



Srpsko hemijsko društvo  
Serbian Chemical Society



Sekcija za hemiju i zaštitu životne sredine  
Chemistry and Environmental Protection Division



# **6. simpozijum Hemija i zaštita životne sredine EnviroChem 2013**

sa međunarodnim učešćem

*6<sup>th</sup> Symposium*  
**Chemistry and Environmental  
Protection EnviroChem 2013**  
*with international participation*

## **KNJIGA IZVODA BOOK OF ABSTRACTS**

**Vršac, Srbija  
21 - 24. maj 2013.**



6. simpozijum  
**Hemija i zaštita životne sredine**  
sa međunarodnim učešćem

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*6<sup>th</sup> Symposium*  
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Republika Srbija  
MINISTARSTVO PROSVETE,  
NAUKE I TEHNOLOŠKOG RAZVOJA





# PROGRAM PROGRAMME

UTORAK / TUESDAY, 21.05.2013.	
17:30	PRIJAVLJIVANJE / REGISTRATION
18:30-19:30	Zajednički koktel / Get together cocktail
20:00-22:00	Sastanak koordinatora na MCHEM-TEMPUS PROJEKTU / Meeting of the MCHEM-TEMPUS PROJECT coordinators: An overview of the achieved outcomes
22:00	KRAJ DANA / END FOR THE DAY
SREDA / WEDNESDAY, 22.05.2013.	
09:00-09:30	<b>SVEČANO OTVARANJE SIMPOZIJUMA / OPENING CEREMONY</b> Predsedavajući / Chairpersons: Bojan Radak, Ivan Gržetić
09:30-09:45	Razvoj hemije životne sredine u Srbiji - osvrt prof. Petra Pfendta <b>P. Pfendt</b>
09:45	<b>SEKCIJA 1 / SESSION 1</b> Predsedavajući / Chairpersons: Branimir Jovančičević, Branka Žarković
09:45-10:15	<b>PLENARNO PREDAVANJE / PLENARY LECTURE</b> <i>Environmental analysis. The power and the beauty of mass spectrometry.</i> <b>A. Lebedev</b>
10:15-10:45	<b>PREDAVANJE PO POZIVU / INVITED LECTURE</b> <i>Water soluble polymers - a new threat for the environment?</i> <b>J. Schwarzbauer</b>
	<b>USMENA IZLAGANJA / ORAL PRESENTATIONS</b>
10:45-11:00	<i>Monitoring of organic compounds in atmospheric aerosols of West Siberia</i> <b>G.S. Pevneva</b>
11:00-11:15	<i>Modeling of transformation in oil polluted soils</i> <b>A. Golovko</b>
11:15-11:30	<i>Pauza / Break</i>
11:30	<b>SEKCIJA 2 / SESSION 2</b> Predsedavajući / Chairpersons: Bojan Radak, Petar Pfendt, Jelena Radonić
11:30-12:00	<b>PLENARNO PREDAVANJE / PLENARY LECTURE</b> <i>Biotransformation of Methanol and Formaldehyde, atmospheric pollutants, by cloud microorganisms. Comparison with radical chemistry</i> <b>A.M. Delort</b>

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12:00-12:30	<b>PREDAVANJE PO POZIVU / INVITED LECTURE</b> Značajni procesi pri rečnoj filtraciji u aluvijalnim izdanima: mehanizmi i uloga <i>Significant processes during river bank filtration in alluvial aquifers: mechanisms and role</i> <b>M. Dimkić</b>
	<b>USMENA IZLAGANJA / ORAL PRESENTATIONS</b>
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12:45-13:00	Karakteristike i segregacija masenih koncentracija urbanog aerosola centralnog Balkana (Beograd) <i>Characteristics and size-segregated mass concentration of urban aerosol of the central Balkans (Belgrade)</i> <b>D. Đorđević</b>
13:00-13:15	Fotokatalitička redukcija ugljendioksida do metanola pomoću kompozitnog katalizatora <i>Photocatalytic reduction of carbon dioxide to methanol using composite catalyst</i> <b>B. Adnađević</b>
13:15-13:30	<i>Biodisel production and characterisation</i> <b>B. Škrbić</b>
13:30-13:45	Adsorpcija jona bakra i cinka na prirodnom zeolitu <i>Adsorption of Copper and Zinc Ions by Natural Zeolite</i> <b>G. D. Bogdanović</b>
13:45-14:15	Sponzorsko predavanje / Sponsor's presentation ANALYSIS D.O.O.
14:15-16:00	<i>Pauza za ručak / Lunch break</i>
16:00-18:00	<b>IZLET / EXCURSION</b>
18:00-19:30	<b>POSTER SEKCIJA 1 / POSTER SESSION 1</b> Komisija za ocenu postera / Poster Presentation Evaluation Committee Mališa Antić, Olga Cvetković, Dragan Veselinović, Milena Jovašević Stojanović, Tatjana Anđelković
20:00-22:00	Sastanak učesnika na MCHEM-TEMPUS PROJEKTU / Meeting of the MCHEM-TEMPUS PROJECT participants
22:00	<b>KRAJ ZA DAN / END FOR THE DAY</b>

ČETVRTAK / THURSDAY, 23.05.2013.	
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09:00-09:30	<b>PLENARNO PREDAVANJE / PLENARY LECTURE</b> <i>Identification of specific pollutants in Serbia: a case study for Novi Sad municipality</i> <b>I. Špánik</b>
09:30-10:00	<b>PREDAVANJE PO POZIVU / INVITED LECTURE</b> <i>Pseudo-persistence and low doses effects - Emerging and priority substances - Challenges and perspectives</i> <b>M. Vojinović Miloradov</b>
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10:15-10:30	Primena frakcionog faktorskog dizajna za određivanje fluora u uglju <i>Application of Fractional Factorial Design for Determination of Fluorine in Coal</i> <b>I. Sredović Ignjatović</b>
10:30-10:45	<i>Degradation of chlorantraniliprole on plants, soil and in water</i> <b>P. Trebše</b>
10:45-11:00	<i>Development of sustainable technologies for organic and inorganic pollutants removal</i> <b>I. Villaescusa</b>
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12:45-13:00	<i>Rapid determination of pollutants by colorimetric reactions in <math>\mu</math>FIA with thermal lens microscopic detection</i> <b>M. Franko</b>
13:00-13:15	<i>Modernisation of Post-Graduate Studies in Environmental Sciences - an example of TEMPUS project activities</i> <b>M. D. Antonijević</b>
13:15-13:45	Sponzorsko predavanje / Sponsor's presentation SHIMADZU CORP.
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10:15-10:30	Određivanje lekova i pesticida u komunalnoj otpadnoj vodi <i>Determination of pharmaceuticals and pesticides in urban wastewater</i> <b>N. Antić</b>
10:30-10:45	<i>Basic chemical and physical characteristics of soils in four Belgrade parks</i> <b>L. Kaluđerović</b>
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**Modeling of transformation in oil polluted soils**

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**PLENARNA PREDAVANJA**

*PLENARY LECTURES*

## **Biotransformation of Methanol and Formaldehyde, atmospheric pollutants, by cloud microorganisms Comparison with radical chemistry**

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Large quantities of Volatile Organic Compounds (VOCs) are emitted into the atmosphere by natural and/or anthropogenic sources. Oxidation of VOCs leads to the formation of gaseous and particulate secondary products which, in turn, have significant impact on the atmospheric composition, and therefore on atmospheric processes, climate and human health. Among these VOCs, methanol is the second most abundant organic molecule in the atmosphere after methane, 11 to 20 % is of anthropogenic origin and from oxidation taking place in the atmosphere, while the major part (80 to 90 %) is of biogenic origin, mainly issued from plant metabolism. Formaldehyde is a primary emission product from biomass burning and fossil fuel combustion, but its principle source in the atmosphere is the photochemical oxidation of methane and non-methane hydrocarbons. Methanol and formaldehyde are soluble and efficiently transferred into atmospheric waters. It is generally admitted that the reactivity of methanol and formaldehyde in clouds is driven by the presence of free radicals ( $\cdot\text{OH}$ ,  $\text{NO}_3\cdot$ ). However, recent studies raised the idea that microbial activity can play a significant role in the liquid phase transformation of some organic compounds [1]. It is now well established that living microorganisms are present in clouds and are metabolically active [2]. This implies the uptake of nutrients from the liquid phase by cells and suggests that they can develop within cloud water. One key question for cloud chemistry now is to quantify biological oxidation as respect to chemical and photochemical processes.

We present here two recent studies showing that microbial activity may have a real impact on the transformation of methanol and formaldehyde in clouds.

### **1. Biotransformation of methanol and formaldehyde in a model system [3]**

The kinetics of biodegradation of methanol and formaldehyde in phosphate buffer at pH 7 by 4 bacterial strains (*Pseudomonas* spp., *Bacillus* sp. and *Frigoribacterium* sp.) isolated from cloud water at the puy de Dôme mountain (France) have been investigated at 5 °C (annual average temperature) using NMR spectroscopy.

A detailed *in vivo*  $^{13}\text{C}$  NMR study of the strain *Bacillus* sp 3B6 allowed to describe the various metabolic routes used for formaldehyde biodegradation: Using *in situ*  $^1\text{H}$  NMR it was possible to measure the average (for the 4 strains) biodegradation rates of formaldehyde ( $10^{-19}$  mol cell $^{-1}$  s $^{-1}$ ) and of methanol ( $10^{-21}$  mol cell $^{-1}$  s $^{-1}$ ). The biodegradation rates measured were compared with rates related to the reactivity of organic species with free radicals  $\cdot\text{OH}$  (daytime chemistry) and  $\text{NO}_3\cdot$  (nighttime chemistry) under two cloud situations (urban and remote cases). Clearly, measured biological and chemical reaction rates were in the same range of magnitude.

## 2. Biotransformation of formaldehyde in real cloud water samples [4]

Real cloud waters with contrasting features (marine, continental, urban) were sampled at the puy de Dôme mountain exhibiting high microbial biodiversity and complex chemical composition. These media were incubated in the dark and subjected to UV-light radiation in specifically designed photo-bio-reactors. Under these conditions it was shown that formaldehyde was clearly biodegraded while it was photoproducted, the combination of both photo and biodegradation gave rise to a constant formaldehyde concentration. This work also showed that microorganisms remained metabolically active in the presence of hydroxyl radicals ( $\cdot\text{OH}$ ) photo-produced from  $\text{H}_2\text{O}_2$ . This oxidant was actually biodegraded by the endogenous microflora. This work suggests that microorganisms could play a double role in atmospheric chemistry: first, they could directly metabolize organic carbon species; second they could reduce the available source of radicals due to their oxidative metabolism. Consequently, molecules such as  $\text{H}_2\text{O}_2$  would be no longer available for photochemical or other chemical reactions, decreasing the cloud oxidant capacity.

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## **Environmental analysis**

### **The power and the beauty of mass spectrometry**

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The power, beauty, simplicity and applicability of the modern mass spectrometry are really remarkable. Actually it is hardly possible to mention a branch of science where mass spectrometry cannot be efficiently applied. Besides classic disciplines dealing with mass spectrometry like chemistry, physics, biology this method may be efficiently used in medicine, cosmic studies, archeology and anthropology, anti terrorist activity, expertise of art exhibits, environmental control, doping-control, metrology, nuclear physics, etc. Due to mass spectrometry new disciplines like petroleomics, huminomics, metabonomics, proteomics have been created recently.

Environmental problems first attracted serious interest in the mid 1970s; this attention coincided with the development of organic mass spectrometry and the appearance of commercially available gas chromatography-mass spectrometry (GC/MS). The first list of priority pollutants created by US EPA contained mainly organic compounds amenable to GC/MS method. Vast implementation of LC/MS created a growing interest towards “new” natural or anthropogenic compounds. These compounds are called “emerging” contaminants. They represent an extremely wide group of chemicals including pharmaceuticals and their metabolites, musks, nanomaterials, perfluorinated compounds, hormones, disinfection by-products, flame retardants, sunscreen filters, naphthenic acids, and many others. Due to human activities these compounds enter into environment (usually at ng-μg/L levels). Although there is a lot of information concerning the danger of many of these pollutants for the environment and humans, they are not regulated in their majority so far. Some rules and restrictions exist but their safe values are not determined. mass spectrometry appeared to be the most efficient method for their detection, identification, and quantification.

During last 15-20 years mass spectrometry has converted into an indispensable method for qualitative and quantitative analysis of the most various substances: from isotopes of chemical elements to synthetic and natural polymers. It allows studying individual compounds as well as complex mixtures of thousands ingredients without any preliminary separation. Modern environmental mass spectrometry can handle any potential ecotoxicant. The corresponding methods have demonstrated excellent results in studies of extremely complex mixtures. The absence of a mass spectrometric method for a certain anthropogenic pollutant means that this compound has not yet attracted the attention of researchers.

The sensitivity of mass spectrometry is unsurpassed. The method deals with femto-zepto ( $10^{-15}$  –  $10^{-21}$ ) Mole levels of analytes in the samples. Taking into account Avogadro number ( $6.022 \times 10^{23}$ ) one can realize that mass spectrometry approaches the absolute theoretical limit of any analysis. The classic impracticable tasks of fairy tales like finding a rye grain in a sack of wheat grains or finding a needle in a haystack may be easily and rapidly accomplished with mass spectrometry. Actually when it deals with  $10^{-18}$  levels it is more fantastic than finding a single needle in 1 million haystacks.

Sometimes the analysis result may be quite surprising and fascinating for anybody. For example just measuring the abundance of isotopes of carbon, oxygen or nitrogen one can define the region of production of drugs of abuse, the part at fault of an oil spill, the authenticity of liquor, or even to differentiate between ancient Europeans and Americans using the bones of the discovered skeletons.

Environmental mass spectrometry is an important brunch of science because it provides many of the data that underlie policy decisions that can directly influence the health of people and ecosystems. Environmental mass spectrometry is currently undergoing rapid development. Among the most relevant directions are a significant broadening of the lists of formally targeted compounds; a parallel interest in nontarget chemicals; an increase in the reliability of analyses involving accurate mass measurements, tandem mass spectrometry, and isotopically labeled standards; and a shift toward faster high-throughput analysis, with minimal sample preparation, involving various approaches, including ambient ionization techniques and miniature instruments. A real revolution in analytical chemistry could be triggered in not distant future with the appearance of robust, simple, and sensitive portable mass spectrometers that can utilize ambient ionization techniques. If the cost of such instruments is reduced to a reasonable level, mass spectrometers could become valuable household devices.

## Enantioselective analysis of PCBs in Environmental Samples

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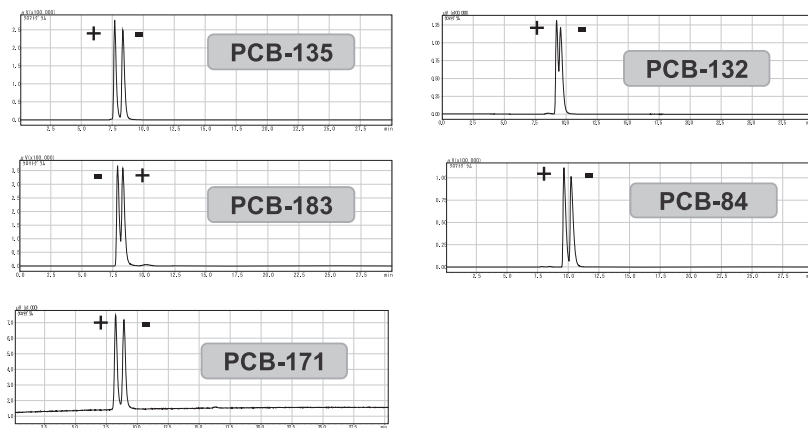
The electronic circular dichroism(CD) spectra of a pair of enantiomeric 2,2',3,4,4',5',6-heptachlorobiphenyls (PCB-183) were investigated for the first time experimentally and theoretically[1]. Geometrical optimization at the DFT-D3-B-LYP/TZVP level revealed that the two phenyl planes of PCB-183 are nearly orthogonal. Due to the sterically large chlorine atoms, PCB-183 becomes atropisomer. Thus, optical resolution was performed by chiral HPLC (column: OJ-H), affording enantiomerically pure first elute (100% ee) and optically enriched second elute (74% ee). Their experimental UV-vis and CD spectra in n-hexane were compared with those obtained by theoretical calculations at the RI-CC2/aug-TZVPP level. Determination of absolute configuration is crucial in the structure elucidation and their biological activities of chiral compounds, and it is also true for PCB atropisomer. However, the determination of absolute configuration of PCB has never been performed. Here absolute configuration of PCB-183 (aS and aR) were determined, aS-PCB-183 and aR-PCB-183 in human sample are determined enantio-selectively.

Pure enantiomers of chiral polychlorinated biphenyls (PCBs) obtained by high-performance liquid chromatography were used to establish the gas chromatographic elution sequences of the (+)- and (-)-enantiomer of eight PCB atropisomers on BGB-172. The elution order using BGB-172 was found to be (-/+) for PCBs 45, 84, 91, 132, 135, 139, and 171 and (+/-) for PCBs 183. Haglund et al reported as follows; the elution order using Chirasil-Dex was found to be (-/+) for PCBs 84, 132, 136, and 176 and (+/-) for PCBs 135 and 174. [2]

GC and LC conditions for chiral separation: To determine absolute configuration of each PCB atropisomers, the enantioselective separation of PCB atropisomer was performed using HPLC(TOSOH CO-8020, SHIMADZU LC-10AT) with CHIRAL-CEL (DAICEL) OJ-H (4.6mmIDx150mm). The adsorbent is cellulose tris(4-methylbenzoate) silica gel coatingtype, particle size 5  $\mu$  m, sample loop : 20  $\mu$  L, column temp : 38°C, n-hexane was used as elution solvent with flow rate 0.3mL/min, UV 291nm. PCB-183 in human sample was enantio-selectively determined by GC/HRMS.(JEOL JMS-800D) using BGB-172 column (20% *tert*-butyldimethylsilylated *beta*-cyclodextrin in methyl phenylcyanopropylpolysiloxane, 30m length x 0.25mmID, 0.25  $\mu$  m Film Thickness, BGB Analytik AG). Carrier gas was helium, and injector and transfer line temperature were 230°C and 245°C. 1  $\mu$  l of samples were injected splitless at an initial temperature of 120°C, 4°C/min to 180°C, 1°C/min to 230°C, and held for 10minutes. The ion source was operated in the electron-impact mode (EI, 38eV, 250°C).

## Experimental data and theoretical calculation results

The concentrations is calculated as  $\epsilon(209)=73000$ . Experimental CD spectra of aR/M are roughly similar in comparison with theoretical calculation of aS/P.(aS: axial S). In experimental CD spectra, comparison between fraction A(100%ee) and fraction B(74%ee) multiply 1.35 with inversion of sign were in excellent agreement. The first elution peak on BGB-172 column by GC/MS is assigned as aS/P. The first elution peak on OJ-H column by LC/MS was also assigned as aS/P.



**Figure 1.** LC chromatograms for the optical resolution of PCB-atropisomers

**Table 1.** Parameters of HPLC and GC for Enantiomer Separation of PCBs 183, 171, 132, 135, 84.<sup>a</sup>

	PCBs	$\tau_0$ ,(min)	$\tau_1$ ,(min)	$\tau_2$ ,(min)	W1	W2	$\alpha$	Rs
HPLC	183	4.04	7.58	8.03	0.25	0.27	1.13	1.72
	171	4.04	6.46	7.04	0.23	0.28	1.24	2.25
	132	4.04	7.28	7.54	0.27	0.32	1.08	0.878
	135	4.04	6.47	7.04	0.21	0.27	1.23	2.36
	84	4.04	8.44	8.92	0.29	0.35	1.11	1.51
GC-MS	183	2.00	41.4	41.6	0.15	0.18	1.00	1.21
	171	2.00	45.4	45.7	0.16	0.19	1.01	1.51
	132	2.00	37.5	37.8	0.12	0.13	1.01	2.36
	135	2.00	32.3	32.5	0.12	0.12	1.01	1.53
	84	2.00	29.0	29.1	0.09	0.10	1.01	1.70
<sup>a</sup> $\alpha = (\tau_2 - \tau_0) / (\tau_1 - \tau_0)$ . $Rs = 2(\tau_2 - \tau_1) / (W1 + W2)$ .								

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## **Identification of specific pollutants in Serbia: a case study for Novi Sad municipality**

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The Directive 2000/60/EC of the European Parliament and of the Council dated 23 October 2000 established a framework for Community action in the field of water policy and set the objectives to prevent deterioration in status of all Community waters, inland and coastal, in order to ensure achievement and maintenance of their good status by year 2015 [1], in order to establish a “good” ecological and chemical quality status. The definition of ecological and chemical status requires establishment of intensive monitoring programmes to receive reliable information about chemical substances or groups of substances present in aquatic environment. However, local environmental monitoring data of the quality of surface water is scarce, and there are particular deficits in the area of priority and emerging substances measurements and human exposure studies in most countries. The highest level of environmental monitoring and scientific findings related to the occurrence of emerging contaminants in surface, ground and wastewater in Serbia have been established through international projects and co-operation (NORMAN, ICPDR, EMCO). These projects provided comprehensive data on the occurrence of WFD priority substances and selected emerging contaminants in water bodies and effluents in some Western Balkan (Serbia, Croatia) and EU countries.

The aim of this work was to establish a list of priority specific pollutants found in Danube River near Novi Sad based on previous screening and target monitoring results. The GC-MS screening and determination of 69 target organic and inorganic contaminants were performed in winter, spring/summer and autumn period in 2012. Organic compounds were extracted by liquid-liquid extraction and stir bar sorptive extraction. The GC analysis was performed using Agilent 7890 gas chromatograph coupled to Agilent 5975 mass spectrometric detector. The system was equipped with PTV injector system. Helium was used as carrier gas. The MSD was used in the SCAN mode for all samples. The target analyses were performed according to ISO standards.

A prioritization approach has been tested on both, substances tentatively identified by non-target GC-MS screening as well as target analyses in 34 surface water and waste water samples collected from 11 sampling points. The concentration of tentatively identified compound from GC-MS screening was estimated through comparison of the signal of an unknown compound to the signal generated by the known concentration of an internal standard. It should be clear that this method



provides only rough estimation of the actual concentration, but as published previously, this error usually varies within one order of magnitude, which is well within the range of uncertainty associated with the ecotoxicological predictions [2]. The prioritization step was based on the evaluation of the extent of exceedance of measured environmental concentrations over the reference value - predicted no effect concentrations (PNEC), determined for identified organic compounds monitored in the river system.

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**PREDAVANJA PO POZIVU**

*INVITED LECTURES*

## Water soluble polymers – a new threat for the environment?

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Production, use and discharge of synthetic polymers are activities with a potential for environmental concern. Currently, plastics with an annual production rate of over 100 million tons get an extended attention of environmental scientists. Plastics are dominantly used as package material or durable raw material due to its high resistance and stability. However, it has been estimated that up to 10% of the annually produced amount are disposed to the marine environment.

Interestingly, a larger proportion of polymers is not used for plastic production but is added as water soluble constituents to several commercial products. These macromolecules also exhibit partially a high environmental stability and are disposed to the aquatic environment as well. However the knowledge about the environmental fate and relevance of these dissolved polymers is scarce.

Here we report on recent research activities on soluble polymers as potential contaminants of the aquatic and soil environment. These investigations are based on the same analytical methodology using pyrolysis coupled with GC/MS analysis either in online or offline mode. The principal approach consists of identification of specific pyrolysis products which can be attributed unambiguously to the former polymer. Further on, these pyrolysis products shall act as indicator molecules for tracing and quantifying the emissions of the polymers or related technical formulations.

Firstly, we focussed on a selected group of polymers, the **polyacrylamide based flocculants** commonly used in waste water treatment plants for precipitating heavy metals and other contaminants. The irrigation of sewage sludge on agricultural soils as fertilization leads to the spreading of the associated flocculants into the pedosphere. Analytical methods for detecting flocculants in soil samples are not published so far. Thus pathways in the environment or accurate correlation with toxic effects cannot be pointed out.

In a first step an analytical procedure induced the pyrolytic decomposition of the polymers. Specific low molecular pyrolysis products were identified by an on-line coupled Pyrolysis-GC-MS system (s. Fig. 1). Structure elucidating analysis applied to these characteristic compounds led to glutarimide-based substances. The method developed was tested on sewage sludge and contaminated soil samples [1].

Secondly, **poly(vinylpyrrolidone) (PVP)** is a synthetic polymer widely used in a variety of industries, because of its unique spectra of properties, particularly good solubility not only in water but also in a large number of organic solvents, low toxicity, high complexing ability and good film-forming characteristics. As a result of its very frequent usage and its suggested environmental stability, it is proposed that PVP has to be detected in the polluted water samples, however, an appropriate analytical method was missing so far.

Our Py-GC/MS based method applied on different sewage waters indicated the presence of PVP in particular in two waste water samples (municipal waste water from Aachen, Germany, and industrial waste water from Pancevo, Serbia). The concentrations of PVP reached up to 7.1 mg/L (Aachen) and 2.9 mg/L (Pancevo)[2].

Lastly, current research deals with the application of cellulose based polymers in drilling fluids used for on-shore and off-shore drilling. The usage of drilling fluids is not a strictly closed system application, hence continuously emission of drilling fluids towards ecosystems are evident.

Py-GC/MS analyses of different technical formulations of drilling fluids were performed in order to identify specific products. The polymers used in the investigated formulations are dominantly based on chemically modified cellulose (**carboxyethyl cellulose CMC and hydroxyethyl cellulose HEC**). Hence, our work was related to optimization pyrolysis conditions and optimum parameters concerning temperature and time. Further on, online derivatisation by TMAH has been proven as useful tool for a more comprehensive detection of pyrolysis products.

Generally, the development of pyrolysis based analytical methods for polymer identification and quantification at trace levels opens the possibility to detect soluble polymers in the environment, which has not been done so far. The analytical restrictions in the past hindered the environmental characterisation of polymer emissions and, consequently, their environmental assessment.

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## Active moss biomonitoring of airborne trace elements in the Belgrade urban area: State of the art

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The urban atmosphere is subjected to large inputs of anthropogenic contaminants produced by both mobile and stationary sources. Trace elements are widely dispersed pollutants in an urban environment and their interaction with different natural components results in toxic effects on the biosphere. Biomonitoring is a rapid and cost-effective method that has commonly been used for assessing environmental quality and potentially detrimental effects of pollutants on the biosphere. Due to their morphological and physiological characteristics, bryophytes have proved to be suitable biomonitors for trace element air pollution. However, in urban areas, where mosses are often scarce or even absent, the “bags technique”, i.e. active biomonitoring, has been initiated and developed with the aim of spatial and/or temporal assessment of contaminant deposition in such highly polluted areas. The *Sphagnum* species are especially recommended as the most suitable moss for active biomonitoring of trace and other elements due to several features including a large surface area and a number of protonated anionic functional groups (ion exchange sites) in the form of uronic acids [1].

In the Belgrade urban area, the research of air quality applying *Sphagnum girgensohnii* moss bags has been taking place since 2005, with special reference to development and adjustment of the methodology. Thus, starting from July 2005, a one-year study was performed at three representative heavy traffic sites where moss bags were exposed to atmospheric deposition for five 3-months consecutive periods during the summer and winter seasons. This study focused on trace element accumulation by moss *S. girgensohnii* in relation to the comparative atmospheric bulk deposition data. Additionally, in order to gain an insight into the role of water supply on the moss accumulation ability, an experiment with dry and irrigated (wet) moss bags was carried out. According to the results, for  $\approx 30$  elements determined by INAA, the significant increase of concentration was obtained in exposed moss in comparison with the unexposed one. Also, majority of the elements were more accumulated in wet than in dry moss bags during each exposure period [2]. High correlations were found between the certain element concentrations in bulk deposits and moss samples [3].

The second experiment was performed between June and November, 2007 where *S. girgensohnii* moss bags were exposed to atmospheric deposition for different exposure periods (0.5–5 months), i.e. for ten consecutive 15-day periods. Since the exposure period is especially critical in such moss biomonitoring

surveys, the aim of this study was to assess cumulative properties of the moss bags *versus* time. Again, different treatments, with and without irrigation, were applied to the moss exposed in parallel. According to the results, both dry and wet moss bags showed a linear trend of accumulation during 1–5 months of exposure for a majority of the 50 elements measured by HR-ICP-MS. Again, slightly higher accumulation of some elements in wet moss bags was evident in comparison with the dry ones [4].

In 2011, two experiments, in five street canyons and one city tunnel was carried out aimed at evaluation of the possibility of using *S. girgensohnii* moss bags for investigation of the small scale vertical and horizontal distribution patterns of trace elements. In the street canyons, the moss bags were hung at heights of about 4, 8 and 16 m for 10 weeks, and also, for the same time, the moss bags were exposed inside, in front of, and out of the tunnel. About 15 elements in the moss were determined by ICP-OES. In all street canyons, the vertical distribution patterns of the moss element concentrations showed statistically significant decrease from the first to the third heights of bag exposure. However, in two canyon streets, the highest elemental concentration was determined in the moss exposed at the second height. Thus, the residents of some canyon streets may be exposed to higher air pollution than pedestrians. In the tunnel experiment, from inner to outside of the tunnel, a decreasing trend element concentration from inner to outside was observed. Otherwise, significantly higher concentration of the elements in moss bags was pronounced for the city tunnel in comparison with the street canyon data [5].

The results of all these studies generally confirmed that the use of *Sphagnum girgensohnii* moss bags could be a simple, sensitive and inexpensive way of obtaining extensive information on deposition levels of certain airborne trace elements in urban area.

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## **Low-cost sensor technologies as a complement to science and management of air quality**

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The boom of sensor technologies for monitoring air quality presents a new opportunity to engage with the public on environment. A FP7 project CITI-SENSE (“Development of sensor based Citizen’s Observatories for better life quality in cities”, a 4-year project co-funded from the 7th EC RTD Framework Program, contract nr. 308524, started in October 2012) investigates how low-cost sensors can be made available to the public, what questions can be investigated, and how to link sensor measurements to other information sources including monitoring networks. This presentation overviews the concepts and methods used in the project, and first lessons learned.

