration may vary both between countries and over time fluctuating not only on an annual basis, but also from one year to the next. In addition, the continually ageing population and improving quality of life worldwide mean that their consumption is set to increase in future years. Once administered, pharmaceuticals are metabolized to varying degrees, and their excreted metabolites and unaltered parent compounds can also undergo further modification due to biological, chemical and physical processes in both sewage treatment facilities and receiving water bodies. Finally, municipal wastewater treatment plants (WWTPs) are generally not equipped to deal with complex pharmaceuticals, as they were built and upgraded with the principal aim of removing easily or moderately biodegradable organic compounds and microbiological organisms, which regularly arrive at the WWTP in concentrations to the order of mg L^{-1} and at least 10^6 MPN/100 mL, respectively. Pharmaceuticals in raw wastewaters are generally in the range of 10^{-3} – 10^{-6} mg L^{-1} , and their chemical and physical properties, such as solubility, volatility, adsorbability, absorbability, biodegradability, polarity and stability, vary greatly with consequences on their behavior during the treatments and consequently their removal efficiencies.

Pharmaceuticals have been found in river biota, some at high levels, thereby evidencing the risk that environmental concentrations of EmS/pharmaceuticals can be higher than their predicted no-effect concentrations (PNECs), especially in effluent-of dominant rivers whose dilution capacity and self-purifying processes are insufficient to pose the risk to aquatic life.

Based on the collected data, it could be evaluated the average daily mass load $\text{mg}/1000 \text{ inh}/\text{d}$ in the secondary effluent for the majority of the compounds.

CASE STUDIES

Occurrence of Ems in Danube River

The Danube River (2850 km) is the longest river in the European Union and Europe's second longest river after the Volga. Danube passes through several Central and Eastern European countries, before it flows into the Black Sea via the Danube Delta in Romania and Ukraine. The Joint Danube Survey 2 (JDS2) was organized by the International Commission for the Protection of the Danube River (ICPDR) and is the world's biggest river research expedition ever. An important objective of the JDS2 was the implementation of the European Water Framework Directive (WFD). The Directive's goal is to ensure that rivers and lakes, water bodies, have “good chemical and ecological status” by 2015 – meaning that they should provide clean water as well as good conditions. Article 8 of the WFD contains the requirements to establish monitoring programs “for the monitoring of ecological and chemical water status in order to establish a homogeny and consistent overview of water status within each river basin district”.

Within the Joint Danube Survey 2, polar water-soluble organic contaminants were analyzed in the dissolved liquid water phase of river water samples from the Danube River and its major tributaries. Analyses were performed by solid-phase extraction (SPE) followed by triple-quadruple liquid chromatography mass spectrometry (LC-MS2). Thirty four different polar emerging organic compounds were screened. Focus was given on pharmaceutical compounds (such as ibuprofen, diclofenac, sulfamethoxazole, carbamazepine), pesticides and their degradation products (e.g. bentazone, 2,4-D, mecoprop, atrazine, terbutylazine, desethylterbutylazine), perfluorinated acids (PFOS; PFOA), and endocrine disrupting compounds (nonylphenol, NPE1C, bisphenol A, estrone). The most relevant polar compounds identified in the Danube River basin in terms of frequency of detection, persistency, and concentration levels were 1H-benzotriazole (median concentration 185 ng/L), caffeine (87 ng/L), tolyltriazole (73 ng/L), nonylphenoxy acetic acid (49 ng/L), carbamazepine (33 ng/L), 4-nitrophenol (29 ng/L), 2,4-dinitrophenol (19 ng/L), PFOA (17 ng/L), sulfamethoxazole (16 ng/L), desethylatrazine (11 ng/L), and 2,4-D (10 ng/L). The highest contamination levels were found in the area around Budapest and in the tributary rivers Arges (Romania), Timok (Bulgaria), Rusenski Lom (Bulgaria), and Velika Morava (Serbia).

The highest maximum concentrations in the Danube River were found for caffeine (1467 ng/L), benzotriazole (380 ng/L), NPE1C (307 ng/L), nonylphenol (240 ng/L), tolyltriazole (130 ng/L), bisphenol A (68 ng/L), carbamazepine (66 ng/L), and terbutylazine (63 ng/L), and in the tributaries for caffeine (6798 ng/L), 4-Nonylphenoxy acetic acid (NPE1C) (3352 ng/L), nonylphenol (1400 ng/L), carbamazepine (945 ng/L), ibuprofen (718 ng/L), bisphenol A (490 ng/L). Median concentrations however were lower in the tributary rivers for many compounds, e.g. for 2,4-D, mecoprop, ibuprofen, PFOA, PFOS, caffeine, carbamazepine. Nonylphenol and bisphenol A were detected in only a few samples, but at relatively high concentrations, which shows that these substances are apparently only used in some areas. They are relatively fast degraded in the river water.

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Mass discharge and chemical emissions to the Black Sea

By knowing the concentrations of persistent chemicals in the river water and the river flow of the river (m³/s), it is simple to calculate the mass load of the substances emitted to the Black Sea (kg/day or tons/year).

The total flux of a big river (the Danube) is relatively constant over time. The concentrations of persistent emerging chemicals are relatively constant as well, because they are discharged

continuously from industry and households. During the JDS2 the river flow of the Danube was measured at several points; it was 1180 m³/s in Austria, 1400 m³/s in Hungary after Budapest, 2460 m³/s in Serbia (downstream Tisa), 3200 m³/s downstream the Velika Morava tributary (Romania), 4830 m³/s downstream the Timok, and 6420 m³/s downstream the Arges. The corresponding mass loads for the most relevant persistent chemicals to the Black Sea are reported in Table 1.

Table 2: Mass discharge loads/emissions of persistent chemicals from the Danube River to the Black Sea; river flow = 6420 m³/s

Chemical	Concentration downstream Arges; before Danube delta [ng/L]	Mass load [t/year]
Benzotriazole	167	33.8
Caffeine	152	30.8
Tolyltriazole	84	17.0
Carbamazepine	25	5.1
Sulfamethoxazole	23	4.7
PFOA	12	2.4
Terbutylazine	7	1.4
Desethylterbutylazine	6	1.2
Desethylatrazine	7	1.4
PFOS	6	1.2

Occurrences of pharmaceutical and personal care products as EmS/micropolutats in rivers from Romania

The occurrence of pharmaceutical and personal care products (PPCPs) was investigated in the Somes River, Transylvania. 15 emerging compounds including pharmaceuticals, metabolites, intermediates and musk fragrances were detected in concentration ranging from 30 ng/l to 10 µg/l. The detected pharmaceuticals belong to the following therapeutic groups: analgesics, antiepileptics, psychiatric, stimulants, anticoagulants, antineoplastic and disinfectants.

In every country some pharmaceuticals are used in quantities of more than 100 tonnes/year. Specific studies exhibit that an appreciable proportion of administrated pharmaceuticals are present in the domestic wastewater.

The polycyclic synthetic musk as Galaxolide (HHCB) and Tonalide (AHTN) has large applications as fragrances in soaps, perfumes, air fresheners, detergents, fabric softener and other cleaning products. There are indications that the polycyclic musks are not only to be found in various environmental compartments but also in the aquatic food chain as well as in fatty tissues and human milk.

Due to an incomplete elimination in wastewater treatment plant (WWTP) residues of PPCPs are found both in waste and surface waters. Although most pharmaceuticals are designed to target specific metabolic pathways in humans and domestic animals, they can have numerous often unknown effects on metabolic systems of nontarget organisms, especially on invertebrates.

Caffeine was detected on 4 sites in the range of 430 to 9700 ng/l, respectively, 2800 ng/l in site 1, 9700 ng/l in site 2, 1020 in site 3 and 430 in site 4. The corresponding loads for sites 1–4 are 4790, 18 850, 2160 and 2380 g/d. Caffeine could be used as excellent marker for discharge of untreated wastewater in surface water. It seems that the load of caffeine in Somes River is around of 2200 to

2400 g/d except the points where the discharge of either the effluent of WWTP or of the untreated wastewater is important.

Galaxolide and Tonalide were detected around of 300 ng/l and 100 ng/l. Due to their environmental stability Galaxolide and Tonalide were selected as suitable tracers for musk fragrance . In every studied sample the ratio of Galaxolide with respect to Tonalide was around of 3. The concentrations of pentoxifylline are around 300 ng/l.

The acetylamino phenazone (AAP) and formylamino phenazone (FAP) were detected in relative high quantity in every place. Their concentrations were, respectively, 1248 ng/l and 260 ng/l in the site 1, 1560 ng/l and 509 ng/l in the site 2, 849 ng/l and 214 ng/l in the site 3 and 312 ng/l and 103 ng/l in the site 4.

The Ibuprofen (as analgesic) has been detected in WWTP effluents, surface and ground water. It was detected in almost every sample of the effluent from Europe, which is probable a result of their high prescription extent and wide usage. The annual production of Ibuprofen is estimated to hundreds of tones. It is applied in relative high amounts of 200–800 mg per tablet. In many papers Ibuprofen is investigated as a representative drug of the antirheumatic group of medicaments. The early pharmaceuticals studies show that 14% from Ibuprofen consumed is eliminated as an unchanged drug. The summarized data on elimination of Ibuprofen in a WWTP have shown values ranging from 65% to 90%. In the Somes river the concentrations at selected sites 1, 2, 3, and 4 were 85, 115 and 61 and under LOQ, respectively, corresponding to loads of 146, 224 and 130 g/d. The prescription of Ibuprofen in the studied area is rather high and, as a consequence, discharging the untreated wastewater increases the concentration in the site 2.

Carbamazepine is widely used as antiepileptic and is antidepressant drug and is known as a persistent substance with extremely low removal rate (fewer than 7%) in WWTP. Carbamazepine was detected in quantities of 65, 72 and 75 of ng/l in the sites 1, 2 and 3 but under limit of detection in site 4 (by dilution). The values of loads are around of 115, 140 and 160 g/d for sites 1–3, respectively.

Diazepam is a psychiatric drug used as tranquilliser. In the WWTP effluent was found in the maximum quantity of 40 ng/l but in rivers was not detected above 30 ng/l. The measured values of 30 ng/l (34 ng/l in site 1; 31 ng/l in site 2; 28 ng/l in site 3 and under of LOQ in site 4) and its calculated load values are constant around of 60 g/d.

Moldovan (2005) showed in his study that codeine, cyclophosphamide, triclosan, acetylsalicylic acid (Aspirin) were also detected.

Acetylsalicylic acid (Aspirin) is an analgesic and anti-inflammatory drug very frequently used in medical practice. It was sold in 2000 in quantities exceeding 1000 tonnes/year in EU countries. In UK the used amount is of over 18 tonnes/year . It was found in effluent sewage up 1500 ng/l and in surface waters up 340 ng/l . The WWTP removal efficiency was reported around of 80% . In the influent WWTP the reported quantities of acetylsalicylic acid was of 1500–5000 ng/l, therefore it is expected that in effluent quantity to be 300–1000 ng/l. Early papers reported maximum values of 340 ng/l. In Somes River a quantity of 37 ng/l, 36 ng/l and 28 ng/l in sites 1–3, respectively (under LOQ in site 4), the loads being around of 65 g/d. The constant concentration in the site 1–3 can be explained by the fact that the degradation quantity is substituted by quantity resulting from untreated wastewater discharged along of the river.

A number of two compounds used probably as intermediate in synthesis of pharmaceuticals were also detected. The first one is N,N-bis(3,3-dimethyl-2-oxetanyl)-3,3-dimethyl-2-oxetan-amine in quantities of 92 ng/l, 77 ng/l and 57 ng/l (loads decreasing from 160 to 140 and 120 g/d) in sites 1, 2 and 3, respectively. The second one is p-chlorophenylsulfone in quantity of 108 ng/l (load of 187 g/d) in site 1 (in sites 2–4 were under LOQ). The behaviour of these compounds confirms that the point source is located close to site 1 (Cluj-Napoca city).

Screening Analysis of Wastewater and Danube Surface Water in the vicinity of Novi Sad, Serbia

This research was focused on collecting reliable information on water quality for the part of the Danube River in the vicinity of Novi Sad and conducted within the framework of international project. Sampling of wastewater discharged into Danube in Novi Sad and Danube surface water was performed on December 2011. Collected water samples were analysed by GC-MS. The most frequently compounds occurring in studied water samples were phthalates, PAHs, terpenes and fatty acids. Phthalates are commonly used as plasticisers, industrial and lubricating oils and defoaming agents. Dibutyl phthalate, diethyl phthalate, dioctyl phthalate which are on the NORMAN list of emerging substances and di(2-ethylhexyl) phthalate, which is on the list of WFD priority substances, were detected in all samples. Special groups detected in all waste and river water samples were terpenes like nerol, citronellol, menthol, ionone and other compounds like camphor, ethyl citrate or methyljasmonate that could occur in cosmetics, care products, and home cleaning products. Wide variety of hormones, derivatives of benzene and polycyclic aromatic hydrocarbons (PAHs) were detected in many studied water samples. Presence of hormones in all samples of surface water indicates human or animal faecal pollution and the presence of bacteria in the Danube River could also be expected.

Novi Sad municipality faces a specific problem, deriving drinking water either from the Danube River or from several groundwater aquifers that are under the pressure of different serious pollutant sources. Drinking water abstraction point is located only several hundred meters downstream of the municipality waste disposal point. Several groundwater abstraction points are also used, however, all of them are located under densely settled urban areas, while one of them is located near the oil refinery. Moreover, industries wastewater without treatment systems and extended agricultural activities could be another major source of pollution.

The Novi Sad Municipality Water Supply System is based exclusively on using the groundwater from alluvial aquifers ($Q_{tot,av} = 47 \text{ m}^3/\text{yr}$), tapped by more than 20 horizontal wells situated at three locations along the Danube River. These aquifers belong to the so-called “rapidly rechargeable aquifer” category, since they depend on the hydrological regime of river. The abstraction of water is achieved using bank filtration, meaning that approximately 80-90 % of water in these layers originates from the Danube River and 10-20 % from the backland.

The Oil Refinery of Novi Sad is located in the Sever IV (North IV) industrial zone of the city, and it represents a complex of processing and appurtenant facilities, accompanying storage capacities, auxiliary premises, and other structures. The total Refinery area covers about 250 ha. Apart from the refinery, a thermoelectric and heat generating plant is located in the Sever IV zone. A shipping canal, with loading and unloading facilities for barges, runs along the southern edge of the refinery directly into the Danube River. A system of artificial collecting channels within the refinery compound takes surface runoff to the Danube River, via a wastewater treatment plant equipped with oil separators.

Downstream, on the Danube left bank, close to the refinery, there is the water supply source Ratno ostrvo, feeding the city waterworks. The sewage system is located in the area of the water supply source, collecting wastewater from the refinery and atmospheric water from the Šangaj settlement, as well as the discharge site of the sewage collector Ratno ostrvo. In addition to the refinery, another source of pollution is the agricultural activity in this area.

Although the available information about pollution of water used for abstraction of drinking water in Novi Sad municipality are insufficient, there is clear evidence that numerous harmful inorganic and organic substances, EmS, including detergents, pharmaceuticals, pesticide residues, perfluorinated substances, personal care products chemicals, heavy metals and microbial pollution were detected in the Serbian part of the Danube surface water, including sampling sites downstream of Novi Sad. It is interesting to point out, that the highest contamination levels of EmS in the Danube surface water were found in the area around Budapest which could be in the direct connection with occurrence of EmS in the vicinity of Novi Sad.

The main objective of the study presented in the paper was to gain more insight into organic and inorganic contaminants present in wastewater and Danube surface water in the vicinity of Novi Sad, in order to establish a coherent and comprehensive quality overview of raw water used for drinking water production, to evaluate the risks for human health and environment and to enable the future designing of an up-to-date early warning system (EWS) for the monitoring of selected hazardous pollutants.

Phthalates, PAHs, terpenes and fatty acids belong to the most frequently occurring compounds in wastewater and Danube surface water near Novi Sad. Dibutyl phthalate, diethyl phthalate and dioctyl phthalate that are already on the NORMAN list of emerging substances, as well as di(2-ethylhexyl) phthalate that is on the list of WFD priority substances, were detected in all water samples, which confirmed their ubiquitous presence.

The sources of the most commonly found pollutants in the aquatic environment are, mainly, degradation processes of petroleum hydrocarbons, cosmetic and care products, as well as home cleaning products. Wide variety of hormones, derivatives of benzene and polycyclic aromatic hydrocarbons (PAHs) were detected in many studied water samples. Presence of hormones in all samples of surface water indicates human or animal fecal pollution and the presence of bacteria in the Danube River could also be expected.

The raw water entering water treatment plant contained more than 140 organic compounds and many of them (phthalates, indeno derivatives, alkyl substituted benzenes, naphthalene and phenol derivatives, PAHs, hormones, triphenyl phosphate) are also found in the surface water from the Danube River.

Results obtained during the quantitative analysis of typical municipal alkaloid caffeine confirmed a widespread occurrence in surface and wastewater. Amount of caffeine ranged from 0-84 ng/L. The presence of caffeine confirmed the existence of human waste in the Danube River.

Presented study of the surface water quality was performed for the first time in Novi Sad and its surroundings, where municipal and industrial wastewaters are directly discharged, without any treatment, into the Danube River.

CONCLUSION

Phthalates, PAHs, terpenes and fatty acids belong to the most frequently occurring compounds in wastewater and Danube surface water near Novi Sad. Dibutyl phthalate, diethyl phthalate and dioctyl phthalate that are already on the NORMAN list of emerging substances, as well as di(2-ethylhexyl) phthalate that is on the list of WFD priority substances, were detected in all water samples, which confirmed their ubiquitous presence.

The sources of the most commonly found pollutants in the aquatic environment are, mainly, degradation processes of petroleum hydrocarbons, cosmetic and care products, as well as home cleaning products.

The raw water entering water treatment plant contained more than 140 organic compounds and many of them (phthalates, indeno derivatives, alkyl substituted benzenes, naphthalene and phenol derivatives, PAHs, hormones, triphenyl phosphate) are also found in the surface water from the Danube River. Results obtained during the quantitative analysis of typical municipal alkaloid caffeine confirmed a widespread occurrence in surface and wastewater. Amount of caffeine ranged from 0-84 ng/L. The presence of caffeine confirmed the existence of human waste in the Danube River.

Presented study of the surface water quality was performed for the first time in Novi Sad and its surroundings, where municipal and industrial wastewaters are directly discharged, without any treatment, into the Danube River.

Nowdays, EmS are detected in biotic and abiotic matrices, but dominantly in the waste water, effluent, surface and ground water. Although the detectable concentrations are in very low or sublow doses, hazardous effect of EmS is evident and can have teratogenic, mutagenic and carcinogenic effect. One of the main characteristics of EmS, old or new chemicals, are their presence in very low – doses, their pseudo – persistency and hormone disrupting agents.

Research in emerging contaminants needs to continue as it is one of the most needed and challenging aspects of environmental issues. This research should also be developed in a preventive direction to help and encourage industry to develop commercially viable substituents which are not hazardous as well as to produce adeguated decontaminants. The direction of emerging contaminant research should be toward clean, safe and healthy environment, and towards the future free of emerging contaminants. These newly recognized old and new contaminants represent progressive shift in traditional thinking about protection scenario and a higher level eco status of whole environment, and water bodies in particular.

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**II International Conference
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**A COMPARISON OF BRACKET DEBONDING FORCES BETWEEN
THE TWO ADHESIVES: CON TEC LC AND CON TEC DUO**

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ABSTRACT

Fixed technique for applying brackets would be impossible without using adhesives for their fixation to the tooth enamel. Potentially serious drawback concerning adhesives might be their eventual negative influence once they enter the bloodstream. The use of adhesives entails a number of problems which are a consequence of their imperfection, besides the fact that they have been actually applied for a number of decades already. The paper will analyze the debonding force values for bracket-tooth interface by using Con Tec LC and, Con Tec Duo. For comparative analysis of the strength of bracket-tooth interface, with the application of different types of adhesives, 80 extracted teeth of the frontal region were used (central, lateral incisor teeth and canines of the upper and lower tooth arch). For the debonding process of applied orthodontics brackets, single-axial Stretch system for examination of tissues was applied to determine the value of the force necessary to separate the bracket from tooth surface, i.e. it was used to test debonding force. The direction of the used force for debonding was under angle of 90 degrees to the vertical axis of the tooth. By comparison of mean values of the strength of interface among the tested groups, it was determined that the highest average value of bond strength was with the group of teeth with which Con Tec Duo was used, a little lower mean value was recorded with the use of Con Tec LC adhesive.