The aim is to develop citizens’ observatories, to enable public participation in environmental decision making, and to investigate the properties of the data and develop methods to use it for environmental research. Specifically, we aim to develop a number of applications relevant to air quality and exposure to air pollutants both indoors and outdoors, to communicate with citizens through citizens’ observatories, and to investigate how citizens’ observatories can contribute to global observing systems.

On the general level, the project joins three elements: technological platforms for distributed monitoring, information and communication technologies compatible with global observing systems, and societal involvement. Pilot studies (Empowerment Initiatives) focus on urban air quality, public spaces and indoor environment at schools, in nine European cities.

The project is organized in work packages that follow the chain in which information is passed, from sensors that monitor the required entities, through communication platforms where the information is made available and globally connected, products where the properties of collected data are investigated and data is made available as information. In addition, a dedicated work package addresses the citizen involvement to ensure that the citizen’s perspectives are taken



into account. These work packages interact with the Empowerment Initiatives that provide implementation of all the project methods and products through the Citizens' Observatories.

Several environmental stressors are targeted: criteria air pollutants (including NO<sub>2</sub>, NO<sub>x</sub>, particulate matter, CO, CO<sub>2</sub>, and selected VOCs), noise, meteorological parameters, and ultraviolet radiation. A number of sensor platforms are available in the consortium, and as much as possible, these will be utilized. The sensor signals will be entered in a communication platform based on a service-oriented architecture that utilizes a number of international standards for access to data, sensors and services. In this way, data will be compatible with the INSPIRE-directive requirements and the GEOSS architecture, and thus widely available.

In dialogue with users, the Empowerment Initiatives will develop locally relevant sensor-based information products. One of the selected nine European locations is Belgrade, largest town in Serbia and Western Balkan region, with more than 1,5 million inhabitants. CITI-SENSE use case will enhance existing air quality monitoring platforms and provide two kinds of products, one relevant to outdoor air pollution, and one to help improve indoor environment in our schools. The Belgrade initiative will be extended to Pančevo, known as industrial "hot spot", a town with more than 100,000 inhabitants, located about 12 km east of Belgrade's city center.

To be able to evaluate air pollution in real time over an urban area, the Belgrade and Pančevo urban air quality study will develop own air quality assessment network incorporating GPS and GPRS adapted for high resolution air quality measurements using static and mobile platforms. Air pollution levels and exposure collected from personal platforms carried by volunteers from selected user groups (for example healthy citizens and patients groups) will be compared with levels and other exposure information. In addition, selected biomarkers will be measured. Data collection for outdoor air will start with a pilot, to be implemented in about a 6 months time. The Belgrade indoor air in schools initiative started recently with a pre-prototype example installed in a school in New Belgrade residential area.

In the first 6 months of the project, the consortium has developed protocols for four pre-prototype examples that were testing feasibility of the project concept and connectivity of the different technologies. The first prototype provides locally specific information about UV exposure (based on routine meteorological monitoring and a specific exposure modeling) through a mobile phone application. The second prototype was to demonstrate to the school authorities the feasibility of monitoring of the indoor environment in the classroom, and the kind of information they may expect, for example through school web portal or mobile phone applications. The third prototype will demonstrate an application for collecting data from the users (school children/staff) on their perceptions of indoor air environment (cold, hot, stuffy air etc). The fourth prototype aims at testing connectivity of the different elements for air quality in Barcelona where existing applications already provide parts of the necessary products.

## Huminske supstance - od strukture ka ekološkoj ulozi

### Humic Substances - From Structure Toward Ecological Role

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Huminske supstance (HS), najvažnija frakcija prirodne organske materije, prisutne su u svim terestričnim i akvatičnim sredinama i učestvuju u skoro svim važnim hemijskim procesima životne sredine. Njihova perzistentnost i rasprostranjenost u biosferi, uvršćuje ih u dominantne regulatore važnijih procesa životne sredine.

Definisanje strukture HS je neophodno u cilju definisanja njihove reaktivnosti, biološke i fizičko-hemijske uloge u procesima u životnoj sredini. Iako je nemoguće dati preciznu strukturnu formulu HS, moguće je dati procenu prisustva različitih funkcionalnih grupa u HS. Imajući u vidu da prevashodno kiseonične grupe, učestvuju u kompleksiranju sa jonima metala, važno je poznavanje zastupljenosti ovih grupa u HS. Najveći deo kiseonika funkcionalnih grupa HS je prisutan u karboksilnim, a manji deo u fenolnim i alkoholnim grupama. Određivanje koncentracije  $pK_a$  vrednostikarboksilnih i fenolnih grupa doprinosi modelovanju aciditeta HS. U literaturi su navedene različite metode određivanja kiseoničnih grupa HS [1], ali sve one pokazuju izvesne nedostatke. Neki autori preporučuju diferencijaciju različitih hidroksilnih grupa HS njihovom derivatizacijom [2]. Selektivnim blokiranjem funkcionalnih grupa, moguće je odrediti njihov pojedinačni doprinos ukupnoj kiselosti HS, kao i interakciji sa protonima i metalnim jonima [3]. Blokiranjem (a) karboksilnih, (b) fenolnih i alkoholnih i (c) karboksilnih i fenolnih grupa, i ispitivanjem kiselinsko-baznih i kompleksirajućih karakteristika derivata, moguće je uočiti doprinos interakciji sa protonima i jonima metala, svake od navedenih kiseoničnih grupa. Hemijske modifikacije specifične za karboksilne, fenolne i alkoholne grupe se mogu efikasno postići esterifikacijom, acilovanjem i metilovanjem. Selektivnim blokiranjem karboksilnih grupa, metanol/tionil-hloridnom metodom esterifikacije, moguće je dobiti derivat sa čak 93% blokiranih karboksilnih grupa, dok metilovanjem sa  $CH_3I/Ag_2O$  u  $N,N$ -dimetilformamidu kao rastvaraču svih kiseoničnih grupa huminskih kiselina moguće je dobiti derivat sa oko 96% blokiranih grupa. Smanjenje ukupne kiselosti esterifikovane HA može se koristiti kao merilo sadržaja karboksilnih grupa, dok se njena ukupna kiselost može uzeti kao merilo sadržaja fenolnih grupa. Porast vrednosti konstanti kiselostiderivatizovanih HA, je u saglasnosti sa razlikama u hemijskim strukturama kiselina. Parametar distribucije konstanti kiselosti se može uzeti kao merilo hemijske heterogenosti HA [3]. Odsustvo karboksilnih grupa za interakciju sa metalima, dovodi do smanjenja stabilnosti kompleksa, odsustvo fenolnih

grupa, do stvaranja još slabijeg kompleksa, dok metilovaniderivat sa blokiranim karboksilnim i fenolnim grupama, gradi najslabiji kompleks.

Ekološka uloga interakcije katjona sa HS leži u kontroli procesa acidifikacije zemljišta i voda, dostupnosti nutrijenata, površinskog razlaganja minerala, nastanka zemljišta, vezivanja, transporta i biodostupnosti teških metala, pesticida, ksenobiotika, radioaktivnog otpadnog materijala, svojstvima sedimenata, zemljišnoj strukturi. Modelovanje interakcije katjon–HS hemijskim ravnotežnim modelima je relativno kompleksno, pošto su HS heterogeni ligandi. S obzirom da HS mogu da se jave i u rastvornoj i u nerastvornoj fazi, važno je uzeti u obzir vezivanje katjona i za rastvorne HS i za humine. Postoje različiti alternativni modeli proračuna katjonskog vezivanja za HS: Gausov, Stokholm Model i NICA-Donan Model. Procena heterogenosti njihove strukture može doprineti proceni njihovih interakcija sa komponentama sredine u kojoj se nalaze. HS u svojoj strukturi sadrže i hidrofilne i hidrofobne fragmente, tako da mogu stupiti u interakcije i sa polarnim i sa nepolarnim jedinjenjima, što ih čini veoma bitnim konstituentima geosorbenata [4,5].

Ekološka uloga HS, određena njihovom polifunkcionalnošću, leži u činjenici da HS s jedne strane kontrolišu fizičko-hemijske procese zagađivanja voda i zemljišta, dok sa druge strane definišu i same procese prečišćavanja zagađenih sredina [6]. Tako, HS se koriste za uklanjanje toksičnih metala, antropogenih organskih hemikalija i drugih zagađujućih supstanci iz vode. Materijali na bazi kalcijum-humata pogodni su za uklanjanje teških metala kao što su Fe, Ni, Hg, Cd i Cu iz vode, za uklanjanje radioaktivnih elementa iz vode koja se ispušta iz nuklearnih elektrana, za prečišćavanje kanalizacije (u vidu filtera na bazi humusa), čišćenje od hromata iz otpadnih voda topionica, uklanjanje ulja i boja iz otpadnih voda i akvatičnih sistema, za filtraciju urbanih i industrijskih otpadnih voda, uklanjanje pesticida iz kanalizacije i uklanjanje fenola iz vode. Materijali koji sadrže humus se takođe koriste za sorpciju štetnih gasova poput vodonik-sulfida, merkaptana i sumpor-dioksida.

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## **Pseudo-persistence and low doses effects Emerging and Priority substances Challenges and perspectives**

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In the recent time, considerable interest has grown concerning the presence of the emerging substances (EmS). The most of EmS are widespread in every day life and applied in different fields of industrial activities as pharmaceuticals both for human and animal uses, personal care products, household chemicals, nanomaterial, additives, anticorrosives, and others. The NORMAN [1] is open and dynamic list which clasifies more than 750 emerging chemicals in 25 classes and subclasses (latest update approved March 2011). EmS are currently not included in routine monitoring programmes at EU level and their fate, behaviour and (eco) toxicological effects are not well understood.

According to Annex II of Directive 2008/105/EC, 33 priority substances and 8 hazardous substances (carbon tetrachloride, p,p'-DDT, aldrin, dieldrin, endrin, isodrin, tetrachloroethylene and trichloroethylene) were shown to be of major concern for European Water Directive. Selected EmS are proposed to be on the list of priority substances (carbamazepine, sulfamethoxazole, diclofenac, ibuprofen, naproxen, bezafibrate, atenolol, ciprofloxacin, erythromycin and gemfibrozil).

Municipal and industrial waste effluents with limited treatment are hotspots for EmS. Although the concentration levels of EmS are very low, they are detectable in WWTP effluents by sophisticated analytical equipment HPLC-TOF-MS/MS.

The dominant and specific physicochemical characteristics for EmS are: low doses occurrence and effects, pseudo-persistency, stable structure, low/non degradability, hydrophilicity and lipophilicity (Log Kow 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 effects in low and sub-low doses. EmS are volatile, non - or semivolatile compounds, water soluble molecules, but could be lipid soluble and polar/nonpolar molecules. EmS interfere and store in protein tissue components of liver or other organs.

Their main physical and chemical properties are characterized by following constants of: protonation (Log pKa) in the range of 9.6 – 2.5, octanol–water partition coefficient (Log Kow) in range 0.35 – 6.02 and solubility (Sw) in range from 106 mg/l to 0.02 mg/l.

Chemicals continually released into aquatic environment essentially become „persistent“, i.e. pseudo-persistent pollutants even if their half-lives,  $t_{1/2}$ , are short.

Thermodynamic kinetic equilibrium for pseudo-persistence phenomena could be presented by mathematical relation  $V_i \gg V_{out}$ , in which the rate of input of EmS ( $V_i$ ) is considerably higher than the rate of observed EmS output ( $V_{out}$ ). That means that the rate of input (release, emission, generation) of EmS into receiving water is much higher than the rate of output/removal. The supply of EmS is continually replenished.

Very low and sub-low doses effect of EmS as the new phenomena showed the hormonally active emerging agents causing a variety of adverse effects, mainly reproductive and developmental.

Within the NATO Project SFP 984087 more than 150 organic compounds in surface water were detected (Institute of Analytical Chemistry, Slovak University of Technology in Bratislava) as the first screening results of the occurrence of EmS in the river Danube in the vicinity of Novi Sad [2,3,4].

Research, detection and evaluation of EmS is one of the most needed and challenging aspects of environmental issues. These newly recognized old and new emerging contaminants require progressive shift in traditional thinking, new perspectives for the modern protection scenario for higher level of eco status of whole environment and further advancement for more integrated, quantitative approach.

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## **Procena potencijalno zagađenih voda za proizvodnju zdravstveno bezbedne hrane**

### **Capability evaluation of potentially polluted water for the safe food production**

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Uvođenjem principa "zagađivač plaća" u evropskim zemljama, zagađenje površinskih i podzemnih voda je drastično smanjeno. Svi zagađivači su dužni da obezbede sredstva za neophodne mere i radove koji će sprečiti zagađenje životne sredine i uticaj na poljoprivrednu proizvodnju. Savremeni potrošač zahteva visoko kvalitetnu hranu, tako kvalitet i zdravstvena bezbednost postaju prioriteta, *European Food Safety Authority* (EFSA) i *Food Standards Agency* (FSA), su akteri kontrole kroz standarde za proizvodnju hrane. EUREGAP je standard za voće i povrće (EUREGAP, 2004) kriterijum za kvalitet vode za navodnjavanje zastupljen je pored ostalih.

Savremena poljoprivredna proizvodnja kao značajne probleme podjednako tretira i mikrobiološku i hemijsku kontaminaciju voda. Akumulacija zagađujućih materija organske ili neorganske prirode smatra se uzrokom. Posebna pažnja posvećena je nitrata i teškim metalima. Povećani sadržaj nitrata najčešće je posledica nekontrolisane upotrebe mineralnih ili organskih đubriva. Vrlo su mobilni u životnoj sredini, veća količina u vodi za navodnjavanje negativno utiče na kvalitet gajenih biljaka. Nitrati se u organizmu redukuju do nitrita koji sa hemoglobinom grade methemoglobin, a sa aminima kancerogene nitrozoamine, pa konzumiranje povrća sa viškom nitrata izaziva ozbiljna oboljenja kao što su methemoglobinemija i kancer. U svetu su vršena ispitivanja sadržaja teških metala u vodama za navodnjavanje (*Al-Subu i sar., 2003; Sharma i sar. 2007*), uticaj povećanog sadržaja na distribuciju metala u zemljištu i navodnjavanjem biljkama (*Kalavrouziotis i Drakatos, 2002*). Rezultati pokazuju da vode zagađene ovim metalima (Cr, Pb, Ni, Cd idr.) značajno utiču na sadržaj istih u gajenim biljkama, a nekima se sadržaj povećava i u zemljištu. Toksičnost teških metala kod čoveka izaziva oštećenja bubrega, jetre, centralnog nervnog sistema, možda pojavu kancera (*Vapa i Vapa, 1997*). Pored đubriva u vode dospevaju industrijskim i urbanim otpadom i sago-revanjem fosilnih goriva.

Savremeni pristup kontaminaciji voda za navodnjavanje identifikuje kontaminanate (mikrobiološke i hemijske) i prenošenje kontaminacije u sistemu voda/zemljište/navodnjavane biljke i primenu metoda dekontaminacije. Multidisciplinarni pristup zastupljen je u svih 5 projekata predstavljenih u daljem tekstu, čiji su rezultati potencijal za formiranje bonitetnih klasa.

"WATERWEB Water Resource Strategies and Drought Alleviation in Western Balkan Agriculture" - EU FP6 projekat je realizovan u slivu reke Bolečice i potoka koji prolazi kroz školsko dobro Poljoprivrednog fakulteta "Radmilovac". Vršena



su hidrološka istraživanja, određivan kvalitet vode, a akcenat projekta bio je razrada metoda za merenje hemijske kontaminacije površinske i dubinske vode korišćene za navodnjavanje, kao i metoda za ispitivanje prenošenja kontaminanata u sistemu zemljište/biljka/voda.

*"SAFIR Safe and High Quality Food Production using Low Quality Waters and Improved Irrigation Systems and Management"* – EU FP6 projekat – ispitivanja su vršena na lokalitetu Surčina, praćen je transport teških metala iz vode za navodnjavanje u krtole krompira. Testirane su metode za dekontaminaciju vode kroz primenu filtera za uklanjanje teških metala kao dela sistema za navodnjavanje. Efikasnost metode procenjena je preko sadržaja teških metala u krtolama.

*"CROPWAT A Centre for Sustainable Crop-Water-Management"* – EU FP6 projekat – razvoj ekspertize za ocenu stepena kontaminacije biljaka vodom za navodnjavanje. Zamisao projekta je bila kalibracija metoda praćena stvaranjem osnove za formiranje mreže bonitetnih klasa.

*"Multidisciplinarni pristup upravljanja vodom za potrebe proizvodnje zdravstveno-bezbedne hrane i ublažavanja efekta suše u poljoprivredi"* – TR 20025 – na osnovu ekspertize iz prethodnih EU projekata sastaviti hidrološku studiju (GIS mapu) kanala za odvodnjavanje jugoistočnog Srema kao potencijalni model rešenja navodnjavanja u drugim delovima Srbije i revitalizaciju zapuštenih kanala za navodnjavanje. Paralelni cilj je razvoj ekspertize praćenje prenošenja hemijskih kontaminanata iz vode za navodnjavanje na gajene biljke u okolini kontaminiranih izvorišta.

*"Ispitivanje mogućnosti korišćenja kontaminiranih voda za gajenje alternativnih, zdravstveno bezbednih žita"* – projekat TR 31006 koji je u toku -lokacija na deponiji pepela termoelektrane Nikola Tesla B. Zamisao je multidisciplinarna – zemljište je deposol sa oštećenjem antropogenog porekla, voda iz kanala je proceđena iz pepelišta, potencijalno kontaminirana As, Pb i Zn, a gaji se alternativno žito kvinoja, poželjno zbog otpornosti na sušu i odsustva glutena. Svrha gajenja je proizvodnja hleba namenjenog osobama sa intolerancijom na datu supstancu.

Tri civilizacijske epohe izazvale su najznačajnije promene u životnoj sredini. Poljoprivredna revolucija, koja je trajala sve do početka XVII veka. Industrijska revolucija, završetak oko 1985. godine. Na kraju, tehnološka revolucija čiji smo svedoci, praćena borbom za spašavanje dovoljnih količina vode odgovarajućeg kvaliteta, koju uz tehnološki napredak vodi čovek, a posledica je ljudske nepromišljenosti i nemara. Ta apsurdna činjenica nas je navela da kroz rezultate realizacije 5 naučnih projekata pristupimo pokušaju bonitiranja voda, prema različitim parametrima i raznovrsnom karakteru.

## **Značajni procesi pri rečnoj filtraciji u aluvijalnim izdanima: mehanizmi i uloga**

### **Significant processes during river bank filtration in alluvial aquifers: mechanisms and role**

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Podzemne vode su izuzetno značajan element sistema voda na planeti Zemlji. Podzemne vode nisu samo prirodni resurs već i bitan segment životne sredine i jedan od osnovnih činilaca hidrološkog ciklusa. Širom sveta ljudi ih koriste kao resurs za obezbeđenje pijaćih voda. Vodosnabdevanje stanovništva u Republici Srbiji vrši se najvećim delom eksploatacijom podzemnih voda. Eksploatacija aluvijalnih podzemnih voda iznosi preko 50% ukupno zahvaćenih podzemnih voda. Samoprečišćavajući efekti filtracije kroz poroznu sredinu, menjaju kvalitet podzemnih voda od reke ka bunarima, najčešće u smeru njegovog poboljšanja [1]. Strujanjem podzemne vode, rastvorena materija izložena je različitim fizičkim, hemijskim i biohemijskim procesima. Procesi prečišćavanja teže da eventualno promenjeni kvalitet podzemnih voda dovedu do bazičnog, koji je zavistan od mineraloškog sastava stenske mase na putu filtracije, oksičnosti sredine i dinamike kretanja podzemnih voda. Aluvijalne izdani se mogu se samim tim mogu posmatrati kao složen fizičko-biogeohemijski reaktor.

Za razliku od površinskih voda podzemne se vode kreću znatno sporije i kroz ekstenzivne kontakte i procese na relaciji tečna faza-skelet izdani-vazduh poprimaju bazični kvalitet karakterističan za određeno vodno telo. Antropogeni uticaji se filtracijom podzemne vode smanjuju i kvalitet vode teži bazičnom kvalitetu izdani. Ovo je važno za ispravno određivanje zaštitnih zona, kao i procesno tehnološke linije izvorišta podzemne vode [1], [2].

Dugogodišnjim istraživanjima aluvijalnih sredina, koja su sprovedena u Institutu Jaroslav Černi kroz različite projekte, ispitivani su procesi koji se odvijaju u podzemnoj sredini na putu filtracije od reke do bunara. Ova obimna ispitivanja obuhvatila su procese transformacije kvaliteta kao i procese starenja bunara i opadanja kapaciteta vodozahvata. Posebna pažnja usmerena je na vezu između procesa koji se odvijaju u podzemnoj sredini i stepena oksičnosti akvifera. U okviru naučnog projekta „Metodologija ocene, projektovanja i održavanja izvorišta podzemnih voda u aluvijalnim sredinama u zavisnosti od stepena aerobnosti“, kao i projekta „Starenje bunara i održavanje izvorišta“ izvršena su istraživanja hemijsko-mikrobiološkog sastava, sadržaja farmaceutika, pesticida [3] i njihovih metabolita u aluvijalnim i površinskim vodama, kolmiranja gvožđem vodozahvatnih bunara u zavisnosti od stepena oksičnosti sredine [4], [5], kao i istraživanja veza na genezu aluvijalnih sedimenata. Istraživanja su sprovedena na: beogradskom izvorištu podzemnih voda, regionalnim izvorištima Ključ i Trnovče, izvorištu



Medijana za vodosnabdevanje Niša, kao i drenažnim sistemima Kovin-Dubovac i Kničanin-Čenta. Efikasnost obalske filtracije i veštačkog prihranjivanja pri uklanjanju organske materije (huminske kiseline, hidrofilne kiseline, belančevine, lipidi, amino kiseline i ugljovodonici) može se pratiti na osnovu sumarnih parametara kao što su ukupni organski ugljenik i rastvoreni organski ugljenik [6]. Rezultati pokazuju da se filtracijom kroz vodonosnu sredinu, smanjuju se koncentracije ukupnog organskog ugljenika (TOC) a takođe i koncentracije mikropolutanata, pre svega farmaceutika i njihovih metabolita [7]. Sadržaj ukupnog organskog ugljenika iznosi prosečno 2,5 mg/l u reci Savi dok je u bunarima beogradskog izvorišta sadržaj oko 1 mg/l.

Prezentovani rad obuhvatiće procese koji se odvijaju u aluvijalnim akviferima, istraživanja i dobijene rezultate, koji pokazuju značaj podzemnih voda za vodosnabdevanje.

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## **Pharmaceuticals and pesticides in sediments, surface and groundwater of Danube river basin in Serbia**

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Contamination of surface water by different pharmaceuticals and pesticides has been reported in the last decade in a number of studies. Due to the high water solubility and often poor degradability polar organic compounds such as residues from pharmaceuticals and polar pesticides may, under unfavorable conditions, pass through all natural filtrations and leach into the groundwater aquifers. Standard water treatment plants are not equipped to remove pharmaceuticals as well as some pesticides from water and ultimately they can reach drinking water. Recently, pharmaceuticals have been detected at trace levels in drinking water in United States, Canada as well as in Europe. Despite of growing concern, drugs have not yet been included in the environmental regulations.

In 2009, in collaboration with Jaroslav Černi Institute, we have started the extensive task of monitoring pharmaceuticals and pesticides in surface and groundwater of Danube river basin in Serbia. At the beginning of this project we have developed the multiresidual methods for preconcentration of quantitative analysis of multiple classes of pesticides [1] and pharmaceuticals [2] based on solid phase extraction and HPLC-MS/MS analysis using ion trap mass spectrometer with electrospray ionization source.

Residues of 14 pesticides, belonging to the different chemical classes, were monitored. Pesticides were selected based on the existing regulations and the extent of their use in Serbia. Eighteen most frequently used pharmaceuticals in Serbia that belong to major groups of antibiotics, sedatives, antiepileptics, analgesics/antipyretics and cardiovascular drugs were chosen for the study. In addition two metamizole metabolites (4-FAA and 4-AAA) were analyzed and used as indicators of sewage contamination and markers for natural water pollution with wastewater

The surface water samples were collected from 11 sampling sites of the river Danube in different cities, and four sampling sites of its tributaries Tisa, Sava, Morava and Pek near their confluence with the Danube. The groundwater samples were collected from observation or operation wells in the vicinity of the surface water sampling sites. More than 100 samples were analyzed in last 4 years. The list of trace level pharmaceuticals and pesticides detected in surface and groundwater is presented in table 1. During the spring campaign 2011 we have analyzed river sediments from the Danube and its tributaries Tisa, Sava, Morava and the results are also included in table 1.

**Table 1.** Pharmaceuticals and pesticides detected in sediments and water samples

Sample	Pharmaceuticals	Pesticides
River water	4-FAA, 4-AAA, carbamazepine, azithromycin, lorazepam, metoprolol, bisoprolol, trimethoprim	carbendazim, atrazine, dimethoate, propazine, carbofuran,
Groundwater	4-FAA, 4-AAA, carbamazepine,	carbendazim, atrazine
River sediment	carbamazepine, diazepam, clopidogrel, erythromycin	dimethoate, atrazine, propazine, malathion, carbofuran

In the surface water samples, carbamazepine and metamazole metabolites (4-FAA and 4-AAA) were the most frequently detected drugs [3]. The residues of carbamazepine were detected in the concentration range below 100 ng l<sup>-1</sup>. The frequency of its detection can be explained by low sorption, resistance to biodegradation and low removal rate in waste water purification plants, as well as high administered doses of this antiepileptic drug. Carbamazepine residues detected in the Danube in Serbia are lower than those found in the surface waters in Germany, USA and Switzerland but higher than those reported for Finland and Canada. Carbamazepine is also detected in river sediments where it is partially removed. However, this drug is passing through natural filtrations, reaching the groundwater.

The pesticides found in the highest concentrations in the water of the Danube River Basin are atrazine and carbendazim [4]. Among monitored pesticides the most frequently found was carbendazim. However, concentrations of atrazine, one of the pesticides which is on the list of the priority substances, was present at levels far from those established in the legislation as maximum allowable concentrations. Both pesticides were also found in groundwater. The adsorption ability of these pesticides to the soil is low as they have not been detected in the sediments. Therefore the pesticides leaching to groundwater is expected.

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**USMENA IZLAGANJA**

*ORAL PRESENTATIONS*



## 6. simpozijum Hemija i zaštita životne sredine

*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

1.

### **Metode određivanja i praćenja stanja zagađenosti životne sredine**

*Methods of determining and monitoring  
environmental pollution*

## **Upotreba policikličnih alkana tipa sterana i terpana u identifikaciji zagađivača naftnog tipa u sedimentima reke Tise**

### **The use of polycyclic alkanes of sterane and terpane types in the identification of petroleum pollutants in the river Tisa sediments**

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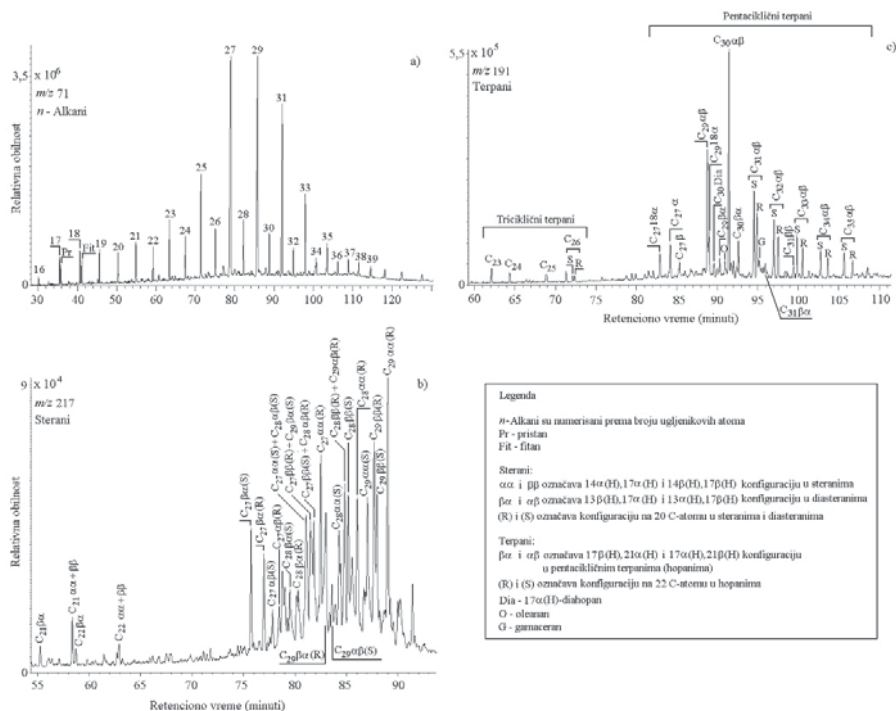
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Koncentracija nativnog bitumena (organske supstance rastvorne u organskim rastvaračima) u recentnim sedimentima nije definisana. Teorijski, ona može da bude u opsegu od 0% do 100% („sipeće nafte“). Zbog toga, na osnovu količine bitumena u sedimentima ne može pouzdano da se utvrdi da li je organska supstanca nativnog tipa, ili je u pitanju naftna zagađujuća supstanca antropogenog porekla. U nekim slučajevima u karakterizaciji organske supstance mogu da posluže *n*-alkani i izotopski sastav ugljenika. Međutim, imajući u vidu da nafta sadrži policiklične alkane tipa sterana i tri-, tetra- i pentacikličnih terpana sa karakterističnim raspodelama termodinamički stabilnijih, geolipidnih, i manje stabilnih, biolipidnih izomera, čvrsto se može pretpostaviti da se oni mogu upotrebiti za pouzdanije utvrđivanje prisustva naftnih zagađujućih supstanci u različitim segmentima životne sredine, uključujući i rečne sedimente [1].