Keywords: Adhesives, bracket, debonding, stretch system.

INTRODUCTION

Orthodontics, as science and practice, has developed through its history depending on the development of biology, medicine and technique. Advancement of technique in general and the knowledge derived from it made possible the use of that information to design orthodontic devices with certain elements comprising orthodontic device itself: bracket, screws, wires, rubber cups for traction, rubber bands etc, with quite precisely defined characteristics required by the therapy, all of which makes work significantly easier and provides a safer therapy outcome [1,2].

One of the problems encountered relatively frequently by an orthodontist in his everyday work while using the fixed technique is occurrence of failure of brackets fixed to the tooth by adhesive. This requires re-application of the bracket, implying a waste of time both for the patient and the therapist, and entails other consequences too. One of the consequences is that if the bracket fails for the second time, it is not advisable to adhere it for the third time. Another drawback in such situation is that new amount of adhesive has to be used, providing another contact with tissue.

Numerous studies of the material used for bonding brackets have been undertaken because of the reasons mentioned above. These materials differ both by their chemical composition, the curing method, and sensitivity to moist environment during bonding of brackets etc., as well as by the existence of extensive correlative dependence between these elements. This additionally complicates

the deriving of absolutely safe conclusions as to “which is the best adhesive agent for bonding brackets in every specific case”, depending on the age of the patient etc.

Taking into account the importance of the mentioned problems and the views of these processes and phenomena that are frequently contradictory, we have chosen this study in order to exactly determine the difference between the various types of adhesives (bonding agents), in terms of their adhesiveness, the course and comfort during work, with an aim to precisely define the guidelines and operating instructions for specific types of adhesives.

Nowadays, based on extensive research, there is a belief that the strength of bracket-tooth interface within the range 3–7 MPa is satisfactory for the clinical work of an orthodontist [3–5], while other authors state a somewhat bigger range of values 2.8 – 10.0 MPa [6–7], whereas, according to Newman et al. [8] an acceptable minimum of the bond strength with regards to etched enamel ranges between 6–8 MPa. On the one hand, orthodontists require as safe (strong) adhesive bond as possible, thus decreasing the possibility of undesired separation of bracket (bracket failure) during the therapy; on the other hand a stronger enamel-adhesive bond increases the risk of damaging tooth enamel during debonding [9–11]. It is more fortunate a circumstance if during debonding bracket is separated from the adhesive, with adhesive remaining on the tooth, rather than a situation where adhesive is bonded more strongly to the bracket, thus, separating adhesive together with the bracket may entail damage of enamel if the enamel-adhesive bond is strong. In the former case it is better to carefully remove the remaining part of the adhesive on the tooth with hard polishing rubber cups, rather than with turbine and diamond drill. This enamel damage that occurs relatively frequently should be repaired according to certain generally accepted principles that apply to such cases and situations.

MATERIALS AND METHODS

80 extracted teeth of the frontal region (central, lateral incisors and molars of upper and lower dental arch) were used for comparative analysis of bracket-tooth bond strength for application of Con Tec LC and Con Tec Duo adhesives. The criteria for teeth selection for the study were the following: no caries on labial surface, no cracks of enamel that can be caused by the pressure of forceps during tooth extraction, no hypoplastic macroscopically visible areas, and no decalcification caused by any reason. The common procedure of tooth preparation for bonding brackets (regardless of adhesive type) was in accordance with the procedure that most commonly used for in vitro studies [12–14].

The procedure consisted of storing the freshly extracted human teeth in a solution of 0.1% (weight/volume) thymol. Teeth were cleansed and polished. The procedure of bonding brackets to teeth was done only after finishing the preparation (Figure 1).



Figure 1. Bracket bonded on a molar (prepared for experimental analysis)

During bonding brackets a protocol was applied determined by the requirements, i.e. manufacturer's instructions for each of the mentioned adhesives used in the study, i.e. the adhesives tested for the purpose of comparative analysis of bracket-tooth bond strength.

The study was done *in vitro* as this was done by many other investigators before [15–20] who tested certain characteristics of adhesive types in order to understand their specific properties, advantages and shortcomings compared to each other. An *in vitro* study of adhesives is more favorable compared to *in vivo* study, because it eliminates the factor of speed of work depending on researcher's dexterity, thus reducing the possibility of contamination of the working area with saliva, (which in turn reduces the adhesive strength of the bonding agent), having in mind that most adhesives are sensitive to moist as “one of the most common causes for bracket failure”. Besides, laboratory study may indicate potential clinical success in certain conditions [21].

In order to avoid the influence of type of the bracket on bracket-tooth bond strength, the same type of metal bracket Discovery Slot 0,56 x 0,76 mm / 22 x 30 inch, Cuspid brackets with hooks was used with tested adhesives.

Con Tec LC adhesives were used with the first group, in which curing was done by chemical activation, while in the second group Con Tec Duo adhesives were used which are chemically and light-cured.

The process of debonding of placed orthodontic brackets aimed at determining the size of force necessary to separate the bracket from tooth surface was measured in the Centre for Bioengineering of Kragujevac University. For the purpose of this study, the Centre for Bioengineering modified its device, a single-axial Stretch system for tissue testing [22,23], so that a new sensor for force of 300 N was mounted and used to test the force of separation of bracket from the tooth. The device on which testing was done is presented in Figure 2, and the position of the tooth before starting debonding is presented in Figure 3. The direction of application of debonding force was at the angle of 90 degrees at the vertical axis of tooth.

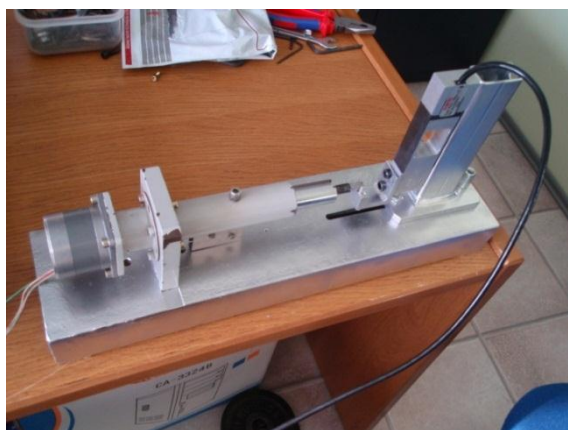


Figure 2. Device on which study was performed (Stretch system)



Figure 3. Position of tooth in the device Stretch system, before starting debonding

Tensile force was accomplished at constant speed of 1 mm/min. The device automatically recorded the force accuracy with 0.3 N. The graph presents the forces in the function of time with 0.15 second intervals.

RESULTS OF STUDY

Table 1 presents the results of statistical analysis of debonding force for adhesive Con Tec LC while table 2 presents the results for adhesive Con Tec Duo.

Table 1: Results of statistical analysis of debonding force for adhesive Con Tec LC

Descriptive parameter (Debonding force (N) – adhesive Con Tec LC)	Dental arch		Total
	Upper	Lower	
N	20	20	40
MIN	82,98	42,43	42,43
MAX	118,6	64,81	118,57
I	35,59	22,38	76,14
Me	105,1	55,27	73,90
Xsr	102,3	53,99	78,15
SD	13,88	7,59	26,84
CV	13,57	14,06	34,35

Table 2: Results of statistical analysis of bond strength obtained with ConTec Duo adhesive

Descriptive parameter (Debonding force (N) – adhesive Con Tec Duo)	Dental arch		Total
	Upper	Lower	
N	20	20	40
MIN	90,89	48,78	48,78
MAX	137,76	71,47	137,76
I	46,87	22,69	88,98
Mo	116,67	61,12	61,12
Me	116,67	60,95	81,18
Xsr	113,44	60,69	87,07
SD	15,33	6,83	29,17
CV	13,51	11,25	33,50

Table 3 presents comparative results of statistical analysis for debonding force with Con Tec LC and Con Tec Duo adhesives. The obtained total results for debonding force of teeth of the upper and lower dental arch show that the biggest average value $X_{sr} = 87.07$ N was obtained with the group of teeth in which Con Tec Duo adhesive was used for bonding brackets, whereas a somewhat lower average value $X_{sr} = 78.15$ N was obtained with the group of teeth in which Con Tec LC was used. The results of testing of significance of differences by t-test show that there is no statistically significant difference between the mean values of debonding forces for brackets fixed with Con Tec LC and Con Tec Duo adhesives ($p = 0.158601$).

Table 3: Comparative results of statistical analysis for parameter F (debonding force) with tested adhesives total results (summary for all tested teeth of the upper and lower tooth arch)

Analyzed statistical elements for parameter F (debonding force)	Con Tec LC	Con Tec Duo
N	40	40
MIN	42,43	48,78
MAX	118,57	137,76
I	76,14	88,98
Mo	–	61,12
Me	73,90	81,18
Xsr	78,15	87,07
SD	26,84	29,17
CV	34,35	33,50

CONCLUSIONS

Based on comparative analysis of the results of the debonding force with tested adhesives for fixing brackets to tooth enamel, the following conclusions may be derived:

- Comparison of mean values of debonding forces between tested adhesives showed that the highest average value of debonding force was with the group of teeth in which the adhesive Con Tec Duo was used, whereas somewhat lower value was obtained by use of Con Tec LC adhesive.
- The results that gave a clear insight in the bracket-tooth bond strength achieved by the tested adhesives that are nowadays most commonly used in practice have the following clinical-theoretical implications.
- If the degree of tooth dislocation is bigger, which requires higher activation of arch, i.e. stronger force to move the tooth, it is necessary to use the adhesive by which the strongest tooth-bracket bond is achieved, in order to avoid undesirable failure of the bracket (Con Tec Duo).
- If the degree of disruption of tooth position is smaller, adhesives that achieve a lower bracket-tooth bond may be used too (Con Tec LC).

Using mentioned strategy for usage of adhesives one manage to use lower amounts of adhesive and therefore to minimize the possibility of potentially negative effect of adhesives towards tissue.

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**II International Conference
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**POPULATION EXPOSURE TO IONISING RADIATION: DOSE
MAGNITUDE AND BASIC RADIATION PROTECTION PRINCIPLES**

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ABSTRACT

The paper presents major sources of population exposure to ionizing radiation and the magnitude and distribution among various sources. Natural radiation sources are part of human environment. Due to external exposure from space radiation, external exposure from terrestrial radiation, internal exposure from inhalation of radon and thoron and their progeny and due to internal exposure from radionuclides in the body, as a global average, the natural background radiation is 2.4 mSv per year. Apart from natural radiation, nuclear and isotopic techniques represent a wide range of human activities, and for more than a century have very important applications in various areas of life. A brief overview of these methods used in agriculture, industry, science and research, archaeology, history and medicine and their radiation impact will be provided. Parallel to expansion of radiation application, the concerns related to health effects of ionizing radiation have been raised. The scientific discipline called radiation protection has an aim to protect people and environment from excessive and unnecessary exposure to ionizing radiation. There are three basic principles in radiation protection: justification, optimisation of protection and individual dose limitations, and overview of these will be given in the paper.

Key words: radioactivity, radiation dose, radiation source, population, environment.

INTRODUCTION

Radioactivity and radiation is a part of our natural environment, which existed on Earth before any sign of life. Later, humans learned how to use radiation and it has become an important part of our life (Bethge et al., 2004; Bushberg et al., 2003; Eyre, 1996; UNSCEAR, 2010). Nuclear and isotopic techniques present a wide range of human activities. For more than a century, they have been applied in different areas, as nuclear energy, agriculture and biotechnology, in the management of water and marine resources, industry, science and research, archaeology, history and medicine (Magill and Galy, 2005). Different nuclear technologies bring on daily basis immense benefits in diagnosis and treatment of disease, in control of industrial processes, for development of science and power generation. In general, application of radiation and nuclear methods are based on various properties of nuclei and radiation, such as the interaction of radiation with matter, radiation detection, biological effects of radiation and static and dynamic nuclear properties (magnetic properties, stability, radioactive decay) (Bethge et al., 2004).

In parallel with the expansion of application of radioisotopes and nuclear methods, awareness about of the harmful effects of ionizing radiation has increased (IAEA, 2004) . The new findings resulted in the development of new scientific and professional discipline that is now known today as the Radiation Protection. This discipline pervades all applications of radiation sources and nuclear methods with an aim to protect people and the environment from unnecessary and excessive exposure to ionizing radiation, seeking to maximize the benefit and minimize the risk in any practice that is associated with radiation (ICRP, 2007).

Although the terms "radiation", "radioactive" or "nuclear" cause of fear and concern, the fact that radiation is a part of our natural environment and has outstanding role in medicine, industry and technology, often is not well understood. The paper presents major sources of population exposure to

ionizing radiation, the magnitude and distribution among the various sources of radiation exposure. Different categories of radiation exposure sources are presented: natural radiation sources, medical procedures, consumer products or activities involving radiation sources, industrial radiation sources and exposure of workers due to their occupation.

RADIATION PROTECTION STANDARDS

Dose quantities

Human body does not possess receptor for ionizing radiation and thus, we cannot detect the presence of radiation by our senses. We use other means and specific instrument to detect and measure presence of radiation as gas, solid-state, chemical detectors and other detectors (Cherry et al., 2003; Martin, 2006). We interpret measurements in a way to express the amount of energy deposited in human body or any part of it, or, alternatively, we can calculate the dose absorbed by a organ followed by radionuclide deposition (internal dosimetry).

The amount of energy deposited per unit mass is called absorbed dose. It is expressed in units gray (Gy=J/kg). Types of ionizing radiation (alfa, beta, gamma, neutrons...) differ in a way they interact with biological material. When different biological effectiveness of different radiation types is taken into account a new quantity is introduced, called equivalent dose. This quantity includes radiation weighting factors assigned to different radiation types, ranging from 1 for gamma radiation to 20 for alpha particles. It is expressed in units sievert (Sv=J/kg) and provides an index of likelihood of harm for particular tissue or organ. The risk varies from organ to organ and to assess the overall detriment to human body by multiplying organ dose by a tissue weighting factor related to risk for a particular organ. The sum of weighted equivalent doses is called effective dose (ICRP, 2007):

$$E = \sum_T w_T \cdot H_T \tag{1}$$

where w_T presents tissue weighting factor (Table 1) and H_T corresponding equivalent dose for tissue T.

Table 1: Tissue weighting factors, w_T (ICRP, 2007)

Tissue/organ	w_T
Bone-marrow (red), Colon, Lung, Stomach, Breast, Remainder tissues*	0.12
Gonads	0.08
Bladder, Oesophagus, Liver, Thyroid	0.04
Bone surface, Brain, Salivary glands, Skin	0.01

* Remainder tissues: Adrenals, Extrathoracic (ET) region, Gall bladder, Heart, Kidneys, Lymphatic nodes, Muscle, Oral mucosa, Pancreas, Prostate (male), Small intestine, Spleen, Thymus, Uterus/cervix (female).

The effective dose allows to represent exposure by a single number and to compare different exposures types. It takes into account type and energy of radiation and tissue radiosensitivity, it applies to both external and internal exposure and thus, gives a broad indication of the health detriment. As a measure of dose to group of people and whole population, collective effective dose is used. It is a sum of effective doses for all exposed people with units man Sv (IAEA, 2004; ICRP, 2007).

Radiation sources in global prospective

Ionizing radiation enters our lives in a variety of ways. It is merely fact of our life, which arises both from nature and artificial processes (UNSCEAR, 2010). According to their origin, we classify radiation sources to natural and artificial or man-made. Each source has two important properties: the dose that it delivers and possibility of humans to affect this dose. Until recently, natural radiation was pure background phenomena, however it is well know that in some cases exposures to natural radiation can be remarkably high. In the case of radon exposure, there possible actions that can lead to dose reduction, however, exposure to other natural sources almost cannot be altered. Since more than a century ago, use of radiation and radioactivity has become important element of human activates which include energy production, medicine, fire detection, light prevention, agriculture, geology, industry and many others. All these activities in spite to huge benefit increase exposure to ionizing radiation, which varies immensely between different applications. Variations in radiation exposure are much larger due to man-made sources of radiation compared to natural sources. Exposure man-made sources is by far more controllable, and extend of this process is based on balance of benefits and associated risks.

The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) regularly publishes data on doses from all sources. According to UNSCEAR report form 2010, annual dose, averaged over the population worldwide is about 3.0 mSv in total. About 2.4 mSv of this is from natural sources and 0.6 mSv from man-made sources (Table 2).

Table 2: Annual average doses and ranges of individual doses of ionizing radiation (UNSCEAR, 2010)

Source	Annual average dose (mSv)	Typical range of individual doses (mSv)
Natural		
Radon	1.26	0.2-10
External terrestrial	0.48	0.3-1
Ingestion	0.29	0.2-1
Cosmic	0.39	0.3-1
Total natural	2.4	1-13
Man-made		
Medical diagnostics	0.6	0-80
Atmospheric nuclear tests	0.005	-
Occupational	0.005	0-20
Chernobyl	0.002	-
Nuclear fuel cycle	0.0002	-
Total man-made	0.6	-

Radiation effects

Ionizing radiation has enough energy to cause damage in cells which can further increase the risk of cancer later in life. However, the health effects of ionizing radiation are dependent on the dose received. Health effects of ionizing radiation are classified into two types: those that are visible, documented and confirmed within a relatively short time - weeks to a year or so (called tissue reactions or formerly deterministic effects: skin erythema, hair loss, cataract, infertility, circulatory disease) and others which are only estimated and may take years or decades to manifest (called stochastic effects: cancer and genetic effects). Tissue reactions have thresholds, which are typically quite high (order of magnitude of couple of Gy) which is mainly related to accidental situation (ICRP, 2007; IAEA, 2004). Stochastic effects include cancer and genetic effects, but the scientific evidence for cancer in humans is stronger than for genetic effects. According to ICRP Publication 103 (2007), detriment-adjusted nominal risk coefficient for stochastic effects for whole population after exposure to radiation at low dose rate is 5.5% per Sv for cancer and 0.2% per Sv for genetic effects. This gives a factor of about 27 more likelihood of carcinogenic effects than genetic effects. There has not been a

single case of radiation induced genetic effects documented in humans so far, even in survivors of Hiroshima and Nagasaki.

Basic radiation protection principles

Radiation protection standards are way to control exposure to ionizing radiation. The standards in this area are consistent trough the world, mainly due to internationally recognized framework. The standards are based on the conservative assumption that the risk is directly proportional to the dose, even at the lowest levels, though there is no evidence of risk at low levels, i.e. “linear no-threshold (LNT) hypothesis”, which is recommended for radiation protection purposes only such as setting allowable levels of radiation exposure of individuals (ICRP, 2007).

In any country, radiation protection standards are set by government authorities, generally in line with recommendations by the International Commission on Radiological Protection (ICRP), International Atomic Energy Agency (IAEA) and coupled with the requirements of basic radiation protection principles. The three key points of the ICRP's recommendations are (ICRP, 2007):

1. Justification, according to which no practice should be adopted unless its introduction produces a positive net benefit;
2. Optimization, according to which all exposures should be kept as low as reasonably achievable, economic and social factors being taken into account;
3. Dose limitation, stating that exposure of individuals should not exceed the limits recommended for the appropriate circumstances.

National radiation protection standards are based on ICRP recommendations. They set dose limits for both occupational and public exposure categories, whereas this does not apply to medical exposures. The ICRP recommends that the maximum permissible dose for occupational exposure should be 20 mSv per year averaged over five years (i.e. 100 mSv in 5 years, about 8 time average dose from natural background) with a maximum of 50 mSv in any one year. For public exposure, 1mSv per year averaged over five years is the dose limit (ICRP, 2007). In both categories, the figures are over and above background levels, and exclude medical exposure.

Practices are activities that involve deliberate use of ionizing radiation. They are clearly defined and regulated. On the other hand, we do not take measures to reduce exposure from natural radiation, although there are some interventions in the case of high exposures in homes and at work.