U ovom radu ispitivani su sedimenti reke Tise u delu toka od mesta Kanjiža do ušća u reku Dunav (ukupno 11 uzoraka, dužina rečnog toka 153 km).

Uzorci su uzeti sa površine rečnih sedimenta (0-20 cm). Pošto su osušeni na vazduhu, metodom ekstrakcije po Soxhletu iz njih je izolovan bitumen. Metodom hromatografije na stubu iz bitumena su izolovane alkanske frakcije i zatim analizirane gasnohromatografsko-masenospektrometrijski (GC-MS). *n*-Alkani su identifikovani na osnovu jona  $m/z$  71, sterani na osnovu  $m/z$  217, a terpani na osnovu jona  $m/z$  191 (Slika 1).





**Slika 1.** Rapodele *n*-alkana (a), sterana (b) i terpana (c), tipične za 11 ispitivanih sedimenata reke Tise.

Svi ispitivani uzorci sedimenata sadrže približno istu količinu organske supstance sa potpuno identičnim raspodelama *n*-alkana, sterana i tri- i pentacikličnih terpana. Na osnovu raspodela *n*-alkana (u opsegu C<sub>16</sub>-C<sub>22</sub> neparni i parnih homolozi su ravnomerno raspoređeni; u opsegu C<sub>23</sub>-C<sub>37</sub> dominiraju neparni homolozi, Slika 1a) ne može se pouzdano utvrditi poreklo organske supstance. Međutim, tipične „nafte raspodele“ sterana i terpana (Slika 1b i c) čvrst su dokaz da je u delu toka reke Tise od mesta Kanjiža do ušća u reku Dunav prisutan isti tip zagađujuće supstance, čije raspodele biomarkera ukazuju na sirovu naftu.

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## **Određivanje lekova i pesticida u komunalnoj otpadnoj vodi**

### **Determination of pharmaceuticals and pesticides in urban wastewater**

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Komunalne otpadne vode, se svakodnevno ispuštaju u prirodne vodotokove i imaju negativne efekte kako na zdravlje ljudi tako i na životnu sredinu. Njihovim ispuštanjem dolazi do smanjenja kvaliteta vodenih resursa u meri u kojoj prirodni mehanizam prečišćavanja ne može nadoknaditi posledice zagađenja, kojima su svakodnevno izloženi. Nepoznavanje kvantiteta i kvaliteta otpadnih voda, uticaja na recipijente, kao i veoma nizak stepen prečišćavanja urbanih otpadnih voda kako u Srbiji tako i u Beogradu, predstavlja ozbiljan problem u oblasti zaštite životne sredine. Navedeni problemi i harmonizacija propisa sa Evropskom unijom, naglašavaju potrebu za praćenjem zagađenja životne sredine komunalnim otpadnim vodama pre svega da bi se utvrdio njihov sastav pre nego što budu ispuštene u prirodne vodotokove.

S obzirom na to da značajne količine lekova i pesticida koje dospevaju u prirodne vodotokove upravo potiču iz komunalne otpadne vode, predmet ovog rada je ispitivanje sadržaja ovih zagađujućih materija u komunalnoj otpadnoj vodi Beograda. Takođe je ispitivan sadržaj lekova i pesticida u komunalnoj otpadnoj vodi pre i posle tretmana u dva postrojenja za prečišćavanje otpadne vode (PPOV). Oba postrojenja imaju primarni i sekundarni tretman prečišćavanja. Odabrani su najčešće korišćeni pesticidi i lekovi u Srbiji, koji po svojoj strukturi pripadaju različitim grupama. Analizirani su sledeći pesticidi: simazin, atrazin, propazin, linuron, monuron (herbicidi); monokrotofos, dimetoat, malation, tebufenozid, imidakloprid, acetamiprid, karbofuran, karbaril (insekticidi); i karbendazim (fungicid). Ispitivani su sledeći lekovi: trimetoprim, sulfametoksazol (antibiotici); bromazepam, lorazepam, diazepam, karbamazepin (sedativi); i diklofenak (analgoantipiretik). Uzorci komunalne otpadne vode Beograda uzeti su na sedam različitih lokacija ispusta u junu i julu 2011. godine (Sajam, Ušće, Lasta, Istovar, Ada Huja 1, Ada Huja 2 i Višnjica). Otpadna voda pre i posle PPOV uzorkovana je u februaru i martu 2011. godine. Metode posebno razvijene za analizu tragova pesticida, a zatim i lekova u površinskoj i podzemnoj vodi su objedinjene u jednu multirezidualnu metodu koja je nakon validacije primenjena na uzorke otpadne vode [1, 2].

Kao tehnika pripreme uzorka korišćena je metoda ekstrakcije na čvrstoj fazi, čija je prednost istovremeno izolovanje, prečišćavanje i koncentrovanje analita iz tečnog uzorka na čvrstom adsorbensu. Za identifikaciju i kvantitativno određivanje

pesticida i lekova, korišćena je tačna hromatografija visoke performanse u sprezi sa tandem masenom spektrometrijom, za koju je pokazano da je metoda izbora za analizu polarnih jedinjenja iz složenih matrica, poput otpadne vode.

Najčešće detektovani analiti u uzorcima komunalne otpadne vode iz Beograda su pesticid karbendazim i lekovi lorazepam i diklofenak. Prisustvo karbendazima detektovano je u većini uzetih uzoraka, izuzev u onim sa mernih mesta Ušće i Lasta. Diklofenak je detektovan u svakoj tački uzorkovanja, dok lorazepam nije samo na mernom mestu Višnjica. Najviše analita detektovano je na mernom mestu Sajam. Ovo se može objasniti činjenicom da se upravo ovde sakuplja najveća količina otpadne vode Beograda. Lekovi su detektovani na svim mestima uzorkovanja, dok pesticidi nisu detektovani u uzorcima uzetim na mestima Ušće i Lasta. Od 14 ispitivanih pesticida 8 nije detektovano, dok od lekova nisu detektovani bromazepam i karbamazepin. Pronađene koncentracije pesticida kreću se u opsegu od 12,2 ng l<sup>-1</sup> (propazin) do 144,5 ng l<sup>-1</sup> (malation). Najniža koncentracija za lekove izmerena je za diklofenak (58,4 ng l<sup>-1</sup>), a najviša za sulfametoksazol (1184,2 ng l<sup>-1</sup>).

Tragovi lekova su detektovani u svim uzorcima iz postrojenja za prečišćavanje otpadnih voda, dok pesticidi nisu pronađeni. Od ispitivanih 7 lekova u uzorcima pre i posle tretmana detektovano je 5 i to: trimetoprim, sulfametoksazol, karbamazepin, lorazepam i diklofenak. Najviša koncentracija izmerena je u uzorcima pre tretmana (karbamazepin, 2675 ng l<sup>-1</sup> diklofenak, 5927 ng l<sup>-1</sup>). Kada se uporede koncentracije detektovanih lekova u uzorcima pre i posle tretmana može se zaključiti da su u izvesnoj meri lekovi uklonjeni iz otpadne vode i da se efikasnost uklanjanja kreće od 23,2 % (trimetoprim) do 97,5 % (lorazepam).

### Zahvalnica

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## Primena frakcionog faktorskog dizajna za određivanje fluora u uglju

### Application of fractional factorial design for determination of fluorine in coal

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Fluor, pored hlora predstavlja najznačajniji halogeni element u uglju. Tokom sagorevanja uglja fluor uglavnom isparava u obliku toksičnih gasovitih jedinjenja, što može izazvati niz ekoloških, ali i zdravstvenih problema [1]. Iz navedenih razloga, od posebnog značaja je razvoj metoda za određivanje sadržaja fluora u uglju.

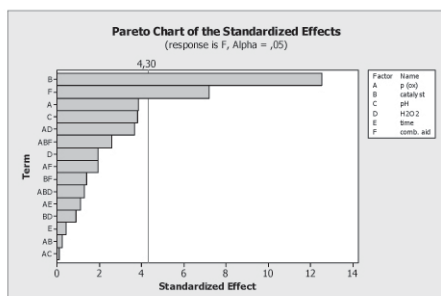
Cilj ovog rada je statistički pristup ispitivanju uticaja različitih parametara na ekstrakciju fluora iz uglja sagorevanjem u kiseoničnoj bombi, primenom frakcionog faktorijskog dizajna. Ekstrakcija fluora iz uglja sagorevanjem u kiseoničnoj bombi ispitana je promenom sledećih parametara: pritiska kiseonika, sadržaja katalizatora ( $V_2O_5$ ), koncentracije apsorpcionog rastvora, koncentracije  $H_2O_2$  u apsorpcionom rastvoru, sadržaja pomoćnog goriva (ulja) i vremena hlađenja kiseonične bombe nakon sagorevanja uzorka. Za svaki parametar izabrana su dva nivoa, minimalni (-1) i maksimalni (+1), koji su sistematizovani i prikazani u tabeli 1. Primenom statističkog programa *Minitab*, za šest parametara, na dva nivoa dobijena je matrica od 19 eksperimenata. Sadržaj fluorid-jona u apsorpcionom rastvoru određivan je primenom fluorid-selektivne elektrode (ISE27B, Consort, Belgija).

**Tabela 1.** Eksperimentalni parametri i njihovi nivoi

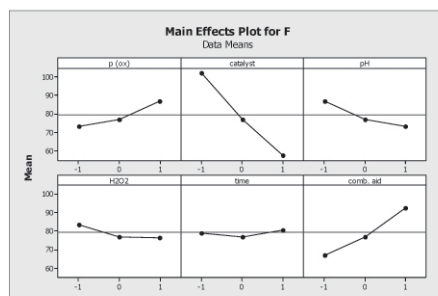
Br.	Parametar	Nivo 1 kodirana vrednost (-1)	Nivo 2 kodirana vrednost (+1)
1	p(O <sub>2</sub> ), atm	15	25
2	m(V <sub>2</sub> O <sub>5</sub> )/m(uglja)	0	0,25
3	c(NaOH), mol/L	0	1
4	w(H <sub>2</sub> O <sub>2</sub> ), %	0	1
5	t <sub>hlađenja</sub> , min	5	25
6	V(ulja), μL	0	100

Svrha primene eksperimentalnog dizajna je da se u što manjem broju eksperimenata (sagorevanja u kiseoničnoj bombi) odredi koji parametri najviše utiču na izdvajanje fluora iz uglja. Tri tipa grafičkih prikaza korišćeni su pri analizi i poređenju rezultata. Komparacija apsolutnih vrednosti efekata ispitivanih parametara na

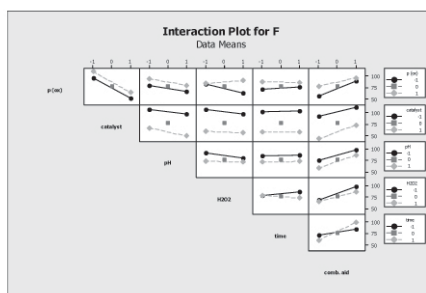
izdvajanje fluora iz uglja izvršena je konstruisanjem Pareto-grafika (slika 1). Analiza rezultata prikazanih na slici 1 ukazuje da na određivanje fluora u uglju sagorevanjem u kiseoničnoj bombi najveći uticaj imaju katalizator i dodatak pomoćnog goriva.



Slika 1. Pareto-grafik



Slika 2. Grafik glavnih efekata



Slika 3. Dijagram interakcija parametara

Drugi tip grafika su grafici glavnih efekata (slika 2) koji pružaju dodatne informacije o tome na koji način se koncentracija fluora izdvojena iz uglja menja sa promenom parametara sagorevanja između dva zadata nivoa. Na osnovu rezultata prikazanih na slici 2 uočava se da se sa dodatkom katalizatora značajno smanjuje koncentracija fluorid-jona u adsorpcionom rastvoru, odnosno sprečava se izdvajanje fluora iz uglja. Nasuprot tome, ekstrakcija fluora sagorevanjem uglja u kiseoničnoj bombi se povećava sa povećanjem količine dodatog pomoćnog goriva.

Interakcije između parametara, prikazane na slici 3, omogućavaju da se razmatraju ne samo apsolutni uticaji parametara na izdvajanje fluora iz uglja sagorevanjem u kiseoničnoj bombi, već i kako promena jednog parametra (između dva nivoa) utiče na izdvajanje fluora pri konstantnoj vrednosti drugog parametra.

Na osnovu prikazanih rezultata zaključuje se da primenjeni frakcioni faktorijski dizajn, omogućava da se u daljem eksperimentalnom radu pristupi optimizaciji analitičke metode [2] utvrđivanjem optimalnih vrednosti pritiska kiseonika i količine pomoćnog goriva.

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## **Rapid determination of pollutants by colorimetric reactions in $\mu$ FIA with thermal lens microscopic detection**

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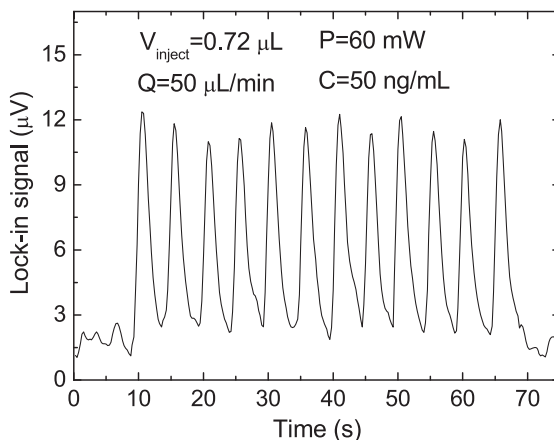
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Thermal lens microscope (TLM) [1] is one of recent promising developments of thermal lens spectrometry (TLS) towards miniaturization and automation. TLM not only has the advantage of high sensitivity as conventional TLS, but also has its unique capabilities such as high temporal ( $\sim$  ms) and spatial resolution ( $\sim$   $\mu$ m). These enable high sample throughput and small-volume detection of a variety of compounds by TLM with low sample/reagent consumption, when it is coupled to lab-on-chip chemistry [2]. In microfluidic chips, which offer a state-of-the-art environment for colorimetric reactions needed to enhance the specificity of TLM detection, the microchannels provide short diffusion distances and large specific interface areas, contributing to considerable reduction of analysis time compared to conventional chemical analysis. This was however not yet exploited for determination of analytes in flow injection analysis (FIA) mode. To demonstrate the advantages and potentials of TLM in such  $\mu$ FIA systems, a combined microfluidic-FIA-TLM method is proposed for the first time for rapid determination of pollutants by colorimetric reactions.

A new highly sensitive  $\mu$ FIA system with thermal lens microscopic detection was developed for rapid determination of analytes in water. Detection of on-line generated coloured compounds and complexes in a microchip eliminates unavoidable additional measures employed in conventional FIA-TLS to obtain a satisfactory FIA-TLS signal, such as the employment of a reversed FIA for higher sensitivity and the addition of extra solvents to the sample to match the physical properties of the reagent. More importantly, compared to the conventional FIA-TLS [3], 100 times lower sample/reagent consumption and 10 times shorter analysis time for one injection were obtained in such an experimental setup. Besides, the influence of the excitation power density and flow rate on the photodegradation of the analyte was investigated in detail.

It was found that under high excitation power densities (e.g.  $> 3 \times 10^4$  W/cm<sup>2</sup>) the photolabile analytes can be partially degraded, while by increasing the flow rate (e.g. from 20 to 50  $\mu$ L/min) the photodegradation of photolabile analytes can be reduced. Analytical signals for twelve sample injections in one minute (Fig. 1) can be recorded on this setup. For injections of sub- $\mu$ L samples into the microfluidic stream in a 50- $\mu$ m deep microchannel at excitation power 60 mW, limits of detection corresponding to an absorbance of  $9 \times 10^{-6}$  AU were achieved.

As an example of practical application of  $\mu$ FIA-TLM, determination of hexavalent chromium [Cr(VI)] in aqueous solution, following the colorimetric reaction with diphenylcarbazide, will be illustrated. For this case, which was previously studied in detail by conventional FIA-TLS, the LOD of 4 ng/mL was achieved with excitation at 514.5 nm. This LOD is lower than achieved by spectrophotometry in 1 cm cell, despite 200 times shorter optical pathlength in case of  $\mu$ FIA-TLM.



**Figure 1.**  $\mu$ FIA-TLM signal of Cr-DPC complex for twelve consecutive injections of Cr(VI) standard solution (50 ng/mL)

The presented  $\mu$ FIA-TLM setup offers possibilities for high throughput detection of pollutants in micro space by replacing the currently used injector with a more powerful and automated system to facilitate fast and consecutive injection of multiple samples.

### Acknowledgement

We thank the Slovenian Research Agency for financial support through the research program grant P1-0034 and the young researcher fellowship to M. Liu.

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## TOC kao indikator naftnog zagađenja u zemljištu

### TOC as an indicator of oil hydrocarbon pollution in soil

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Uparedni pregled primene koncentracije ukupnog organskog ugljenika (TOC - total organic carbon) kao indikatora naftnog zagađenja u zemljištu pokazuje mogućnost primene u eksperimentalnoj istraživačkoj praksi.

Specifičnost zemljišta koje je ispitivano je izuzetno visoka opterećenost i koncentracija naftnih ugljovodonika. Radi pojednostavljenja, u modelu koji će se koristiti u istraživanju, primenjena je koncentracija ukupnih naftnih ugljovodonika (TPH – total petroleum hydrocarbons) i njihova povezanost sa koncentracijom ukupnog organskog ugljenika u zemljištu (TOC - total organic carbon).

TOC je analiza kojom se mogu kvantifikovati sve težinske frakcije TPH.

Količina naftnih ugljovodonika se može utvrditi oduzimanjem količine TOC u nezagađenim uzorcima zemljišta, vode ili sedimenata od količine koja je izmerena u kontaminiranim uzorcima.  $TPH = TOC_{ncont} - TOC_{cont}$ .

Koncentracija TOC u vsoko kontaminiranoj vodi pokazala je značajnu pozitivnu korelaciju ( $r = 0,67$ ,  $P = 0,05$ ) sa TPH. Sa povećanjem koncentracije naftnih ugljovodonika, koncentracija organskog ugljenika se povećavala prema jednačini:  $TOC = -0,29 + 0,073 \text{ TPH}$  [1]

TOC je korišćen za praćenje kontaminacije uzoraka zemljišta naftnim ugljovodicima u rafineriji koja više nije u funkciji. [2] TOC je meren na terenu putem vlažne oksidacije korišćenjem hromne kiseline i kolorimetrije. U odabranim uzorcima merena je koncentracija ukupnih naftnih ugljovodonika. Poređenjem rezultata za TOC i TPH pokazano je da su vrednosti TOC više od 30 000 mg/kg.

Pokazana je linearna veza između ukupne koncentracije PAH (policikličnih aromatičnih ugljovodonika) i TOC ili BC (black carbon – crni ugljenik), sa koeficijentom linearne regresije 0,7277 i 0,9245, respektivno. [3]

Pokazano je da se TOC može koristiti kao indikator naftnog zagađenja u sedimentima zagađenim naftom. [4]

Određene vrednosti TPH, TOC PAH i PCB poslužile su da se definiše veza između TPH i TOC u sedimentima. Utvrđeno je da je veza između TPH i TOC u sedimentima:  $TOC = 0,45324 + 0,00011 \text{ TPH}$ , sa značajnom pozitivnom korelacijom ( $r = 0,98105$ ). [5]

Regresionom analizom sadržaja TOC i TPH pokazana je visoka korelacija između ova dva parametra u oba profila zemljišta ( $R^2 = 0,9906$ ,  $P$ -vrednost = 0,000 za profile zemljišta sa lokacije L1  $R^2 = 0,3553$ ,  $P$ -vrednost = 0,492 za profile zemljišta sa lokacije L2). Ovim je potvrđena validnost merenja TOC kao indikatora kontaminacije naftom prisutne u suvom zemljištu zagađenom izlivanjem nafte u Kuvajtu. [6]



U mnogim izvorima je potvrđena visoka korelacija između koncentracije ukupnog organskog ugljenika i sadržaja naftnih ugljovodonika u zemljištu, sedimentima i vodi, što potvrđuje da TOC može da se koristi kao indikator opterećenosti zemljišta naftnim ugljovodonicima.

Eksperimentalna istraživanja u okviru preliminarne rada na doktorskoj tezi su u toku.

### **Ključne reči**

*naftni ugljovodonici - TPH; ukupni organski ugljenik - TOC; kontaminacija; zemljište; sedimenti.*

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## MALDI-TOF-MS Characterization of Environmental Bacterial Isolates

### MALDI-TOF-MS karakterizacija bakterija izolovanih iz životne sredine

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#### Introduction

Various traditional and modern microbiological methods are available for the analysis and characterization of pure bacterial cultures. However, for some of them sample preparation can be very time-consuming. Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS) has the advantage of short measuring time, fast sample preparation and negligible sample consumption. With the utilization of MALDI-TOF MS biomolecules, such as proteins, peptides, oligosaccharides and oligonucleotides in the range of 400 and up to 350,000 Da, can be analysed within a few seconds [1]. Recently, determination of the bacterial samples as intact (whole) cells and also bacterial extracts has been developed [2]. Ten bacterial environmental isolates were characterized using 16SrRNA and subsequently MALDI-TOF-MS, with the use of the Maldi Biotyper database.

#### Material and Methods

**Isolation and media.** Hydrocarbon degrading bacteria were isolated as a pure culture using media with diesel as a sole source of carbon. Ferrous iron and sulphur oxidizing thionic bacteria were isolated as a pure culture after enrichment in 9K liquid medium and growth in microwell plates using the method of most probable number.

**Analysis of 16S rRNA gene sequences.** The genomic DNA of bacteria was extracted with the use of DNeasy Blood & Tissue Kit (Qiagen, Germany). The 16S rRNA genes were amplified by PCR using 27F (5'-AGAGTTTGATCMTGGCTCAG-3') and 1492R (5'-CGGCTACCTTGTTACGACTT-3') primers and amplified fragments were sequenced using the commercial MACROGEN (Netherlands) service.

**MALDI-TOF MS.** Autoflex II Bruker Daltonics, and Microflex Bruker Daltonics MSTM, software flexControl, flexAnalysis and Maldi biotyper were used. Matrix  $\alpha$ -Cyano-4-hydroxycinnamic acid; shots: 300; laser intensity: 35-40%; masses

in the range 2-20 kDa were determined in linear positive mode at an accelerated voltage of 19 kV. Bacterial samples were analysed as intact (whole) cells and also as ethanol extracts.

## Results

According to 16S rRNA gene analysis, 10 strains were *Brachybacterium* sp. CH-KOV3, *Rhodococcus* sp. H33-7, *Rhodococcus* sp. H63-1, *Acidithiobacillus ferrooxidans* strains B1 & B2, *Planomicrobium* sp. RNP01, *Micrococcus* sp. RNP04, *Rhodococcus* sp. RNP05, *Planococcus* sp. RNP07, and *Pseudomonas* sp. NS22. Through the comparison of the identification made by 16S rRNA gene sequencing and MALDI Biotyper software, positive identification was made only for two samples. *Rhodococcus erythropolis* (RNP05) and *Micrococcus luteus* (RNP04) were identified positive as secure genus identification and probable species identification. However, software was not able to identify genera *Brachybacterium*, *Acidithiobacillus*, *Planomicrobium*, *Planococcus* and *Pseudomonas*. In this case, the spectral/protein profile is referenced to a compiled database with 3,900 strains from over 2,000 well-characterized microbial species. However, it was shown that this database was not reliable for environmental samples and that the database was optimized for clinical samples. In addition, differentiation between two different phyla (Proteobacteria and Actinobacteria), genus (*Planomicrobium* and *Planococcus*), species (*Rhodococcus rhodochrous* and *Rhodococcus erythropolis*) and strains (*Acidithiobacillus ferrooxidans* strain B-1 and B-2) was studied. It was confirmed that the mass spectra of evolutionary close related environmental bacteria are more similar than between phylogenetically remote bacteria. The similarity of mass spectra was about 15% for evolutionarily distant phyla versus more than 90% similarity for close related strains. Dominant protein peaks are present in genus and species spectra, suggesting that the method is reliable for genus and species differentiation and identification.

## Conclusion

The results have confirmed that MALDI-TOF-MS is a fast and reliable automated method for clinical isolates but that the current database is not appropriate for the identification of bacterial environmental isolates. It is necessary to expand the database and analyse a number of bacteria from different habitats. MALDI-TOF-MS is an excellent method for a quick fingerprinting of intact bacterial cells.

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## Tečno-hromatografsko ponašanje i određivanje 6- i 8-supstituisanih hinolina

### Liquid chromatographic behaviour and determination of 6- and 8-substituted quinolines

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Hinolin,  $C_9H_7N$ , 129,16 g/mol, kao i njegovi supstitucionni derivati, su heterociklična jedinjenja sa sve većom primenom: u poljoprivredi (kao fungicidi i herbicidi), kozmetičkoj industriji (kao konzervansi, baktericidi i dezinfisijensi), medicini (u terapiji tuberkuloze, aritmije srca, hepatitisa B i malarije), elektronici (organske svetlosnoemisione diode), prehrambenoj industriji (prehrambene boje) kao i kompleksirajuće sredstvo u hemiji i hemijskoj industriji. Osim ovih namena, u životnoj sredini mogu da se nađu kao posledica nepotpunog sagorevanja organskih supstanci u motornim gorivima. S druge strane, ova grupa jedinjenja je, od strane Međunarodne agencije za istraživanje kancera, svrstana u grupu 2A verovatnih ljudskih kancerogena. Iz navedenih razloga postoji interes da se razvije pouzdana, jednostavna, selektivna i osetljiva metoda za njihovo određivanje.

U ovom istraživanju proučavana je mogućnost primene visoko-performansne tačne hromatografije (HPLC) za kvalitativno i kvantitativno određivanje 6-aminohinolina (6AQ), 6-hidroksihinolina (6HQ), i 8-hidroksihinolina (8HQ). Izvršen je razvoj HPLC metode pri čemu su sledeći parametri pokazali najbolje rezultate: razdvajanje je izvršeno izokratski na Bischoff C18 Prontosil ACE-EPS (250 x 4 mm, 5  $\mu$ m, 120 Å) koloni uz eluent 5% metanol/5% Briton-Robinson pufer/90% voda (pH 7,3). Komponente smeše se detektuju UV detektorom (Bischoff, 1010) na 240 nm, protok (Bischoff HPLC pumpa 2250) 1,0 ml/min. Injektovano je 20  $\mu$ l rastvora uzorka. Kolona je termostatisana na temperaturi od 25 °C.

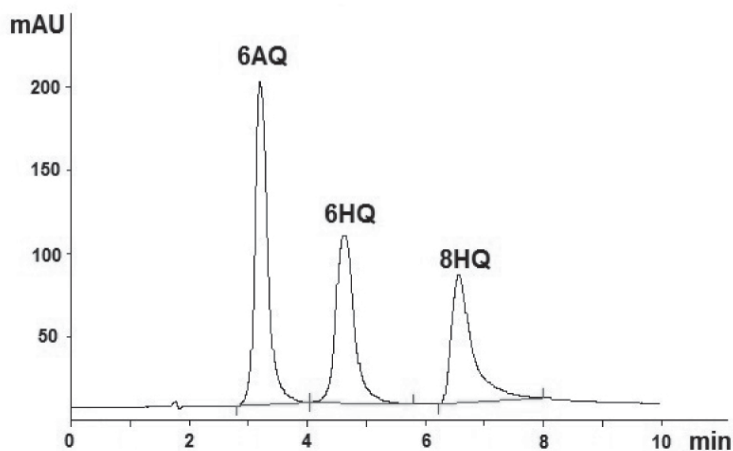
Polazeći od literaturnih podataka 1, pri referenznofaznom separacionom modu, jedna od stacionarnih faza od izbora je C18, a eluent smeša metanola i vode. U skladu sa tim izvršen je izbor kolone i eluenta za ispitivanja proučavanih hinolina, tako što je pri izokratskom načinu rada menjan sadržaj metanola u mobilnoj fazi, kao i njena pH vrednost. UV spektrofotometrijskim merenjima utvrđeno je da sve tri ispitivane supstance apsorbuju u oblasti  $250 \pm 20$  nm, i to dajući jedan apsorpcijski pik. Pri pH 7,3 (koja je utvrđena kao optimalna prema teorijskim i izmerenim  $pK_a$  vrednostima) utvrđeno je da je optimalna detekciona talasna dužina 240 nm, pri čemu su molarne apsorptivnosti,  $a$  ( $10^4$  dm<sup>3</sup>/mol cm):  $a$  (6AQ) = 3,7;  $a$  (6HQ) = 5,0 i  $a$  (8HQ) = 4,2. Linearna zavisnost apsorpcije od koncentracije, pri debljini spektroapsorbujućeg sloja od 10 mm i zapremini rastvora od 10  $\mu$ L, utvrđena je u širokom opsegu koncentracije. U Tabeli ispod su data retencionna vremena ispitivanih supstanci za neke od sastava mobilne faze.

**Tabela 1.** Ukupna retenciona vremena 6HQ, 6AQ i 8HQ za eluente različitog sastava (v/v/v)

Eluent MeOH/BR/H <sub>2</sub> O	8/2/90	5/5/90	2/8/90
Jedinjenje	Ukupno (bruto) retenciono vreme (min)		
6HQ	2,18	4,85	36,22
	2,32	4,84	36,95
6AQ	2,03	3,29	14,94
	2,03	3,27	14,93
8HQ	2,68	7,35	-
	2,69	7,64	-

Na osnovu podataka prikazanih u prethodnoj Tabeli (kao i na osnovu separacionih koeficijenata pikova i broja teorijskih platoa) može se zaključiti da eluent od izbora za izokratsko HPLC određivanje ispitivanih hinolina ima sastav 5% Mtanol/5%BR pufer pH 7,3/90% H<sub>2</sub>O.

Na Slici ispod prikazan je jedan od hromatograma smeše ispitivanih hinolina.



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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

2.

**Transformacije i  
rasprostiranje zagađujućih  
supstanci**

*Transformation and propagation  
of pollutants*

## **Karakteristike i segregacija masenih koncentracija urbanog aerosola centralnog Balkana (Beograd)**

### **Characteristics and size-segregated mass concentration of urban aerosol of the central Balkans (Belgrade)**

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Aerosoli su važne komponente sistema Zemlje. Smanjuju vidljivost, pogoršavaju zdravlje ljudi, deponuju zagađujuće materije u ekosisteme i direktno i indirektno utiču na radijacioni bilans klimatskog sistema. Sastav aerosola je u vezi sa toksičnošću i oštećenjem zdravlja ljudi. Radiacioni bilans Zemlje, globalna klima i efekat aerosola na planetarni energetski bilans, distribucije masenih veličina čestica i njihovih hemijskih karakteristika su još uvek nedovoljno razjašnjeni.

#### **Metode merenja**

Ispitivanje segregacija veličina urbanog aerosola Beograda (44°49'14"N, 20°27'44"E) rađeno je u periodu jun – decembar 2008. Kao reprezentativna lokacija, u zoni uticaja urbanih izvora emisija aerosola, izabrana je centralna zona grada - Studentski trg. Za sakupljanje i segregaciju uzoraka aerosola korišćen je High Volume Cascade Impactors, Model TE-236. U periodu uzorkovanja sakupljeno je 32 seta uzoraka, dinamikom svaki šesti dan. Vreme trajanja sakupljanja svakog pojedinačnog seta je bilo 48 sati. Segregacija čestica urađena je u šest intervala aerodinamičkog prečnika ( $D_p$ ):  $D_p \leq 0.49 \mu\text{m}$ ,  $0.49 \leq D_p \leq 0.95 \mu\text{m}$ ,  $0.95 \leq D_p \leq 1.5 \mu\text{m}$ ,  $1.5 \leq D_p \leq 3.0 \mu\text{m}$ ,  $3.0 \leq D_p \leq 7.2 \mu\text{m}$  and  $D_p \geq 7.2 \mu\text{m}$ . Mase sakupljenih uzoraka aerosola na vlaknastom filteru su izmerene gravimetrijskom metodom koristeći vagu KERN ABT 120-5DM (klase tačnosti I i preciznosti 0.01 mg). Vaga i filteri su čuvani na temperaturi  $20 \pm 5^\circ\text{C}$  i vlažnosti  $45 \pm 5\%$  u struji azota, pre i za vreme merenja. Proširena nesigurnost gravimetrijskog merenja mase bila je do 4% [1].

Oblik, veličine i hemijski sastav finih i čestica krupnog moda su analizirani SEM tehnikom. Mikrofotografije su dobijene pomoću Nova NanoSEM 230, FEI, USA. Isti uređaj je korišćen i za EDX analizu. Hemijska karakterizacija



čestica je urađena na semi-kvantitativnom nivou. Čestice sakupljene na filteru nakon SEM analize su prekrivene slojem Pt (4nm) u cilju poboljšanja provodljivosti uzoraka.

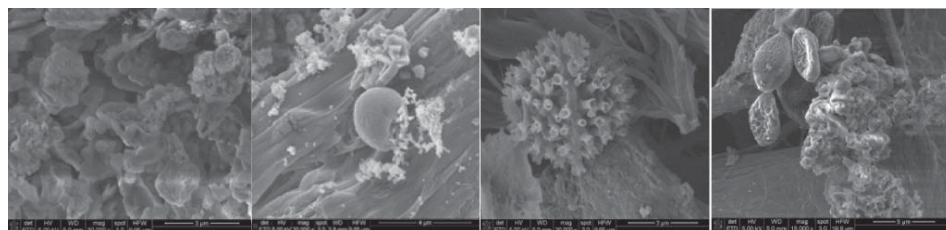
## Rezultati

Vrednosti masenih koncentracija čestica, uključujući srednje vrednosti, standardne devijacije ( $\sigma$ ) i doprinose finog i moda krupnih čestica u mernoj kampanji date su u Tabeli 1.

**Tabela 1.** Masene koncentracije aerosola  $m_{GM}$  ( $\mu\text{g m}^{-3}$ ) prema intervalima veličina aerodinamičkog prečnika čestica  $D_p$  ( $\mu\text{m}$ )

	Mean $\pm \sigma$	% of total $\Sigma$
$D_p \leq 0.49$	$7.9 \pm 5.0$	41.6
$0.49 \leq D_p \leq 0.95$	$2.7 \pm 1.5$	14.2
$0.95 \leq D_p \leq 1.5$	$1.8 \pm 1.0$	9.5
$\Sigma_{(fine)}$	$12.4 \pm 6.6$	65.3
$1.5 \leq D_p \leq 3.0$	$2.0 \pm 1.2$	10.5
$3.0 \leq D_p \leq 7.2$	$3.3 \pm 2.0$	17.4
$D_p \geq 7.2$	$1.3 \pm 0.8$	6.8
$\Sigma_{(coarse)}$	$6.6 \pm 3.7$	34.7
Total $\Sigma$	$19.0 \pm 9.7$	100

Na slici 1. prikazane su mikrofotografije nekih od uzoraka sakupljenih u mernoj kampanji sa karakterističnim česticama neorganskog i organskog porekla.



**Slika 1.** Morfologije nekih uzoraka sakupljenih u mernoj kampanji

Morfološki i hemijski sastav čestica je pokazao najobilnije prisustvo ugljeničnih čestica, prisustvo organskih kao i neorganskih materija prirodnog i antropogenog porekla. Sadržaj ugljenika se kretao do oko 70% pa i više. U uzorcima su dominirali i drugi elementi prema redosledu obimnosti: O, Mo, Si, Fe, Ca, Al, K, Mg.

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## **Basic chemical and physical characteristics of soils in four Belgrade parks**

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This paper presents basic physical and chemical characteristics of soils from four Belgrade parks. Soil samples were collected in May of 2011 from four city parks: Studentski Park (SP), Botanicka Basta (BB), Zemunski Park (ZP) and Karadjordjev Park (KP). At each site, composite samples were taken below the tree crowns and from the open space not sheltered by tree branches. Samples taken below trees were taken at each 10 cm, up to 50 cm depth, except at the KP site where the sampling was up to 30 cm depth. At the open space, samples were taken from first 10 cm. Soils at all sites were characterized as Anthrosols. Anthrosols are group of soils that have been formed or heavily modified by long-term human activity [1].

Soil physical and chemical characteristics were analyzed using standard methods. Soil reaction in water (1:2.5) and in 1 M KCl (1:2.5) suspension was determined potentiometrically [2]; organic matter content was determined by Tjuri method [2]; calcium-carbonate content was determined by volumetric method using Scheibler calcimeter [3], and particle-size distribution was analyzed by the sieve and pipette method [4].

Soil in Studentski Park has medium texture. It varies from loam, silt loam to silty clay loam [5]. Organic matter content in the first 10 cm is 4.38% and it gradually decreases with depth, having the lowest content between 40-50 cm, 3.23% respectively. Soil reaction in water solution ranges from 7.44 to 7.93, while in 1 M KCl, it ranges from 6.94 to 7.39, gradually increasing with depth. Lime content ranges from 11.9% to 26% and it also increases with depth.

Soil in Botanicka basta also has silt loam and silty clay loam texture with more than 50% of silt [5]. Organic matter content in the first 10 cm is around 5% and it decreases gradually from 2.1% at second depth to 1.4% at the deepest soil layer. Soil reaction in water solution ranges from 7.43 to 8.05, while in 1 M KCl it ranges from 7.12 to 7.60, increasing gradually with depth. Lime content ranges from 9.8% to 22.2% and it also increases gradually with depth.

Soil in Zemunski Park has silt loam to loam texture [5]. Organic matter content in the first 10 cm is around 5% and it decreases to 1.52% at the 40-50 cm depth. Soil reaction in water solution and in 1 M KCl varies from 7.72 to 8.05 and from 7.07 to 7.50, respectively. Lime content ranges from 12.4% to 20.8% and it also increases with depth.

Soil in Karadjordjev Park has lower lime content, from 3.8% to 8.8%, and it has silty clay loam texture. Organic matter content varies from 2.6 to 2.77% in all samples. Soil reaction in water solution ranges from 7.73 to 7.94, while in 1 M KCl it ranges from 7.15 to 7.3.

The samples from all sites have silt content higher than 45%, and they have loam, silt loam or silty clay loam texture. The samples from SP, BB and ZP sites are slightly to moderately alkaline, rich in carbonates, with organic matter content around 5% in the first 10 cm, which gradually decreases with depth. The results of soil analysis at KP site indicate lower organic matter content which does not vary with depth, and lower content of carbonates compared to other sites.

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## **Modeling of transformation in oil polluted soils**

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The degree and time of oil transformation in the biosphere depend on the content of its light fraction (boiling below 200 °C), paraffin waxes, aromatic hydrocarbons, hetero-organic compounds, resins and asphaltenes, and on the time elapsed since the oil pollution episode, as well as on the climatic and hydrological conditions. A significant portion of the light oil fractions decomposes and volatilizes already on the soil surface. Paraffin waxes are less destructible and hardly oxidized in air, and, getting into the soil pores, they inhibit free water exchange and ventilation in the soil, which results in a complete degradation of biocenosis. Aromatic hydrocarbons are hard to decompose; they present the most toxic oil components. Resins and asphaltenes are not easily digestable by microorganisms, their metabolic process is so slow that it can last tens of years. Any form of sulphur contained in oil (hydrogen sulfide, sulfides, mercaptans, thiophenes, free sulfur, etc.), exerts a toxic effect on the living organisms.

In order to develop effective measures for remediation of contaminated soils, it is necessary to know the natural purification mechanisms, the factors that accelerate this process, the quantitative criteria that characterize different stages of change of oil, soil, and vegetation, and the recovery rate of the latter.

The purpose of this investigation is to obtain the data for monitoring of environmental pollution by oil and oil products.

To achieve the goal, special model experiments using natural objects were carried out. A high-sulfur oil (Stotal = 2.3%) with an average density of 875 kg/dm<sup>3</sup> was used as a pollutant. An oil sample was applied on soil (humidity of 2.1%) in the amount of 4% by weight. The natural soil microflora served as decomposing microorganisms. Simultaneously, an experiment was conducted on the use of nitrogen and phosphate fertilizers to stimulate the growth of microorganisms. A sterile soil sample coated with oil (4%) was used as a reference. The investigation was carried out at 16-18 °C. During the experiments, the influence of microflora on the change of chemical composition of the oil was evaluated in 30, 60, 90 and 120 days. Residual oil from the soil was extracted with chloroform, whose resin and asphaltene content was determined and the composition of saturated and aromatic hydrocarbons was analyzed. To obtain the data on the change in the composition of oil contamination, use was made of infrared spectroscopy and gas chromatography-mass spectrometry (GC-MS).

According to the IR spectroscopy data, the number of oxygen-containing compounds in residual (biodegraded) oil increases with time, while the number of CH<sub>2</sub> and CH<sub>3</sub> groups decreases (absorption bands 1470 and 1380 cm<sup>-1</sup>).

The content of asphaltenes in the original oil is 3.1%, that of resinous components is 10.3%, and the amount of oils (hydrocarbon concentrate) is 86.6% by weight. The amount of oils decreases, while that of resin-asphaltene substances increases in biodegraded oil in comparison with the original oil. In the original oil and biodegraded samples, the maximum number of n-alkanes are low molecular n-C<sub>14</sub> + n-C<sub>17</sub> (factor odd/even 0.9-1.0). Higher values of the coefficients  $K^* = (Pr + Ph)/(n-C_{17} + n-C_{18})$  for biodegraded samples indicate a decreased content of normal alkanes in the residual oil in contrast to that of isoprenanes, which is due to the fact that normal alkanes are the first to be subjected to biodegradation.

A change in the oil composition correlates with the changes in the microbial community. The microbiological analysis data demonstrated that within the first two months of the experiment the number of heterotrophic organisms tended to decrease in the scenario with a mineral fertilizer compared to that without any addition. Note that the number of hydrocarbon-oxidizing microorganisms (COMs) is noticeably increased as a result of application of biogenic elements. The side effects are attributed to the tendency in the microbiological community towards a higher population of the bacteria capable of assimilating oil hydrocarbons as a sole source of carbon. An application of additional sources of nitrogen and phosphorus was found to favor a fast growth of this group of microorganisms in the 3-rd scenario of our experiment. The above-mentioned decrease in the total number of heterotrophic microorganisms is likely to be due to the cumulative soil toxicity resulting from a fast accumulation of oil degradation products. A higher level of soil toxicity in the soil sample with a mineral fertilizer is also indicated by a larger number of lower fungi (12 million colony forming unit CFU/1g soil) versus the sample without mineral fertilizers (8 million CFU/1g soil).

A decrease in the total number of microorganisms and, in particular, hydrocarbon-oxidizing microorganisms is due to a gradual depletion of biogenic elements in the soil.

## **Degradation of chlorantraniliprole on plants, soil and in water**

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Chlorantraniliprole (CAP) belongs to the third generation of pesticides with a new and specific mode of action as activator of ryanodine receptors [1]. This anthranilamide compound is formulated as Coragen, and is becoming widely used on fruit trees, vines, cereals and potatoes for control of pests, especially those belonging to the order of Lepidoptera.

According to producer's observations, chlorantraniliprole features high photo and thermal stability, short withdrawal period and high persistence on agricultural crops. However, several questions of insecticide's fate in the environment remain. Besides data provided by producers which are accepted also by organisations such as EPA and Health Canada, and besides scientific publications that are based on research conducted in the laboratories of producers, there is no independent scientific research carried out about the behavior of chlorantraniliprole in the environment, including its degradation pathways and transformation products, into which the pesticide transforms.

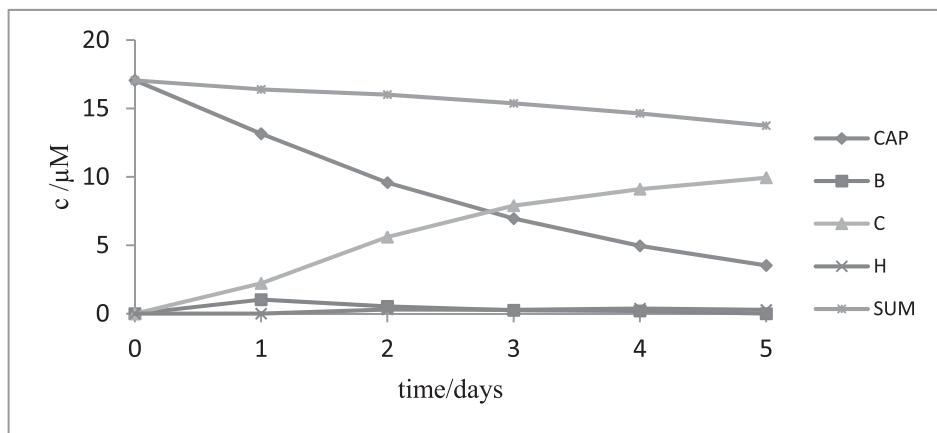
In the present study, we aimed to obtain an overview of CAP's fate in the environment by studying its stability in natural environment (vineyard) as well as under simulated sunlight conditions in the laboratory. The concentrations of CAP were monitored in vegetation (grass) and soil several months after application.

It was observed that under given meteorological conditions over three months were required for removal of 90% CAP from vegetation. However, CAP was removed from soil in less than a month, which was attributed to washing off of the top soil layer containing CAP. This indicated that CAP can represent a hazard for aquatic environment exposed to run-off waters from vineyards or other agricultural areas. This experiment suggested that considerable amounts of CAP might end up in the aquatic environment due to the runoff in case of rain-showers. Once reaching the water compartment, various transformations of CAP may take place. For this reason chemical and photochemical degradation of CAP in aqueous solutions was investigated under laboratory conditions.

Photodegradation studies of CAP in aqueous solutions were carried out using simulated sunlight, irradiating at high intensity (750 W/m<sup>2</sup>). Because of low solubility of CAP in water, solutions of CAP (17 µM) were prepared in acetonitrile – tap water mixture (1:4 v/v). Dark control was prepared in a same way, but wrapped in an aluminium foil. Samples were irradiated with simulated solar light for 5 days and their degradation was monitored daily by HPLC.

Photodegradation of CAP with simulated solar light followed the first order kinetics with a half life of 2.4 days. Series of experiments showed that CAP's early-stage photodegradation pathway leads to three degradation products, which have been

characterized by IR, NMR and MS. With the photodegradation of CAP, compound C was the main product observed (Fig 1.). It accounted for transformation of about 65% of initially present CAP, while other products were detected only in traces. In dark controls, the concentration of CAP in 5 days dropped to approximately 75% of its starting concentration, indicating that CAP undergoes chemical degradation also in the absence of light. Only one product (compound H) was detected in dark controls. Compound H was found also in irradiated sample, but probably due to its phototransformation, its concentration remained low.



**Figure 1.** Chemical and photochemical degradation of CAP and formation of products (B, C, H) under simulated sunlight.

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## The influence of metal ions on interactions of water with aromatic pollutants

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Understanding interactions in water solutions is very important in assessing the impact of water pollutants. Rapid water flow through hydrophobic environments can be applied in processes of water purification [1]. Water-aromatic interactions are thus of great importance in these processes, primarily by using carbon nanotubes [2]. Moreover, aromatic compounds are commonly encountered as toxic constituents of water. In addition, properties of water are influenced by metal ions that are commonly present in water. Here we present our results on metal ion influence on water/benzene interactions.

By searching Cambridge Structural Database (CSD), conformations in which water molecule or one of its O-H bonds is parallel to the aromatic ring plane were discovered. Calculated interaction energies at CCSD(T)/CBS level show that interactions are significant at large horizontal displacements of water (-2.45 kcal/mol at 2.6 Å), i. e. out of the aromatic ring and out of the C-H bond region (*Figure 1*). These energies are comparable with energy of slipped-parallel benzene/benzene dimer [3]. Interaction energies also reveal that at longer horizontal displacements (3.5 Å) interactions are also substantially strong, up to -1.5 kcal/mol.

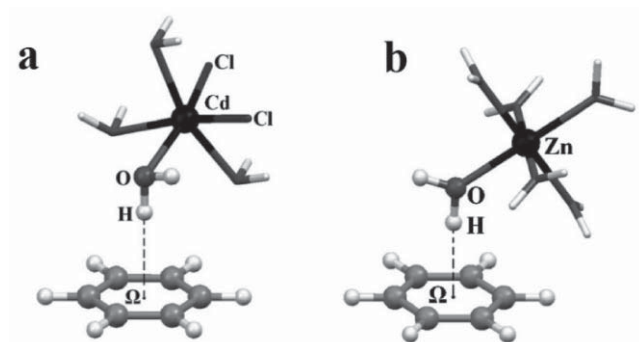


**Figure 1.** Benzene/water interactions at large horizontal displacements

Water/benzene interactions become significantly stronger when the water molecule is coordinated to a metal ion. Energies of OH/ $\pi$  interactions between benzene molecule and various neutral and positively charged aqua complexes were calculated at MP2/def2-QZVP level of theory. OH/ $\pi$  interactions of coordinated water with benzene are stronger than OH/ $\pi$  interactions of non-coordinated water with benzene (-3.36 kcal/mol), even if the aqua complex is neutral (energy for  $[\text{CdCl}_2(\text{H}_2\text{O})_4]$ , *Figure 2a*, is -6.86 kcal/mol). Positively charged aqua complexes form much stronger OH/ $\pi$  interactions with benzene (up to -14.85 kcal/mol, for  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ , *Figure 2b*) [4]. Additionally, long-range interactions are strong. At



the H-Ω distance of 3.0 Å, the interaction energy is up to -4.91 kcal/mol for neutral complexes and up to -10.76 kcal/mol for positively charged complexes. The reasons for stronger interactions of coordinated water are larger partial positive charges of the water hydrogen atoms in the complexes and the larger size of aqua complexes compared to the water molecule. The existence of coordinated water/benzene interactions was confirmed by performing CSD search.



**Figure 2.** OH/ $\pi$  interactions of neutral (a) and positively charged (b) aqua complexes with benzene molecule

Our results show that interactions of benzene with water that contains metal ions are much stronger. This substantially influences the solubility of aromatic pollutants, since metal ions are regularly present in liquid water in the environment.

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## 6. simpozijum Hemija i zaštita životne sredine

*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

3.

### **Sistemi za prečišćavanje, nove čistije tehnologije i oprema**

*Purification systems, new cleaner  
technologies and equipment*

## Fotokatalitička redukcija ugljendioksida do metanola pomoću kompozitnog katalizatora

### Photocatalytic reduction of carbon dioxide to methanol using composite catalyst

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Evidentni efekti promene klime - globalno zagrevanje izazvani su povećanjem koncentracije u atmosferi tzv. gasova staklene bašte: CH<sub>4</sub>, CFC a posebno ugljendioksid. Uslovljeno time, kao imperativ, nameće se potreba za razvojem novih procesa i tehnologija koje bi selektivno, efikasno i ekonomski opravdano omogućavale smanjenje sadržaja CO<sub>2</sub> u atmosferi.

Fotokatalitička redukcija CO<sub>2</sub> sa vodom do metanola je relativno nov i atraktivan postupak za smanjenje sadržaja CO<sub>2</sub> u atmosferi i osnova za razvoj novih procesa, tehnologija i proizvoda [1-3].

U ovom radu ispitan je uticaj niza tehnoloških parametara: vreme ozračivanja ( $t_{oz}$ ), koncentracija fotokatalizatora ( $C_{FK}$ ), pritisak CO<sub>2</sub> ( $P_{CO_2}$ ) i koncentracije metala u katalizatoru ( $C_M$ ) na katalitičku aktivnost i kvantnu efikasnost postojećih (P-25 i TiO<sub>2</sub>) i novo-razvijenog kompozitnog fotokatalizatora (M/TiO<sub>2</sub>).

Fotokatalizator P-25 je komercijalni pirogeni TiO<sub>2</sub> proizvođača Degussa, Nemačka. Katalizatori TiO<sub>2</sub> i M/TiO<sub>2</sub> su sintetisani prema postupku opisanom u radu Adnađevića i saradnika [4].

Fotokatalitička redukcija CO<sub>2</sub> sa vodom vršena je u cilindričnom kvarcnom reaktoru u kojim je određena masa fotokatalizatora suspendovana u 0,2 N rastvoru NaOH. Ugljendioksid je uveden u reaktor pri kontrolisanom pritisku i protoku. Fotoaktivacija sistema vršena je sa Hg lampom ( $\lambda=254$  nm) postavljenom u centar fotokatalitičkog reaktora, a energetska fluks je meren luks metrom (Oriel inst.). Koncentracija metanola određena je gasno hromatografskom metodom (GC-FID Varian 3300, kolona PORAPAK Q).

Na osnovu dobijenih rezultata utvrđeno je da:

- Povećanje vremena ozračivanja ( $t_{oz} \geq 2$  h),  $C_{FK} = 1$  g/L;  $P_{CO_2} = 125$  kPa;  $C_M = 2\%$ , dovodi do povećanja prinosa metanola kod ispitivanih fotokatalizatora. Prinos metanola kompozitnog katalizatora M/TiO<sub>2</sub> je od 2 do 10 puta veći od prinosa P-25 i TiO<sub>2</sub>. Povećana fotoaktivnosti M/TiO<sub>2</sub> je posledica redistribucije električnog naelektrisanja između TiO<sub>2</sub> i metala, gde metal služi kao lovac elektrona i na taj način poboljšava separaciju elektrona od šupljina.
- Energetska efikasnost kompozitnog fotokatalizatora, pri  $C_{FK} = 1$  g/L;  $P_{CO_2} = 125$  kPa;  $C_M = 2\%$ , je šest puta veća od energetske efikasnosti P-25 fotokatalizatora i četiri puta veća od energetske efikasnosti TiO<sub>2</sub>.

- c) Kvantna efikasnost kompozitnog fotokatalizatora, pri  $C_{FK} = 1\text{g/L}$ ;  $P_{CO_2} = 125\text{kPa}$ ;  $C_M = 2\%$ , je skoro sedam puta veća od kvantne efikasnosti P-25 i  $\text{TiO}_2$  fotokatalizatora. Ono što je posebno važno je da je kvantna efikasnost  $\text{M/TiO}_2$  fotokatalizatora gotovo duplo veća od maksimalne prirodne efikasnosti koja se ostvaruje kod makro algi [5].
- d) Promenom koncentracije metala u  $\text{M/TiO}_2$  fotokatalizatoru, pri  $C_{FK} = 1\text{g/L}$ ;  $t_{oz} = 6\text{h}$  i  $P_{CO_2} = 125\text{kPa}$ , prinos metanola raste do koncentracije metala od 2%, a zatim opada sa porastom koncentracije metala.
- e) Promenom pritiska  $\text{CO}_2$ , pri  $C_{FK} = 1\text{g/L}$  i  $t_{oz} = 6\text{h}$ , prinos metanola raste sa porastom pritiska u opsegu od 100 do 125 kPa, a zatim opada. Povećanje prinosa metanola na pritiscima  $\text{CO}_2$  manjim i jednakim 125 kPa posledica je ubrzanje fotokatalitičke redukcije sa porastom pritiska ugljendioksida. Smanjenje prinosa metanola pri pritiscima ugljendioksida većim i jednakim 125 kPa je najverovatnije uzrokovano formiranjem viših ugljovodoni-ka ( $\text{C}_2\text{H}_5\text{OH}$ ) u koje se metanol dalje konvertuje.
- f) Porast koncentracija fotokatalizatora od 0 do 1g/L, pri  $C_M = 2\%$ ;  $t_{oz} = 6\text{h}$  i  $P_{CO_2} = 125\text{kPa}$ , dovodi do povećanje prinosa metanola. Nasuprot tome, pri koncentracijama fotokatalizatora većim i jednakim 1g/L, povećanje koncentracije dovodi do smanjenja prinosa metanola. Smanjenje prinosa metanola, pri koncentracijama fotokatalizatora većim i jednakim 1g/L, najverovatnije je posledica smanjenje penetracije UV zračenja od strane fotokatalizatora

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## Uticaj visokofrekventnog elektromagnetnog polja na merenje pH staklenom elektrodom

### The influence of high frequency electromagnetic field on pH measurement with the glass electrode

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U literaturi postoje podaci o delovanju visokofrekventnog elektromagnetnog polja na voltometrijsko ponašanje jona teških metala u prisustvu butanola[1] kao i na striping voltometriju[2]. Nisu nađeni podaci, u literaturi, o uticaju visokofrekventnog elektromagnetnog polja na merenje pH rastvora.

U cilju ispitivanja uticaja visokofrekventnih elektromagnetnih polja, različitih frekvencija, izgrađen je sistem sa mogućnošću promene frekvence elektromagnetnog polja u opsegu 20MHz - 200MHz i promenljive snage do 3W. Ovaj sistem čine RF signal generator GW Instek GRG-450B i pojačivač LZY-22.

Za merenje pH korišćen je pH-metar ISKRA MA 5730 i kombinovana staklena elektroda Metrhrom NTC/3MKC1.

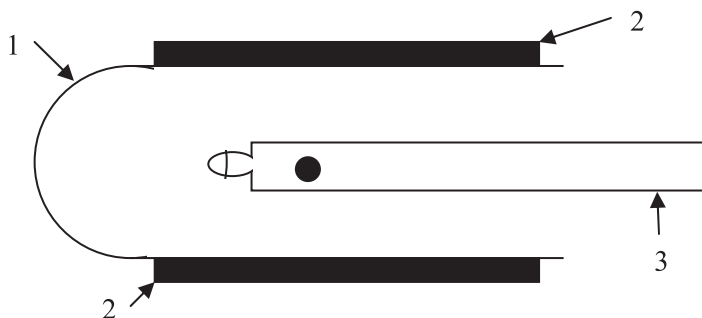
U ispitivanjima je korišćen puferski rastvor,  $\text{pH}=7.00\pm0.02$  na  $25^{\circ}\text{C}$ , Entech Instruments. Merenje pH puferskog rastvora vršeno je u cilindričnoj ćeliji, prečnika 20 mm i visine 80 mm (sl. 1), od stakla, u kojoj se nalazio puferski rastvor i kombinovana staklena elektroda. Sa spoljne strane ćelije nalazile su se, priljubljene uz zid i pričvršćene lepljivom trakom, dve elektrode od bakarnog lima (visine 57 mm i širine 30, odnosno 37 mm). Elektrode su spojene sa izvorom elektromagnetnog zračenja.

#### Postupak merenja

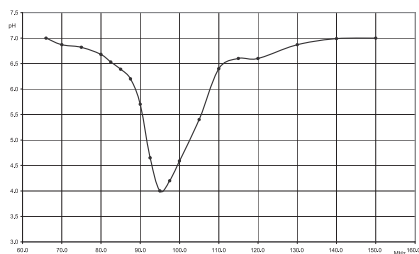
Na spoljne bakarne elektrode dovođen je visokofrekventni elektromagnetni signal snage 1 W, čija je frekvencija u opsegu 20MHz - 200MHz u početnim merenjima a kasnije u užem opsegu. Nakon svake promene frekvencije stabilizovala se vrednost pH za najduže 10 s, tako da je jedna serija merenja izvršena za najduže vreme od 16 min, tako da je sobna temperatura za taj period bila konstantna.

Na slici br. 2 date su očitane vrednosti pH u zavisnosti od frekvencije elektromagnetnog zračenja. Dobijena kriva nedvosmisleno ukazuje da elektromagnetno polje utiče na pH vrednosti koju pokazuje sistem za merenje pri čemu su očitane vrednosti pH manje od pH vrednosti puferskog rastvora. Smanjenje očitane vrednosti pH zavisi od frekvencije elektromagnetnog zračenja. Kriva koja se dobija povezivanjem dobijenih tačaka na grafikonu koji pokazuje promenu očitane vrednosti pH od frekvencije elektromagnetnog zračenja ima maksimum, tj. najmanju

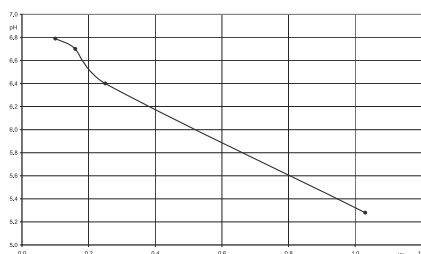
očitanu vrednost pH pri frekvenciji od 95MHz, u ovom slučaju to je pH=3.9, tj. očitana vrednost pH je za tri pH jedinice niža od vrednosti pH korišćenog pufer-skog rastvora.