The first requirement of the system of radiological protection for practices is the need to consider harmful costs in the light of benefits. In most cases, radiation effects are just one of the possible harmful outcomes, taking into account social and economical effects. This applies to all practice, including medical applications of ionizing radiation where each procedure has to be judged on its own merits, both for patients and population as a whole. As we assume that no dose is free from risk, it is important to reduce all doses as low as reasonably achievable (ALARA). Constrains are imposed to optimize exposure, usually as a fraction of annual dose limit related to particular practice or industry. For member of the public, in the phase of planning of new practice pr source, typical dose constraint is 0.3 mSv. Application of dose constraint and diagnostic reference levels (DRL) in the case of medical exposures have provided practical means for reducing doses globally (IAEA, 2004; ICRP, 2007).

NATURAL RADIATION SURCES AND EXPOSURE PATTERNS`

Natural radioactivity is a source of continuous exposure to human beings. It is present in the human environment due to the presence of cosmogenic and primordial radionuclides in the Earth's crust.

Natural environmental radioactivity and the associated external exposure due to gamma radiation depend primarily on the geological and geographical conditions, and appear at different levels in the soil of each region in the world. There are three naturally occurring decay series, headed by the radionuclides ^{238}U , ^{235}U , and ^{232}Th . These series are commonly called the uranium series, the actinium

series, and the thorium series respectively. The three families of radioactive heavy elements account for much of the background radiation to which humans are exposed. Also the primordial radionuclide ^{40}K , which is everywhere present, produce significant human exposure.

Exposure to natural radiation represents the most significant part of the total exposure to radiation in the environment. Worldwide average annual effective dose from natural sources is 2.4 mSv (UNSCEAR, 2010). Almost the one fifth of total dose (0.48 mSv) belongs to external exposure from terrestrial radiation and 0.39 mSv to exposure from cosmic rays (Table 2).

A significant contribution to natural exposure of humans is due to radon gas, which emanates from the soil. Radon (^{222}Rn) is a natural radioactive gas produced upon uranium (^{238}U) decay. Its physical properties are: colorless and odorless gas. In the living environment, the gas is found diluted in low concentrations (5-10 Bq/m³). In the indoor spaces, such as apartments, radon may be accumulated. The indoor radon concentration depends on building construction, construction site characteristics and meteorological conditions, as well as on the construction materials. It is believed that exposure to certain levels of radon concentrations increase the risk of lung cancer. The risk depends on its concentration in the apartment and time spent in the area. Public exposure to radon and its radioactive daughters, present in the environment, results in largest contribution to the average effective dose received by human beings. Worldwide average annual effective dose from radon is 1.26 mSv (Table 2, UNSCEAR, 2010). The results of the radon concentration measurement in Belgrade showed that in the most of the apartments radon concentration is below 200 Bq/m³ (Eremić-Savković et al, 2002; Popović et al, 1996).

Human activities involving the use of radiation and radioactive substances cause radiation exposure in addition to the natural exposure. Some of those activities simply enhance the exposure from natural radiation sources. Examples are the mining and use of ores containing naturally radioactive substances and the production of energy by burning coal that contains such substances (Pantelic et al, 2002).

ENVIRONMENTAL POLLUTION

The global source of artificial radionuclide contamination in our country are fallout due to nuclear testing throughout the 20th century and deposition of radionuclides from the regions of nuclear accidents.

Partial meltdown of the reactor at Chernobyl in April 1986 released high amounts of radionuclides into the environment. As a result of the accident, the reactor was destroyed and about $14 \cdot 10^{18}$ Bq was ejected in the environment during 10 days. ^{131}I , ^{134}Cs and ^{137}Cs were the most important and the most dangerous radionuclides released and spread over a large part of Europe (IAEA, 2006). The deposition of radiocesium from the Chernobyl accident in Serbia occurred at the beginning of May 1986. The ^{137}Cs was deposited on the ground, forage crops, grass and feed plants of ruminants. During the following years, ^{137}Cs entered all compartments of the affected ecosystems. The main pathways of radionuclides in the human body are inhalation and ingestion through food and drinking water. ^{137}Cs activity was monitored in the environment after the Chernobyl accident. ^{137}Cs is one of the radionuclides of public health importance because of its long half-life (30 years) and its nearly complete gastrointestinal absorption in humans. When ingested from contaminated food, the absorbed caesium accumulates into all tissues. The effective dose from ^{137}Cs due to food ingestion in 1986 was 0.66 mSv and decreased in subsequent years. (Maksic et al, 1997).

The Fukushima Daiichi nuclear power plant accident caused a large regional release of radionuclides into the atmosphere and subsequent radioactive contamination of the environment. Once released into the atmosphere, a long-range atmospheric transport processes can cause widespread distribution of radioactive matter. The fallout consisting of short-lived and long-lived radionuclides, eventually affects humans either directly or indirectly by entering the food chain through plants and animals. The occurred radioactive contamination originating from Fukushima was detected not only in Japan and Asia, but also in the entire northern hemisphere, including USA and Europe.

Gamma spectrometry measurement of aerosol samples in Belgrade showed clear evidence of fission products ^{131}I , ^{134}Cs and ^{137}Cs within two weeks after the accident (Nikolić et al, 2012). The activity diminished with time due to dispersion in air and, in case of ^{131}I , short half life.

MAN-MADE RADIATION SOURCES AND EXPOSURE PATTERNS

Industrial application of ionizing radiation

Application of radiation sources is of paramount importance in the industry, primarily in the field of processes control as well as in the radioactive gauges, for measuring the level, density and thickness of various products. Radiation sources are used for detection of defects in materials, for the corrosion detection and control and error detection in welds. Radiographies similar to industrial are nowadays of immense importance in the field of security and prevention of illegal traffic of goods (Magill and Galy, 2005). The properties of material can be successfully determined by detecting changes in the intensity of radiation emitted by the source. This principle is used different radioactive (nuclear) gauges. In general, these devices consist of a radiation source and detector, which is usually a gas (Geiger-Miller counter) or scintillation (usually a crystal) detector. When industrial process requires determination of level of liquid in the container or in the pool, the device consists of a radiation source and detector positioned opposite the source at the level of liquid. In this situation, the change of liquid level results in a change of the signal on the detector. This method has been used successfully to control the content of cans of soft drinks and in the industrial production of thin films, such as plastic or metal foils, floor coverings or paper (IAEA, 2004; Magill and Galy, 2005).

Neutron beams from nuclear reactors and spallation sources are successfully used in radiography of objects consisting of parts with different cross sections for neutrons. Given that materials such water and hydrocarbons efficiently scatter thermal neutrons (which is not the case with the gaseous mediums and metal), neutron radiography is an ideal technique for analysis of density variations in materials that absorb and scatter neutrons. In contrast to the x-radiation interactions, neutrons interactions do not depend systematically on atomic number of media, although some lighter atoms (boron and hydrogen) have a significant cross section for interaction (Magill and Galy, 2005; Martin, 2006).

Application of radioactive tracers is old as the knowledge of radioactivity. Presence of radioactive traces enables detection of radiation and non-invasive analysis of physical and chemical properties of materials to which these tracers have been added in very small quantities. For example, the labeling of pesticides and insecticides by ^{14}C isotope of carbon, it is possible to monitor the degradation products in the biosphere. In other areas, such as biochemistry, hydrogen isotope tritium ^3H or ^{32}P isotope of phosphorus is being successfully used. This enabled successful monitoring phosphorus absorption in plants (IAEA, 2004; IAEA, 2011).

Based on biological effects of ionizing radiation, various nuclear methods have found a significant place in the sterilization of food and insect control. Also, the results of the analysis of radiation effects in different materials enabled the use of radiation for modification of material properties. Effects of ionizing radiation are successfully used to destroy pest populations by male insect sterilization, for improving sanitary conditions for both humans and animals and to prevent the spread of infectious disease (IAEA, 2011). In radiation sterilization of food, by exposing samples to doses on the order of kGy, the taste is preserved, which is great advantage of this method in comparison to some alternative methods such as pasteurization (Martin, 2006; IAEA, 2011).

Industrial radiography is a discipline in which the sources of ionizing radiation are used for testing and analyzing the internal structure of materials and objects. These methods are entirely non-destructive and are based on the application of x- or gamma radiation. In addition to industrial applications, x-radiography and gamma radiation and is widely used for baggage and cargo control in air and other modes of transport.

Medical application of ionizing radiation

Nuclear technologies are the basis of modern medicine today. Medical procedures and techniques based on the application of radiation, radioisotopes and nuclear methods take a central place in modern health systems. These methods are an example of transfer of high technology and modern scientific knowledge in daily medical practice, whether in terms of diagnosis or treatment of disease.

First applications of radiation sources linked specifically to medicine are almost as old as the human knowledge of radioactivity and x-radiation. In addition to the long history of medical use of radiation cause the least controversy in public, primarily because of clear awareness among the population about the benefits arising from use of radiation sources for diagnosis and treatment of disease. For more than a century, medical imaging is used for the study of anatomical, morphological, biochemical and physiological properties of the human body. These methods allow the presentation of complementary structures (anatomy), composition (biology and chemistry) and function (physiology and metabolism) of the human body. Depending on the methods and techniques you use to generate images of internal body structures, imaging methods can be classified broadly in the imaging by x-radiation, (nuclear) magnetic resonance imaging and radioisotope (PET, SPECT) imaging and hybrid imaging based on fusion of images obtained by different methods (Ciraj-Bjelac et al., 2012).

Application of x-radiation in medical imaging has a mass application in the world and a clear trend of growth over the past few decades (Ciraj-Bjelac et al, 2011, UNSECAR, 2010). These techniques include conventional radiography and fluoroscopy, computed tomography (CT), mammography and interventional procedures in radiology and cardiology. Despite the great diversity and different technological levels, all these methods are based on a selective absorption of x-radiation in anatomical region that is a subject of investigation (Bushberg et al, 2002).

Radioisotope imaging is the subject of diagnostic nuclear medicine. Images resulting from the emission of radiation from radiopharmaceuticals are reflecting the spatial and time distribution of radionuclides. If based on emission of photons, the technique called SPECT (Single Photon Emission Tomography), while emission of photons from positron annihilation is called PET (Positron Emission Tomography). Nuclear diagnostic imaging methods provide valuable information on physiological and biochemical processes and are complementary to other imaging methods such as conventional radiology, MRI and ultrasound (Hendee et al, 2002; Iniewski, 2009). These methods are very important in the diagnosis of diseases of the heart, brain, lung, and kidney or in the diagnosis of malignant disease and their follow up. One of the most common applications of nuclear methods in medicine is its basis has use of gamma camera (NaJ scintillator) which detects the radiation emitted by the radiopharmaceutical selectively bound to the region of interest (Christioan et al, 2007). More than 20 000 gamma cameras are in use worldwide. They are used to perform more than 33 million examinations annually (UNSEAR, 2010).

Hybrid imaging methods, e.g. PET is now available in more than 1000 hospitals in the world (UNSECAR, 2010). Modern PET systems are integrated with units for computed tomography, forming a hybrid imaging system PET/CT. By annihilation of positrons from the accumulated radiopharmaceutical and electrons from the surrounding tissue, two photons of energy 0511 MeV are emitted. Using coincident technique, it is possible to determine a place of their origin in the organ. Used radionuclides belong to the chemical elements that are embedded in complex organic compounds of the body, so this technique is suitable for testing *in vivo* metabolism (Christioan et al, 2007) .

One of the most important applications of radionuclides in radiotherapy is based on the use of sealed radiation sources for external beam therapy, the use of implants for the treatment of prostate cancer, intravascular radiotherapy and use of radiopharmaceuticals in for therapeutic purposes. In addition to these methods, rapid development and implementation of a range of new and effective techniques, such as radioimmunotherapy and ion beams is expected in near future (Johns and Cunningham, 1983; Hohloch et al., 2011, Mayles et al., 2007, Nakaya et al, 2010). External beam radiotherapy, dose of

ionizing radiation is produced by radiation sources outside the body, using photons or electrons of energies of several MeV, which is sufficient for the penetration of radiation to tumour sites in the body. A source of radiation in radiotherapy (radionuclide) is mainly ⁶⁰Co or linear accelerators. Recently, devices containing a large number of sources of ⁶⁰Co, known as "Gamma Knife", which allows for very sophisticated and highly-localized brain therapy have been developed (Mayles et al., 2007, Nakaya et al, 2010). Hundreds of thousands of patients each year is referred to brachytherapy treatment (in the Greek language *brachys* means close). In this technique, an sealed source of radiation is introduced into the body cavity or tissue and its proximity to the tumors, provides the necessary dose for tumor and minimal dose to surrounding healthy tissue (Mayles et al., 2007).

Radiation exposure for medical use of ionizing radiation

Diagnostic and interventional procedures involving x-rays are the most significant contributor to total population dose from man made sources of ionizing radiation with ever increasing use (UNSECAR, 2010). X-ray imaging generally covers a diverse range of examination types, many of which are increasing in frequency and technical complexity. Trends in radiation exposure from diagnostic radiology are presented in Table 3. Due to increasing importance of radiation burden for medical x-ray examination, clinical dosimetry is becoming an active research and practical area. Objectives of clinical dose measurements in diagnostic and interventional radiology are multiple, as assessment of equipment performance, optimization of practice through establishment of diagnostic reference levels (DRL) or assessment of risk emerging from use of ionizing radiation.

Table 3: Trends in radiation exposure from diagnostic radiology, adopted from (UNSCEAR, 2010)

Year	Number of examination (million)	Annual per caput dose (mSv)	Collective dose (man Sv)
1988	1380	0.35	1 800 000
1993	1600	0.3	1 600 000
2000	1910	0.4	2 300 000
2008	3100	0.6	4 000 000

Various dosimetric quantities are needed to assess radiation exposures to humans in a quantitative way, in order to assess dose–response relationships for health effects of ionizing radiation which provide the basis for setting protection standards as well as for quantification of exposure levels. As an example, typical effective doses for diverse x-ray examinations in Serbia are presented in Table 4. Nevertheless, radiation burden from medical exposure depends immensely on health care levels, as presented in Table 5.

Table 4: Typical effective doses from x-ray examinations in Serbia

X-ray examination	Effective dose (mSv)	Equivalent number of chest radiographies	Equivalent number of days of exposure to natural sources
Chest PA	0.05	1	5
Pelvis	0.6	12	60
Lumbar spine	0.8	16	80
Urinary tract	0.4	8	40
Barium enema	4.8	96	480
CT chest	2.1	42	210
CT abdomen	8	160	800
Coronarography	10	200	1000

An estimated annual number of nuclear medicine examinations worldwide is approximately 33 million, with collective dose of 202 000 man Sv, which represents 35% increase in the last decade. Typical effective doses from nuclear medicine examinations range from 1 mSv for examinations of kidneys, thyroid or lung to 7 mSv for brain scintigraphy (UNSCEAR, 2010).

Table 5: Annual collective dose due to medical exposures, adopted from (UNSCEAR, 2010)

Health care level	Population (million)	Collective dose (man Sv)		
		Diagnostic x-rays	Nuclear medicine	Total
I	1540	2 900 000	186 000	3 100 000
II	3153	1 000 000	16 000	1 000 000
III	1009	33 000	82	33 000
IV	744	24 000	-	24 000
World	6446	4 000 000	202 000	4 200 000

In Serbia, the total annual number of nuclear medicine procedures is approximately 35000, with associated collective dose of 125 man Sv. Average effective per caput was estimated to 17 μ Sv. Total number of x-ray procedures is approximately 5 million, with associated collective dose of 4500 man Sv and average effective per caput of 0.6 mSv.

Occupational exposure to ionizing radiation

Occupational exposure occurs in many professions. In many areas of industry and medicine, workers are exposed to man-made sources of radiation, whereas some workers, as aircrews or mines can also be exposed to natural sources due to their occupation. All occupational exposures are monitored for external radiation, usually by passive dosimeters, and sometimes also by active personal monitors. Special doses assessment methods are developed for internal exposures (UNSCEAR, 2010). Average annual occupational effective doses are presented in Figure 1.

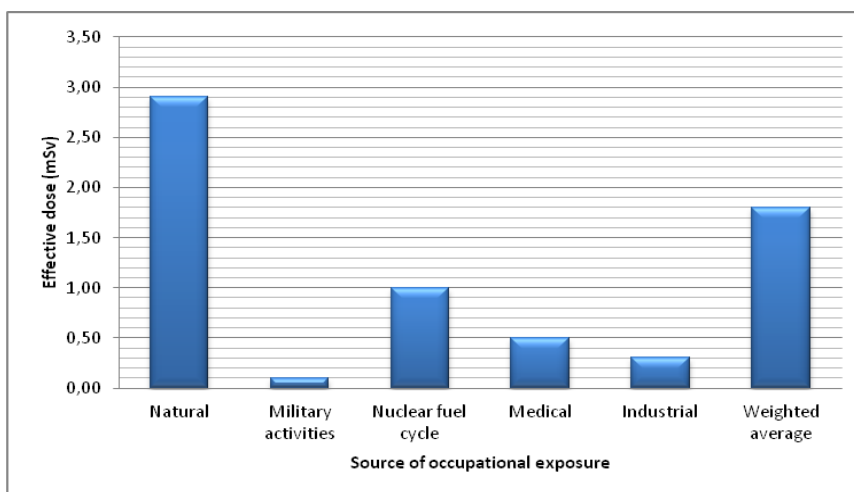


Figure 1. Typical annual effective dose from occupational exposure

Exposure of the general public

Different sources contribute to population exposures. Radionuclides of artificial origin are discharged to the environment from nuclear power industry, military establishments, research organization, hospitals or general industry. These discharges must be controlled and authorized.

Nuclear power industry discharges at each stage of fuel cycle, when variety of gaseous, liquid or solid forms are released to the environment. Estimated radiation burden from these activities is 0.9 man Sv per GW. For approximate power generation of 250 GW annually, estimated collective dose is 200 man Sv and per caput annual dose is approximately 1 μ Sv. Maximum effective dose from the discharge of artificial radionuclides is about 0.014 mSv in a years, with corresponding collective dose of 5000 man Sv. Although radioactive discharges are well controlled nowadays, this was not the case in the past. Around 500 atmospheric explosions were conducted until 1980. The concentration of radionuclides in air, rain and human diet are at present much lower than in 1960-ties, when they reached the maximum.

The most important radionuclides contributing to human exposure are carbon-14, strontium-90 and cesium-137, and total dose from external and internal exposure is estimated to be 0.005 mSv annually. The estimated collective dose is approximately 30 000 man Sv (UNSCEAR, 2010; IAEA, 2004).

CONSLUSIONS

Radiation and radioactivity is a part of our nature, it existed in “big bang” and it has been present in universe. Radioactive material are part of Earth, and even human body. However, only a century ago mankind discovered this universal phenomena and it has become an important element of human development that contributes immensely to technological development and quality of our life. Due to external and internal exposures, as a global average, the natural background radiation dose is 2.4 mSv per year. Apart from natural radiation, nuclear and isotopic techniques represent a wide range of human activities, and for more than a century have very important applications in various areas of life, with contribution of 0.6 mSv annually, mainly due to medical exposures. Internationally harmonized standards in radiation protection are developed to control exposure to ionizing radiation. There are three basic principles in radiation protection: justification, optimization of protection and individual dose limitations, all with aim to protect people and the environment from unnecessary and excessive exposure to ionizing radiation, seeking to maximize the benefit and minimize the risk in any practice that is associated with radiation.

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**DISPOSAL OF ASH FROM THE THERMAL POWER PLANT
„NIKOLA TESLA B“ AND THE IMPACT OF ASH ON THE
ENVIRONMENT AND HUMAN HEALTH IN THE REGION**

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ABSTRACT

The processes of combustion of fossil fuels in power plants produce large amounts of ash. If the resulting ash is not disposed of properly, it can lead to pollution of air, water and soil, which in turn adversely affects the plants, animals and people in the region. In this paper, on the example of thermal power plant „Nikola Tesla B“, ash disposal in landfills is analyzed, as well as maintenance of landfills and prevention of ash dispersion from landfills. Also, the negative impact of ash on the environment is shown, and mathematical model of ash dispersion from the landfill is provided.

Key words: ash, landfills, air, health.

INTRODUCTION

Serbia is among the European countries where coal is the dominant energy source. In 2007, 38978 GWh of electricity was produced in Serbia (excluding Kosovo), of which 27545 GWh in coal-fired power plants (Bošković, 2008). That means that about 70% of electricity is from burning coal.