**Slika 1.** Ćelija za merenje pH. 1.Stakleni sud. 2.Bakarna elektroda 3. Kombinovana elektroda



**Slika 2.** pH vrednosti na različitim frekvencama elektromagnetnog zračenja



**Slika 3.** pH vrednost za različite snage elektromagnetnog polja na 95 MHz

Vrednost pH zavisi i od snage elektromagnetnog polja. Sa povećanjem snage, pri konstantnoj frekvenciji, očitana vrednost pH se smanjuje, što se vidi na sl. 3 za frekvenciju od 95 MHz. Smanjenje je linearno sa snagom polja.

Na osnovu iznetog je utvrđeno da će očitana vrednost pH pri merenju staklenom elektrodom zavisiti od frekvencije i od jačine elektromagnetnog polja u kome se nalazi rastvor sa mernim sistemom.

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## **Bezotpadna tehnologija u preradi lekovitog i aromatičnog bilja**

### **Free waste technology in the processing of medicinal and aromatics plants**

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Proizvodnja i promet aromatičnih biljaka je u svetu izuzetno značajna, organizovana i bitna privredna delatnost. Smatra se da se samo biljke iz familije Lamiaceae gaje na više od 500.000 hektara. Promet tih materija se u zemljama zapadne Evrope za poslednjih deset godina udvostručio. Takav porast rezultat je jačanja ekološke svesti i saznanja o često neželjenim posledicama upotrebe proizvoda sintetske hemije. Zbog stalnog povećanja obradivih površina zemljišta za gajenje aromatičnih biljaka značajno je razmotriti pitanje upravljanja otpadom koji nastaje nakon destilacije etarskih ulja. Ostaci biljaka nakon destilacije mogu se iskoristiti za đubrenje zemljišta ili za proizvodnju briketa za loženje. Nužno je upoznati domaće firme i proizvođače etarskih ulja sa tehnologijama za proizvodnju komposta i briketa.

U procesu prerade lekovitog i aromatičnog bilja destilacijom u cilju dobijanja etarskih ulja ostaje iskorišćena biljna masa i hidrolat ili mirisna vodica. U većini slučajeva iskorišćena biljna masa za dobijanje etarskog ulja i hidrolat se smatraju otpadom u procesu destilacije i bacaju se. Odluka kojom se prelazi sa nivoa kada se otpaci "bacaju" na nivo njihovog recikliranja, zavisi pre svega od dostupnih tehnologija za preradu otpadaka, a potom i od društveno-ekonomskog razvoja, ekološke svesti i politike jednog društva. U mnogim zemljama razvijenog sveta već postoje strogi zakonski propisi o obaveznom uklanjanju otpadaka, koji sadrže veći udeo organske materije i biogenih elemenata, korišćenjem u poljoprivredi i šumarstvu. Srbija je usvojila Zakon o upravljanju otpadom ("Sl. glasnik RS", br. 36/2009 i 88/2010) kojim se definiše upravljanje otpadom na način kojim se ne ugrožava zdravlje ljudi i životna sredina. Prema ovom zakonu proizvođač otpada dužan je da: sačini plan upravljanja otpadom i organizuje njegovo sprovođenje, ako godišnje proizvodi više od 100 tona neopasnog otpada ili više od 200 kilograma opasnog otpada [1]. Koncept hijerarhije upravljanja otpadom ukazuje da je smanjenje nastajanja otpada najefektivnije rešenje za životnu sredinu. Međutim, tamo gde dalje smanjenje nije praktično primenljivo, proizvodi i materijali mogu biti iskorišćeni ponovo, bilo za istu ili drugu namenu. Ukoliko ta mogućnost ne postoji, otpad se dalje može iskoristiti kroz reciklažu ili kompostiranje, ili kroz dobijanje energije. Samo ako ni jedna od prethodnih opcija ne daje odgovarajuće rešenje otpad treba odložiti na deponiju [2].



Kompostiranje se definiše kao brzo, ali delimično, razlaganje vlažne, čvrste organske materije, otpada od hrane, baštenskog otpada, papira, kartona, pomoću aerobnih mikroorganizama i pod kontrolisanim uslovima. Kao proizvod dobija se koristan materijal, sličan humusu, koji nema neprijatan miris i koji se može koristiti kao sredstvo za kondicioniranje zemljišta ili kao đubrivo [2]. Prednosti su sledeće: krajnji proizvod ima izvesnu tržišnu vrednost, koja treba da rezultira u vraćanju izvesnog dela uložених sredstava; prostor koji je potreban za lokaciju postrojenja je relativno mali i cene transporta nisu tako velike. Najbolje je organski otpad za kompostiranje razdvajati na izvoru i pre odlaganja na deponiju. U principu, kompostiranje se sprovodi u dva nivoa:

- sakupljanje i izdvajanje organskih komponenti (kuhinjski otpad i otpad iz bašti) za kompostiranje na kompostnim poljima ili u posebnim postrojenjima (najčešće regionalnog tipa);
- promocija samostalnog kompostiranja “u svom dvorištu” kroz edukaciju i uspostavljanje malih bunkera za kompostiranje.

Sa razvojem čistijih tehnologija kao što je kompostiranje biljni otpad koji je nastao u procesu prerade lekovitog i aromatičnog bilja mogao bi se ponovo iskoristiti i reciklirati. Iskorišćena biljna masa je bogata belančevinama, ugljenim hidratima, ostalim hemijskim čistim elementima izuzetno važnim za ljudski organizam i drugim hranljivim sastojcima, koji se uz dalju pripremu može koristiti kao sirovina za proizvodnju komposta, briketa ili dijetetskih preparata u ljudskoj i veterinarskoj medicini. Otpad nakon destilacije etarskog ulja je izuzetan resurs i može se iskoristiti za pravljenje visoko vrednog organskog đubriva što predstavlja jedan vid bezotpadne tehnologije, imajući u vidu da bi sam ostatak predstavljao ozbiljan ekološki problem. Mnogobrojna istraživanja poslednjih godina, posebno u razvijenim zemljama, poklanjaju izuzetnu pažnju traženju načina za korišćenje ovih otpadaka i njihovom preradom u kvalitetna organska đubriva – komposte.

To znači da bi se uz adekvatne tehnologije nus proizvodi nastali u preradi lekovitog i aromatičnog bilja mogli doraditi i prodavati po visokim cenama. Na taj način firme koje se bave proizvodnjom etarskih ulja bi imale dvostruku korist i povećanje rentabilnosti, prvo kroz prihode od etarskog ulja, a zatim i kroz prihode od prodaje komposta, briketa i hidrolata.

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## 6. simpozijum Hemija i zaštita životne sredine

*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

4.

### **Zelena hemija i alternativna tehnološka rešenja**

*Green chemistry and alternative  
technologies*

## Development of sustainable technologies for organic and inorganic pollutants removal

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During the last two decades our research group has been investigating the potential application of natural by-products and vegetable wastes for water treatment. The evaluation of sorption performance of several materials such as olive stones, cork, exhausted coffee and grape stalks has been evaluated to select the most effective by-product for the elimination of each pollutant. The adsorption of organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs), pesticides, dyes and pharmaceutical compounds) [1] and inorganic pollutants (divalent metals, hexavalent chromium, and arsenic) [2,3] were investigated in batch and continuous modes. The knowledge acquired on sorption performance of these sorbents allowed us to develop sustainable technologies. At present two applications are available: a utility model based on cork to remove PAHs from natural waters and a pilot plant for electroplating wastewater treatment based on the use of grape stalks for hexavalent chromium reduction.

### Cork filter for the purification of natural water contaminated by PAHs

A cork filter was designed for water contaminated by polycyclic aromatic hydrocarbons (PAHs) remediation [4]. Phenanthrene was chosen as a model for PAHs. This filter is able to reduce PAHs contamination to values below the limits set by the regulations (Directive 98/83/CE and WFD 2000/60/EC). The following features characterize the filter: 1) the cork filter is based on by-products of the cork industry (e.g. cork strips after being punched out of the cork stoppers) (Fig. 1); 2) granulated cork bed of particle size within 0.5 and 0.7 mm are confined in a cylindrical glass tube (10 mm x 85 mm length) (Fig. 2); 3) porosity of the bed ranges between 15% and 25% 4) cork particles density is 0.0546 g mL<sup>-1</sup>. Experimental data showed that after passing 720 mL of water contaminated with 30 µg L<sup>-1</sup> phenanthrene through the cork filter, the outflow concentration was reduced to 1 µg L<sup>-1</sup>. After 72 min, the outflow concentration was less than 0.1 µg L<sup>-1</sup> and the total amount of phenanthrene retained by the cork was about 22 µg.



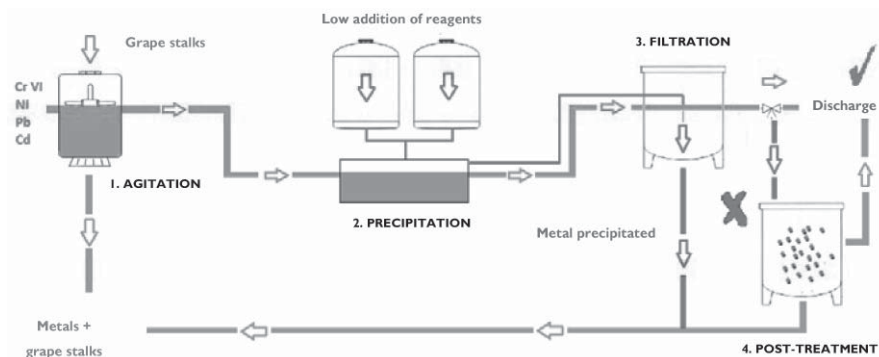
**Figure 1.** Cork strip after being punched out of the cork stoppers



**Figure 2.** Granulated cork bed and its dimensions confined in a cylindrical glass tube

## Grape stalks based technology for electroplating wastewater treatment

This technology is based on the use of grape stalks waste particles as sorbent and reduction material for the elimination of hexavalent chromium and divalent metals present in the electroplating industries wastewaters. The experimental set-up of the pilot plant designed for wastewater treatment is presented in Figure 3.



**Figure 3.** Pilot plant for electroplating wastewater treatment

In a first step, grape stalks of particle size within 1.6-3.15 mm are put into contact with the contaminated water in a stirred batch reactor. The amount of grape stalks added to the reactor varies as a function of initial metal concentration in a ratio 26 g of grape stalks per g of Cr(VI) in solution. After 48 hours contact, more than 67% of total chromium is eliminated, a partial elimination of other metals is achieved and no hexavalent chromium is present in solution. A second step by using precipitation reagents is needed to eliminate the remaining metal ions in solution. After the overall water treatment process, metal ions concentrations are below the regulated discharge limits.

The technology is sustainable, economically favourable due to the reduction in energy costs, lower reagents consumption and lesser equipment maintenance resulting in a total 40% costs saving compared to the cost of the treatment in a standard treatment plant.

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# Adsorpcija jona bakra i cinka na prirodnom zeolitu

## Adsorption of Copper and Zinc Ions by Natural Zeolite

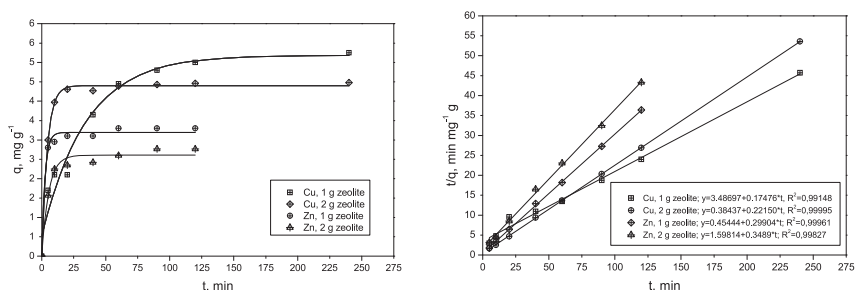
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Uklanjanje jona metala iz različitih efluenata dovelo je do razvoja različitih postupaka za tretman otpadnih voda. Bakar, cink, nikl, olovo, kadmijum, hrom i živa često su prisutni u otpadnim vodama, koje mogu nastati prilikom rudarskih aktivnosti, preradi nafte, proizvodnji boja, pesticida, proizvodnji i recikliranju papira i sl. Više postupaka je korišćeno za tretman industrijskih otpadnih voda, uključujući neutralizaciju i precipitaciju, redukciju, jonsku izmenu, adsorpciju, biosorpciju, reversnu osmozu itd. Adsorpcija se dosta ispituje kao metoda za uklanjanje jona metala. Usled visoke cene aktivnog uglja za tretman voda, vršena su i vrše se i dalje istraživanja drugih adsorbensa. Neki istraživači su proučavali [1,2] manje skupe materijale za izdvajanje Cu(II), Zn(II), Mn(II), Fe(II), Fe(III) iz otpadnih voda kao što su gline, zeoliti, lignit i sl.

U radu je ispitivana adsorpcija bakra i cinka iz sintetičkih rastvora na prirodnom zeolitu (klineptilolit). Eksperimenti su izvođeni u čaši, dovodenjem u kontakt 1 i 2 g zeolita sa 50 ml rastvora jona teških metala određene početne koncentracije. Korišćen je zeolit klasa krupnoće < 0,4 mm. Zeolit i vodena faza održavane su u suspenziji pomoću magnetne mešalice (brzina mešanja 300 min<sup>-1</sup>). Nakon mešanja, suspenzija je filtrirana i filtrat je analiziran. Analiza uzoraka je vršena metodom AAS i na UV/VIS spektrofotometru Rayleigh UV 9200 Promena kapaciteta adsorpcije sa vremenom za jone bakra i cinka prikazana je na slici 1.

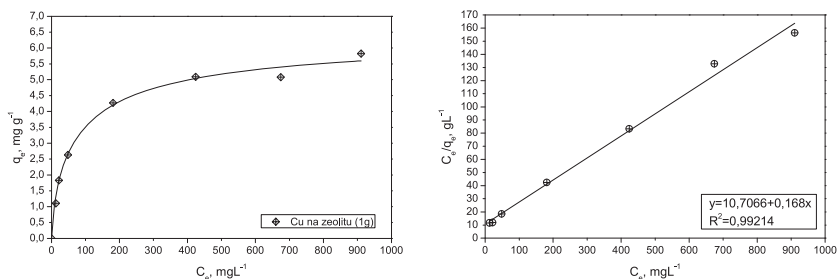


**Slika 1.** Promena kapaciteta adsorpcije sa vremenom za jone bakra i cinka; zeolit (-0,4+0)mm;  $C_0=250 \text{ g/dm}^3$ ; pH=3,5

Sa slike1 (leva kolona) se može videti da se proces adsorpcije odvija u dva koraka: u prvih 20-25 minuta procesa adsorpcija je brza, da bi se ravnoteža uspostavila već posle 40 minuta. Nakon toga, nema značajnijih promena kapaciteta. Na slici

se može videti da se kapacitet adsorpcije ispitivanih jona smanjuje sa povećanjem mase adsorbensa. Maksimalni kapacitet adsorpcije za bakar iznosi 5,25mg/g, a za jone cinka 3 mg/g adsorbensa.

Zavisnost kapaciteta adsorpcije zeolita od različitih koncentracija polaznog rastvora bakra prikazana je na slici 2. Uočava se, da sa porastom početne koncentracije dolazi do porasta kapaciteta korišćenog adsorbensa. Najveći kapacitet adsorpcije je postignut pri adsorpciji jona bakra iz polaznog rastvora koncentracije 1026,85 mg/dm<sup>3</sup> i iznosio je 5,82 mg/g.



**Slika 2.** Adsorpciona izoterma (levo) i Langmuir-ova zavisnost (desno) za jone bakra; zeolit (-0,4+0)mm; pH=3,5; t=90 min

U literaturi se brzina adsorpcije najčešće opisuje pomoću modela Langmuir-a i Freundlich-a [2,3]. U našem slučaju, Langmuir-ov model je pokazao bolje slaganje sa eksperimentalnim rezultatima. Na osnovu adsorpcione izoterme za bakar, određeni su parametri po modelu Langmuir-a i prikazani u Tabeli 1.

**Tabela1.** Parametri Langmuir-ove adsorpcione izoterme za Cu<sup>2+</sup>

Metal	$K_L$ (dm <sup>3</sup> /mg)	$Q_m$ (mg/g)	$R^2$
Cu	63,73	5,952	0,99214

Na osnovu prikazanih rezultata, očigledno je da se prirodni zeolit može koristiti za uklanjanje jona Cu i Zn iz razblaženih rastvora. Adsorpcija metala zavisi od vremena, vrste jona koji se adsorbuje, mase adsorbensa, od početne pH vrednosti rastvora, kao i početne koncentracije metala.

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## **Biodisel production and characterisation**

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Rapidly growing fossil energy consumption, particularly in the transport sector, caused problems over the last two centuries such as increasing greenhouse gas emissions, growing energy dependency and supply insecurity. To overcome these problems, the use of biofuels derived from renewable sources has recently been receiving increased attention due to its economic and environmental benefits. The use of biofuels is strongly promoted by the European Union through Directive 2009/30/EC. This Directive encourages suppliers to reduce life cycle greenhouse gas emissions at least 6% by 2020 compared to the EU-average level in 2010 through the use of biofuels and alternative fuels (apart from reductions in flaring and venting at production sites). One of two biofuels considered by this Directive is biodiesel.

Biodiesel (fatty acid alkyl esters), a substitute to diesel fuel, is produced from renewable natural sources such as vegetable oils, animal fats and microalgal oil. It is biodegradable, sustainable, and also environmentally beneficial fuel considered to be carbon neutral, as biodiesel yielding plants absorb carbon-dioxide to a greater extent than that contributed to the atmosphere when used as fuel in engines. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The use of waste cooking oils as raw material is one of the primary options to be considered to lower the cost of biodiesel. It is also environmentally acceptable as waste frying oils have been regularly poured down the drain, resulting in problems for wastewater treatment plants and energy loss, or integrated into food chain by animal feeding, causing human health problems. The most commonly used method for biodiesel production is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by operating parameters like molar ratio of glycerides to alcohol, catalysts, etc.

The aim of this paper is to present the results of the laboratory-scale biodiesel production performed at the Faculty of Technology Novi Sad by the base-catalyzed transesterification of different feedstocks, including sunflower and waste cooking oils. The investigations of biodiesel production have been focused on transesterification using homogeneous and heterogeneous catalysts. Characteristics of the obtained products like density at 15°C, kinematic viscosity at 40°C, acid value, iodine value, fatty acid (methyl ester) composition, etc., were determined and compared to the results of the relevant literature data and the quality standard EN 14214. The results revealed the most influential characteristics of feedstocks onto the biodiesel purity and yields. Effectiveness of different purification procedures of the biodiesel has been examined and compared. The chemometric



approach has been additionally used in order to characterize biodiesel produced on the base of their fatty acid methyl esters (FAMES). It pointed out variables (FAMES) most important for the discrimination of biodiesels produced from edible and non-edible feedstocks.

### Acknowledgment

*The results presented here are obtained within the project no. 172050 supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia and coordinated by Prof. Dr. B. Škrbić, and COST Action TD1203 "Food waste valorisation for sustainable chemicals, materials & fuels (EUBis)".*

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**5.**

**Antropogeni uticaji na  
životnu sredinu**

*Antropogenic impacts on the  
environment*

## Monitoring of organic compounds in atmospheric aerosols of West Siberia

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Natural biological and geological processes as well as human activity cause organic compounds to occur in atmosphere and subsequently to play an important role in the formation of atmospheric aerosols. Lack of information on spatial and high-altitude distributions of the organic compounds in the aerosols stimulates scientific research in this area. We have investigated saturated hydrocarbons and aldehydes in the atmospheric aerosols, which were sampled by the aircraft-laboratory "Tu-134 Optic" at altitudes ranging from 500 to 7000 m. The sampling was performed from January to June 2012. To detect the saturated hydrocarbons we filtered the atmospheric air (more than 1 m<sup>3</sup>) using Teflon analytical membranes Grimm 1.113A with a pore diameter of 1.2 µm. The samples of atmospheric aerosols were extracted with acetone, concentrated in vacuum and analyzed by chromatography-mass-spectrometer (50 - 250 °C at a rate of 5 °C/min, isotherm at the initial and final temperatures – 3 and 45 min, respectively). The hydrocarbons were identified using library data bases of mass spectra NIST11, NIST02 and Wiley22. In the aerosols sampled in January and May 2012 we identified n-alkanes C<sub>14</sub>-C<sub>26</sub>, among which C<sub>17</sub>H<sub>36</sub> was identified at maximum concentration. Homologous series of n-alkanes identified in the aerosol sampled in March 2012 was composed by the compounds with a number of carbon atoms in a molecule ranging from 13 to 24. The maximum in molecular-weight distribution fell on C<sub>24</sub>H<sub>50</sub>. In the aerosol sampled in June in addition to normal alkanes C<sub>12</sub>-C<sub>24</sub> we also identified unsaturated hydrocarbons (alkenes). It should be noted that the aerosol sample contained alkenes only with an even number of carbon atoms in a molecule. Among n-alkanes in the aerosol sampled in June 2012 homologues with an even number of carbon atoms predominated over those with an odd number of carbon atoms in a molecule. The concentration of hexadecane was maximal in this sample. Hexa- and octadecene predominated among alkenes.

Aldehydes were detected as derivatives – hydrazones at air pumping through absorbing tubes with acidified solution of 2,4-dinitrophenylhydrazine. The air atmospheric samples were collected with an altitude gradient of 500 – 1000 m. The formed hydrazones were analyzed using a microcolumn liquid chromatograph Milichrome A-02 equipped with UV detector with a column filled with a

reversed-phase sorbent ProntoSIL 120-5-C18 AQ #1810. Acetonitrile mixed with water was used as an eluent.

In the aerosol sampled in May 2012 maximum concentrations of formaldehyde ( $0.256 - 0.552 \text{ mg/m}^3$ ) were registered at altitudes ranging from 5,500 to 7,000 m, whereas those of acetaldehyde ( $0.0710 - 0.215 \text{ mg/m}^3$ ). – at altitudes ranging from 1,000 to 3,000 m. Minimum concentrations of both formaldehyde and acetaldehyde ( $<0.004 \text{ mg/m}^3$ ) were registered at 500 and 4,000 m. Aldehyde content in June aerosol sample was significantly different: maximum concentrations of formaldehyde ( $0.076 - 0.106 \text{ mg/m}^3$ ) were registered at altitudes ranging from 1,000 to 3,000 m, maximum concentration of acetaldehyde ( $0.629 \text{ mg/m}^3$ ) corresponded to the altitude of 5,000 m. Minimum concentrations of both formaldehyde and acetaldehyde ( $0.014$  and  $0.019 \text{ mg/m}^3$ , respectively) were registered at the altitude of 7000 m.

Thus, it was found that the compositions of n-alkanes in the aerosols sampled in winter-spring period had no significant differences. In the summer aerosol sample the concentrations of n-alkane homologues with an even number of carbon atoms exceeded the concentrations of a-alkanes with an odd number of carbon atoms in a molecule. In addition, the summer sample contained alkenes with an even number of carbon atoms. Contrary to expectations at an altitude of 7,000 m we detected formaldehyde, the concentration of which was more than 2 times higher than the concentration of this aldehyde in smog conditions, suggesting that it was not completely consumed in the ground air and moved with air masses to a considerable altitude. Besides, vertical migration of hydrocarbons is possible (for example, terpenes evolved by coniferous forests), during photo-oxidation of which significant amount of formaldehyde is formed at already a high altitude. Chemical compositions of atmospheric aerosols will be monitored every month during 2-3 years.

*The work was performed as a part of SB RAS interdisciplinary integration project № 35*

## **Level and source identification of polycyclic aromatic hydrocarbons associated with atmospheric coarse particles in Belgrade urban area, Serbia**

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The aim of this paper was to determine level, seasonal variation and potential sources of polycyclic aromatic hydrocarbons (PAHs) associated with atmospheric PM<sub>10</sub> in wider Belgrade area: rural-industrial, suburban-industrial and traffic measurement site in the local monitoring network established by Institute of Public Health of Belgrade. Sixteen U.S. Environmental Protection Agency polycyclic aromatic hydrocarbons were analyzed in PM<sub>10</sub> aerosol fraction during 2010 and 2011. Collected samples are prepared according to EPA Compendium Method TO-13A using Gass Chromatography with Mass Selective Detector (GC-MS) [1].

PM<sub>10</sub> mass concentrations were higher during the heating than the non-heating season with a number of PM<sub>10</sub> samples exceeding the limit value. PAH concentrations had the same trend as the PM<sub>10</sub>. The total PAHs in PM<sub>10</sub> fractions were more than 10 times higher in winter than summer.

The contribution of PAH sources to the total PAH concentration in PM<sub>10</sub> were identified using the ratio of some PAH also and receptor modelling-Positive Matrix Factorization analysis (PMF) [2,3,4]. 16 species of PAHs were used as input data to receptor model to afford three factors. These factors were designated as (1) stationary sources (combustion of oil and coal, power generated, residential heating) [5,6], (2) diesel and gasoline vehicle exhaust [5,7,8,9] and (3) biomass burning [5,10].

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## **Uticaj polietilena visoke gustine (HDPE) na prinos i sastav tečnog pirolizata kerogena tipa III**

### **The influence of high density polyethylene (HDPE) on the yield and composition of liquid pyrolysate of type III kerogen**

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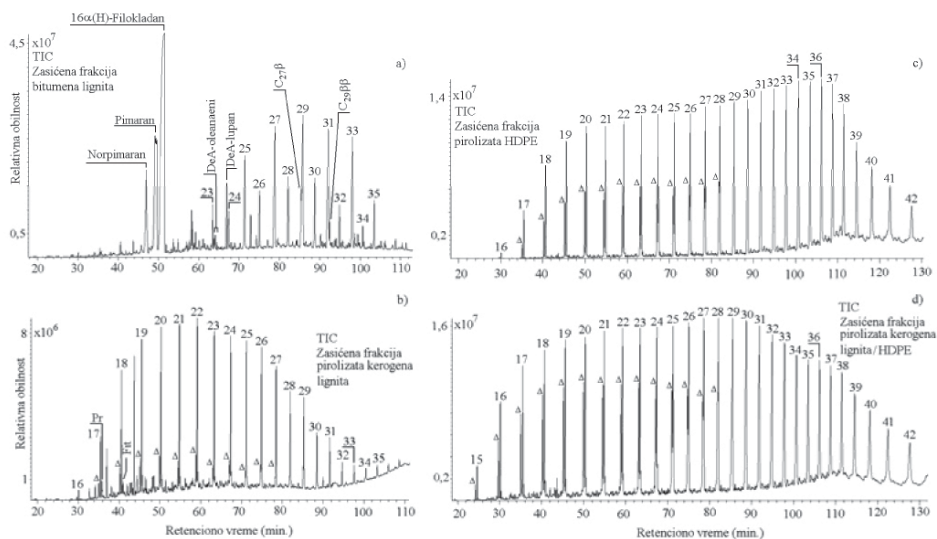
Pirolizom kerogena uglja i uljnih škriljaca dobijaju se tečni pirolizat, gas, i čvrsti ostatak, bogat ugljenikom [1]. Cilj ovoga rada bio je da se ispita uticaj polietilena visoke gustine (HDPE) na prinos i sastav tečnog pirolizata kerogena tipa III (iz lignita). Osim toga, analiziran je sastav bitumena polaznog lignita, pirolizata kerogena, pirolizata kerogena u prisustvu HDPE (kerogen/HDPE) i samog HDPE. Kao supstrat upotrebljen je uzorak lignita iz polja Smederevsko Pomoravlje Kostolačkog basena (bušotina A1J-369) sa dubine 83,2-85,2 m. U svojstvu HDPE korišćena je plastična kesa za pakovanje hrane. Iz polaznog uzorka lignita, bitumen je izolovan ekstrakcijom po Soxhletu. Piroliza kerogena lignita, kerogena lignita u prisustvu HDPE (maseni odnos 1:1) i samog HDPE izvođena je na temperaturi 400 °C, u trajanju od 4 sata u inertnoj atmosferi azota. Iz bitumena i tečnih pirolizata su posle taloženja asfaltena, primenom hromatografije na koloni izolovane frakcije zasićenih ugljovodonika, aromatičnih ugljovodonika i polarnih jedinjenja sa azotom, sumporom i kiseonikom (NSO). Zasićena frakcija je analizirana gasnohromatografsko-masenospektrometrijskom tehnikom (GC-MS).

Prinosi tečnih pirolizata kerogena lignita, HDPE i kerogena lignita u prisustvu HDPE iznosili su 1,43%, 15,25 % i 6,01 %. Prinos tečnog proizvoda značajno se povećeva kada se piroliza kerogena tipa III vrši u prisustvu HDPE. HDPE deluje kao proton donor, koji aktivira degradaciju kerogena, i kao rastvarač tokom pirolize. Grupni sastav pirolizata kerogena i kerogena/HDPE značajno se razlikuje u odnosu na grupni sastav bitumena polaznog lignita i ukazuje na značajno smanjenje sadržaja asfaltena (sa 74 % na manje od 2 %) i obogaćivanje maltenske frakcije u sadržaju ugljovodonika (od 7 u % polaznom lignitu do 40 % u pirolizatima).

TIC (Total Ion Current) zasićenih frakcija pirolizata se znatno razlikuju u odnosu na TIC zasićene frakcije bitumena lignita (slika 1). Pirolizati kerogena, kerogena/HDPE i HDPE imaju tipičnu naftnu raspodelu. U svim pirolizatima dominiraju *n*-alkani, a za njima po obilnosti slede *n*-alkeni. *n*-Alkani su najčešće



najobilnija klasa jedinjenja u sirovim naftama. Prisustvo reaktivnih *n*-alkena u pirolizatima, omogućava njihovu relativno laku konverziju u račvaste i ciklične ugljovodonike tokom prerade. Dobijeni rezultat pokazuje da su piroliza HDPE i njegova ko-piroliza sa kerogenom alternativni načini za dobijanje sintetičke nafte i neutralizaciju plastičnog otpada.



**Slika 1.** TIC zasićene frakcije izolovane iz bitumena lignita (a), pirolizata kerogena lignita (b), pirolizata HDPE (c) i pirolizata kerogena lignita/HDPE (d) *n*-Alkani su numerisani prema broju C-atoma; Δ – 1-*n*-alkeni sa istim brojem C-atoma kao i *n*-alkani; ββ- označava konfiguraciju na 17 i 21 C-atomu u hopanima.

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## 6. simpozijum Hemija i zaštita životne sredine

*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

6.

### **Uticaj zagađujućih supstanci na biohemijske procese**

*Effects of harmful substances on  
biochemical processes*

## Protein-polyphenol interactions in complex food systems

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Both high-affinity binding and non-specific adsorption of polyphenols to proteins are of importance in complex food systems. The biological significance of the high-affinity non-covalent binding to globular dietary proteins is often investigated by fluorophore quenching method. The majority of studies on the interactions between polyphenols and proteins yielded the binding constants, the identity of the putative polyphenol-binding sites, the character of forces important for recognition, and effects of the complex formation on the stability and antioxidant activity of polyphenols[1]. Apart from a recent study in which it has been shown that polyphenols exhibit potent dose-dependent inhibitory activity on  $\alpha$ -synuclein aggregation, very few studies focused on biological ramifications of the stable protein-polyphenol complexes[2].

It has recently been shown that consumption of polyphenol-enriched apple extract reduced symptoms of food allergy to ovalbumin in a mice model of allergy [2]. Proposed mechanisms of anti-allergic action of apple polyphenols were related, at least in part, to polyphenol-protein interactions, which presumably reduced the allergenicity of the allergen by epitope modification. Gruber et al. reported similar results with the major cherry allergen Pruav 1[3] the major allergen from cherry (*Prunus avium*). In particular, it has been shown that the interaction of Pruav 1 with various polyphenols, including epicatechin, gallic acid and quercetin, led to permanent modification of the tertiary structure of the allergen, which resulted in a strong reduction of its IgE-binding capacity. Recently, similar findings were reported, demonstrating reduced allergenicity of peanuts after interaction with polyphenols[4].

Protein conformation, digestibility and aggregation are important for biological activities of dietary proteins that elicit hypersensitivity reactions in humans, such as IgE-binding capacity, uptake by antigen-presenting cells, activation of effector cells in allergy, and sensitizing potential of food allergens [5].

Complexation of polyphenols and proteins can also affect antioxidant activity of polyphenols by affecting their electron donation capacity and reducing the number of hydroxyl groups available in the solution. However, due to the prolonged life of polyphenols in the complex, the effect of complexation may be beneficial for the overall antioxidant activity of the polyphenols. In the gastrointestinal tract, dietary protein encounters mixtures of polyphenolic compounds present in various foods. Thereby, our approach was to examine the interactions between a model globular whey protein ( $\beta$ -lactoglobulin) and complex polyphenol mixtures

as isolated from various polyphenol rich sources (green and black tea, coffee, cocoa). All the mixtures were analyzed for the exact composition by high resolution mass spectrometry [6].

We demonstrated that changes in pH that occur in the human GIT (1.2-2.5 in the stomach and 7.2 in the intestine and saliva) affect binding affinity of polyphenolic compounds to the protein. The most profound effect of pH on the binding affinity was observed for polyphenol extracts rich in phenolic acids. The obtained binding constants were analyzed relative to the known biological effects of polyphenols – i.e. protein digestion inhibition and masking of the antioxidative power of formed complexes. All tested polyphenol extracts, regardless of the chemical composition, protected protein secondary structure at extremely acidic pH of 1.2. A positive correlation was observed between the binding strength of protein-polyphenol interactions in solution, half time of protein decay during gastric digestion and masking of the total antioxidant capacity of protein-polyphenol complexes [6]. The anti-nutritive properties of polyphenols increase upon processing of complex food systems with phenol-oxidases which results in formation of stable protein-polyphenol complexes and aggregation of proteins [7].

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## Bitan uticaj PM10 na kvalitet vazduha u Srbiji Substantial influence of PM10 on AQ in Serbia

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Implementacija Zakona o zaštiti vazduha manifestuje se i kroz uspostavljanje i operativno funkcionisanje državne mreže automatskog monitoringa kvaliteta vazduha na nivou Republike Srbije. To je omogućilo dobijanje većeg obima validnih podataka o ambijentalnim koncentracijama zagađujućih materija za potrebe ocenjivanja kvaliteta vazduha (sumpordioksid, azotdioksid, suspendovane čestice PM10, ugljenmonoksid, prizemni ozon), [1]. Ocena kvaliteta vazduha se daje na godišnjem nivou, saglasno domaćoj zakonskoj regulativi u koju je transponovana EU regulativa iz ove oblasti.

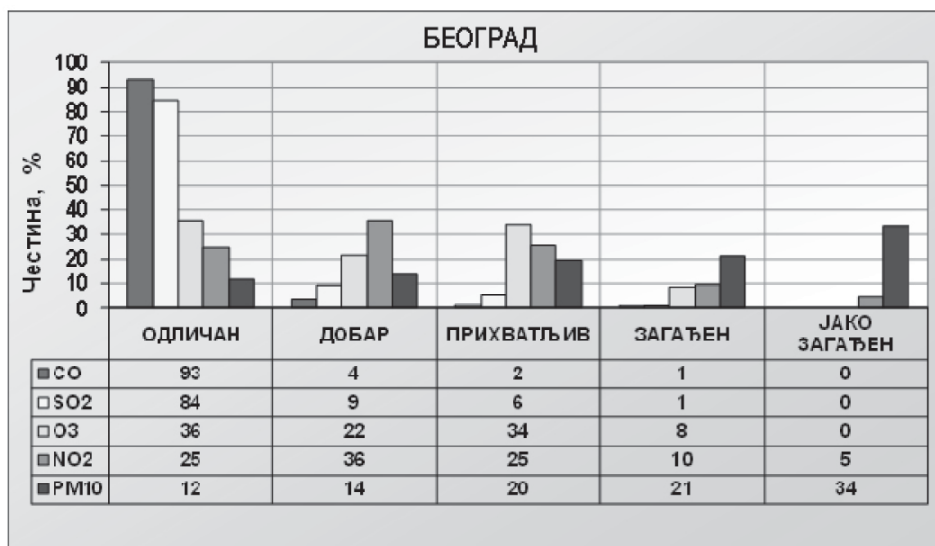
Saglasno zakonskoj regulativi a prema nivou zagađenosti, polazeći od propisanih graničnih i tolerantnih vrednosti, na osnovu rezultata merenja, utvrđuju se sledeće kategorije kvaliteta vazduha: *prva kategorija* - čist ili neznatno zagađen vazduh gde nisu prekoračene GV nivoa ni za jednu zagađujuću materiju; *druga kategorija* - umereno zagađen vazduh gde su prekoračene GV nivoa za jednu ili više zagađujućih materija, ali nisu prekoračene TV ni jedne zagađujuće materije i *treća kategorija* - prekomerno zagađen vazduh gde su prekoračene TV za jednu ili više zagađujućih materija.

Parcijalni doprinos pojedinih zagađujućih materija ukupnoj oceni kvaliteta vazduha se može jasno predstaviti primenom Indeksa kvaliteta vazduha SAQI\_11, [1]. Ocena uticaja suspendovanih čestica PM10 na kvalitet vazduha u Srbiji urađena je analizom dnevnih koncentracija PM10 tokom 2011. godine primenom Indeksa SAQI\_11. Komparacija parcijalnih uticaja pojedinih polutanata na kvalitet vazduha ukazuje da je uticaj suspendovanih čestica PM10 na kvalitet vazduha u Srbiji dominantan.

	Београд					Нови Сад					Ниш					Бор				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
CO	93	4	2	1	0	97	1	1	0	0	95	3	2	0	0	100	0	0	0	0
SO <sub>2</sub>	84	9	6	1	0	99	0	0	0	0	97	1	0	1	0	37	7	11	12	33
O <sub>3</sub>	36	22	34	8	0	44	23	28	6	0	52	35	13	0	0	28	27	42	3	0
NO <sub>2</sub>	25	36	25	10	5	56	19	8	4	13	68	26	5	1	0	90	8	1	0	0
PM10	12	14	20	21	34	30	28	24	15	3	6	20	28	16	30	22	24	29	18	7

**Tabela 1.** Procentualna zastupljenost klasa kvaliteta vazduha na osnovu dnevnih vrednosti koncentracija zagađujućih materija tokom 2011.

Dok su u našoj regulativi i praksi dominirale manuelne metode monitorin- ga kvaliteta vazduha čestično zagađenje je ocenjivano koncentracijama čađi. Iako su sezonske veze između koncentracija čađi i PM10 različite čvrstine, [2], čađ je imala najveću učestalost prekoračenja GVI. Bitan uticaj čestičnog zagađenja na kvalitet vazduha u Srbiji je nastavljen, [3], [4] i posle donošenja i usvajanja nove zakonske i podzakonske regulative.



**Slika 1.** Grafički prikaz učestalosti (%) klasa kvaliteta vazduha na osnovu dnevnih koncentracija pojedinih zagađujućih materija tokom 2011. u aglomeraciji Beograd – koncentracije PM<sub>10</sub> su najčešće uslovljavale klase “zagađen” i “jako zagađen” vazduh

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## 6. simpozijum Hemija i zaštita životne sredine

*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

7.

### **Obrazovanje o životnoj sredini**

*Environmental education*

## Specialist Academic Study - New Curricula on Toxicological Risk Assessment of Environmental Contaminants

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The study programme is designed to give course participants a broad understanding of regulatory toxicology *i.e.*, the relationships between toxicological information and the legal aspects of chemical regulations.

New curricula, Toxicological risk assessment of environmental contaminants starts in October 2013. Key topics covered: principles and current issues relating to regulatory toxicology including the history of risk assessment, toxicity testing and regulation, an introduction to toxicology, regulatory toxicity testing, specific toxicity, organ toxicity, toxic substances, human data

General requirements laid down by the Law of the University of Belgrade and special requests defined by the general act of the Faculty of Pharmacy. Students who completed master degree at the following faculties have right to apply for the programme: Faculty of Chemistry, Faculty of Pharmacy, Faculty of Medicine, Faculty of Dental Medicine, Faculty of Biology, Faculty of Veterinary Medicine, Faculty of Technology and Metallurgy, Faculty of Agriculture.

Programme details are given in the table below.

**Table 1.** Subject schedule per semesters

No.	Subjects Name	Status	ECTS	Total number of classes			Year of st. prog.
				Lect.	Prat.	Oth.	
1.	General Toxicology	o.	10	15	15	60	1.
2.	Principles of Ecotoxicology	o.	10	15	15	60	1.
3.	Environmental Contaminants	o.	10	30	15	60	1.
4.	Toxicity Testing	o.	10	30	30	30	1.
5.	Chemical Risk Assessment	o.	10	30	45	30	1.
6.	Elective block*	e.	5	15	15	30	1.
		e.	5	15	15	30	1.

\*Pharmaceutical waste, Toxicovigilance, Regulatory toxicology, Toxicological laboratory and Good Laboratory Practice, Management of Chemical Accidents

Proposed study programme provides an opportunity for specialisation of the staff that work or are interested to work in the field of toxicology and ecotoxicology. It aims to provide chemists, pharmacists, biologists, technologists, physicians, dentists, veterinarians and agricultural engineers with extensive knowledge and skills in various fields of toxicology. This study program also provides a possibility of further professional development of the ones already employed

in the institutions of environmental health. The programme aims to provide intensive training in both the theoretical basis and required skills in the various specialties, *i.e.* principles of general toxicology, hazardous chemicals and their risk assessment.

After competition of this specialist programme students are expected to be able to apply the gained knowledge in the field of toxicology, ecotoxicology and the risk assessment of hazardous chemicals. The owner of the diploma has the right to enroll in doctoral academic studies according to the requirements provided by corresponding rule books of the University of Belgrade and the Faculty of Pharmacy on the enrollment of doctoral academic studies.

## **Modernisation of Post-Graduate Studies in Environmental Sciences - an example of TEMPUS project activities**

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Zoran D. Matović<sup>6</sup>, Vesna Marjanović<sup>7</sup>, Jan Schwarzbauer<sup>8</sup>,  
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With the ever increasing progress and achievement in science and technology it is evident that higher education is under pressure to continue to produce new generations of highly skilled individuals who will be capable of contributing further intellectual and technical advances in the 21<sup>st</sup> century. Therefore, higher education (HE) systems around the globe are facing an enormous challenge to develop programmes that will help produce such scientific graduate leaders and the necessary new generations of scientists and technologists.

Interdisciplinary sciences face challenges in developing broad understanding of their graduates required to equip them with valuable knowledge that they will use in their day-to-day duties upon graduation.

To further this aim of developing modern scientists who are competitive on a world stage we have created a joint-project, funded by the European Union's TEMPUS programme, which aims to respond to current societal needs to develop and modernise existing Chemistry and Environmental Science programmes in Serbia with a view of making programme outcomes consistent with best practice in the rest of Europe. To achieve this aim the following objectives and work programmes have been formulated:

- Revisit current benchmarking statements and align them with 21<sup>st</sup> century needs.
- Modernisation of the HE quality assurance (QA) system.
- Staff development – both pedagogical and scientific.
- Implementation of modern technologies in teaching practice.
- Aligning assessment criteria and methodology with new teaching strategies.

Higher education modernisation is often driven by its desire to establish the most effective ways of delivering teaching and learning. When talking about modernisation of curricula in the 21<sup>st</sup> century we often think about the use of interactive boards, public response systems and virtual learning environments. Although, it is evident that computer aided teaching and learning processes are often dominant, implementation of new teaching strategies is often dictated by:

- An effective understanding of how learners learn (teaching theories).
- The desired learning outcomes (stake holders input)
- Available tools (technologies).
- Latest scientific discoveries (research informed teaching).



**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**POSTER PREZENTACIJE**  
**Sekcija 1**

*POSTER PRESENTATIONS*  
*Section 1*

## Software modeling and dispersal of industrial pollutants forecasting

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The following study presents the results of pollutants modelling in the oil and petrochemical industry. These industries are the greatest emitters of two important pollutants: SO<sub>2</sub> and NO<sub>2</sub>, and we evaluated their influence on the environment. No study that deals with the pollution in this manner has ever been made. An EPA (Environment Protection Agency) model was used for the dispersion of pollutants into the air, called ALOHA (Areal Locations of Hazardous Atmospheres). ALOHA is a modelling program that estimates hazardous releases of chemicals, including toxic gas clouds, fires and explosions. ALOHA is a good programme because it takes into an account physical and chemical characteristics of pollutants (density of the gas, molar mass, and boiling point) for its analyses. Danger zone is an area where a hazard has exceeded a user specified Level of Concern (LOC). Data used for the analyses have been taken from the project documentation and measurements of emissions performed by the certified institutions. Certified institutions are accredited organizations that perform the tests; they fulfil all of the set conditions and they have permission from the ministry, which is in charge of environmental problems, to perform air monitoring and/or the measuring of emissions.

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## Contents of radionuclides in soils of urban area (Belgrade city parks)

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The paper presents the results of activity concentration (Bqkg<sup>-1</sup>) determination of natural (<sup>238</sup>U, <sup>226</sup>Ra, <sup>232</sup>Th, <sup>40</sup>K, <sup>210</sup>Pb) and man-made (<sup>137</sup>Cs) radionuclides in soils of urban area (Belgrade city parks). Main soil physical and chemical properties (pH value, particle size distribution, organic matter and carbonates percentages) were also determined. Soils that were classified as Anthrosols are characterised by a strong influence of human activities and therefore becomes the main concern due to their impact on human health and environment.

In May of 2011, soil samples were collected from four city parks: Studentski Park (SP), Botanicka Basta (BB), Zemunski Park (ZP) and Karadjordjev Park (KP). At each site, composite samples were taken mixing three subsamples from soil bellow the tree crowns and from soil of an open area not sheltered by the tree branches. Soil under the trees was sampled at each 10 cm up to 50 cm depth (except at the KP site up to 30 cm) and at an open area from the first 10 cm.

Soil samples were air – dried, sieved, packed in 500 ml Marinelli beakers and kept sealed for one month to attain radioactive equilibrium between <sup>238</sup>U, <sup>232</sup>Th and their progenies. Measurement of radionuclides activity concentration in soil samples were done by standard gamma spectrometry using HPGe detector (CANBERRA, relative efficiency 20%).

Radioisotope activities (Bqkg<sup>-1</sup>) are in the range of 14-46 for <sup>238</sup>U, 1.2-3.4 for <sup>235</sup>U, 33-50 for <sup>226</sup>Ra, 29-63 for <sup>210</sup>Pb, 28-50 for <sup>232</sup>Th, 424-576 for <sup>40</sup>K and 0.7-36 for <sup>137</sup>Cs. The obtained values of radionuclides activity concentration are in agreement with the values for background gamma radiation reported in previous studies for soils in Serbia [1, 2].

Coefficient of variation of natural radionuclides content (<sup>238</sup>U, <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>232</sup>Th and <sup>40</sup>K) is within experimental uncertainty of their activity determination, estimated to be 25%. At each site, <sup>137</sup>Cs varies significantly along the soil depth and among sites with total coefficient of variation 92%.

<sup>238</sup>U series activity ratios <sup>226</sup>Ra/<sup>238</sup>U and <sup>210</sup>Pb/<sup>226</sup>Ra were calculated referred to quite immobile <sup>226</sup>Ra nuclide that stays constant down the soil depth [2] and no important disturbances from radioactive equilibrium in soil were found [3].

At each location, for natural radionuclides (except  $^{210}\text{Pb}$ ) slightly higher activity concentration was noticed in the first layer of soil (0-10 cm) taken from soil of an open area compared to the same layer taken under the tree crown. This could be explained by the fact that main pathway of natural radionuclides accumulation in leaves is through resuspension from soils [1] and since tree's foliage is regularly removed from the parks, part of soil radioactivity could be lost.

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## Procena radijacionog opterećenja mahovina Sokobanje

### Evaluation of the radiation load of moss from the Sokobanja

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Akcidentom u nuklearnoj elektrani Lenjin u Černobilju (1986. godina) u okolini je izbačeno oko  $12 \times 10^{18}$  Bq radioaktivnog materijala. Najznačajniji i najopasniji radionuklidi izbačeni u atmosferu bili su  $^{131}\text{I}$ ,  $^{134}\text{Cs}$  i  $^{137}\text{Cs}$ . Vodećim radionuklidom sa tačke posmatranja formiranja tkivnih doza i radiobioloških posledica, smatra se  $^{137}\text{Cs}$  zbog dugog vremena poluživota (30,17 godina). Jon cezijuma je hemijski i biohemijski homolog kalijuma, u organizmu prati njegov metabolizam, potpuno je rastvorljiv u telesnim tečnostima i ravnomerno se raspoređuje u organizmu [1]. Organizmi su u toku svog života konstantno izloženi radioaktivnom zračenju, koje može biti različite prirode i porekla. Izlaganje jonizujućim zračenjima predstavlja radnju ili uslove pri kojima dolazi do ozračivanja organizma jonizujućim zračenjima. Jonizujuće zračenje može izazvati funkcionalne, morfološke i genetske promene u organizmu, a ukoliko su doze kojima je organizam izložen viske može izazvati i njegovu smrt. Dozimetrija radioaktivnog zračenja predstavlja direktno praćenje emisije radioaktivnog zračenja u prirodi.

Mahovine su veoma stara i primitivna grupa organizama i lako upijaju zagađujuće supstance iz svoje okoline. U zavisnosti od vrste i starosti mahovina, njihovih morfoloških i fizioloških karakteristika, mesta i podloge nalaženja, nadmorske visine, pokazalo se da mahovine usvajaju i radioaktivne ostatke ( $^{137}\text{Cs}$ ). Procena radijacionog opterećenja organizama iz životne sredine u ovom slučaju, za mahovine je kompleksna. Proračun doza zahteva informacije o unutrašnjoj i spoljašnjoj distribuciji radionuklida, o njihovom ponašanju u životnoj sredini, koje su malo dostupne, posebno za pojedinačne vrste i zbog toga je neophodno izvršiti uprošćavanja i uopštavanja podataka [2].

Uzorci mahovina sakupljeni su metodom slučajnog uzorka na teritoriji Sokobanje u periodu od 2000. do 2012. godine, na lokalitetima: Ozrena i Lepterijske. Svi uzorci su homogenizovani i mereni u Marinelli posudama zapremine 1L. Gamasppektrometrijska merenja su vršena na HPGe detektoru sa 8192 kanala, rezolucije 1,65 keV-a i relativne efikasnosti od 34% na 1,33 MeV-a za  $^{60}\text{Co}$ . Vreme merenja jednog uzorka je bilo 60000s. Relativna greška pripreme uzorka i merenja je do 10%. Obrada spektra je vršena pomoću softverskog paketa Gamma Vision 324. Aktivnost veštački proizvedenog radionuklida  $^{137}\text{Cs}$  je merena preko  $\gamma$ -linije na energiji od 661,6 keV-a. Imajući u vidu prodornost čestica, realno je pretpostaviti da su sve emitovane čestice (gama i beta) apsorbovane u tkivu koje je akumuliralo  $^{137}\text{Cs}$ , izmerenu aktivnost smo preračunali u dozu.

Jačina apsorbovane doze u ispitvanim uzorcima mahovina Lepterije je bila 0,051-0,503 mGy/god, a u mahovinama Ozrena 0,018-0,284 mGy/god. Iz tabele sledi da su mahovine dobri modeli za istraživanja jačine apsorbovanih doza, da jačina apsorbovane doze opada u posmatranom vremenskom periodu, kao i da su jačine apsorbovanih doza u mahovinama sa teritorije Sokobanje niže od doza koje izazivaju promene u reprodukcijom ciklusu biljnih i životinjskih organizama (0,4 do 1 Gy godišnje) i letalnih doza (4 Gy i 0,4 Gy godišnje).

**Tabela 1.** Jačina apsorbovane doze, standardna devijacija, minimalna i maksimalna vrednost jačine apsorbovane doze u mahovinama

GOD.	Jačina apsorbovane doze u mahovinama			
	(mGy/god)			
	Lepterija		Ozren	
	sr. vred.± st. dev.	min-max	sr. vred.± st. dev.	min-max
2000	0,503	---	---	---
2001	0,418±0,119	0,332-0,503	0,236±0,088	0,173-0,298
2002	0,367±0,122	0,264-0,500	0,284	---
2006	0,293±0,020	0,279-0,304	0,145±0,162	0,008-0,546
2007	0,105	---	0,173±0,108	0,028-0,287
2008	0,094 ± 0,054	0,013-0,136	0,055±0,047	0,008-0,148
2009	0,074 ± 0,054	0,010-0,139	0,027±0,021	0,007-0,071
2010	0,074 ± 0,060	0,013-0,153	0,046±0,0248	0,003-0,080
2012	0,051 ± 0,037	0,010-0,117	0,018±0,009	0,009-0,035

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## **Nova alternativna tehnološka rešenja tretmana galvanskog otpadnog mulja**

### **New alternative treatment technology solutions galvanic sludge**

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Metode prečišćavanja galvanskih otpadnih voda koje se najčešće primenjuju u Republici Srbiji pripadaju tipu konvencionalnih sistema za prečišćavanje (hemijska oksidacija i redukcija, neutralizacija, koagulacija, flokulacija i taloženje). Ovi sistemi u drugoj fazi tretmana, nakon reakcije sa krečnim mlekom, imaju za posledicu taloženje toksičnih metala, na pH=9,5, uz stvaranje sekundarnog zagađenja, u vidu galvanskog mulja ( $\text{Me}(\text{OH})_x$ ) [1].

Toksični metali se ne razgrađuju biološki i trajno se akumuliraju u životnoj sredini, čime dospevaju u lanac ishrane i samim tim indirektno utiču na život i zdravlje ljudi.

Stabilizacija toksičnih metala iz galvanskog mulja vrši se različitim tehnološkim postupcima, kao što su: inkorporacija toksičnih metala u opeku [2], reciklaža i ponovna upotreba u metalurgiji [3], implementacija u keramiku od gline [4], inkorporacija u borsilikatno staklo [5], inkorporacija u staklo-keramiku sa aluminijumskom šljakom [6], prevođenje pepela nastalog sagorevanjem uglja i otpadnog stakla u staklo-keramiku [7], vitrifikacija [8], očvršćavanje galvanskog mulja asfaltnom emulzijom [9], stabilizacija galvanskog mulja korišćenjem sulfoaluminatnog cementa [10], sinteza  $\text{Cr}^{3+}$  u  $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3(\text{Al}_2\text{O}_3)$  prozirnu staklo-keramiku [11] i drugi.

S obzirom na značaj navedenih istraživanja, izvršena je karakterizacija galvanskog mulja, dat je tehnološki postupak stabilizacije u koristan eko-sinterovan materijal i navedene su metode nekonvencionalnih sistema prečišćavanja otpadnih voda koje nemaju sekundarno zagađenje životne sredine.

Prema Pravilniku o uslovima i načinu razvrstavanja, pakovanja i čuvanja sekundarnih sirovina [12] muljevi nastali iz pogona galvanizacije mogu se klasifikovati prema katalogu otpada pod indeksom 11, kao otpadi iz hemijskog tretmana površine metala. Muljevi svrstani pod indeksom 19 iz kataloga otpada, predstavljaju otpade iz objekata za obradu i tretman otpadnih voda, navedeni su pod indeksnim brojem 19 02 05, kao muljevi iz fizičko-hemijskog tretmana koji sadrže opasne supstance.

Stabilizacija galvanskog mulja izvršena je inkorporiranjem toksičnih metala u eko-sinterovani proizvod u obliku čvrstih rastvora, dodavanjem otpadnog stakla, metalnih strugotina i aluminijumske šljake. Na taj način se hemijski aktivne materije ( $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) prevode, faznim i hemijskim transformacijama, u izuzetno stabilnu strukturu, gde se polutanti ne mogu pokrenuti ni pod kritičnim uslovima, kao što su visoka temperatura, dejstvo kiselina i baza i slično.

Uvođenje nekonvencionalnih sistema za prečišćavanje otpadnih voda (elektrohemijska oksidacija i redukcija, jonska izmena, kao i membranski procesi: reverzna osmoza, ultrafiltracija i elektrodijaliza) omogućava regeneraciju toksičnih metala, mineralnih ulja i boja, uz dobijanje takvog kvaliteta efluenta koji može da se recirkuliše u tehnološki proces galvanizacije. Ekonomske su prirode jedino razlozi zbog čega se ove metode ne koriste u našoj zemlji.

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## **Ekotoksikološka analiza rizika u procesu galvanizacije**

### **Ecotoxicological Risk Analysis In The Galvanizing Process**

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S obzirom da se u tehnološkom procesu galvanizacije koristi veliki broj zagađujućih materija, koje zbog specifičnosti procesa i operacija ne dovode samo do zagađenja radne sredine i oštećenja zdravlja profesionalno eksponirane populacije, nego utiču i na kvalitet otpadnih voda, postoji potencijalna opasnost od zagađenja životne sredine. U tom smislu potrebno je izvršiti ekotoksikološku analizu rizika procesa galvanizacije.

Dosadašnje studije u oblasti ekotoksikološke analize rizika zagađujućih materija, a posebno toksičnih metala, na profesionalno eksponiranu populaciju u tehnološkim procesima galvanizacije ukazuju na značajnost istraživanja. Surgiewicz i Domanski [1] su analizom izloženosti toksičnim metalima u procesima galvanizacije ustanovili da su koncentracije pojedinačnih toksičnih metala, kao i njihovih jedinjenja, u ispitivanim sistemima u dozvoljenom opsegu, ali da prisustvo i malih količina ukazuje na potencijalni zdravstveni rizik. Kasperczyk i dr. [2] su na osnovu studije procene uticaja izloženosti olovu, na koncentraciju cinka, bakra, gvožđa, selena i proteina (transferin, ceruloplazmin i haptoglobin) u krvi profesionalno eksponirane populacije, utvrdili da su koncentracije olova u krvi i cink protoporfirina bile značajno više u eksponiranoj u odnosu na kontrolnu grupu, kao i koncentracije bakra, selena i ceruloplazmina. EPA i mnoge druge agencije i centri za kontrolu bolesti i prevenciju istraživale su procese i informacije potrebne za kreiranje i sprovođenje biomonitoringa u cilju procene ekotoksikološkog rizika. Novija istraživanja, za procenu potencijalnog ekotoksikološkog rizika, daju doprinos razvoju biomonitoringa, uključujući širi opseg zagađujućih materija, a posebno toksičnih metala [3]. Otpadne vode iz procesa galvanizacije mogu sadržati i do 1000 mg/dm<sup>3</sup> toksičnih metala koji, prema ekološkim propisima širom sveta, moraju biti kontrolisani na prihvatljiv nivo pre nego što se ispuste u životnu sredinu [4].

Primenom ekotoksikološke analize, istraživani je rizik toksičnih metala i drugih zagađujućih materija u radnoj i životnoj sredini, koje nastaju u procesu galvanizacije. Takođe, praćeni su i štetni efekti toksičnih metala i drugih zagađujućih materija na eksponiranu populaciju. Izvršeno je ispitivanje biološkog materijala, korišćenjem podataka iz godišnjih izveštaja službe socijalne medicine i statistike, podataka iz zdravstvenih kartona primarne i specifične zdravstvene zaštite zaposlenih. Koncentracija toksičnih metala u biološkom materijalu određivana je spektrofotometrijskim metodama. Statistička analiza rezultata izvršena je softverskim paketima Excel, Matlab i SPSS19.0. Istraživanje je pokazalo da povećanje



koncentracije toksičnih metala u biološkom materijalu predstavlja značajan pokazatelj direktnog ili indirektnog oštećenja zdravlja i zagađenja otpadnih voda, a samim tim i narušavanja kvaliteta radne i životne sredine [5].