One of the problems that accompany the production of electricity from coal is the problem of so-called energy waste. This term means the ash and slag generated as incombustible and unburned residues from coal combustion, and wastes (mainly gypsum) which are obtained by flue gas desulphurization.

In industrial practice, the term ash means the incombustible solid residue which is separated during the coal burning in boilers in power plants and heating plants. Thereby, ash can differ by location of its separation. There are different types of ash in thermal power plants that use classical combustion system of pulverized (crushed) coal:

- Bottom ash, biggest incombustible residue of combustion that is allocated at the bottom of the boiler,
- Boiler ash, larger class ash that leaves boiler with flue gasses, but separates and precipitates under the heater and flue gas channel on the way to the electrostatic precipitator,
- Fly ash, smallest class ash that leaves boiler with flue gasses, but it separated from them in electrostatic precipitators.

From the point of depositing and distribution, distinction between ash and slag is essential, where ash consists from boiler ash and fly ash. Slag stands out because of its specific characteristics, especially the particle size and the deposition rate, which greatly influence the choice of transportation systems.

Classification of ash, adjusted for conditions in Serbia, is presented in (Grbović, 1986). That classification distinguishes three types of ash: silicate, calcium, silicate-calcium ash. Classification is based on the difference in the chemical and mineralogical composition of the ash, and its different behavior upon contact and transportation with water. Silicate ash is completely inert, participation of calcium is minimal, and a major component in the chemical structure is SiO₂ (Knežević, 1988).

Typical representative of silica ash is ash that is produced in power plants which use lignite (from Kolubara and Kostolac coal basin) as fuel. Calcium ash is highly reactive in contact with water, as a result of the high percentage of calcium in the chemical structure. Calcium ash is produced in thermal power plant Gacko. Silicate-calcium ash has SiO_2 and CaO in its structure, but their participation is moderate, and ratio is approximate to 1:1. Mixed silicate-calcium type of ash can be found in Kosovo's power plants.

RELATIONSHIP BETWEEN ASH TYPES AND DEPOSITING TECHNOLOGY

There are three basic systems in the technological process of depositing ash:

- Internal transportation, system for collecting ash and slag inside the main thermal power plant facility (MTF),
- External transportation, transportation system of ash and slag from plant to the landfill,
- Depositing, the final step in which the collected and transported ash and slag is deposited on a specially selected and prepared ground.

Silicate and silicate-calcium ash can be transported within the MTF with hydraulic or pneumatic-hydraulic system, while calcium ash requires dry, pneumatic transport. External transportation is largely dependent on how the internal transportation is resolved. If there was a mixing of water with ash and slag within the MTF, then the external transportation is completely defined and reduced to hydraulic transport. But if the dry (pneumatic) transport is used as internal transportation, than external transportation can be in the form of either dry (pneumatic, mechanical) or wet (hydraulic) transport. Dry external transportation dictates the conditions of dry depositing and formation of dry landfills. The use of hydraulic transport basically offers two options: disposal in the form of diluted slurry and in form of dense slurry. Another option is to solidify the dilute slurry before depositing, but that technology is very complicated.

TRANSPORT AND DISPOSAL OF ASHES

Transport and disposal of ash can be done by:

- Dry processes (mechanical, pneumatic),
- Wet processes (hydraulic).

Dry mechanical processes include transportation with trucks and conveyor belts (more used for slag). In all cases when the mechanical transport is applied, ash and slag must be moistened before loading on the transport medium (truck, conveyor belt). The degree of wetting depends on the characteristics of ash and available water, but the humidity usually ranges between 10 to 30%. The most critical phase in the dry manipulation of ash using the mechanical means of transport is the phase of unloading at the landfill. Because of the duration of the transport cycle, (under-soaked) ash is often dried during transportation, so it causes dusting in the wide area around landfill. Pneumatic ash transport over long distances is not common because of the high power consumption, and due to dusting on the landfill. Wet or hydraulic deposition of ash means that before the external transportation phase, ash is added to water, and after the brief mixing, in the form of the slurry is transported to the landfill where it is unloaded by various methods. In this type of manipulation, there are two basic ways:

- Transport and deposition in the form of diluted slurry,
- Transport and deposition in the form of dense slurry.

Diluted slurry implies the uncontrolled use of water, so that the ratio between the solid (ash and slag) and liquid (water) phase is 1:8 ÷ 1:15. This is a very comfortable transportation system because it does not require special technological discipline, caring, and automation, but it does require a lot of water and energy. Such slurry requires very demanding and controlled landfill with large surface and volume. Deposition within the reservoir (landfill) is done through spigot. Dense slurry implies that the ratio of ash and water is approximately 1:1, and that the ratio is strictly controlled. These systems have strict technological discipline, and they use highly sophisticated systems for automatic control of

slurry density. This kind of slurry allows the use of smaller landfills, and discharge is done through one or more independent pipes. Thermal power plant „Nikola Tesla B“ previously used transport in the form of diluted slurry (1:10 ratio, or more), but few years ago they moved to the transport in the form of dense slurry (1:1 ratio). Free depositing of slurry in the prepared storage space is done through one or more independent pipes. This is technologically the simplest form of depositing. The disadvantage of this method is that large crater is formed on the place where slurry falls from the pipe, which can threaten the stability of the embankment. Today, free depositing is done mostly with dense slurry. Deposition through a spigot is a form of discharge where the main pipeline was drilled at equal distances, so that the slurry can exit through numerous small holes. Discharge of slurry through numerous small holes contributes to a better wetting of a large area along the embankment, and better segregation of material. Specially designed and constructed spigot consists from pipes laid in the form of the comb with several teeth.

THE INFLUENCE OF ASH ON ENVIRONMENT AND PROTECTION MEASURES

The issue of safe deposit may be considered from two aspects, technical and environmental. Relationship between these two aspects is so close, that every aspect of geotechnical instability threatens the ecological and vice versa. From an environmental point of view, the main problems of ash landfills are connected to air, water (surface and groundwater) and soil. Ash particles suspended in the air can cause respiratory diseases and cancer in humans, corrosion on buildings, a destructive effect on plants. In addition, they can cause discomfort in the form of ash accumulation on structures and objects, can interfere with sunlight (the formation of smog and haze) and can act as catalysts for specific reactions. Improving conditions for ecologically stable disposal of energy waste can be considered in three groups of measures:

- Reduction of pollution sources,
- Precautionary measures,
- Subsequent protection measures.

Reduction of pollution sources

Reduction of pollution from landfills involves activities that affect waste reduction and recycling. For ash and slag, these activities are:

- Selective mining of coal,
- Cleaning of coal before combustion,
- Increasing the efficiency of the combustion of coal,
- Finding a potential application of ash.

In the first two cases, power plants have no direct influence, because these are mining activities. The other two activities are direct responsibility of power plants. To minimize generation of ash in combustion processes, it is necessary to use a higher quality coal. One of the methods for obtaining higher quality coal is selective mining. Selective mining of coal is often not feasible, so a homogenization of better quality coal with lower quality coal is only solution. The use of low quality coal is also possible by introducing a system for coal cleaning. However, the problem is in the quantities that need to be cleaned and in the waste water that remains after the process. Use of dry cleaning methods is not suitable because of the low efficiency. Power plants have to invest in their equipment, because modern boilers are achieving better combustion and utilization of coal, so the formation of ash is reduced.

Of the 7000000 t of ash and slag which is annually produced in our power plants, only about 600000 t (less than 10%) is used again for some kind of construction (most of it to create dikes around landfills). Worldwide, the percentage of ash which is used as a raw material goes from 20% up to 100%. Ash and slag are commonly used in road construction to create different layers and embankments, as a cheap material to fill various holes, dents and depressions, in addition to the preparation of cement, for making building blocks, etc.

Precautionary measures

Precautionary measures can very effectively reduce the environmental impact to a minimum, without big additional investments. This group of protective measures is based on engineering solutions and insights, but it could not be achieved without broad support of the community and the population in the region. Precautionary measures include the following activities:

- The choice of a rational transport and disposal technology,
- Optimization of the size of the landfill,
- Selection of the proper location for the formation of landfill,
- Preparation of landfill for depositing.

For many years, there was no special attention paid to the conditions of depositing, nor is it adapted to the characteristics of the waste material and the requirements of the environment. Because of that, most of the power plants in Serbia started with the problems brought by the transport and disposal of ash. With the increasing awareness of environmental preservation, interest in reducing the negative impact of landfills was also growing. One of the first things that was discussed was the adjustment of ash depositing technology to the ash characteristics and specifics of the environment.

Size of the landfill involves analysis of two parameters: occupied area and height of the landfill. This measure of protection prevents the simultaneous use of all the area intended to accommodate the ashes from power plant during its life cycle. Successful reduction of the active area of landfill was carried out at several of our power plants, including the power plant „Nikola Tesla B“. The total area for deposition is usually divided into three cassettes, where only one cassette is active (working cassette), one is a reserve (with all the measures of protection as it is not in the use) for overcoming the situations of possible breakdowns, and the third is completely out of use (in the next 6 to 10 years). With such a mode of operation, 2/3 of the landfill is grass area, and as a possible source of pollution remains 1/3 of the landfill.

The choice of landfill location can be considered as an initial measure for reducing the negative impact of landfills on the environment. Unfortunately, the location of almost all of today's landfills is contrary to the known and long-accepted factors for site selection in the world. Thus, our landfills are located near cities and settlements, near rivers, on the direction of the winds, etc. An obvious example is landfill of thermal power plant „Nikola Tesla B“, which is located near the town of Obrenovac. A possible solution is that the ashes are disposed of in the internal landfills of closest surface mines.

In order to improve the quality of groundwater in the vicinity of the landfill, it is necessary to prepare the area for deposit, prior to the start of the landfill operation. Preparations include hydro isolation of the floor and inner sides of the landfill. World practice shows that the use of plastic sheets in combination with the clay gives the best results.

Subsequent protection measures

Subsequent protection measures have the least effect and require major investments, but they are necessary to protect the environment. Subsequent measures include the following methods:

- Maintaining the maximum allowable size of water mirrors,
- Spraying uncovered parts of the landfill with water or suspension,
- Formation of a biological cover.

Water mirror has long proved to be a good protection for the environment against the air pollution, and it is often used. Water mirror prevents ash dispersion with the wind. The problem, however, is the danger which accumulated water poses to the geotechnical stability of the landfill. The balance can be easily disrupted and the situation becomes critical. In the power plant „Nikola Tesla B“, water mirror covers up to 60% of the total area of the cassette.

Spraying uncovered parts of the landfill (parts that are not underneath the water mirror) is commonly used measure of protection. Overflow and waste water from the landfill is used for the spraying. The effects can be beneficial, especially in terms of air pollution. The problem arises in the need for constant alertness and prediction of conditions that may occur, so the spraying could start on time.

Grassing of inactive areas of landfill is domesticated measure in our power plants. The results, as seen from an environmental point of view, are very positive, but the investment and maintenance costs are high. In the thermal power plant „Nikola Tesla B“, biological recultivation (seeding grass, planting trees and shrub species) is done twice a year (in spring and fall).

MATHEMATICAL MODEL OF ASH DISPERSION IN THE AIR

The problem of modeling the dispersion of ash particles from landfills is not easy. It is necessary to calculate the mass flux of ash rising from the landfill, depending on the strength of the wind, and determine the concentration of ash in the air at a particular location. In this paper will be briefly described the procedure shown by Zoran Gršić et al. (2007).

The first step in the modeling is the parameterization of the lifting mechanism. This can be achieved by comparing the ash to the dust particles. Several authors (Shao et al., 1993; Marticorena et al., 1997) have pointed out saltating (sandblasting) as the most important mechanism for lifting dust aerosols to the atmosphere. A similar idea can probably be applied to the ash. If surface of ashes is sufficiently dry, i.e. if surface of ash/slag depots are not protected with the pond (water mirror), a strong wind is able to roll greater particles or to lift some of them in to the air. Saltating, sand-sized particles sandblast the surface and eject fine particles which remain suspended in the air for a long period of time, and which can be transported to great distances downwind. The most common approach in the parameterization is described in the following equation:

$$q = A \frac{\rho}{g} \sum_{u_*} u_* (u_*^2 - u_{*tv}^2), \quad (1)$$

where:

- q [g/cm s] – instantaneous horizontal (saltation) mass flux,
- A – unit less parameter (usually assumed to be equal to 1),
- ρ [g/cm³] - density of air ,
- g [cm/s²] –acceleration of gravity,
- u_* [cm/s] – wind shear velocity,
- u_{*tv} [cm/s] – threshold shear velocity.

The threshold shear velocity is the minimum friction wind speed assumed to give dust emission. It is related to soil roughness and soil characteristics. The wind shear velocity is related to wind speed at height z under neutral condition (wind speed greater or equal to 6 m/s) by:

$$U(z) = \frac{u_*}{k} \ln \left(\frac{z - D}{z_0} \right), \quad (2)$$

where:

- $U(z)$ [cm/s] - wind speed at height z ,
- k – von Karman's constant (0.4),
- z_0 [cm] – roughness height,
- D [cm] – displacement height.

Because of sandblasting by saltation-sized particles, vertical dust flux is linearly related to instantaneous horizontal (saltation) mass flux (1), by a constant:

$$F = Kq, \quad (3)$$

where:

- F [g/cm² s] – vertical dust flux,
- K [cm⁻¹] – a constant.

The value of K is strongly dependent on depots surface texture, crusting, moisture, and it is typically on order $10^{-5} - 10^{-6}$.

Dispersal of ash and its concentration can be calculated in several ways (Eulerian models, Gaussian models, Lagrangian models). Here is presented the Gaussian model:

$$C(x, y, z) = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left\{ \exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right] \right\}, \quad (4)$$

where:

- $C(x, y, z)$ [μ/m³] – air pollution concentration at grid poin (x, y, z),
- y [m] - lateral distance from plume axis,
- z [m] – height of the receptor above ground,
- Q [kg/h] – source strenght,
- H [m] – effective height of source emission,
- σ_y, σ_z [m] – diffusion coefficients in y and z directions,
- u [m/s] – average wind speed.

Source strenght Q is described by:

$$Q = FS, \quad (5)$$

where:

- S [m²] – area of source emission.

With this calculation, the corresponding meteorological data, particle size distribution, surface characteristics of disposal sites like roughness, threshold shear velocity, and their texture, it is possible to determine the concentration of ash in the air, in the vicinity of cities like Obrenovac and Belgrade.

CONCLUSION

Most of the economic and social activities cause emissions of air pollutants. Their presence directly affects the health of people and ecosystem. The main sources of air pollution are the sectors of: energy, transport and agriculture. In Serbia, the main sources of electric energy are thermal power plants that burn poor quality coal. Because of that, and generally old equipment in power plants, they emit a lot of sulfur and nitrogen oxides, and their landfills are major sources of particulate matter (ash). With increasing environmental awareness, people have begun to think about reducing pollution from power plants. One way to do that is to focus attention on the processes and systems for the disposal of ashes.

This paper presents an overview of the processes and systems for disposal of ashes, and it gives the mathematical model of propagation of ash in the air. It also gives some of the measures that can reduce the impact of ash on the environment. In order to really solve the problem of pollution from landfills, it is not just required to invest one time and solve the current problems. Only through continuous and thorough work on improving the conditions for transport and disposal of ash, as well as on the prevention of ash dispersion from landfills, it is possible to permanently reduce pollution and make life easier and healthier for everyone.

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**REMEDIATION POLICY OF RADIOLOGICALLY CONTAMINATED
SITES: PERSPECTIVES IN SERBIA**

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ABSTRACT

Radiologically polluted land are a relatively new area for policy and legislation within the states of the European Union and there is little resemblance in approach. Policy aims and principles pertaining to contaminated land are similar within the states but regimes vary according to local pollution levels and socio-economic circumstances. Serbia as a representative of the transitional economy still do not has policy in this area. Herein, policy objectives in Serbia are discussed, showing both the similarities and some of the many differences in relation to other Member States. Policy direction, aims, principles and goals are considered. The main policy instruments for controlling contaminated land are also examined.

Key words: remediation, policy, contaminated land, radionuclides.

INTRODUCTION

Remediation of contaminated land is a relatively novel domain for policy and legislation within the European Union (EU) with many variations of range development among the Member States. The nature of the contaminants and the hazards they present vary greatly from site to site. Contaminated land may contribute to pollution of ground water, surface water, ambient air and foods, creating additional potential human exposure routes.

Most commonly, radioactive residues are the result of human activities that have been carried out in the past without being regulated, where the termination of the activity and the handling of the remaining residues would most probably not have been adequately considered when the activity was initiated, like ancient practice of mining and milling operations of ores containing natural radioactive substances. Radioactive residues may also remain from past events that may have been unforeseeable at the time of occurrence, such as accidents releasing long-lived radioactive materials to the environment. Finally, a largest amount of radioactive residues in the human habitat are a legacy from past military operations.

Reductions in the doses to individuals and environmental impacts were to be achieved by means of interventions aimed at: (1) removing the existing sources of contamination; (2) modifying the pathways of exposure; and/or, (3) reducing the numbers of individuals or other receptors exposed to radiation from the source. In some cases the restricted use of human habitats may be the outcome of the optimization process for remediation (IAEA, 2007). The requirements established a generic reference level for aiding decisions on remediation as an existing annual effective dose of 10 mSv from all environmental sources, including the natural background radiation (IAEA, 2007)..

The objectives of remediation were now formulated as: (1) to reduce the doses to individuals or groups of individuals being exposed; (2) to avert doses to individuals or groups of individuals that are likely to arise in the future; and, (3) to prevent or reduce environmental impacts from the radionuclides present in the contaminated area (IAEA, 2007).

Although in 2006 the majority of EU countries reported either national or regional inventories of contaminated sites, progress in the management of these sites varies significantly across Europe - depending on different national management approaches and legal requirements. Approaches to clean up, including different remediation targets also vary across EU countries, and countries differ in the degree and extent to which they finance clean up.

As the other Balkan countries Serbia does not have well developed legislative of remediation of contaminated areas. The policy framework of the existing Law on Waste Management does not refer to the radiological contaminated sites. Due to its turbulent past and inadequate environmental consciousness Serbia is facing with many problems of land degradation caused both, radionuclides and the municipal waste. Here we consider and emphasize fundamental principles and objectives of remediation in the EU that can serve as examples in which direction Serbia should go toward the remediation policy making. Here is also presented a model policy in its ideal form.

EUROPEAN REMEDIATION POLICY PERSPECTIVES

Around the Europe, each Member State has its own critical areas and more or less acute radiological contamination problems to be solved. In the last 30 years soil protection policies have been gradually developed and implemented, both nationally and at EU level.

A number of references concerning soil safety and remediation can be found somewhat spread through the European Community regulatory system. They are usually related to the measures and implements that have direct or indirect effect on the quality of soil. The Waste Framework Directive (2006/12/EC) sets requirements for waste disposal and recovery and for regulating the recycle and reuse of contaminated wastes thereby contributing to a more sustainable remediation of contaminated sites and prevention of soil contamination. Environmental Liability Directive (2004/32/EC) includes terms for addressing new contamination problems and remediation of land damage whenever a risk associated with contaminated land potentially endanger human health. New regulatory framework, REACH (Registration, Evaluation, Authorization, and restriction of Chemicals) (CEPIC, 2003) came into force on June 1, 2007, and Common Agricultural Policy which also address the problems related to soil contamination. Although different, these policies focus primarily on diffuse rather than local contamination aspects and they are quite limited when dealing with historical contamination and site development cases (Rodrigues et al.2009). However, soil contamination is essentially a local problem, and unless there is as sufficient concern within the local community and the appropriate mechanisms are in place to pressure on higher tiers of government, it is unlikely to become a subject of higher policy.

A new legislative proposal - draft Soil Framework Directive, SFD was presented by the European Commission in 2006. (EC, 2006). The draft SFD demands a precautionary approach to be followed and defines a list of potential sources of soil contamination, such as industrial facilities, mines and waste landfills both operating and after closure, former military sites, ports and airports, dry cleaners and waste water treatment installations and considers a broad group of dangerous substances for which future soil contamination must be prevented and past contamination must be remediated (EC, 2006). Sites are considered contaminated and needing remediation whenever “they pose a significant risk to human health or the environment”, but the mechanisms through which “significant risk” is assessed are yet to be defined. It allows local soil and land use to be taken into account and includes the possibility to delegate the enactment of policy aims and measures to local authorities. Concerning contaminated land, the SFD includes a systematic inventory of contaminated sites, the definition of National Remediation Strategies and a soil status report to be made available to competent authorities whenever a site on which a potentially polluting activity has been developed, is to be sold.