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## Air quality in urban parking garages: Instrumental monitoring vs active moss biomonitoring

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Traffic-related air pollutants (e.g. PM<sub>10</sub>, trace elements) are considered to have negative effects on human health [1]. Due to very intensive vehicle activities in semi-enclosed space, urban parking garages are potentially hotspot microenvironments where employees and attendants are usually exposed to high concentration of these pollutants. It is well-documented that instrumental monitoring gives a reliable picture of pollution patterns, but active moss biomonitoring has proven to be one of the most flexible and cost effective approach to achieve information mainly about trace elements pollution. The current study was performed in four multi-level underground and semi-enclosed parking garages in the centre of Belgrade (Pionirski park-PP, Masarikova-M, Zeleni venac-ZV and Obilićev venac-OV) with aim to provide multi-pollutant assessment (PM<sub>10</sub> and trace elements). Also, possibility of using *Sphagnum girgensohnii* moss bags for monitoring of trace elements air pollution in semi-enclosed places was evaluated. The moss bags were hung at similar positions in all garages: near the ground floor entrance and at one in the interior. After ten weeks of the moss exposure, concentrations of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were determined in moss samples by ICP-OES. Along with the moss bag experiment, MiniVol air samplers were placed near the tollbooths in two garages (M and PP). Twenty-four hour air samples of PM<sub>10</sub> were collected for ten weeks. In the filter samples, PM<sub>10</sub> mass concentrations were calculated by gravimetric method. Concentrations of the element listed above were determined in the filter samples by ICP-OES as well.

According to the results obtained, in 77% and 93% samples from M and PP, respectively, mass concentrations of PM<sub>10</sub> exceeded the daily air quality set value-50 µg m<sup>-3</sup>. Although prescribed value is related to outdoor air quality, it could also be applicable to indoor spaces [2]. Also, the obtained daily concentrations of some heavy metals (Ni, Pb and Cd) in PM<sub>10</sub> samples, exceeded the air quality limit values set by EU Directive and WHO guideline [2, 3]. In general, concentrations of PM<sub>10</sub> and trace elements associated with PM<sub>10</sub> showed deacresing trend from weekdays to weekend which corresponded with the reduction of traffic volume. Additionally, total concentrations of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni and Sr were significantly higher in moss bags exposed at the entrance than in the interior of parking garage, indicating that pollution level depends on the traffic intensity. Comparing the trace element concentrations, obtained in two garages both by moss bags and instrumental monitoring, it was observed that in case the concentration of a given element is higher in moss from one of the garages, the concentration

of the same element was also higher in the PM<sub>10</sub> sampled from that garage. Thus, the results confirmed that *S. girgensohnii* moss bags can be used as alternative or complementary method to classical instrumental measurements of trace elements content in semi-enclosed spaces such as urban parking garages.

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## Phase Transformation Kinetics during Isothermal Decomposition of Iron-Zinc Concentrate in Nitrogen Atmosphere

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Zinc is an important element especially for the steel industry and the formation of Electric Arc Furnace Dust (EAFD) leads to strong recycling activities. Zinc in primary fluidized bed calcine as well as in EAFD exists besides as simple oxides in a spinel form called zinc ferrite  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ . A lot of studies have been conducted to find the most efficient way of zinc and iron recovery from the EAFD material due to environmental, technical and economical needs. Because of that there is a necessity for treatment of wastes containing zinc ferrites [1]. In this paper, we present a concept based on JMA theory of nucleation and growth of a new phase [2,3], to explain the mechanism of the isothermal decomposition of zinc ferrite from neutral leach residues.

After 15 minutes of heating the samples (Zinc leach residue was obtained from former company Ruhr-Zink, Datteln, Germany, with a moisture content of 23%) in order to eliminate the contained moisture, these were used in the thermal treatment experiments performed in the tube furnace. At the fixed operating temperatures (600, 750, 950, 1150 °C), the four experiments were performed at each operating temperature in the certain time intervals (15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 minutes). The experiments were repeated three times. After reaching the aimed temperature, 1 g of the zinc leach residue was inserted in a tubular furnace, under a constant nitrogen gas, with a flow rate of  $\varphi = 1 \text{ L min}^{-1}$ . After beginning of the thermal treatment of dried sample at the fixed operating temperature, the reaction time was measured by chronometer (in digits form). After that, the specimen was taken out from the furnace and placed in the exiccator. The weight results were noted as an average mass loss of the specimen, in order to calculate the decomposition rate.

The values of Avrami rate constant ( $K_A$ ) and Avrami constant ( $n$ ) were calculated from the linear relationship  $\ln[-\ln(1-\alpha)] = n \ln K_A + n \ln t$  [3], at the different operating temperatures (600 °C, 750 °C, 950 °C and 1150 °C). The conversion data for  $0.15 \leq \Delta\alpha \leq 0.95$  are almost located on straight lines (not shown). The logarithmic values of  $K_A$  ( $\ln K_A$ ), values of  $K_A$ , as well as the values of the Avrami constant ( $n$ ), are listed in Table 1.

**Table 1.** Values of  $\ln K_A$ ,  $K_A$  and  $n$  calculated from the linear dependence of  $\ln[-\ln(1-\alpha)]$  against  $\ln t$  at different operating temperatures (600, 750, 950, 1150 °C) in considered conversion ranges ( $\Delta\alpha$ ), for the decomposition process of zinc ferrite from neutral leach residues

T (°C)	Conversion range, $\Delta\alpha$ (-)	$\ln K_A$ , $K_A$ ( $\text{min}^{-1}$ )	$K_A$ ( $\text{min}^{-1}$ )	$n$	$R^2$ <sup>a</sup>
600	0.15-0.95	-3.41046	0.03303	$2.96 \pm 0.03$	0.99165
750	0.15-0.95	-3.26080	0.03836	$3.78 \pm 0.05$	0.99210
950	0.15-0.95	-3.18499	0.04138	$4.32 \pm 0.07$	0.99198
1150	0.15-0.95	-3.15298	0.04272	$4.74 \pm 0.09$	0.98775

<sup>a</sup> Adj. R-Square.

It can be observed that the values of Avrami rate constant ( $K_A$ ) increased as the operating temperature increased, which directly suggests the following facts: the higher operating temperature, the faster the decomposition process, which is in good agreement with the general rule of chemical reactions [4]. Normally,  $n$  should not exceed 4 (i.e. the value for three-dimensional bulk nucleation). In the latter case, it can be assumed that the surface induced abnormal grain growth expected for Fe crystallization compounds is responsible for the high value of  $n$  for advanced crystallization at high operating temperatures ( $T \geq 950$  °C).

In the case of  $T = 600$  °C, for which we have the value of  $n = 2.96$  ( $\approx 3.00$ ) (Table 1), we can expect that the two-dimensional (2D) crystallization mechanism with a disc growth exists. The Avrami constant of  $n = 3.00$  implies that the main crystallization mechanism is interface-controlled three-dimensional isotropic growth and early nucleation-site saturation [5]. At the elevated operating temperature of 750 °C, where the value of  $n = 3.78$  was identified, the investigated process proceeds through the three-dimensional (3D) crystallization mechanism, with a sphere morphological units [5]. In fact, the transformation for which  $3 < n < 4$  (Table 1) is considered to imply that the process is interface-controlled with a decreasing nucleation rate. On the other hand, an increasing nucleation rate with time can result in the value of  $n > 4$  [5], as can be clearly seen for our investigated system at operating temperatures of 950 and 1150 °C. Having in mind that the value of  $n$  in a given region varies over  $n = 4.00$  ( $n$  exceeds 4.00), the crystallization of probably presented »amorphous« phase (probable formation of amorphous ZnO - cinkite) (which is formed on the observed operating temperatures) should take place in the *autocatalytic stage* of the crystallization process, under the conditions where the rate of nucleation rapidly increases [6].

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## Upotreba akumulatora toplotne i termohemijske energije u sistemima za iskoriscavanje obnovljivih izvora energije

### Thermal and Thermochemical Energy Storages Coupled With Renewable Energy Systems

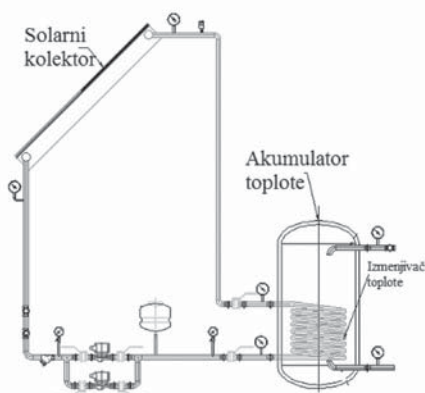
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Jos od 70-tih godina 20. veka, na globalnom nivou, raste svest o potrebi da se pronadje alternativa fosilnim gorivima kao glavnom izvoru energije, s obzirom na njihove ograničene rezerve i negativne posledice njihovog korišćenja po okolinu. U 21. veku unapređivanje tehnologije za korišćenje obnovljivih izvora energije postalo je praktično najznačajniji strateški cilj za najrazvijenije zemlje, koje u tim naporima predvode EU i Japan. Jedan od osnovnih problema pri korišćenju obnovljivih izvora energije je taj što potražnja za energijom i dostupnost energije iz obnovljivih izvora (npr. solarne energije ili energije vetra) nisu vremenski usaglašeni. Ključnu ulogu u rešavanju ovog problema imaju akumulatori energije [1], koji mogu biti bazirani na razlicitim tehnologijama.

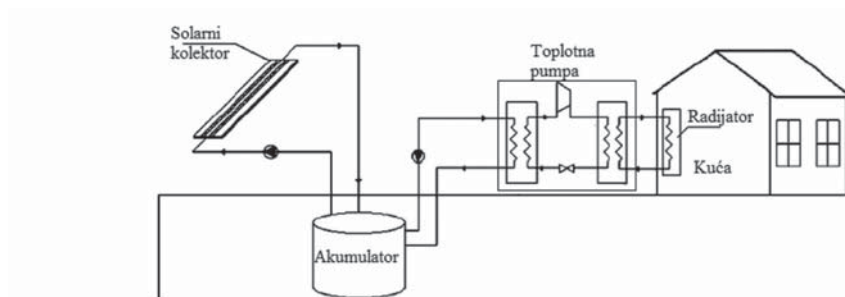
Ukoliko se solarna ili geotermalna energija koriste u sistemima za grejanje i/ili hladjenje, za efikasan i fleksibilan rad ovakvih sistema, sa energetske i ekonomskog aspekta, neophodna je upotreba akumulatora toplotne ili termohemijske energije [1,2]. Ovo važi i za industrijske upotrebe [3], ali i za upotrebe u oblasti zgradarstva [4,5].

Na slici 1 je prikazana šema sprezanja akumulatora toplote sa solarnim kolektorom. U ovom slučaju temperaturna stratifikacija radnog fluida u akumulatoru toplotne energije značajno utiče na efikasnost čitavog sistema.



**Slika 1.** Akumulator toplotne energije spregnut sa solarnim kolektorom

Na slici 2 je prikazan još složeniji sistem gde osim solarnog kolektora imamo i toplotnu pumpu, koja može da koristi energiju okolnog vazduha ili geotermalnu energiju.



**Slika 2.** Akumulator toplotne ili termohemijske energije spregnut sa izvorima obnovljive energije

Akumulatori toplotne energije koriste osetni i/ili latentni deo unutrašnju energiju radne supstance. Akumulatori termohemijske energije uz to koriste i energiju hemijske veze i fenomen povratne reakcije poput  $\text{MgO} + \text{H}_2\text{O} + 81 \text{ kJ/mol} \leftrightarrow \text{Mg(OH)}_2$

Važne osobine akumulatora toplotne i termohemijske energije su gustina usklađene energije i vreme skladištenja (odnosno gubici energije sa vremenom). Sa druge strane dva ključna problema koji se javljaju pri konstituisanju akumulatora toplotne energije su izbor radne supstance i konstrukcija izmenjivaca toplote.

Naša istraživanja su usmerena na energijsku i eksergijsku analizu uticaja sprežavanja akumulatora energije u sistemima za korišćenje obnovljivih izvora energije (poput toplotnih pumpi i solarnih kolektora), kao i na ispitivanje materijala koji mogu da se koriste u akumulatorima toplote, kao i istraživanja vezana za uticaj tipa izmenjivaca na rad akumulatora toplotne energije.

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## Bioassays for toxicity evaluation of azo dye electrochemical degradation using Zr and C electrodes

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Worldwide, 10.000 different textile dyes with an estimated annual production of  $7 \cdot 10^5$  metric tons are commercially available [1]. More than half of them have azo compounds. Azo dyes are of great concern because of their widespread use, toxic aromatic amine intermediates and recalcitrance for aerobic wastewater treatment [2]. There is a need to determine technologies that achieve technically and economically efficient reduction of color in textile industry discharges. While various treatment strategies exist for azo-dye removal and degradation, electrochemical treatment as a method has been studied by a number of researchers with different types of electrodes. Electrochemical treatment can be considered as solution for decolorization and degradation of dye molecules [3]. We were interested in application of zirconium (Zr) and graphite (C) electrodes, but also in the ecotoxicity assessment. Important advantages of using electrochemical methods are that they do not produce sludge and processes are commonly conducted at room temperature and atmospheric pressure.

In undivided cell Fisher platinum electrode was employed as anode and Zr (or C) electrode as cathode. Applied voltage during the electrolysis was 12V. The optimal conditions for degradation were previously determined in a palladium (Pd) / platinum (Pt) model system for Reactive Green 15 (pH value of 9.00 and power of 12V) so electrolysis with other electrodes were done under the same conditions. Samples were taken at beginning and the end of the treatment to test for toxicity potential of the intermediates. Decolorization was monitored spectrophotometrically (UV-Visible Cintra 6 spectrometer, GBC Scientific Equipment Pty Ltd., Australia) and degradation was measured by HPLC techniques, Dionex ULTIMATE 3000 chromatograph with a DAD detector. *Daphnia magna* acute toxicity test was performed according to standard protocols (USEPA, 2002) [4]. Reconstituted hard water was prepared according to standard method ISO 6341 [5]. Test vessels were placed in a  $20 \pm 2^\circ\text{C}$  room under 16h:8h / light:dark regime. The endpoint was the mortality of neonates. The number of dead neonates was recorded after 24h and 48h. Tests were considered valid if the mortality in the control did not exceed 10 %.

The LC 50 values were estimated by regression models: Probit and Spearman-Kärber using TesTox software (Teodorovic and Mauric 2003) [6]. For the test of acute toxicity the brine shrimp *Artemia salina* was used according to Vanhaecke and Persoone (1981). *A. salina* cysts (DAJANA PET, Czech Republic) were



hatched in seawater (Reef Crystals tm, Aquarium Systems - USA). Using instar II–III larvae, an acute toxicity test was performed in darkness at a temperature of  $26 \pm 1$  °C, for the respective test period of 24h. Validity criterion and data analysis were same as in *Daphnia magna* acute toxicity test. The objectives of this study were to evaluate the sensitivity of two bioindicators *Artemia salina* and *Daphnia magna* to degradation products after electrochemical treatment of Reactive Blue 52 and Reactive Green 15.

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## **Toxicity evaluation after *para*-chlorophenol degradation in Dielectric Barrier Discharge Reactor**

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Chlorophenols (CPs) are listed among the 65 priority pollutants by the US Environmental Protection Agency – EPA as most of them are toxic for humans and animals. The 4-chlorophenols (C<sub>6</sub>H<sub>5</sub>ClO) are classified as hazardous substance and may cause long-term adverse effects in the aquatic environment [1]. They are not readily biodegradable and it is difficult to remove them from the environment. Chlorophenols are introduced into the environment in several ways; they are intermediers in synthesis of many pesticides, herbicides, fungicides, paints, as well as by-products formed during bleaching of pulp with chlorine and in chlorination of drinking water for disinfection. So they could be found in surface water, groundwater and especially in wastewater [2]. Decomposition of 100 mg/L aqueous solutions of 4-chlorophenol using falling film dielectric barrier discharge (DBD) reactor was examined in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and homogeneous catalyst (Fe<sup>2+</sup>). The kinetic of 4-chlorophenol degradation in several successive passes through the DBD reactor was monitored using HPLC. Products of degradations such as acetic, formic and oxalic acids were quantified using ion chromatography (IC).

The genus *Artemia* is one of the animal models used for toxicity tests in laboratory conditions as a rapid preliminary screening for the presence of biochemical activity. *Artemia salina* was used to estimate both potential and consequences of using DBD reactor (non-thermal plasma) in water treatment. After degradation the measured concentration of 4-chlorophenol and degradation intermediates revealed very efficient removal of these substances from the water during the DBD treatment with an addition of a catalyst. Concerning bioassay, a significant difference was established between treatments when DBD was applied and when the solutions were not exposed to DBD reactor, but also depending on the presence of a catalyst.

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## Indeks geoakumulacije u proceni zagađenja sedimenata

### Geoaccumulation index in assessment of sediment contamination

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U ovom radu analiziran je sadržaj Cd, Cu, Co, Mn, Cr, Ni, Pb i Zn u uzorcima sedimenata najvećih reka u Srbiji (35 lokacija) i računanjem indeksa geoakumulacije ( $I_{geo}$ ) je izvršena procena da li dobijeni sadržaji elemenata predstavljaju fonski sadržaj ili ukazuju na postojanje kontaminacije.

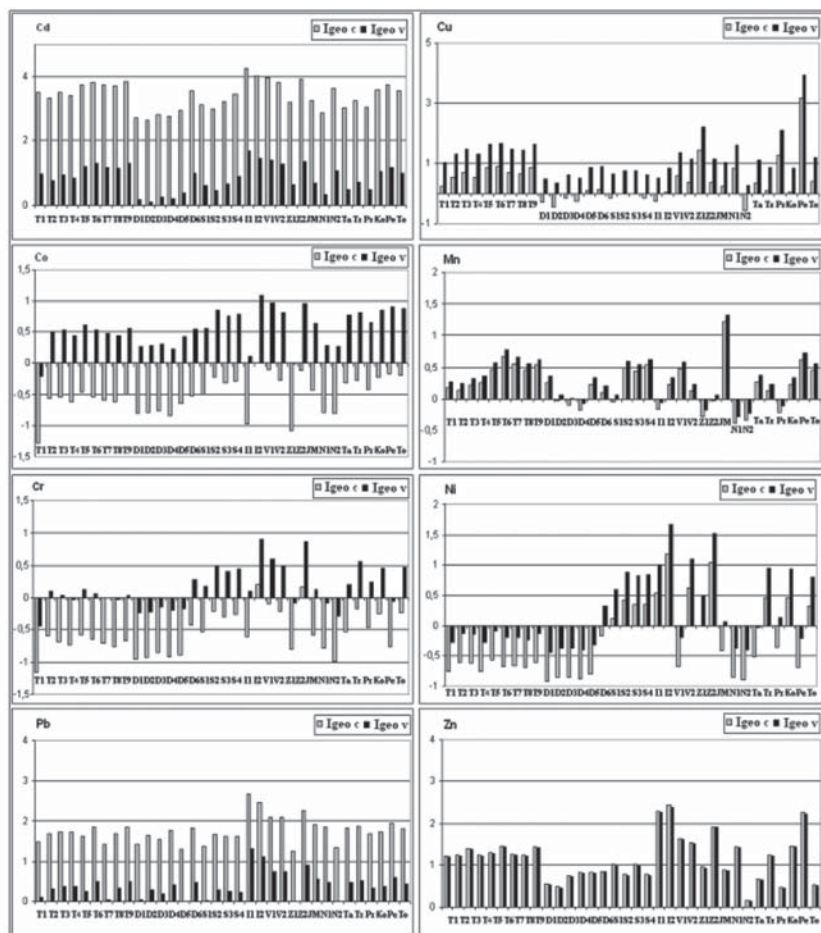
Indeks geoakumulacije ( $I_{geo}$ ) predstavlja kvantitativnu meru zagađenja rečnog sedimenta toksičnim elementima.  $I_{geo}$  se za metale računa po sledećoj formuli:  $I_{geo} = \log_2 (Cn) / 1.5 (Bn)$ , gde je Cn koncentracija metala u uzorcima sedimenta, a Bn predstavlja geohemijski fon metala (n). Indeks geoakumulacije se računa na sadržaj elemenata u frakciji sedimenta  $< 2\mu m$  [1]. Faktor 1.5 predstavlja fonski faktor za korekciju matriksa zbog litogenih efekata. U kvantifikovanju indeksa geoakumulacije, postoji sedam stepeni ili klasa

- Klasa 0 (praktično nekontaminiran):  $I_{geo} \leq 0$ ;
- Klasa 1 (nekontaminiran do umereno kontaminiran):  $0 < I_{geo} < 1$ ;
- Klasa 2 (umereno kontaminiran):  $1 < I_{geo} < 2$ ;
- Klasa 3 (umereno do jako kontaminiran):  $2 < I_{geo} < 3$ ;
- Klasa 4 (jako kontaminiran):  $3 < I_{geo} < 4$ ;
- Klasa 5 (jako do ekstremno kontaminiran):  $4 < I_{geo} < 5$ ; i
- Klasa 6 obuhvata sve one vrednosti indeksa koje su veće nego što su definisane za Klasu 5.

$I_{geo}$  je u ovom radu računat koristeći dve različite vrednosti za fonski sadržaj i dobijeni rezultati su upoređivani. Uočeno je da postoje razlike u vrednosti  $I_{geo}$  u zavisnosti od toga da li su za fonski sadržaj korišćene prosečne vrednosti za sadržaj elemenata u Zemljinoj kori ili izračunate vrednosti za ispitivani sediment. Najmanja razlika u vrednosti  $I_{geo}$  je uočena za Zn, sto je posledica malih razlika između korištenih fonskih koncentracija ovog elementa.

Dobijeni rezultati ukazuju da najveći broj sedimenata i elemenata pripada Klasu 1 (Slika 1), tj. Klasi nekontaminiran do umereno kontaminiran (Cd, Co, Cr, Cu, Ni i Pb), Klasi 2 (Cd, Cu, Zn, Cd i Pb u nekim sedimentima), Klasi 3 (Cu u rekama Pek i Zapadna Morava i Zn u uzorcima Ibra i Peka). Najveća dobijena vrednost za  $I_{geo}$  je 3.92 u sedimentu reke Pek za Cu (Klasa 4, jako kontaminirano). Rezultati

ukazuju da su od svih ispitivanih elemenata Cu i Zn najznačajniji zagađivači reka. Negativne vrednosti Igeo, uglavnom za As, Cr i Ni su rezultat nepostojanja značajnih izvora kontaminacije ovim elementima u ispitivanim rečnim sistemima.



Slika 1. I<sub>geo</sub> u zavisnosti od izbora fonskog sadržaja.

Moguće je zaključiti da izbor fonskog sadržaja ima značajnu ulogu u interpretaciji geohemijskih podataka i utvrđivanju stepena zagađenosti. Izračunate vrednosti indeksa geoakumulacije ukazuju da u ispitivanim sedimentima postoje značajni izvori kontaminacije elementima Cu i Zn. Najzagađeniji rečni sistemi ispitivanim toksičnim elementima su Ibar, Pek i Zapadna Morava.

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## **Sadržaji isparljivih organskih jedinjenja u ambijentalnom vazduhu urbane zone (Beograd)**

### **Contents of volatile organic compounds in ambient air of the urban zone (Belgrade)**

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Isparljiva organska jedinjenja (Volatile Organic Compounds – VOCs) se definišu kao grupa ugljovodonika visokog napona pare, različitih vrsta i svojstava. Uglavnom VOCs uključuje ugljovodonike nemetanskog tipa (Non-methane hydrocarbons – NMHC), oksidovane i halo-ugljovodonike. Biogeni i antropogeni VOCs u ambijentalnom vazduhu utiču na kvalitet vazduha kako u regionalnoj skali tako i na velikim rastojanjima širom sveta. VOCs su dobro poznati kao prekursori prizemnog ozona koji nastaje u fotohemijskim reakcijama. Oni takođe doprinose stvaranju fotohemijskog smoga, uključujući sekundarni organski aerosol (Secondary Organic Aerosols – SOA). Većina VOCs ima kancerogeno, mutageno i teratogeno dejstvo. Glavni izvori emisija VOCs su prirodni (biogenog porekla) i antropogeni (korišćenje rastvarača, sagorevanje biomase, saobraćaj..).

#### **Metode merenja**

Ispitivanje je rađeno je u periodu april - maj 2012.g. na lokaciji centralne zone grada - Studentski trg. Uzorci su sakupljani metodom pasivnog uzorkovanja u trajanju od 12 sati, za dnevni i noćni ciklus, korišćenjem kombinacije adsorbenasa Carbopack C / Carboback B / Carbosieve S111 koja omogućava adsorpciju najšireg opsega C<sub>n</sub>. Analiza je rađena pomoću GC/FID/ECD (Agilent 7890A) koji je povezan sa termodesorberom (Unity 1 MARKES). Razdvajanje komponenata je rađeno na kapilarnoj koloni DB-624, dužine 60 m. Za identifikaciju i kvantitativno određivanje korišćena je standardna gasna smeša TO – 15 Scotty Analyzed Gases 110 L, od 62 komponente (po 1ppm u azotu).

#### **Rezultati merenja**

Rezultati (Tabela 1) pokazuju da postoji razlika u sadržajima pojedinih jedinjenja u dnevnom i noćnom režimu. Tako na primer metil izobutil keton i n-oktan se pojavljuju samo noću dok su sadržaji o-ksilena, etilhlorida i trihloretilena znatno viši danju.

**Tabela 1.** Prosečan sadržaj najzastupljenijih VOCs u ambijentalnom vazduhu centralne zone Beograda; dan (08 – 20h) i noć (20 – 08h)

	dan		noć	
	Sr. vrednost	St. devijacija	Sr. vrednost	St. devijacija
Propilen	0,278	0,475	0,777	1,382
1,3-Butadien	0,697	2,159	5,215	25,098
Etanol	0,085	0,143	0,723	2,145
Aceton	0,204	0,321	1,805	7,797
Ugljen disulfid	0,552	0,767	0,342	0,603
izopropil alkohol	0,031	0,119	0,833	2,896
n-Heksan	0,919	0,903	2,530	10,650
vinil acetat	0,196	0,437	1,256	4,508
2-butanon	0,312	0,910	0,623	1,427
etil acetat	0,338	0,397	0,398	0,618
tetra hidro furan	0,152	0,347	0,322	0,953
cikloheksan	0,083	0,250	0,088	0,341
Benzen	5,230	7,863	11,272	24,849
Heptan	3,193	7,808	13,357	64,339
1,4- Dioksan	3,481	10,076	2,154	3,537
Metil izobutil keton	0,000	0,000	0,272	0,627
Toluen	0,082	0,249	0,218	0,961
n-oktan	0,000	0,000	0,277	1,439
Metil n-butil keton	0,752	0,696	0,990	0,673
Etilbenzen	2,948	6,031	5,359	7,860
m-Ksilen	1,657	1,023	1,927	2,079
p-Ksilen	1,212	0,636	1,853	2,080
o-Ksilen	10,720	18,080	102,950	249,282
Stiren	0,542	2,917	0,000	0,000
1-Etil-4-metilbenzen	0,748	0,917	1,065	1,792
n-dekan	0,121	0,398	4,905	16,393
1,2,4-Trimetilbenzen	2,333	3,059	14,478	37,248
1,3,5-trimetilbenzen	1,193	1,058	2,591	4,191
dihlorodifluorometan	0,076	0,365	0,209	1,009
etil hlorid*	11,629	30,662	5,614	8,829
trihlorofluorometan*	0,423	1,405	1,047	5,092
etilen 1,2-dihloro (trans)*	0,218	0,554	0,466	1,642
1,1,2-trihlorotrifluoroetan	0,029	0,154	0,104	0,396
metil hlorid	0,042	0,171	7,535	38,371
metilen hlorid	0,007	0,027	0,162	0,581
cis-1,2-dihloroetilen	0,842	1,247	0,793	2,117
1,1-dihloroetan	0,110	0,350	0,022	0,102
1,1-dihloroetilen	0,121	0,457	0,347	1,576
trihloretilen	20,629	111,038	0,256	1,259
1,2-dihloropropan	0,028	0,151	0,000	0,000
cis-1,3-dihloropropan	0,229	1,231	0,000	0,000
trans-1,3-dihlorpropen	0,308	1,587	0,016	0,026
1,1,2-trihloretan	0,009	0,023	0,024	0,084
edibromohlorometan	0,056	0,303	0,000	0,000
1,2-dibromoetan	0,652	2,445	0,075	0,099
tribromometan	0,040	0,130	0,086	0,256
1,1,2,2-tetrahaloroetan	0,016	0,021	0,017	0,019
1,4-dihlorobenzen	0,009	0,049	0,028	0,094
benzil hlorid	0,028	0,046	0,049	0,104
1,2-dihlorobenzen	0,006	0,008	0,018	0,034
heksahloro-1-3-butadien	0,430	0,488	4,725	12,788

## Stroncijum-90 u uzorcima mleka iz Srbije

## Strontium-90 in milk samples from Serbia

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<sup>90</sup>Sr svojim prisustvom u životnoj sredini, u koju je dospao usled nuklearnih proba 60-tih godina prošlog veka, postao je jedan od najznačajnijih radioekoloških faktora. Dospевši na Zemljinu površinu, ulazi u ciklus bioloških procesa koji se odvijaju na Zemlji. On prolazi složen put migrirajući po različitim karikama ekološkog lanca da bi dospao do ljudskog organizma gde učestvuje u fiziološkim procesima. Depozicija u koštanom tkivu i spora eliminacija ovog izotopa iz organizma čine ga jednim od najštetnijih radiotoksičnih elemenata. Unošenje <sup>90</sup>Sr u ljudski organizam u velikoj meri zavisi od navika potrošača. Veći deo ljudske populacije konzumira mleko, tako da ono predstavlja značajan izvor unošenja <sup>90</sup>Sr u organizam. Iz tog tazloga ideja za ovaj rad je ispitivanje sadržaja <sup>90</sup>Sr u mleku koje se može naći na teritoriji Republike Srbije.