NATIONAL POLICIES ON CONTAMINATED LAND IN EU

Some Member States have already developed national policies for the management of contaminated sites or specific legislation regulating investigation and clean-up of contaminated land. Areas with a

shortage of land, due to the geography and climate conditions along with population pressures are particularly affected. This joint with pressures on potable water will likely to incite the emergence of legislation on contaminated land.

National soil policies from different perspectives can be found in literature (Ferguson, 1999, Prokop, 2005, Smith et al., 2006; D'Aprile et al., 2007; Thornton et al., 2007, Bouma and Droogers, 2007; Carlon, 2007). These authors analyse soil policies from different countries in an international context, discussing issues such as legal frameworks, financial incentives, risk assessment and soil remediation standards.

Early in the 1980s Norway defined very specific provisions related to soil pollution via the “Pollution Control Act” (based on the “polluter-pays” principle) and by assigning responsibilities for the regulation of contaminated sites (Ferguson, 1999)

In Denmark, potential problems with contaminated sites were identified in the early 70s leading to the revision of waste regulations to deal with soil contamination arising from waste management and twenty years later, to the development of a broader “Soil Contamination Act”, more able to deal with liability issues (Ferguson, 1999)

The Netherlands was one of the first EU Member States to establish specific legislation on soil protection. Soil remediation was given legal status in 1983, and later, in 1987 the Dutch “Soil Protection Act” came into force (Wesselink et al., 2006.) Soil policy developments in the last 20 years in the Netherlands also included: the revision of remediation criteria; developments on soil quality objectives and risk assessment procedures; increase in flexibility for local authorities in regulating contaminated land; encouragement of local participation in the decision making process; a distinction between mobile and immobile cases of soil contamination; and the stimulation of private funding for soil remediation (Wesselink et al., 2006). A new framework of soil quality standards has been developed in the scope the Dutch Soil Quality Decree than entered into force in January 2008.

In the UK the first institutional mechanism to address contaminated land issues was the Inter-departmental Committee on the Redevelopment of Contaminated Land (ICRCL) which was set up in 1976 with the role of developing and co-ordinating advice and guidance on human health hazards arising from the re-use of contaminated land and coordinating advice on remedial measures. In England, Scotland and Wales the contaminated land regime is implemented through The Contaminated Land Regulations (2000, 2001 in Wales) which enforces Part IIa of the Environment Protection Act (1990). Section 57 of Part IIa was introduced into the Environment Protection Act 1990 by the Environment Act 1995 and was implemented in April 2000 in England, in July 2000 in Scotland and in July 2001 in Wales. Part IIa introduced a new statutory regime for the identification, assessment and remediation of contaminated land in the UK and in response to this the DEFRA and the UK Environment Agency have developed risk-based procedures for assessing harm from contaminated sites to ecosystems and human receptors. Comprehensive packages of technical guidance relevant to the assessment of human health risks arising from long-term exposure to contaminants in soil has been published by DEFRA and the UK Environment Agency (DEFRA and EA 2002; DEFRA, 2006).

In Belgium, Flanders adopted its Soil Remediation Decree in 1995 that contains an obligation to carry out an investigation at every transfer of land on which a “risk activity” is or has been developed. In 2006. the Flemish Parliament adopted a new decree that will enter into force during 2008, although the basic principles of soil remediation criteria remain the same from 1995 (Dries et al., 2008). A distinction between “historical contamination” and “new contamination” is made and remediation which is primarily triggered by land transfer processes follows rules appropriate to each case. The legal framework for contaminated land management in the Walloon region is constituted by the Law of the Walloon government for the cleaning of contaminated sites and rehabilitation of brownfield and three kinds of risk-based standards have been developed for soil and groundwater quality assessment on contaminated sites: reference values, trigger values and intervention values.

Following a series of provisions related to remediation of contaminated land that were included in waste management policies, a Ministerial Decree concerning soil contamination (M.D. no. 471/99) came into force in Italy in 1999. In 2006, provisions for the management of contaminated sites have been included in the Legislative Decree no.152/06 (revised by the Legislative Decree no. 04/ 08) which include the development of human-health site specific risk assessment whenever defined screening levels for soil, subsoil and groundwater are exceeded (D'Aprile et al., 2008).

The German Federal Soil Protection Act came into force in 1998, and the accompanying sublegal regulations in 1999 and integrates aspects of soil protection, remediation and pollution prevention (Carlson, 2007).

A Spanish regulation on contaminated soils was published in January 2005 (Royal Decree, RD 9/2005) and has been recently explained by Tarazona et al. (2005). This regulation is supported by the previous Spanish Waste Law (Ministerio de Presidencia 1998), and encompasses exclusively soils polluted by industrial activities.

REMEDICATION POLICY PERSPECTIVES IN SERBIA

Serbia to date has been faced with a number of issues associated with radiological contamination. A civil war on the territory of former Yugoslavia in the last decade of the twentieth century, economic sanctions to Serbia and NATO conflict in the 1999. were additional reasons for radioactive contamination of the regional ecosystem. Furthermore, the main sources of environmental contamination by uranium in Serbia were cheap import of poor quality and often radiologically unsafe phosphate fertilizers as a consequence of reduction of national production capacity (Stojanovic et al 2006).

A lack of required legislation mechanisms, defective economic climate and institutional constraints resulted in burden with a legacy of environmental degradation due to decades of unrestrained economic activity and governmental neglect of environmental control.

Available reports states that the ammunitions containing depleted uranium (DU ammunition) used in the NATO raids on the Federal Republic of Yugoslavia in 1999 against targets in Kosovo and Metohija, Montenegro and Serbia (Document on-line). During the NATO aggression in Yugoslavia 112 sites in Kosovo and Metohija and 12 locations in southern Serbia with the ammunitions containing depleted uranium (DU ammunition) were bombing (Stojanovic et al 2011).

To date have been published decontamination of four “hot spots” in Serbia (Bratoselce and Reljan near Preševo, Pljačkovica above Vranje and Borovac near Bujanovac. The decontamination was carried out between 2002. and 2007. in cooperation with expert teams from the Ministry of Defence of the Republic of Serbia, Serbian military and the *Vinča* Institute. The decontamination of locations contaminated with DU ammunition in southern Serbia has been carried out by way of physical separation It was financed by the Ministry of the Environment of the Republic of Serbia. Hereinafter was stated that upon completion of the decontamination process, the locations and their environs have been placed under continual radiation monitoring (Document on line)

Although the decade passed since these events, in Serbia a very little have been done in terms of the adoption of required legislation relating to the management of radiological waste. Also, the state of municipal waste management in the Serbia is far beneath EU objectives (Hempfling et al. 2009) The National Waste Management Strategy in Serbia is the first fundamental document in the creation of conditions for a rational and sustainable waste management at the national level (NWMS, 2003). The NWMS provides guidance on the implementation of waste legislation. It establishes systems for the management of specific waste streams. However, one of the key obstacles to the achievement of NWMS goals is lack of s of waste management at regional and local levels which have to be developed.

Due to its characteristics, like in many other European countries in Serbia, contaminated sites and contaminated site management (i.e. identification, assessment, prioritization, remediation and monitoring of sites) are addressed by different fields of legislation. The most relevant legal documents referring to contaminated sites or contaminated site management are Law on Environmental Protection (LEP), Law on Privatisation and The National Waste Management Strategy for the Period 2010-2019 (Ausserleitner et al. 2011). The provisions of the Law on Waste Management do not apply to radiological waste.

In Serbian legislation regarding contaminated site management, contaminated locations are defined as locations with confirmed concentration of chemicals, which could cause significant risk to human health and environment, including waste disposal sites, commercial and industrial sites, locations of accidents and brownfields. From a legal point of view no difference is made between historical contamination and “new” contamination. In accordance with the “polluter-pays-principle” and the principle of “liability of polluters” outlined in the Law on Environmental Protection, sites with polluters, which can be held liable, are distinguished from sites, where the state is responsible for remediation. The latter includes sites with unknown polluters or pollution with its source outside the territory of the Republic of Serbia (“principle of subsidiary liability”). Environmental damage caused by former state-owned companies should be remediated by the state prior to privatization (LEP). Brownfield locations, which are potentially contaminated due to former (industrial) activities, are addressed as contaminated sites as well and are referred to as “industrial devastated locations”. Every change in ownership shall be accompanied by an assessment of environmental status and liability for environmental pollution. Within the framework of Serbian legislation two approaches to identify contaminated sites can be identified: (i) by systematic soil quality monitoring at national and local level and (ii) by environmental inspection activities (LEP). A methodology specifically dedicated to identify potentially contaminated sites has not been introduced to Serbian legislation so far.

The decision whether a contaminated site needs to be remediated, is based on generic criteria only, i.e. no risk assessment has to be carried out. Apart from this, EU “best practice” methodology has been introduced recently, combining elements of both, an “early-stage” risk assessment and a classical risk assessment based on field data. According to LEP this methodology shall serve to “determine the status of endangered environment and priorities for rehabilitation and remediation”. Deduced from the qualitative and quantitative criteria given in the the LEP, overall remediation goal is to re-establish the “natural status”, allowing a “multi-purpose” use of soil and groundwater (“precautionary principle”). No reference is made to land-use or site-related aspects. A link between spatial and urban planning and “endangered parts of the environment” can be identified.

Serbia, although the basic regulatory principles remediation includes in LEP, still does not have Policy of remediation on radiological contaminated land. Remediation has to take into account all of the variables on the site, as well as institutional, regulatory and technical consideration. It also has to address the results of risk analysis and cost.

MODEL REMEDIATION POLICY

In simple terms, remediation should be expected if there is contamination and there will be contamination if the levels of radioactivity per unit area are above given values considered unsafe (IAEA 2007).

The first aim of the Policy document should be identification of the radiological contaminated sites and soils from past activities and prevention of any future environment contamination by existing practices and nuclear accidents. Secondly, the Policy document should promote the prevention as the best option for the country and strengthens the national legal and institutional framework for radiation safety through implementation of international standards and best practices.

The objectives of the Policy are to protect people; environment and water resources from harmful radiation exposure from the existing practices and from the practices in past where large and small

sites have been radiological contaminated by industrial activities, coal mining and production of electricity, unsafe RadWaste management and activities within nuclear research.

The guiding principles of Policy is the continuing responsibility of the Government to use relevant legislation, regulations, international standards and best practices as well as all practical means to improve, coordinate programs and resources to the end that the country may; protect the human health from harmful effects of ionizing radiation and other non-ionizing elements that could pollute human environment and water resources; protect and sustain the environment to future generations; protect and preserve the important natural, cultural and historic aspects as a national heritage and maintain the environment which supports diversity and variety; promote and enhance the quality of renewable resources and use of recycling of deplorable resources.

The remediation process need to be justified and must aim, above all, to maximize the net benefit from the remediation within and optimization process.

The overall radiological impact from the site or sites in question should be assessed, if necessary the identification of options for reducing these impacts, the evaluation of the achievable dose reduction, and the assessment of harm and costs associated with these remediation options. Decisions taken on this basis include benefits from dose reductions, financial expenditures required and other factors of influence.

It shall be ensured by means of the legal framework the polluter to pay for the pollution. If organizations or individuals are unable to meet their liabilities the government will ensure adequate funding to be available for remediation actions.

The relevant National legislation and regulations for environmental protection and preservation of human environment, radiation safety and waste management, categorization of land use, transport, industry as well as National Environmental Strategy and National Environmental Action Plan have to lie lay down the legal framework for this document. The Government to review the existing regulations and to develop a regulation which might give positive support to this policy.

All governmental bodies should review their present statutory authority, administrative regulations and current policies and procedures for the purpose of determining whether there are any deficiencies or inconsistencies therein which prohibit full compliance with the purposes and provisions of the Policy, and should purpose such measures as may be necessary to bring their authority and policies into conformity with the intent, purposes and procedures set forth in this document.

The Government should also to recognize that openness, transparency, and effective public and stakeholder engagement and communications are the key to building and maintaining the support, confidence and trust of the public and stakeholders necessary to implement the Policy.

CONCLUSION

There is no single policy model for dealing with contaminated land within EU, and no single model would be workadable for each Member State. However, policy aims and principles refer to contaminated land are much the same across Europe. Remediation on the ground uses analog techniques, which depend on local factors, whenever they are used. Every state has its own system, produced by different goals and different practices, due to different administration, legislation and finances. Even though in Serbia, the policy and legislation is in its beginnings, and therefore, there is a little evidence as to which approaches are more likely to reduce the amount of contaminants, by comparing current experience within Europe a system of best practice could be suggested as the point to the way forward. European policy and directives could also act as catalysts and push Serbian policies onto national agenda. This is especially the case for environmental policies, and contaminated land in Serbia who has land that may be highly contaminated.

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**THE INFLUENCE OF "ZELEZARA SMEDEREVO" ON THE
QUALITY OF THE ENVIRONMENT AND HEALTH OF THE PEOPLE
IN THE SURROUNDINGS**

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ABSTRACT

The uneven development and achieved degree of economy do have negative consequences on the quality of the environment in Smederevo. The most endangered area is the industrial area of "Zelezara Smederevo" which directly threatens the city of Smederevo and a few settlements nearby, like Radinac, Rajca and Vranovo. Using a mathematical pattern the maximum low concentration of SO₂ exhausted from the blast furnace of "Zelezara Smederevo" was calculated. The data from health statistics about prescribed medicine, the structure of diseases and the current information about the degree of endangered environment, were used to illustrate the cause and effect relation between health condition and the influence of certain pollutants existing in the environment.

Key words: air pollution, Zelezara Smederevo, ingredient concentration, the quality of air.

INTRODUCTION

Zelezara-Steelworks Smederevo is an industrial structure situated 7 km southeast of Smederevo and covers the area of 350 hectares. It represents the most important factor for the development of Smederevo (74% of whole production and 97% of export) concerning ferrous metallurgy, the production of crude iron and steel. The main characteristics of Zelezara Smederevo are: high techno-economic and spacious features concerning the usage of water, ban of the sewage, the consumption of electricity, high range of transportation and an emphasized connection in interregional (republic) and trans-regional space dimension. In the same area there is "Messer Technogas" company which produces medical and special gases. The specific form, big quantity and the scope of production cause big ecological pressure on all the factors of environment, which make this area one of the most endangered surroundings. The production of 2.2 million tons exhausts over 70 billion m³ of waste gases (about 32 000 m³ a tone of produced and treated steel or 8.2 million m³ an hour). There are 89 pollutants in "Zelezara Smederevo" sintering plant (34), Blast furnace 1 and 2 (8), Steelshop (32), Hot strip mill (4), Cold rolling mill (10) and Power plant (1) (The group of authors 2007). Apart from the above mentioned pollutants, "Zelezara Smederevo" has 5 landfills of ore and recyclables which belong to the group of special pollutants, that is, the kind of the surface pollutant that exhausts large quantities of dust that pollutes the air of nearby settlements. According to Regulations on limit values for pollutant emission, 18 out of 89 above mentioned pollutants ought to be constantly measured, 55 require isolated measuring, while 10 of these do not need to be measured. By 2005 there had been no continual measuring, but only some of the pollutants were checked. The Institute "1 maj" from Nis had measured the pollution.

At the end of 2005 the then "U.S. Steel Serbia" began measuring according to Regulations on limit values for pollutant emission, the ways and deadlines of measuring and available data. This was performed by Institute of Public Health "Pomoravlje" from Cuprija.

There have been 3 automatic analyzers for monitoring the quality of air in 2007, one in the city center, and the other two near “Zelezara” (Radinac and Ralja). In this way the overall research on the quality of the environment and its impact on the health of its inhabitants started.

Apart from the mentioned pollutants in waste gases, there is the highest concentration of carbon monoxide (CO) (about 25 000 tons). The waste gas contains about 10 000 tons of sulphur dioxide (SO₂) and 1 500 tons of nitrous oxide (NO). The waste gas also contains dust, the quality of which depends on the quality of raw materials and technological process. It has been calculated that the production of 1 ton of iron produces 100 -120 kg of dust, sludge and scalings, which means that the production of 2.2 million tons of iron exhausts 200 000 tons of dust per year. The blast furnace gas contains dust and 30% of carbon monoxide, so after its purification, it is burned in the so-called “candle” before its emission into the atmosphere.

An accident occurred in 2005 due to its not burning and uncontrolled emission into the atmosphere. The fact that the concentration of the CO in the air was 0.4%, which is practically lethal, illustrates the level of the danger. Since then there has been one more “candle” for burning blast furnace gas.

Table 1: Annual statistics of pollutants SO₂, NO₂ and suspended particles of PM₁₀ per hour in the period January 1st 2011- December 31st 2011 on measuring point in Radinac (Agency for Environmental Protection 2011)

parameter	SO ₂	NO ₂	PM ₁₀
Annual statistics of daily data			
GV	125	85	50
minimum	8.1	2.6	17.1
maximum	131.8	53.1	354.8
Number of days >LV	1	0	255
Annual statistics of data per hour			
GV	350	150	
minimum	6.9	0.0	4.7
maximum	602.9	132.9	1063.7
Number of days >LV	7	0	

If there is purification, its efficiency depends on the kind of device and physical-chemical characteristics of dust particles. If the particles are smaller than 10 microns the existing devices can separate them. This kind of dust does not deposit easily, it floats in the air and is the most dangerous for man, because he inhales it. The particles of carbon dust are of this kind. 7-10 000 tons of dust of different physical and chemical content is exhausted in the atmosphere with waste gas.

Apart from this sources in Zelezara, there are 6 deposits of raw material, recyclables and by-products. They represent a special kind of pollutant since they pollute the environment with the dust particles and are called surface line sources.

THE MODEL OF CALCULATING THE MAXIMUM CONCENTRATION OF AIR POLLUTION

Determination of the degree of air pollution by the means of mathematical pattern of air pollution distribution, enables the simulation of the expansion of pollutants with different simulated emissions in determined topological, urban and meteorological situation. By the means of mathematical pattern we get realistic picture of what is going on in connection with the expansion of pollutants, which can be used as a basis for estimation of potential dangers and technical solution of the protection system.

Sulphur dioxide is a part of polluted air, specially in cities. It comes into existence when fossil fuels and other kinds of fuels burn, especially those rich in sulphur. It is also a product of processing mineral ores that contain sulphur (when iron and other metals containing sulphide compounds are produced). This project aims to calculate the distribution of SO₂ in Zelezara Smederevo, that is in blast furnace like the source of pollution in determined topological and meteorological situation using this pattern. Applying this pattern we have calculated the distance from the blast furnace with the maximum concentration SO₂ and its quantity.

The procedure of detecting the surface concentration of dangerous gas materials, stated in this project, is part of regulations used in engineering practise when the structures that produce pollution are constructed.

The aim of this regulation is to estimate the emission of dangerous gases emitted from the defined installed power (and other characteristics of the source) and if it is in accordance with the law.

This procedure has been developed in accordance with empiric and theoretical patterns used in air pollution studies. (Внуков А.К. 1992)

The maximum value of harmful substances concentration measured in mg/m³ in case of the gas emission from certain point source with the round opening under unfavourable weather conditions, at the distance of the x_M (m) from the source is:

$$c_M = \frac{AMFmn\eta}{H^2 \sqrt[3]{V_1 \Delta T}}, \quad (1)$$

A in the formula is the coefficient that depends on temperature stratification of the atmosphere; F – dimensionless coefficient that shows the speed of clogging of harmful substances in the atmosphere;

M (g/s) – represents the quantity of emitted harmful substances in the atmosphere in a unit of time;

m and n are coefficients characterise the conditions of the emission of harmful substance from the opening of the source; H (m) stands for the height of the pollutant compared to the earth's surface;

η is dimensionless coefficient that pictures the influence of relief on the emission of harmful substances;

ΔT (°C) is the difference in temperature between gas mixture which is emitted from the opening and the temperature of surrounding air; V_1 (m³/s) expenditure of the gases determined by the formula:

$$V_1 = \frac{\pi D^2}{4} w_0 \quad (2)$$

D(m) stands for the diameter of the source opening, w_0 (m/s) average speed of the emission of gas harmful substances from the source opening.

$$f = 1000 \frac{w_0^2 D}{H^2 \Delta T} \quad (3)$$

$$v_M = 0.65 \sqrt[3]{\frac{V_1 \Delta T}{H}} \quad (4)$$

The risky speed of wind at the level of pillar of smoke at which the maximum value of surface concentration of harmful substances is :

$$u_M = v_M (1 + 0.12 \sqrt{f}); v_M > 2 \quad (5)$$

$$v_M' = 1.3 \frac{w_0 D}{H} \quad (6)$$

$$f_e = 800(v_M')^3 \quad (7)$$

$$m = \frac{1}{0.67 + 0.1\sqrt{f} + 0.34\sqrt[3]{f}}; f < 100 \quad (8)$$

$$n = 1; v_M \geq 2 \quad (9)$$

$$x_M = \frac{5-F}{4} d H \quad (10)$$

$$d = 7\sqrt{v_M} (1 + 0.28\sqrt[3]{f_e}); v_M > 2 \quad (11)$$

The maximum value of the concentration of harmful substances under unfavourable meteorological conditions at the wind speed $u(m/s)$ is:

$$C_{Mu} = r C_M \quad (12)$$

where,

$$r = 0.67 \frac{u}{u_M} + 1.67 \left(\frac{u}{u_M}\right)^2 - 1.34 \left(\frac{u}{u_M}\right)^3; \frac{u}{u_M} \leq 1 \quad (13)$$

Dimensionless quantity

$$x_{Mu} = p x_M; p = 3 u / u_M \leq 0.25 \quad (14)$$

Is the distance at which with the wind speed $u(m/s)$ the surface concentration of harmful substances has the largest value, p is dimensionless parameter. The calculated gas concentration refers to the time period of 24 hours after the emission from the chimney.

The height of Zelezara Smederevo chimney is 150.2 m, and its width on the top is 6.5 m. Zelezara is situated 7 km southeast from Smederevo. The average elevation of the city area is 120.7 m, the lowest point is 69 m high, and the highest is 273 m. The adopted values of parameters needed for the calculation of the maximum surface concentration of SiO_2 and appropriate distances are:

$$A = 160; F = 1; H = 30.5 \text{ m}; \Delta T = 150^\circ \text{C}; \eta = 1; w_0 = 2 \text{ m/s}; M = 600 \text{ g/s}$$

Using the formulas (1)-(14) it is found that the maximum surface concentration of SiO_2 $C_M = 5.287 \text{ mg/m}_3$ is and that it is found at the distance of $X_M = 1102 \text{ m}$ from the source.

Taking into account the fact that the south wind of 2.6 m/s is the most common one, it can be concluded that the concentration of SiO_2 C_M is 0.284 mg/m_3 and that it occurs at the distance of $x_{Mu} = 3306.5 \text{ m}$ from the source.

Since there are two furnaces in Zelezara and two identical sources of the emission of SiO_2 (when both furnaces are in operation) the total quantity of maximum concentration represents the total of each source, which is in this case $2C_M$ at the same distance X_M .

According to the Regulations on limit values, the methods of measuring, the emission, criteria for setting up measuring points and data records (Official Gazette, RS, no 54/92, 30/00 and 19/2006*) the allowed limited emission of sulphur dioxide is 0.15 mg/m_3 .

Using the theoretical calculation of the limited values of emission of SO₂ and allowed limited values of the emission, we can conclude that Zelezara exceeds the allowed level of the emission of SO₂ under normal meteorological conditions.

THE QUALITY OF AIR

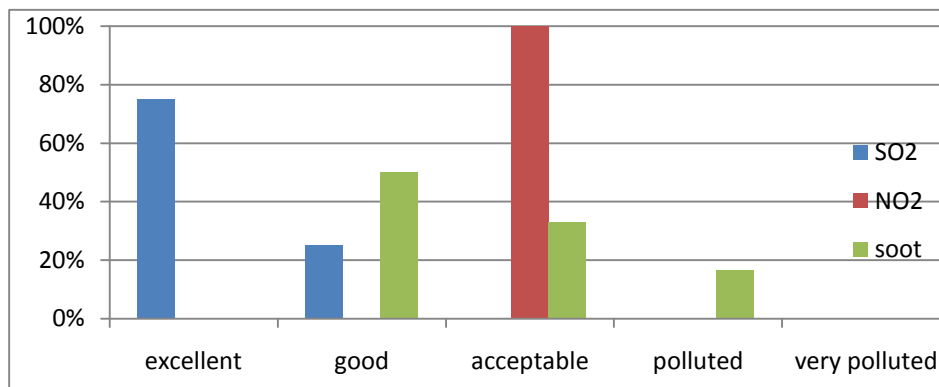
Tabel 2: The results of automatic monitoring parameters of quality of air on measuring point Smederevo – Gimnazija during 2011 (National Institute of Public Health Pozarevac)

month	parameter	SO ₂ µg/m ³			Nu,ber of measuring	NO ₂ µg/m ³			LVI>85	soot µg/m ³			
		number	Average value	Max daily value		LVI150	Average value	Max daily value		Number of measuring	Average value	Max daily value	Number of days above LVI>50
I		31	42,5	96,0	0	31	55,3	94,0	1	31	42,4	126,0	10
II		28	46,2	111,0	0	28	72,8	105,0	10	28	56,1	204,0	8
III		31	43,1	131,0	0	31	63,8	95,0	4	31	31,2	127,0	4
IV		30	19,8	44,0	0	30	58,9	91,0	2	30	16,8	33,0	0
V		31	16,9	39,0	0	31	63,7	106,0	2	31	13,1	48,0	0
VI		30	15,2	57,0	0	30	66,6	98,0	5	30	10,8	20,0	0
VII		31	8,5	17,0	0	31	61,2	92,0	1	31	13,3	24,0	0
VIII		31	12,9	57,0	0	31	66,9	67,0	5	31	16,5	20,0	0
IX		30	14,8	51,0	0	30	70,4	120,0	8	30	17,8	41,0	0
X		31	23,6	64,0	0	31	48,2	89,0	1	31	30,8	99,0	5
XI		30	28,7	74,0	0	30	57,7	99,0	2	30	59,3	161,0	13
XII		31	35,2	79,0	0	30	50,9	178,0	1	31	34,3	90,0	6
year		-	25,6	68,33	0	-	61,36	102,8	3,5	-	28,53	82,7	38,3

Systematic control of the quality of air in the city on measuring point Gimnazija in Smederevo, was done by National Institute of Public Health in Pozarevac. In 2011 a 24 hour measuring of the quantity of SO₂, NO₂, soot and deposited materials in which heavy metals were detected occurred on this point.

The selection of measuring point, sampling and the methods used for the identification of pollutants were chosen in accordance with Law on Air Protection (Official Gazette RS, no 36/2009) and Regulation on the conditions and requirements for monitoring air quality (Official Gazette RS, no 11/2010 and no 75/2010).

On the basis of the adopted criterion of evaluation of air quality and automatic monitoring, near Gimnazija Smederevo, we can estimate the quality of air based on domestic legislation which takes into account the occurrence of GVI exceed and determination of temporary index of air quality.



Picture 1. The quality of air in 2011 on measuring point Gimnazija in Smederevo

On the adopted criterion of evaluation of air quality on measuring point Gimnazija, we can conclude the following: during 2011 according to the average quantity of SO₂, the air was excellent in 75% cases and good in 25% cases. This means that in most cases the imission concentration was less than half of the LV.

In this period it was only in one day that the 24 hour limited and tolerable value of SO₂ was exceeded.

However, the existence of NO₂ has quite different relation; the occurrence of this pollutant is completely between 44-55 mg/m³, which is acceptable. This means that its value is just bellow the level of pollution.

The 24 hour limited value of NO₂ was exceeded during 42 days and for one day the 24 tolerable value was exceeded. Every month there was the exceed of LV, most of which occurred in February (10 days). In winter months the quantity of soot increases and the value of LV is higher from October to March, due to heating. In a half of the cases, the occurrence of soot takes the air to the limit of pollution (33.33%) or is polluted (16.66%) and in 50% of the cases it is of good quality. During 46 days the 24 hour limited value of soot level was exceeded, and during 4 days the 24 hour tolerable value was exceeded as well. These occurred mainly during the winter.

If we assume that the total quantity of exhausted gases and dust stayed in the area of Smederevo and was distributed uniformly during a year, the whole area up to 150 meters would be in waste gas and dust which the inhabitants would have to inhale. Fortunately, favourable geographical position and atmospheric motions spread the exhausted gas and dust and then they cover a much bigger area, which considerably decreases the content of harmful substances. The analysis of wind rose helps us to conclude that south and southeast winds, known as Kosava, prevail in Smederevo. The prevailing circulation of air masses in the north-south direction is caused by orographic factors, i.e. Velika Morava valley.

Since Zelezara is southeast of Smederevo, these atmospheric motions are mitigating circumstances, especially because of the fact that Kosava is a winter wind and, as it is stated, the emissions of gases are higher during winters. Motions of air depressions and anti cyclones over the Pannonian valley and north parts of Velika Morava decrease to certain degree the air pollution in Smederevo. Nevertheless, we can conclude that the air in Smederevo belongs to the third category, as an excessively polluted air.

There is no direct relation between the health of inhabitants and the condition of environment as there are a lot of other factors that affect human health. However, among all the other factors that determine the status of health of the inhabitants, environmental factor together with genetics, individual characteristics, life style and the health care, stands out as one of the most important ones. The quality of air in cities is considered to have more effects on the health than the other environmental factors

and the pollutants of ambient air represents one of the most important reasons for health problems in general.

A number of epidemic studies clearly show that air pollution in the form of respiratory particles is connected with the increased morbidity and mortality caused by respiratory and cardiovascular diseases. The increased number of certain diseases (cardiovascular diseases and hypertension, respiratory diseases, cancer, infective and parasitic diseases) can be the result of modern way of life as well as the result of the pollution of environment. APHEA project “Air pollution and Health: a European Approach” is one of epidemic studies which researches short-termed effects of air pollution on some health parameters, especially on daily variability of lung functioning, the occurrence of hospital treatment and mortality. In Paris, the risk of mortality of respiratory diseases increased to 17% with 100 $\mu\text{g}/\text{m}^3$ increase of concentration of floating particles. Floating particles, black smoke and SO_2 are the cause for urgent hospitalization of respiratory patients. A study in Spain found that oxides, specially NO_2 and ozone, are closely connected with the death of those suffering from cardiovascular diseases, specially in summer.

Cancerous effect of a number of pollutants has been detected, too. Those are polycyclic aromatic hydrocarbons, first of all : wide spread benzopiren, tetraethyl, asbestos, soot and carbon sediments. Some of them, like lead compounds, come into the body in a different way – via the food taken from polluted soil. SO_2 , CO_2 , NO_2 and soot are “classical pollutants”, the most often controlled pollutants both in the world and our country, which separately or together with other pollutants can cause serious health problems. These pollutants cause greatest damages in respiratory tract (Stojanovic S., Nikic D. 2005). They cause respiratory diseases and lead to the changes in pulmonary defence system and also cause the failure of immune system and cancer (Jammes Y. Delpierre, S. Delvolgo M.J. 1998). Human reaction to polluted air depends on the level of concentration of pollutant, the period the person is exposed to it, the current health condition and meteorological conditions. Some groups of the population, children, women of childbearing age, elder people, chronicle patients, are more sensitive and react even when the concentration of pollutants in the air is low. The air pollution with suspended particles consists of tiny liquid or solid particles. Among them those that can reach the deepest parts of lungs are particularly

Important. These particles have the diameter smaller than 10 μm or we could say that there diameter is less than 1/7 of human hair. About 99% of the particles suspended in the air which we inhale, are eliminated from our bodies at the moment we exhale since most of them stay in upper parts of respiratory tract. The rest of 1% stay in human body, come to trachea and further on to lungs. If they reach the lungs, they slow down the exchange of oxygen and carbon dioxide, thus shortening the breath and causing the heart to work harder to compensate the lower intake of oxygen. It is usually, people who are very sensitive to these conditions that fall ill with the respiratory diseases like, enfizem, bronchitis, asthma and heart problems. Particles like liquid and gas substances which are taken in together with particles on which they are absorbed, if inhaled, and are poisonous, can cause the damage of organs like: kidneys and liver (WHO Regional Office for Europe 2007). Although PM_{10} affects the whole human population, some of the categories (children, child-bearing women, the elder and the sick) are more endangered than the others.

According to the quality of air, which depends on the emission of sulphur dioxide, nitrogen oxide, carbon monoxide, soot, powdered substance and others, Smederevo is in the group of 10 most polluted cities in Serbia. The relation between the degree of quality of environment and the health of people in Smederevo has not been researched in detail.

Using health statistics on prescribed medicine, varieties of diseases and data on the degree of the existing pollution, we have tried to find the cause – effect relationship. A general view of health and the range of diseases can be connected with the influence of certain pollutants existing in the environment. We have analyzed health statistics on prescribed medicine. The city of Smederevo is supplied with medicine by Apotekarska ustanova which contains 14 pharmacies. In 2011 the pharmacies gave out 1 080 491 medicines from prescribed prescriptions. We paid special attention to

the prescription of the medicine used to treat the diseases of respiratory organs: enfizem, bronchitis, asthma, lung cancer and infectious diseases which are all caused by the exceeding level of SO₂ and other air pollutants. Close cooperation with the specialists for treating lung diseases and diseases of respiratory organs, helped us to mark the antibiotics used for the treatment and making stronger lung defensive system, pumps which help the asthmatics and those ill with obstructive bronchitis, medicines used for treating lung cancer, tuberculosis, allergies, medicines against cough and fungal diseases.

We have also marked medicines used against pain with patients suffering from late stadium of cancer. We have found out that in 2011, 48 different kinds of antibiotics were prescribed (68822 boxes), which makes 6.4% of the total number of prescribed medicines. 11 kinds of pumps have been prescribed (17216 units) used mostly by children and chronic patients. The total number of marked medicines used in respiratory organ treatment is 123600, which makes over 10% of all prescribed medicines.

Table 3: Development of malignancies in Smederevo and its villages in the period of 1997-2001

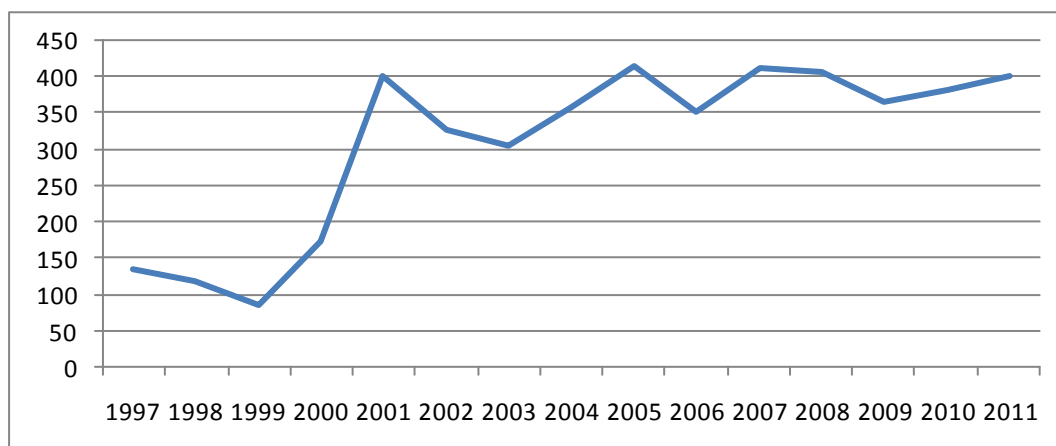
place	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Smederevo	89	77	49	111	221	205	186	151	271	248	260	260	235	250	278
Mihajlovac	5	2	4	11	16	8	14	4	11	7	5	10	12	12	4
Skobalj	2	2	1	2	10	2	6	5	5	7	1	9	12	6	5
Vrbovac	-	-	1	-	6	-	3	3	2	2	5	5	1	5	1
Lipe	4	6	4	4	20	11	8	5	9	6	5	8	6	13	4
Osipaonica	2	-	3	5	17	10	14	8	9	5	13	10	10	4	13
Landol	-	1	-	-	2	2	2	2	2	3	3	3	3	4	1
Vodanj	2	1	1	2	9	4	6	3	4	1	9	3	4	4	5
Radinac	8	7	2	5	16	11	9	14	23	15	23	15	10	12	13
Ralja	-	-	2	1	2	2	1	2	4	4	6	4	6	3	4
Vranovo	2	1	2	5	12	7	9	6	4	5	9	6	10	7	8
Dobri Do	1	3	1	1	4	4	-	1	3	1	5	6	3	3	6
Lugavčina	2	2	-	4	6	10	8	9	11	6	8	13	7	6	10
Seone	2	1	1	1	3	2	4	3	0	2	4	5	2	4	2
Vučak	1	-	1	3	4	5	2	2	7	3	5	5	1	2	6
Drugovac	1	1	1	4	8	6	5	6	9	8	11	6	5	5	6
Udovice	3	1	1	2	6	4	4	3	3	4	2	7	3	4	8
M. Krsna	3	1	2	2	6	6	2	10	10	4	6	6	8	6	8
Binovac	1	-	1	-	6	1	2	2	4	0	-	1	3	2	2
Šalinac	-	1	2	-	3	4	1	1	1	1	5	2	1	2	3
Suvodol	2	-	2	-	1	5	3	-	5	3	-	6	4	3	-
Saraorci	1	3	1	1	7	5	6	3	6	6	10	3	7	6	4
Petrijevo	-	1	-	1	1	3	-	3	4	0	3	2	3	5	-
M. Orašje	-	1	-	2	3	1	-	1	3	0	4	1	1	3	2
Kolari	-	2	-	2	8	4	5	6	3	3	7	6	3	8	5
Lunjevica	-		1	2	1	1	2	3	2	3	2	3	2		
Badljeva	1	1	-	-	2	-	-	1	0	3			1	2	1
Kulič	-	-	-	1	1	4	3	-	0	0	1	1	1	2	1
Sum	132	115	83	172	401	327	305	357	415	350	412	406	364	383	400

The report of Health Center „Sveti Luka“, hospital in Smederevo

From the table in page 8 we can conclude that the number of malignancies increases. This increase has been substantial since 2001 until 2011. The number of the sick has increased almost 3 times. This condition can not be explained only by the polluted environment, but some facts can be connected with the problems of the environment. "Sartid", that is now Zelezara Smederevo, was privatized in 2003, by the American company US Steel. The production had a record increase to historical 2.2 million tons per year and it was for the first time that both blast furnaces were in operation at the same time. Until then only one furnace had been in operation and the other had been rebuilt. A production of

this scope naturally led to extreme emission of harmful substances and contributed to the negative change of the environment and certainly influenced the health of the inhabitants of Smederevo. It is clear from all the data that parameters which endanger the environment occurred over LV in this period. Radinac, the settlement next to Zelezara had in this period the biggest number of the sick (183), which was confirmed by our mathematical pattern about maximum concentration of SO₂.

In settlements situated on Sumadija hills over 100 meters elevation and where the circulation of atmosphere is much bigger, the number of sick inhabitants (dark rows) is considerably smaller. We have stated that the air pollution is closely connected with respiratory organs diseases and malignancies. Thus, we can find a connection between the pollution and the large number of people ill with respiratory organ tumors and thoracic tumors (1074) which represent 25.8% of total number of those ill with malignancies. The number of sick men (878) is much bigger than that of sick women (196) and this can be explained by the working conditions in the very Zelezara. In direct production, where pollution is the biggest, mostly men work while women work in administration. If we add to this the number of those suffering from lip, mouth or pharynx cancer (135), then melanoma and skin tumor (576), this percentage is 43%, which makes half of all the sick and is closely connected with air pollution. Cancerous effect of benzopiren, soot and carbon sediments, and lead compounds contribute to a great extent to the appearance of other malignancies, like endocrine glands tumors, lymphatic and blood tissue of the skin.



Picture 2. Development of malignancies in Smederevo in the period from 1997-2011

The following table could also show the cause – effect relation between the quality of environment and the increase of malignancies. The consequences of lead pollution are: organ damages (kidneys, liver, brain, etc), brain damage and the damage of nervous system (bouts, mental retardation, behaviour disorder, problems with memory, etc.), heart and cardiovascular problems (high pressure. Heart failure etc.).

Chronic mass non infectious diseases (heart diseases and diseases of the blood vesseles, malignancies, obstructive lung diseases, injuries, mental health disorders etc.) have dominated Serbian national pathology. (Aleksic I, 2006.)

Table 4: Malignancies according to locality and sex in the Smederevo's municipality

Malignancies	years	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	
Lips mouth pharynx	00-14	m	3	22	10	9	3	6	10	13	8	4	11	8
		f	2	3	4		3	0	2	4	3	2	5	1
Digestive organs	15-29	m	14	46	39	44	24	39	38	33	42	28	28	19
		f	10	33	36	25	20	25	12	26	19	22	22	23
Respiratory organs thoracic	30-39	m	13	106	76	73	59	82	82	89	71	63	75	89
		f		25	23	11	16	14	13	14	22	14	22	22
Bones and joint cartilage	40-42	m			3				1		1			2
		f		1	1					1	1	1		
Melanoma and skin tumors	43-44	m	20	20	19	27	30	22	21	22	31	22	27	34
		f	11	18	20	10	15	26	32	33	28	25	32	31
Tumors of connective and soft tissue	45-49	m	1	3		2		1	2			2		1
		f	1	3				2	3	2		2		
Breast cancer	50	m	1	1			1		1					
		f	49	55	33	52	38	67	46	42	41	52	37	58
Genitalia tumors	51-63	m	4	3	3	6	6	22	13	39	62	42	43	43
		f	22	43	28	15	22	45	32	49	27	43	35	32
Urinary system tumors	64-68	m	6	5	7	6	1	25	13	14	20	13	17	17
		f	1	1	2	2	3	8	2	7	4	7	6	5
Eye, brain and other tumors	69-72	m	4	2	2	5	1	4	3	4	2	3	3	2
		f		1	2	4	3	2	4	1	2	2	1	1
Endocrine glands tumor	73-80	m		3	4	2	3	7	11	8	2	4	2	4
		f		1	7	3	3	4	4	4	4	4	12	4
Lymphatic, blood and related tissue tumor	81-96	m	6	3	8	5	5	4	3	2	7	4	4	
		f	4	4		4	1	10	2	5	9	5	1	
Total		m	72	213	171	179	133	212	198	224	246	185	210	223
		f	100	188	156	126	124	203	152	188	160	179	173	177
Sum	m+f	172	401	327	305	257	415	350	412	406	364	383	400	

Health center report „Sveti Luka“ OU hospital in Smederevo

CONCLUSION

Having analysed the value of substances that define the quality of the environment we can conclude that Smederevo is a settlement with extremely polluted environment. This especially refers to the polluted air, where the quantity of certain harmful substances exceeds the limit values a few times. It is obvious that there is a real treat to the health of the people. If no measures are taken, we cannot expect any improvement and betterment of the environmental quality. The basic thing that could

contribute to the decrease of air pollution is eliminating harmful substances from the air and the making of cadastre of air pollutants in the city of Smederevo. This way, at every moment there is a clear insight in the quality of air on the whole territory. This, first of all refers to "Zelezara Smederevo" which is the main source of air pollution. The cadastre could be used for producing meteorological and diffuse model of the pollutants for the whole city territory, the usage of which could define procedure in cases of accidents and over limited pollutions. The protection of air from harmful substances can also occur through surveillance over facilities and devices which can pollute the air, and it covers the emission limit to allowed ranges stated by

Regulations on limit values, the way and measure deadlines and recorded data, overtaking technological and other necessary measures for the decrease of the emission as well as the monitoring of the effect that polluted air has on people and the environment. To improve the quality of the environment extra measures, such as the gasification project and the heating system in the city, must be taken.

The existing boilers that use liquid and solid fuels should in the coming period be converted into boilers that use gas. Diversion of transit and freight traffic ought to be redirected to the bypass, thus decreasing the air pollution in the city center. This is the reason for a study on traffic in the city and its surrounding area. Rebuilding, maintenance of the existing and setting up new areas of trees and protective low and medium greenery, with long vegetation near bigger pollutants.

The city of Smederevo in its further development must rely on its ecological component and a general principal of sustainable development, because only that way will it approach European standards, and only that way will it have the possibility of access to European funds and loans for development.

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**WELDING FUME AND GAS EXPOSURE IN THE WELDING
ENVIRONMENT**

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ABSTRACT

Welding produces various contaminants at a sufficient rate to cause both short and long-term health effects if not properly controlled. Epidemiological studies of welders indicate that a large number of welders experience some type of respiratory illness. World health organizations recognize the importance of preventing health risks associated with fumes and smoke generated during welding. In many countries strict standards have been established to limit the permissible exposure limit. In this paper are presented several literature surveys to investigate the nature various fumes and gases generated in welding. Besides the above, listed and other potential hazards associated with this process.

Key words: *Welding, Gases, Ozone.*

INTRODUCTION

Welding is the method of joining two metal parts together by applying intense heat between them, which causes the parts to melt and intermix. This process can be done directly between the two parts or through the use of an intermediate molten filler metal. The filler, base metal and base metal coating used during welding operations and the subsequent gases that are formed during the welding process release small, solid particles into the air creating a plume. This plume is called "welding fume". Welding fume contains elements that, in their pure forms, can be hazardous to worker health if inhaled or ingested. Therefore, the chemical composition of welding fume must be examined when considering fume toxicity. Many different energy sources can be used for welding including gas flames, electric arcs, electric resistance, lasers, electron beams, friction, molten metal baths and ultrasound. Welding includes joining methods as diverse as fusion welding, forge welding, friction welding, braze welding, brazing, soldering and explosion welding (Welding Processes, 2012). The environment surrounding many welding processes contains *fumes* that may be harmful (toxic) or relatively harmless and *gases* that may have pulmonary or non-pulmonary effects. The health risks and effects associated with welding gases and fumes are determined by (CH032, 2009):

- the length of time that welders are exposed to them
- the type of welding
- the work environment
- the protection.

Welding is one of the most important trades, employing 700,000 and 400,000 in the U.S. (NIOSH, 1998) and Japan, respectively. Welding is a high-risk occupation. Welders are exposed to hazardous fumes and gases during welding operation and tends to suffer from occupational respiratory diseases such as welding pneumoconiosis and asthma (Antonini et al., 1998; Jenkins, 2003; Jenkins and Eager, 2005). All welding processes produce hazardous gases. Gases are invisible to the eye, and may or may not have an odour. The heat in both the flame and the arc, and the ultraviolet radiation from the arc, produce gases such as carbon monoxide, carbon dioxide, oxides of nitrogen and ozone. Other gases and vapours may be produced as by-products from the breakdown of solvents or coatings on the metal. Gases used for arc shielding, or as a fuel, are also given off during welding.

THEORY

Fume constituents and their associated health effects

Fumes are particles formed by electrode (and base metal) constituents that are vaporized and subsequently condensed in the welding area. Because of their small size, fume particles may remain suspended in the aerosol form for long periods. Since the particles have mass and size and are affected by air movement, electrical fields, gravity, diffusional forces, and other external forces, they tend to agglomerate into clumps that gradually settle on the floor and other surfaces (Speight and Campbell, 2008). While suspended, however, they are inhaled by all persons in the vicinity. Table 1 includes the most common welding fume constituents and their associated health effects (ACGIH, 2004; Antonini, 2003). Metal fume fever occurs in welders who inhale zinc oxide fumes, although other components, for example, copper, aluminium and magnesium, may also produce this condition. Symptoms of metal fume fever, which resemble influenza, usually occur several hours after exposure and include a metallic or sweet taste, chills, thirst, fever, muscle aches, chest soreness, fatigue, gastro-intestinal pain, headache, nausea and vomiting (National Occupational Health and Safety Commission, 1990). The symptoms usually subside within one to three days of exposure with no residual effect. Due to the presence of chromium, nickel and aluminium, there is concern about the effects of chronic exposure on special groups such as welders of stainless steel and aluminium. At this stage, there is insufficient information to be conclusive about the effects of welding these metals.

In addition to fume particles, there are also gases formed that have toxic effects. These include:

- ozone,
- oxides of nitrogen, and
- carbon monoxide.

Carbon monoxide (CO) is an odorless, colorless gas that may be formed by the incomplete combustion of the electrode covering or flux and by the use of carbon dioxide (CO₂) as a shielding gas. It will also be produced in gas welding when combustion of acetylene is incomplete, as with a reducing flame. Carbon monoxide levels may build up in confined spaces and poorly ventilated spaces. Overexposure to CO inhibits the body's red blood cells to sufficiently carry oxygen to other tissues within the body, which subsequently results in asphyxiation (Spear, 2004). High levels of CO may potentially accumulate when welding or air arc gouging in confined spaces. There is also a potential of an oxygen deficient atmosphere if welding inside of a confined or enclosed space if an inert gas (such as argon) is used as the shielding gas.

Ozone, nitrogen dioxide and nitric oxide are produced by the interaction of ultraviolet light (from the welding arc) with the surrounding air. These compounds are irritating to the eyes, nose and throat. High exposures can also cause fluid in the lungs and other long-term pulmonary illnesses. Exposure to ozone produce excessive mucus secretion, headache, lethargy, eye irritation and irritation and inflammation of the respiratory tract. In extreme cases, excess fluid and even haemorrhage may occur in the lungs. The irritant effects of the gas on the upper respiratory tract and the lungs may be delayed. Inhalation of nitrogen oxides does not always produce immediate irritant effects but may result in excessive fluid in the lung tissues (pulmonary oedema) some hours after exposure ceases.

If the metal has been degreased with a chlorinated solvent, other airborne gases (such as phosgene, hydrogen chloride, chlorine gas, etc.) may be produced (Tabele 2). These gases generally cause irritation to the eyes, nose and respiratory system and symptoms may be delayed. The toxic gas phosgene, also known as carbonyl chloride, is not a normal component of welding gases, but is formed by the oxidation of chlorinated hydrocarbons (for example, trichloroethylene, trichloroethane and perchloroethylene), such as when welding is carried out in the presence of solvent vapours escaping from a nearby degreasing tank or when solvent is left behind after degreasing. Exposure to phosgene produces, after a latent period of several hours, irritation of the respiratory tract or perhaps serious lung damage. Phosgene formation is promoted by ultraviolet radiation, hot metal surfaces, flame and cigarette smoking .

Table 1: Common Constituents in Welding Fumes

Metal Constituent	Common Source(s)	Health Effect(s)
Aluminum	Component of some alloys (such as Inconel, copper, zinc, steel, magnesium, brass, and filler materials).	Lung damage, irritation
Beryllium	Hardening agent found in copper, magnesium, and aluminum alloys.	Cancer (lung), berylliosis
Cadmium	May be contained in plated materials and/or zinc alloys and sometimes used in the manufacture of fluxes in flux-cored electrodes.	Kidney damage
Chromium	Contained in most stainless steel and high-alloy materials. Also used as plating material.	Irritation, dermatitis, liver, kidney, respiratory, cancer (hexavalent chromium insoluble compounds)
Copper	Included in alloys such as Monel, brass, bronze.	Irritation, damage to the gastrointestinal tract, metal fume fever
Fluorides	Common ingredient in electrode coatings and flux material for both low- and high-alloy steels.	Irritation, bone damage, fluorosis
Iron	The major contaminant in all steel welding processes.	Siderosis (i.e., pigmentation of the lungs)
Lead	Common in solder, brass and bronze alloys. May also be contained in the primer/coating on steels.	Central nervous system, blood, kidney, reproductive
Magnesium	Found in light metal alloys.	Irritation, metal fume fever
Manganese	Contained in most welding processes.	Central nervous system, lung damage, reproductive
Molybdenum	Contained in some steel alloys, stainless steel, and nickel alloys.	Irritation, lung damage, central nervous system
Nickel	Contained in stainless steel, Inconel, Monel, Hastelloy and other high-alloy materials, welding rods, and plated steel.	Dermatitis, pneumoconiosis, central nervous system, cancer, lung damage
Silicon	Present in most welding consumables.	Irritation, fever
Tin	Used in some solder alloys and bronzes.	Stannosis (i.e., benign lung disease), central nervous system, irritation, immunotoxicity
Titanium	Common ingredient in many flux-cored electrodes and in the coating of covered electrodes.	Lung damage
Vanadium	May be contained in some steel alloys, stainless steel, and nickel alloys.	Irritation, lung damage
Zinc	Common component of galvanized and coated metal.	Metal fume fever

Phosphine is generated when steel coated with a rust proofing compound is welded. High concentrations of phosphine gas are irritating to the eyes, nose and skin. There may also be serious effects on the lungs and other organs.

Table 2: Health Effects of Gases and Organic Vapours Produced During Welding

Gases	Source(s)	Health Effect(s)
Carbon Monoxide	Formed in the arc.	Absorbed readily into the bloodstream, causing headaches, dizziness or muscular weakness. High concentrations may result in unconsciousness and death.
Hydrogen Fluoride	Decomposition of rod coatings.	Irritating to the eyes and respiratory tract. Overexposure can cause lung, kidney, bone and liver damage. Chronic exposure can result in chronic irritation of the nose, throat and bronchi.
Nitrogen Oxide	Formed in the arc.	Eye, nose and throat irritation in low concentrations. Abnormal fluid in the lung and other serious effects at higher concentrations. Chronic effects include lung problems such as emphysema.
Oxygen Deficiency	Welding in confined spaces, and air displacement by shielding gas.	Dizziness, mental confusion, asphyxiation and death.
Ozone	Formed in the welding arc, especially during plasma-arc, MIG and TIG processes.	Acute effects include fluid in the lungs and hemorrhaging. Very low concentrations (e.g., one part per million) cause headaches and dryness of the eyes. Chronic effects include significant changes in lung function.
ORGANIC VAPOURS		
	Source(s)	Health Effect(s)
Aldehydes (such as formaldehyde)	Metal coating with binders and pigments. Degreasing solvents.	Irritant to eyes and respiratory tract.
Di-isocyanates	Metal with polyurethane paint.	Eye, nose and throat irritation. High possibility of sensitization, producing asthmatic or other allergic symptoms, even at very low exposures.
Phosgene	Metal with residual degreasing solvents. (Phosgene is formed by reaction of the solvent and welding radiation.)	Severe irritant to eyes, nose and respiratory system. Symptoms may be delayed.
Phosphine	Metal coated with rust inhibitors. (Phosphine is formed by reaction of the rust inhibitor with welding radiation.)	Irritant to eyes and respiratory system, can damage kidneys and other organs.

Welding processes and materials

There are about 20 major types of welding processes used on 10 major classes of materials, and hence an extremely wide range of work environments is possible. Figure 1 shows the various welding and allied processes used.

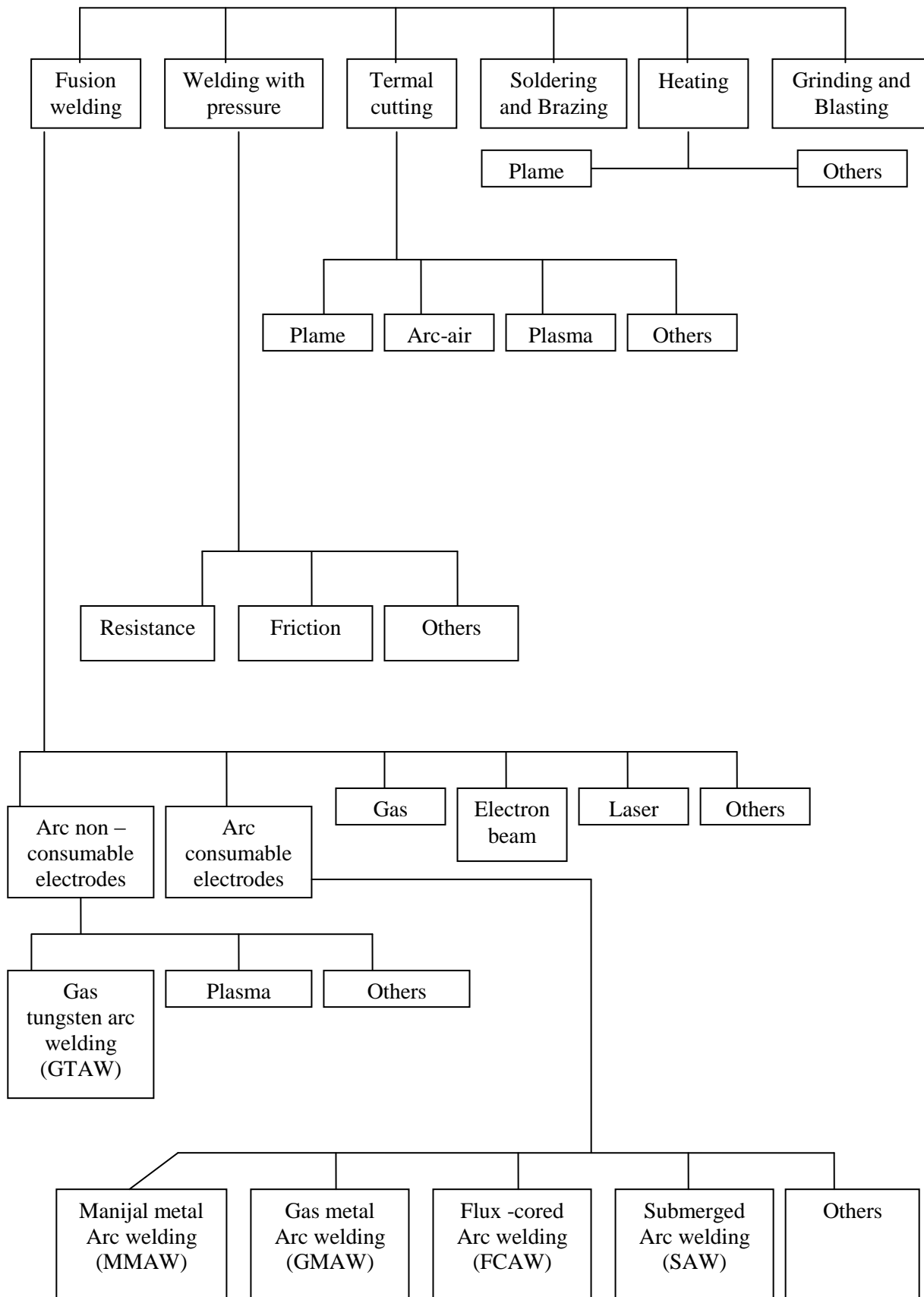


Figure 1. Welding and allied processes

The two most common types of welding used are:

- the electric arc welding of metal using a flux-coated electrode (manual metal arc welding, MMAW); and
- the electric arc welding of metal using a gas-shielded wire electrode (gas metal arc welding, GMAW).

The following five combinations account for 60 to 70 per cent of all welding activity: MMAW/mild steel, MMAW/stainless steel; GMAW/mild steel; GMAW/stainless steel; and GMAW/aluminium.

Materials used in welding

During the welding process is widely used for the following types of materials:

- Core and filler metals are usually made of alloy similar in chemical composition to the materials being welded. The most commonly used material is mild steel. Special steels may contain: chromium, nickel, molybdenum, aluminium, cobalt, vanadium or tungsten.
- Electrode coatings (a complex mixture of materials, ferro-manganese, ferro-vanadium and ferro-silicon, fluoride).
- Coatings on materials to be welded (metal coated with zinc, lead or tin, electroplated with cadmium, copper, chromium or nickel, primed, painted with coatings containing lead pigments, zinc chromate, zinc dust or copper and coated with resins, such as epoxy, phenol formaldehyde, vinyl, polyurethane, bitumen, oil modified alkyd and sodium/potassium silicate).
- Cleaning of welding materials.

FINDINGS AND DISCUSSION

Fume Generation Rates at common Welding Processes

The type of welding process is directly related to the amount of fumes and gases that are generated. Therefore, it is important to have a basic understanding of the welding process in order to assess the risk of exposure.

Shielded Metal Arc Welding (SMAW) is commonly used for carbon steel welding and low alloy welding. SMAW can produce high levels of metal fume and fluoride exposure, but it is considered to have little potential for generating ozone, nitric oxide and nitrogen dioxide.

Gas Metal Arc Welding (GMAW) or metal inert gas (MIG) welding is typically used for most types of metal. This process produces fewer fumes since the electrode has no fluxing agents. However, due to the intense current levels, GMAW produces significant levels of ozone and nitrogen oxides.

Flux Core Arc Welding (FCAW) is used for carbon steels, low alloy steels and stainless steels. This welding process generates a substantial amount of fume. However, FCAW generates little ozone, nitric oxide and nitrogen dioxide.

Gas Tungsten Arc Welding (GTAW) is also known as tungsten inert gas (TIG) welding. High electrical currents are used, which causes this process to produce significant levels of ozone, nitric oxide and nitrogen dioxide.

Submerged Arc Welding (SAW) is another common welding process used to weld thick plates of carbon steel and low alloy steels. The flux material keeps the fumes down and since the arc is not visible, there is little ozone, nitric oxide and nitrogen dioxide that is generated. The major airborne hazard with SAW is the fluoride compounds generated from the flux material.

In addition to the welding technique, studies have shown (Spear, 2004) that the fume generation rate is also influenced by the following factors: electrical current, arc voltage, electrode diameter and angle, shielding gas, speed of welding, steady/current pulsed current welding and tc.

Since most of the fumes are attributed to the welding consumables, there has been a drive to develop a number of “low-fume” consumables. The focus appears to be in the reformulation of the flux-cored wire to low-carbon strip materials for the tube and less mineral compounds for the core (Lyttle, 2004).

Identifying the hazards at welding

The first step in managing risks associated with welding processes is to identify all the hazards that have the potential to cause harm. Risks will depend on various factors, including the (Welding Processes, 2012):

- properties of the materials being welded
- surface coating of the items being welded (for example whether they contain lead or other toxic materials)
- condition of the welding equipment
- conditions under which welding is carried out (for example, confined spaces)
- skills, competence and experience of the welder.

Different welding processes also influence the risk. For example, the risk of electric shock is lower using gas metal arc welding (GMAW) than manual metal arc welding because the open circuit voltages are lower, only direct current is used and the power is switched at the hand piece. The amounts and types of fumes produced vary greatly depending on the process involved and the materials being used such as metals, solvents, flux, paint and plastics. The health effects of exposure to fumes, dust, vapour and gases can vary. Effects can include irritation of the upper respiratory tract (nose and throat), tightness in the chest, asphyxiation, asthma, wheezing, metal fume fever, lung damage, bronchitis, cancer, pneumonia or emphysema. Some welding fumes are easy to see, however, many gaseous fumes and vapours are invisible. Generally, fewer fumes are generated from gas welding than from electric welding processes. Also, intense ultraviolet radiation emitted by arcs may travel significant distances from arcs, especially in reflective environments and may give rise to significant quantities of ozone. To determine the risk of exposure to fumes during welding you should identify what equipment and materials are being used and the level of fumes, dust, vapour and gases generated. Exposure standards represent airborne concentrations of a particular substance or mixture that must not be exceeded. There are three types of exposure standard:

- 8-hour time-weighted average
- peak limitation
- short term exposure limit.

Gas welding emits visible light and infra-red radiation. The potential effect of radiation on the body depends on the type, intensity, the distance worker are from it and the duration of exposure (“Arc eye“ eye disorder, skin burns). Using electrical welding equipment involves a risk of electric shock or electrocution. Exposure to electromagnetic fields is also a potential hazard for workers with some medical conditions. Electric shock may result in serious burns or death by electrocution. The risk of electric shock can be exacerbated by moisture and high humidity. Welding generates heat, flames and sparks—all of which are sources of ignition. When combined with sources of fuel and oxygen, sources of ignition present a significant risk of fire and explosion. Common sources of fuel that can be found in workplaces include flammable and combustible materials such as, flammable gases, (for example, acetylene, hydrogen, methane-natural gas), liquefied petroleum gas (for example, barbeque gas), flammable liquids (for example, mineral turpentine, petrol), combustible liquids (for example, oils) and materials such as wood, leaves, cardboard boxes and flammable metal or self-burning dusts. The risk of fire and explosion could be increased by exposure to an oxygen rich atmosphere.

Burns are one of the most common injuries in welding. The temperature of a welding arc can reach 6000⁰Celsius. Burns occur frequently on hands and other exposed skin, but also in eyes from sparks and metal fragments. The symptoms of exposure to this level of heat are similar to extreme sunburn. Welding can often produce heat at a level that creates an uncomfortable and hazardous working environment. Exposure to extreme heat is particularly hazardous when working outdoors in

direct sunlight, on hot days and in confined spaces. Working in a hot environment can cause heat rash, heat stress, heat stroke and result in permanent injury or death.

Compressed and liquefied gases are used as fuel, a source of oxygen or as shielding gases in certain types of welding. Cylinders contain large volumes of gas under high pressure and precautions need to be taken when storing, handling and using cylinders. The hazards associated with compressed and liquefied gases include fire, explosion, toxicity, asphyxiation, oxidation and uncontrolled release of pressure. Exposure to high noise levels can cause permanent hearing loss. Equipment for performing welding can generate varying levels and frequencies of noise that may cause workers to be exposed to noise that exceeds the exposure standard. Lead can become an airborne contaminant when soldering and welding materials. A welder may be exposed to lead when welding on steel painted with leaded paints, on leaded steel, flame cutting of batteries and materials contaminated with lead (for example, old automotive mufflers). The major risk associated with lead is lead poisoning (plumbism). This affects the blood system and can cause anemia. Other symptoms include abdominal pain, convulsions, hallucinations, coma, weakness, tremors and the possible increased risk of cancer. Lead exposure can also affect both male and female reproductive systems.

CONCLUSION

Approximately one million workers worldwide perform welding as part of their work duties. Pulmonary effects observed in full-time welders have included metal fume fever, airway irritation, lung function changes, susceptibility to pulmonary infection, and a possible increase in the incidence of lung cancer. The potential hazards of welding operations include metal fumes, toxic gases, and ultraviolet and infrared radiation. Fume particles are formed from vaporization of molten metal. They are very fine in size, generally one micron or smaller, and may join together to form larger particles. The mechanisms responsible for the fume formation are complex. Fumes can be sampled by drawing air through a special filter at a controlled rate. The adverse health effects of overexposure to welding fumes and gases include chronic or acute systemic poisoning, metal fume fever (a short-term painful ailment with symptoms of fever and chills), pneumoconiosis (lung disease due to accumulation of mineral or metallic particles), and irritation of the respiratory tract.

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INFECTIOUS MEDICAL WASTE TREATMENT

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ABSTRACT

An exposure to medical waste can pose a significant health threat to people who work in healthcare, general population, as well as to the ecosystem in which such waste is disposed. The primary goal of this paper is to show the means and the results of the management of this type of waste, with emphasis on the management of dangerous infectious medical waste. The results of steam sterilization in an autoclave, at the temperature of 121°C, with the usage of saturated steam, and within a defined time limit are in accordance with the EU Directive STAATT IV when it comes to waste pathogens destruction. After the management, the treated waste is safe and can be discarded on the town's depo.

Key words: *infectious medical waste, medical waste management, infectious waste treatment.*

INTRODUCTION

All waste generated in the health care of people and animals are considered under medical waste. In relation to the composition, properties and their origin, it can be classified into seven major categories: waste, infectious and potentially infectious waste, used sharp medical instruments, pathoanatomical waste, chemical waste, pharmaceutical waste, including cytostatics, canisters, and bottles under pressure.[9]

In the overall pollution of the environment, medical waste does not take a great deal, but it is potentially the most dangerous types of waste, because it can lead to infection and poisoning.

Infectious medical waste contains a sufficient number of virulent, pathogenic organisms so that after contact with it, an infectious disease can occur. Those are the following wastes: a kit for planting and cultivation, blood, blood derivatives and blood products, needles, syringes, pipettes, test tubes and glassware, waste from surgery and the autopsy room, the infectious waste from the quarantine department, human tissues, organs and excreta which contain pathogenic microorganisms, waste generated in hemodialysis or blood transfusion, waste from vaccines and serums and unrecognizable tissue at 3 to 4 mm [4].

In the past, most medical waste was treated by incineration in an inadequate furnace in the hospital. There is evidence in the General Hospital in Šabac, that in the period from 1.1.2007. to 31.12.2007. the total burned waste was 21.478kg. Taking into account that infectious and pathoanatomical waste was burned, the amount of 21.478kg, or 35.44 kg per hospital bed in a year indicates that it is only small amounts of waste, and that is one part of the infectious and pathoanatomical waste ended in the landfill as a communal waste.[6]

Since this type of treatment led to emissions: individually and flue gases and ash, as well as wastewater treatment plant flue gases, the development of alternative systems for medical waste treatment started in the late 1970s in Europe. Systems for the treatment of medical waste can be divided into: systems based on steam, systems on dry heat systems based on chemicals, and radiation based systems.

Alternative treatment of infectious waste steam is based on the process of thermal sterilization. Waste sterilization cycle takes about 90 minutes. The treatment is carried out at elevated pressure (~ 3.2 bars) and temperature (121-134°C) in an atmosphere that is nearly 100% saturated with water vapor, because:

- microorganisms are sensitive to high temperatures in a humid atmosphere,
- saturated steam under high pressure and at elevated temperature acts as a mild acid and destroys organic substances such as microorganisms and
- during condensation, energy enthalpy is released directly to the inner and outer surface of the waste - the location of the microorganisms.[3]

For the quality of the sterilization process on the basis of water vapor, the most important parameters are the complete removal and replacement of air with water vapor in order to avoid "the problem of the cold island" - pockets of air in the treatment chamber where the air is replaced by water vapor (checking with Bowie and Dick test), the quality of the applied saturated steam during treatment and temperature (which is measured after the waste reaches the temperature at which the process is done – testing with thermometric test). [1]

The efficiency of the system depends on the waste packaging procedures, as well as the materials from which autoclave chamber is made. Materials that come in contact with the steam should be resistant to the effects of steam and condensate; they should not have any negative impact on the quality of the steam nor any discharge which are known to be poisonous in quantities that could endanger the health or the environment. In addition, one should take into account the corrosive impact of the waste to be sterilized in the sterilizing chamber, the presence of substances which promote corrosion in steam for sterilization and cooling means, the ability to create layers that are resistant to corrosion as well as to all aspects of environmental protection. The exhaust gases generated by applying negative pressure must be sterilized, and all odors must be removed. The noise produced by the autoclave must be reduced to the legal basis and the maximum 80dB, which, as previously, must be controlled precisely by the prescribed instructions for the operation of the device for sterilizing waste.

INFECTIOUS MEDICAL WASTE MANAGEMENT

According to estimates by the World Health Organization, an average of 1.8 kg of medical waste per hospital bed per day is created in Serbian hospitals, of which about 0.5 kg makes infectious medical waste. This quantity is proportional to the quantity and average applicable to the countries of Eastern Europe. All health institutions in Serbia annually generate about 48000t of waste. Approximately 9600t of waste may be considered as hazardous waste. [6,9]

Poor management of medical waste poses a risk to humans and the environment because of the health risks of exposure to infectious waste. [7] Medical waste management operations include:

- 1) separation of hazardous and municipal waste,
- 2) collection,
- 3) disinfection,
- 4) central collection,
- 5) transportation,
- 6) recycling,
- 7) incineration and
- 8) final deposition which is clearly defined in Medical Waste Management Plan and accompanied by appropriate documentation.

General Hospital, Šabac was appointed in 2008 as the central place for the treatment of infectious waste (CMT) by the Ministry of Health of Serbia. It has the task of organizing, collecting and treating infectious waste arising from medical clinics in the region: the Institute of Public Health Šabac, Šabac health centers, Bogatić, Vladimirci, and Koceljeva., infectious medical waste is delivered to the place of treatment by ADR regulations, properly labeled, and the waybill marked, and in a properly marked means of transport: number - UN 3291, the title - "(BIO) MEDICAL WASTE N.O.S" category - 6.2,

packing Group II, in the amount of <333 kg and usually 2 containers. Containers have a bar code, so that the amount of waste through the information system is available to control all aspects of waste management at the local and national level. The code for infectious or potentially infectious medical waste according to the Waste Catalogue Republic of Serbia is 18 01 03 *. [2]

Main stages of the treatment of infectious medical waste are: sterilizing and crushing. Sterilization prior to the collection and measurement of infectious waste, and after crushing disposal of treated waste follows. The goal of treatment of infectious medical waste with steam autoclaves is in the inactivation of potential microbial agents with which hazardous infectious waste is turned into non-hazardous waste. Figure 1 gives a partial view of the phases of treatment, and in Figure 2 general account of waste management during central treatment of infectious waste.



Figure 1. Phases of treatment of infectious medical waste: measurement, sterilization, crushing, dumping [5]

RESULTS OF INFECTIOUS WASTE TREATMENT

Justification for the treatment of infectious waste is monitored by way of the technical kind, concerning the work of the autoclave, the total volume of treated infectious waste, hospital occupancy capacities, consumption of energy and materials necessary for the operation of the plant, through the training of staff and informing the public about the need for decreasing amounts of infectious waste and dealing with the same...

According to the German experience (Tech Log-Dortmund) medical waste has the following structure:

- a) Similar to municipal waste: 86.8%,
- b) Potentially infectious: 7.3%,
- c) Radioactive waste: 1.4%,
- d) Other hazardous wastes (chemical): 1.2% and
- e) Usable waste (paper): 3.3%.

with the standards of European Union for this type of waste. Data on waste generation and waste-related parameters for the availability of hospital facilities are provided in Table 1.

Table 1: Parameters of hospital capacity and occupancy data on waste generation

CMT "General Hospital Šabac"	2010	2011
The amount of waste, kg	48.501	46.352
Average occupancy, %	46,6	48,18
Number of beds	297	331
The amount of infectious waste per occupied hospital bed-daily, kg	0,45	0,38

In Table 2 and in Figure 3 an overview of the results achieved during 2009 is provided, when the total processing infectious waste was the highest.

Table 2: Review of infectious waste production and consumption aids [5]

General Hospital Šabac	Treated infectious waste (kg)	Number of spent cans for sharp objects 3l (pcs)	Number of spent cans of sharp objects 1l (pcs)	Number of used yellow bags (pcs)
Planned	54 000	2 700	800	20 000
Realized	53 978	2 422	230	15 820

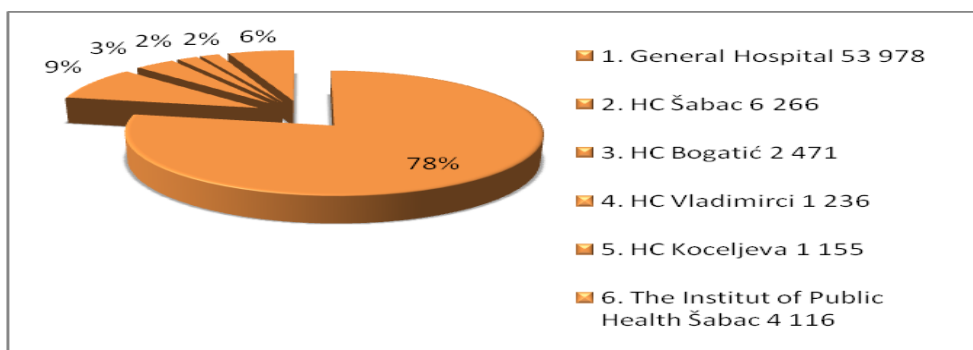


Figure 3. Graphical display of the treated waste share in Šabac CMT [5]

Compared to 2009, taking into account the year 2008 as well, in which the infectious waste treatment started only since July, the continuation of good practice in the management of medical waste can be noticed (Figure 4).

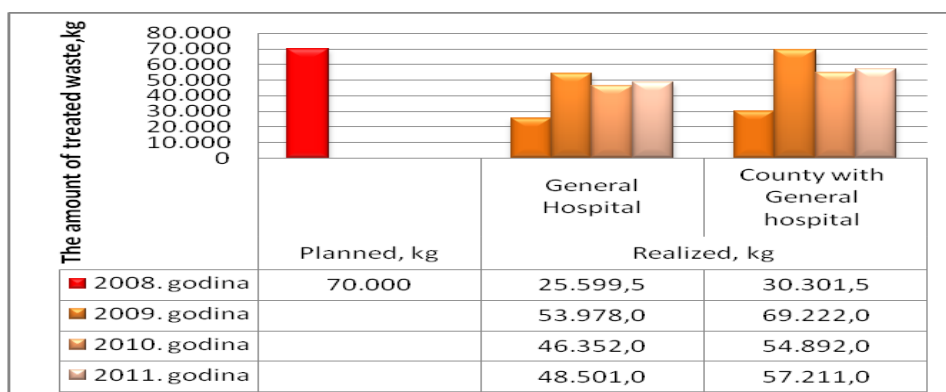


Figure 4. Results of infectious waste treatment in the period 2008-2011.

Figure 5 presents the average monthly cost of CMT's where you can see the materials necessary for the smooth operation of the plant (normative shown in Table 2, in 2009), account for 25% and energy by 12%.

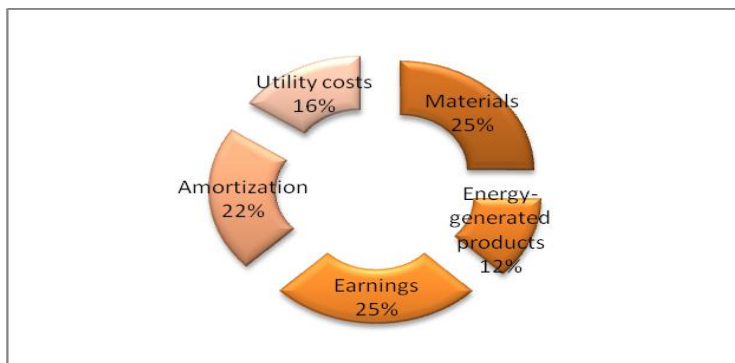


Figure 5. Structure of average monthly costs CMT

An important parameter for justification of treatment of infectious medical waste are the direct capital costs which structure is shown in Figure 6, which shows that they are 90%, and the staff training for the safe operation of the facility and good practices of waste management in the departments of the hospital, where waste and transport is generated, it remains 10%.

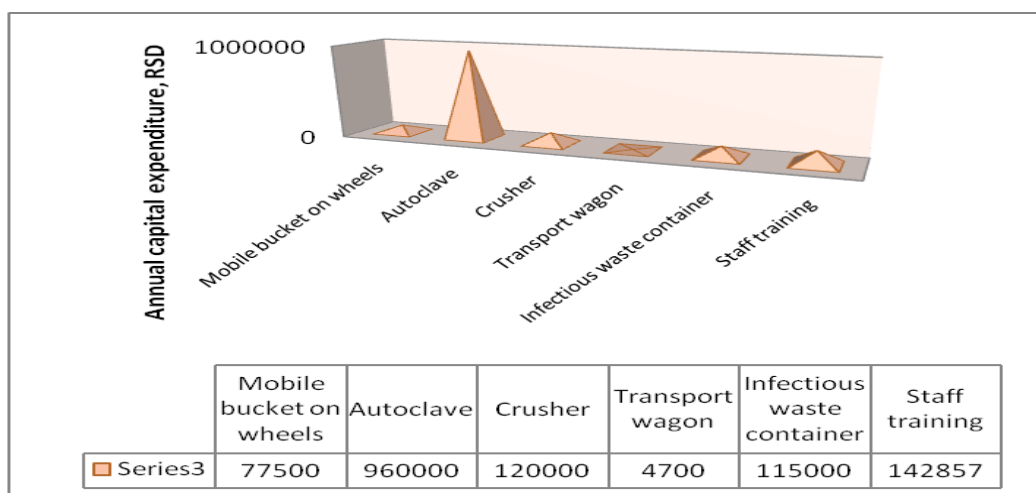


Figure 6. Annual capital costs of facilities for treatment of infectious waste

Getting system ensures that the most resistant of 10^6 microorganisms (including spores) survive maximum 1 (reduction rate is: 6 log 10). The results achieved for sterilization are up to 10 log 10 (which corresponds to STAAT IV). By STAAT III the necessary degree of destruction of the dispute is 4 log 10.[10]

The end product of the treatment is non-hazardous municipal waste disposed of at the city dump.

CONCLUSION

In the section for the treatment of infectious waste in Šabac, they process about 160 kg of waste per day. The degree of destruction of pathogens during treatment corresponds to the steam sterilization, which is prescribed by the EU Directives for medical devices MDD 93/42/EC. The results of treatment testify to the fact that good waste management involves minimizing their processing if all safety standards for humans, the environment, the ecosystem in general are respected.

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