Uzorci mleka sakupljeni su u aprilu 2011. god. na individualnim gazdinstvima i u gradskim mlekarama na teritoriji Republike Srbije. Ispitani su uzorci: kozje mleko (Resnik i Kosovska Mitrovica), ovčije (Studenica), kravlje (Kraljevo i Kosmaj) kao i uzorci kravljeg mleka (pasterizovano kratkotrajno AD Imlek mlekara Beograd, pasterizovano dugotrajno AD Imlek mlekara Beograd, pasterizovano kratkotrajno mlekara Subotica i pasterizovano kratkotrajno AD Niška mlekara). Sadržaj <sup>90</sup>Sr u uzorcima određen je radiohemijski, oksalnom metodom, koja se zasniva na oksalatnom izdvajanju Ca i Sr, žarenju do oksida i korišćenju aluminijuma kao povlačivača za <sup>90</sup>Y. Vreme uspostavljanja radioaktivne ravnoteže između <sup>90</sup>Sr i <sup>90</sup>Y je 18 dana. Nakon ovog vremena, izdvaja se <sup>90</sup>Y na povlačivaču Al(OH)<sub>3</sub> [1], koji se mineralizuje do oksida, a potom se vrši merenje na protočnom niskofonskom α/β brojaču THERMO-EBERLINE FHT 770T. Kalibracija detektora je određena pomoću standardnog izvora: <sup>90</sup>Sr (EM145, Češka nacionalna laboratorija Prag) za beta aktivnost.

U tabeli 1 prikazane su dobijene vrednosti specifične aktivnosti <sup>90</sup>Sr. Koncentracija <sup>90</sup>Sr kreće se u opsegu od 0.08 do 0.25 Bq l<sup>-1</sup>. Najveći sadržaj <sup>90</sup>Sr detektovan je u uzorku kravljeg mleka iz Kraljeva, 0.25 Bq l<sup>-1</sup>, dok je najmanji sadržaj detektovan u uzorcima kravljeg mleka iz Kosovske Mitrovica i Kosmaja, 0.08 Bq l<sup>-1</sup>.



**Tabela 1.** Aktivnost  $^{90}\text{Sr}$  u mleku

Vrsta mleka	Mesto uzorkovanja	A $^{90}\text{Sr}$ (Bq l <sup>-1</sup> )
Kozje	Resnik	0.10 ± 0.02
Kozje	Kosovska Mitrovica	0.08 ± 0.02
Ovčije	Studenica	0.13 ± 0.03
Kravlje	Kraljevo	0.25 ± 0.05
Kravlje	Kosmaj	0.08 ± 0.01
Kravlje	Beograd	0.10 ± 0.02
Kravlje	Beograd	0.23 ± 0.05
Kravlje	Subotica	0.21 ± 0.05
Kravlje	Niš	0.19 ± 0.05

U našoj zakonskoj regulativi ne postoji Pravilnik koji reguliše dozvoljene vrednosti koncentracije  $^{90}\text{Sr}$  u mleku, osim Pravilnika [2] u kome se navodi da je granica sadržaja  $^{90}\text{Sr}$  u mleku i mlečnim proizvodima posle nuklearnog akcidenta ili u slučaju drugog vanrednog radiološkog događaja 125 Bq l<sup>-1</sup>. Rezultati dobijeni u ovom radu ukazuju na to da su koncentracije  $^{90}\text{Sr}$  u analiziranim uzorcima mleka daleko ispod dozvoljenih granica.

U Srbiji se u okviru monitoringa radioaktivnosti, ispituje sadržaj  $^{90}\text{Sr}$  u mleku u zbirnim mesečnim uzorcima iz različitih gradova [3]. Za 2010. god. vrednost koncentracije  $^{90}\text{Sr}$  u mleku je u intervalu od minimalne detekcione koncentracije (mdc) do 0.07 Bq l<sup>-1</sup>. Srednje mesečne vrednosti koncentracije za period od 2000. do 2010. god. [4] bile su u intervalu od mdc do 1 Bq l<sup>-1</sup>. Dobijene vrednosti koncentracije  $^{90}\text{Sr}$  u uzorcima koji su ispitivani u ovom radu su istog reda veličine kao i ranijih godina.

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## Mineral Composition of Clay Fraction in Belgrade City Parks Soils

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The paper presents results of mineral composition of clay fraction from soil samples collected in Botanical garden and City Park in Zemun. Parent material for both locations was determined using geological map, scale 1:100.000, sheet K 34-113 Belgrade [1]. Location in Botanical garden lies on Pontian sands and marly clays, while City Park in Zemun takes part of lower and middle Pleistocene loess sediments, and the sampling site is around 100 m away from Zemun loess plateau. Soils at both locations are classified as a part of Anthrosol reference soil group, known as soils where anthropogenic factor plays a major role in soil formation or further evolution [2].

In May of 2011, soil samples were taken from the 40-50 cm depth, after obvious identification of C horizon (weathered rock). Field identification of parent material did not correspond to the one found on the Geological map at the site in Botanical Garden. Instead of Pontian sands and marly clays, loess was identified. Botanical garden and City Park in Zemun represent small green surfaces within the territory of Belgrade City centre. Soil samples were air dried and sieved through sieves of 2 mm diameter. Wet sieving was performed using 0.05 mm sieves in order to separate silt and clay from sand. Particles of clay smaller than 2  $\mu\text{m}$  were separated by decantation method. Typically, 50 g of soil sample was dispersed in 1 L of distilled water and left to settle for 24 h. A fraction that corresponds to the 1/3 of height from the upper boundary was separated, centrifuged for 5 min at 5000 rpm and left to dry in air. This procedure was repeated several times.

Mineral composition of clay fraction was determined using X-ray diffraction (XRD) method. XRD is one of most important methods for the assessment of soil mineral properties. The diagrams were recorded using  $\text{CuK}\alpha = 1.54184\text{\AA}$  radiation, setting the current of  $I = 18\text{ mA}$  and voltage of  $U = 7\text{ kV}$  (Ni filter). X-ray powder diagrams were recorded in the  $2\theta$  range from  $2^\circ$ - $60^\circ$  with recording speed of  $1^\circ/\text{min}$  and  $R_c=4/2$ . Oriented samples of air dry, ethylene-glycol saturated (EG) and heated ( $550^\circ\text{C}$ ) clay were recorded for both locations.

Mineral analysis of clay fraction reveals that both, City Park in Zemun and Botanical garden, samples have similar composition. In City Park in Zemun, illite is dominant mineral, but small presence of kaolinite, smectite and chlorite was also detected. In Botanical garden, smectite and kaolinite are dominant minerals, while there is also a high content of illite. Chlorite is present, but in lower content than other minerals.

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## **Upravljanje komunalnim i industrijskim otpadom na teritoriji grada Kragujevca**

### **Management of municipal and industrial waste in the city of Kragujevac**

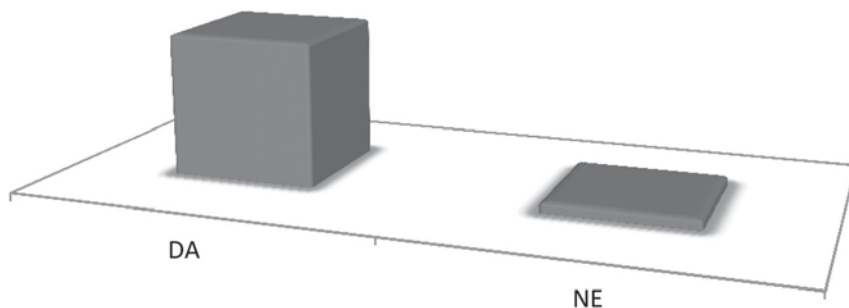
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U Republici Srbiji upravljanje otpadom je u značajnoj meri zastarelo. Do pre deset godina sakupljalo se samo 50% otpada, od čega se 63% odnosilo na sakupljanje komunalnog gradskog otpada i 20% industrijskog otpada. Otpad se nije najčešće sakupljao iz ruralnih područja, gde je uglavnom spaljivan ili se akumulirao na smetlištima i divljim deponijama. Od približno stotinu zvaničnih gradskih deponija, nijedna nije ispunjavala kriterijume sanitarnih deponija. Poslednjih pet godina situacija se nije značajno promenila, jer je zabeleženo par hiljada divljih deponija u Republici Srbiji. Nažalost, usvajanjem Zakona o zaštiti životne sredine i upravljanju otpadom kao i Nacionalne strategije kojom se planiralo formiranje regionalnih centara za upravljanje komunalnim otpadom malo toga je implementirano. Ne može se reći da situacija nije poboljšana ali i dalje postoji veliki broj gradskih smetlišta koje ne ispunjavaju osnovne kriterijume. Opasan otpad, po definiciji, predstavlja otpad koji ima takva fizička, hemijska ili biološka obeležja da zahteva specijalno rukovanje i postupke obrade kako bi se izbegli rizici i štetna delovanja na zdravlje i životnu sredinu [1]. Sam komunalni čvrst otpad podrazumeva otpad iz domaćinstava kao i drugi otpad koji je zbog svoje prirode ili sastava sličan otpadu iz domaćinstava. Nastaje u okviru komunalne infrastrukture u domaćinstvima, administrativnim i obrazovnim ustanovama, turističkim objektima, trgovini, uslužnim delatnostima, kao i otpad sa javnih površina i parkova. Industrijski otpad se u poslednjih nekoliko godina generisao uglavnom zahvaljujući proizvodnji i radu mnogih fabrika i preduzeća. Razvoj mnogih preduzeća doprinela su povećanju količine industrijskog otpada i problematici odlaganja. U cilju utvrđivanja najvažnijih problema u oblasti upravljanja svim vrstama otpada u gradu Kragujevcu i njegovog uticaja na životnu sredinu, kao i načina za njihovo rešavanje sprovedene su dve ankete u okviru Lokalnog ekološkog akcionog plana (LEAP) iz 2010 godine [2]. Jedna anketa bila je namenjena za domaćinstva, a druga za industrijska preduzeća. Utvrđivanje problema u ovoj oblasti u našem gradu i prigradskim naseljima bilo je kroz sagledavanje i evidentiranje vrsta otpada, kao i načina za njegovo zbrinjavanje. Pitanja sprovedena u domaćinstvima odnosila su se na komunalni otpad, njegovu klasifikaciju i odlaganje. Zbrinjavanje elektronskog, farmaceutske i medicinskog otpada takođe je bio sastavni deo ankete sprovedene među građanima. Anketiranje u vezi upravljanja industrijskim otpadom

sprovedena je u preko dvadeset preduzeća na teritoriji grada Kragujevca. Pitanja su uglavnom iziskivala odgovore da li i uolikoj meri generišu otpad kao i da li su upoznati sa zakonskim regulativama (Slika 1) i da li imaju pomoć u tehničko-tehnološkom smislu itd.

**Da li ste upoznati sa novim Zakonom o zaštiti životne sredine?**



**Slika 1.** Grafički prikaz odgovora na jedno od anketnih pitanja

Zbirni statički rezultati pokazali su da među većim procentom građana vlada solidna ekološka svest. Preduzeća su bez obzira na poteškoće (uglavnom, finansijski i nasleđeni problemi) shvatila potrebu i korist da otpadne materije iskoriste ili za ponovnu upotrebu ili da ih pošalju drugim centrima (partnerima) koji se bave procesom reciklaže (ponovne upotrebe). Celokupni rezultati svakako ne treba da budu zadovoljavajući već motivacija da se u ekološkom pogledu dosegne još viši nivo. Potrebno je u narednom periodu izvršiti opsežnu edukaciju na svim nivoima i generacijama kako bi rezultati bili još bolji. “*Misli globalno, deluj lokalno*”.

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## **Dynamics of change in hydrocarbon composition of oil under the influence of peat microflora at lower temperatures**

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In severe climatic conditions of Siberia restoration of oil-polluted soils is considered as a pressing environmental problem. At excess of allowable pollution level soil-vegetable covering loses its self-regeneration ability. Peat-gley bog soils dominate in the territory of West Siberia. Due to their structure and biochemical nature peats have good sorption properties and contain hydrocarbon-oxidizing microorganisms capable to destruct oil hydrocarbons and other components.

We have studied the effect of aboriginal peat microflora on the destruction of different classes of saturated and alkyl aromatic hydrocarbons at lower temperatures.

Oil biodegradation was simulated using high-moor peat at 9 °C. Stripped oil was applied on damp peat (humidity 54 %) in amounts of 15 and 32 wt %. Impact of microorganisms on oil was determined in 15, 45, 75 and 270 days. The residual oil was extracted from the peat with chloroform. In extracts obtained we determined contents of asphaltenes, resins and hydrocarbons. Compositions of saturated and aromatic hydrocarbons were analyzed by gas chromatography-mass spectrometry

Introduction of oil into peat caused marked increase in total number of microorganisms in all the experiments. The growth of microorganisms was observed for 75 days regardless of a pollution level. A sharp decrease in microorganism number occurred in 270 days. It was especially noticeable in the samples with a pollution level of 32 %. Therefore, oil dose in excess of 15 % had a sharp inhibiting effect not only on total number of microflora but also on hydrocarbon-oxidizing bacteria probably owing to general deterioration of peat aeration. Despite periodic (decrease-increase-decrease) changes in the amount of the residual oil we observed a steady tendency to oil utilization by microorganisms.

The content of asphaltenes increased significantly, while contents of resins and hydrocarbons decreased in the residual oils as compared with the initial one.

The results of chromatography-mass spectral analysis of individual hydrocarbon composition evidenced significant changes, which occurred during biodegradation. In the samples with 15 % degree of oil pollution n-alkylbenzenes were subjected to the most destruction in all the experiments – in 45 days their concentration decreases by 1.8, in 75 days – 4.3 and in 270 – by 10.9 times in the

oil sample, the biodegradation period of which was 15 days (Table). Under such conditions n-alkanes degraded slower – in 270 days their concentration decreased only 6.8 times. Alkylphenanthrenes were found to be the stable as compared with the rest of alkylarenes.

**Table 1.** Hydrocarbon composition of residual oils

Compounds	Content, wt %			
15 % of oil in peat				
n-Alkanes	1.79	1.21	0.61	0.26
Isoprenoids	0.52	0.34	0.22	0.12
n-Alkylbenzenes	0.10	0.06	0.02	0.01
Methylalkylbenzenes	0.15	0.10	0.06	0.03
Naphthalenes	0.09	0.05	0.04	0.02
Phenanthrenes	0.04	0.03	0.02	0.02
32 % of oil in peat				
n-Alkanes	5.58	2.06	2.53	2.25
Isoprenoids	1.07	0.49	0.90	0.59
n-Alkylbenzenes	0.24	0.09	0.15	0.10
Methylalkylbenzenes	0.33	0.14	0.33	0.17
Naphthalenes	0.17	0.07	0.15	0.08
Phenanthrenes	0.10	0.04	0.09	0.05

In the samples with 32 % of oil pollution one observed no pronounced dynamics of change in the contents of saturated and aromatic hydrocarbons with increasing experiment duration from 45 to 270 days. The contents of all hydrocarbons decreased in the following way: in 45 days 2.2 – 2.7 times and in 270 days 1.8 – 2.5 times in comparison with the sample, the biodegradation of which lasted for 15 суток

Increased pollution level had a negative impact on vital activity of microorganisms reducing their ability to utilize the oil components.

## **Aromatična jedinjenja u izduvnim gasovima motornih vozila**

### **Aromatic compounds in the exhaust of motor vehicles**

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Zagađenje vazduha od strane motornih vozila predstavlja veliki problem kako zbog konstantnog povećanja broja motornih vozila tako i sve većih pređenih rastojanja svakog vozila tokom godine. Kao primaran izvor energije motorna vozila koriste fosilna goriva čijim sagorevanjem nastaju produkti u obliku gasovitih, tečnih i čvrstih zagađujućih materija. Konstantna emisija u ambijentalni vazduh negativno utiče na globalne procese transporta, distribucije i raspodele između osnovnih kompartimenata životne sredine: vode, vazduha, zemljišta i vegetacije što može podrazumevati i raspodelu između faza unutar određenog kompartimenta životne sredine.

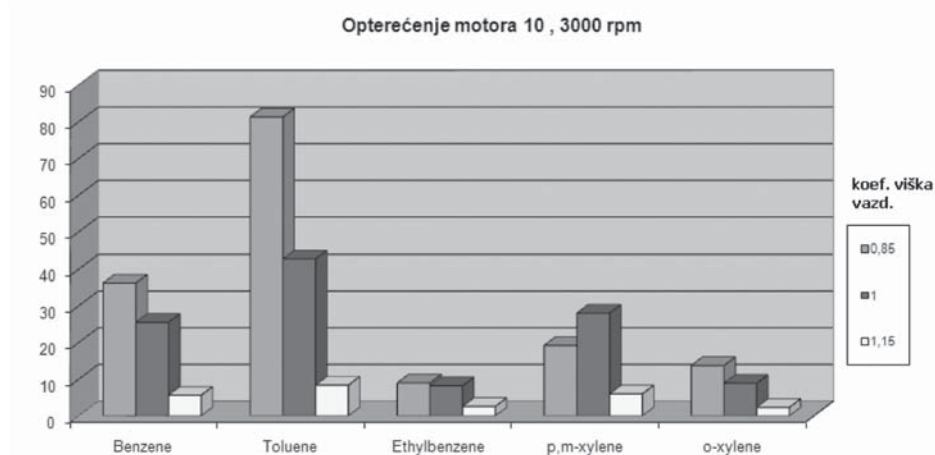
Sagorevanje predstavlja osnovni proces tokom kojeg se hemijska energija iz goriva pretvara u toplotu i dalje u mehanički rad u motorima saunutrašnjim sagorevanjem (SUS). Od ukupne energije koja se oslobađa procesom sagorevanja, oko 42% se koristi za pokretanje vozila, dok preostalih 58% predstavlja gubitke. Načelno, što je motor efikasniji, to su i manje količine štetnih izduvnih gasova. Sagorevanje u motorima SUS predstavlja veoma kompleksan hemijski postupak, okarakterisan naglim promenama temperature, pritiska i koncentracije reaktivnih supstanci. Proces hemijske konverzije u komori za sagorevanje je sve, samo ne jednostavna hemijska reakcija. Zbog čega još uvek nije definisana zadovoljavajuća teorija sagorevanja koja bi opisala navedeni proces u svakom detalju. Usavršavanje komore za sagorevanje, optimizacija procesa izmene radne materije, podizanje sposobnosti sistema za napajanje goriva i visoko efikasni sistemi za naknadni tretman izduvnih gasova proizveli su značajno efikasnije i čistije motore [1].

Ekološki standardi Evropske Unije koji se odnose na izduvne gasove motornih vozila, počev od Euro 1, pa sve do najnovijeg Euro 6 standarda koji će se primenjivati u zemljama EU od decembra 2013. godine fokusirani su, pre svega, na smanjenje emisije gasova staklene bašte: ugljen dioksida, ugljen monoksida, oksida azota i čvrstih čestica. Međutim eksperimentalni rezultati istraživanja ukazuju na relativno visoke koncentracione nivoe aromatičnih jedinjenja u izduvnim gasovima motornih vozila. Prisustvo hazardnih polutanata iz grupe BTEX javlja se pre svega kao rezultat supstitucije olova kao antidetonatora sa aromatičnim jedinjenjima u bezolovnim benzinima, čime je praktično izvršena zamena jednog problema drugim. Globalni procesi raspodele, transporta i distribucije aromata čine ovaj problem još većim.



Prisustvo VOC jedinjenja u ambijentalnom vazduhu utiče na produkovanje ozona i fotohemijskih oksidanata štetnih po zdravlje ljudi i ekosisteme. Sinergija štetnog efekta benzena i ostalih BTEX jedinjenja je očekivana s' obzirom da se u izveštajima koji se odnose na monitoring ambijentalnog vazduha detektuju najčešće kao grupa [2,3].

Eksperimentalna istraživanja u okviru rada sprovedena su u laboratoriji za motore SUS Fakulteta tehničkih nauka u Novom Sadu. Praćeni su koncentracioni nivoi BTEX jedinjenja u izduvnim gasovima benzinskog motora Fiat 1.2, pri promenljivom broju obrtaja, različitom stepenu opterećenja i variranju stehiomstrijskih odnosa smeše vazduh/benzin. Detekcija koncentracionih nivoa BTEX jedinjenja je sprovedena korišćenjem mobilnog gasnog hromatografa Voyager, Photovac. Za razdvajanje komponenti uzorka vazduha korišćena je Supelcowax10- (PEG) kolona, a za detekciju fotojonizacioni (PID) detektor.



Eksperimentalni rezultati ukazuju na prisustvo izuzetno visokih koncentracija BTEX jedinjenja u izduvnim gasovima benzinskih motora, pre svega kao rezultat nepotpunog sagorevanja smeše benzina i vazduha u uslovima bogate smeše (koef. viška vazduha <1) i velikih opterećenja motora do kojih često dolazi u uslovima gradske vožnje.

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## **Degradability of *n*-alkanes during *ex situ* stimulated bioremediation of soil contaminated by heavy residual fuel oil (mazut)**

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In this paper, the *ex situ* stimulated bioremediation of soil contaminated with heavy residual fuel oil (mazut) was conducted during the period of 6 months. The fate of *n*-alkanes in the pollutant was monitored.

According to our previous research [1] it was concluded that during natural biodegradation of oil pollutant, in the conditions of the reduced availability of certain class of compounds (first of all caused by their low amount), microorganisms opt for those which are more accessible, i.e. those which are found in the substrate in higher amount, even if these compounds are less biodegradable.

In the present research we investigated if in the conditions of stimulated bioremediation (with addition of biomass, nutrient substances and biosurfactant) the biodegradation of the compounds which are found in low amount can be stimulated as well.

The soil polluted with heavy residual fuel oil (mazut) was mechanically mixed with softwood sawdust and crude river sand to form a homogenized biopile. Reinoculation was performed periodically with biomasses of microbial consortia isolated from the mazut-contaminated soil. Biostimulation was conducted with addition of nutritional elements (N, P and K). Aeration was improved by systematic mixing. Biosurfactants were used as surface active agents to solubilize mazut.

During the interval of six months the samples were taken five times. Organic substance from in total 5 soil samples was extracted with chloroform (HPLC, J.T., USA) using a Soxhlet apparatus. From these extracts, the hydrocarbons (saturated and aromatic) were isolated by column chromatography and analyzed by the gas chromatography-mass spectrometry (GC-MS) techniques. In the aromatic fraction phenanthrene, methyl-phenanthrenes, dimethyl-phenanthrenes and trimethyl-phenanthrenes were analyzed in detail. The saturated hydrocarbon mixture was separated into *n*-alkane and branched and cyclic alkane fractions by urea adduction. The *n*-alkanes in urea adducts were analyzed by gas chromatography (GC).

In the initial sample the fraction of total saturated hydrocarbons was characterized by a broad and prominent “hump” of an unresolved complex mixture (UCM), typical of oils altered by biodegradation. *n*-Alkanes were present in a very low abundance and their identification was possible only after concentration by urea adduction technique. According to these results the investigated oil pollutant was classified to be at the boundary between the third and the fourth biodegradation level.

During the experiment, a specific biodegradation pattern of methyl-phenanthrene homologues was observed (the most pronounced in comparison with the trimethyl-phenanthrenes and the least in comparison with the methyl-phenanthrenes). It was concluded that this process of applied bioremediation resulted in the increase in the availability of phenanthrene and its methyl derivatives to microorganisms and in that way increased the degradability of homologues with higher level of alkylation [2].

However, in the fractions of saturated hydrocarbons investigated in the present research, the removal of the remaining *n*-alkanes was not observed. The abundance of *n*-alkanes remained at the initial low level, even at end of the experiment, after six months of the intensive stimulated bioremediation.

According to these results it can be concluded that even in conditions of intensive stimulated bioremediation, biodegradation of individual components of oil pollutants will not proceed (not even in the case of *n*-alkanes which are the most biodegradable hydrocarbons in oils) unless they are present in some minimum “threshold” amount.

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## **Fotolitička i fotokatalitička razgradnja herbicida klomazona u prirodnim vodama**

### **Photolytic and photocatalytic degradation of the herbicide clomazone in natural waters**

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Herbicid klomazon (2-(2-hlorbenzil)-4,4-dimetil-1,2-oksazolidin-3-on) se efikasno koristi za suzbijanje korovskih biljaka na poljima soje, kukuruza, duvana, pirinča, šećerne repe i različitog povrća [1]. Pomenuti herbicid se dobro rastvara u vodi, pa nakon primene u okviru agrotehničkih mera lako može dospeti u podzemne vode što predstavlja ozbiljan ekološki problem [2]. Iz tog razloga potrebno je naći pogodno rešenje za njegovo uklanjanje iz vodene sredine. Prema literaturnim podacima heterogena fotokataliza u prisustvu  $\text{TiO}_2$  se u većini slučajeva pokazala kao efikasna metoda za uklanjanje pesticida iz vode [3,4]. Stoga u ovom radu je proučavana fotolitička i fotokatalitička razgradnja klomazona u vodenoj suspenziji  $\text{TiO}_2$  Degussa P25. Kao izvor veštačkog zračenja poslužila je halogena lampa sa odgovarajućim optičkim filtrom ( $\lambda \geq 400 \text{ nm}$ ) koja zrači vidljivi deo spektra odnosno živina lampa (emisioni maksimumi u UV oblasti na 304, 314, 335 i 366 nm, sa najintenzivnijim emisionim maksimumom na 366 nm) uz upotrebu odgovarajućeg konkavnog ogledala. Eksperimenti direktne fotolize izvođeni su pri istim uslovima kao i fotokatalitička razgradnja, ali bez dodatka katalizatora. Na osnovu dobijenih rezultata se može zaključiti da direktna fotoliza nema značajniju ulogu kada je u pitanju ukupna brzina fotokatalitičke razgradnje. Naime, primenom vidljivog zračenja ne dolazi do razgradnje klomazona u prisustvu katalizatora, kao i bez njega. Nasuprot tome, u prisustvu UV zračenja dolazi do razgradnje klomazona, s tim da je razgradnja mnogo brža primenom katalizatora. Ranija istraživanja su pokazala da prisustvo organskih i neorganskih materija u prirodnim vodama utiče na efikasnost fotorazgradnje primenom UV/ $\text{TiO}_2$  [5,6]. Stoga je nakon ispitivanja fotokatalitičke razgradnje klomazona u tri puta destilovanoj vodi, ispitivana njegova razgradnja u rečnoj (Dunav i Tisa), podzemnoj i termalnoj vodi. Nađeno je, da se razgradnja klomazona najbrže odvija u tri puta destilovanoj vodi. Naime, brzina razgradnje je oko devet puta veća nego u termalnoj, odnosno oko osam puta u poređenju sa podzemnom vodom. Nadalje, efikasnost razgradnje klomazona u rečnoj vodi je oko tri (Dunav), odnosno četiri (Tisa) puta manja nego u tri puta destilovanoj vodi. Imajući u vidu prisustvo rastvorenih organskih materija i različitih vrsta jona u prirodnim vodenim sistemima, može se očekivati da oni utiču na sam proces fotorazgradnje. Efekat smanjenja brzine razgradnje supstrata u prisustvu jona je posledica toga što se oni ponašaju kao hvatači hidroksil-radikala. Od jonskih vrsta naročito izražen

uticaj imaju hidrogenkarbonatni joni [6]. Isto tako, od organskih materija huminske kiseline mogu imati funkciju hvatača hidroksil-radikala [7,8] što dovodi do smanjenja brzine fotorazgradnje. U cilju ispitivanja efikasnosti fotorazgradnje u prisustvu hidrogenkarbonata, odnosno huminske kiseline u rastvor herbicida klomazona sa tri puta destilovanom vodom pojedinačno je dodata ista količina pomenutog anjona i huminske kiseline koja je prisutna i u prirodnim vodama. Na osnovu dobijenih rezultata može se zaključiti da dodatak hidrogenkarbonata i huminske kiseline dovodi do smanjenja brzine razgradnje u poređenju sa tri puta destilovanom vodom.

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## **Passive sampling techniques in environmental water analysis**

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Anthropogenic pollution represents the major part of environment contamination. The fate of contaminants in environment is variable, some of them even get without change through cleaning technologies of waste waters. The analysis of pollution of surface waters by chemical contaminants is mandatory according to the Water framework directive 2000/60/EU [1] and the EU directive 2008/105/EU [2] with primary aim in preservation of the waters and their conservation for future generations, the limits of concentrations (environmental quality standards) in surface waters are stated for individual high risk chemicals for aquatic fauna and flora, e.g. pesticides, polycyclic aromatic hydrocarbons, benzene, halogenated solvents, flame retardants, polymer additives, tensides, antivegetative preparations and also some metals. All analytical methods used for programs estimating the state of waters must fulfill minimal working criteria including the rules for measurement uncertainty and limits of quantification [3]. One of the most important tasks of analytical process is the sampling, because it influences overall precision of measurements. The passive sampling couples the sampling process with the isolation and pre-concentration of analyte into one step. Passive sampling represents a technique based on free transfer of analyte from aquatic environment to the receiving phase of passive sampler, as a consequence of difference in chemical potential of analyte in these phases [4]. The procedure includes preparation of the samplers, their exposition to the dissolved fraction of the pollutants in surface water, then the processing of the samplers with aim to isolate the concentrated pollutants into a new phase, an organic solvent and the purification and concentration of extracts. The quantitative analysis is aided by use of performance reference compounds (PCRs), whose elimination from the sampler gives information on the transfer kinetics. The result is obtained in the form of time averaged contaminants concentration in sampled waters. The method and the calculation procedure will be stepwisely explained and documented.

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## **Passive sampling techniques with semipermeable membrane devices for monitoring of PAHs in surface water**

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The pollution of surface water by chemicals can lead to disrupted aquatic ecosystems and loss of biotopes and biodiversity. Based on the European Water Framework Directive 2000/60/EC [1] it is required to monitor priority pollutants in surface waters, complying with the EU directive 2008/105/EU which states the limits of concentrations (environmental quality standards) in surface waters for 41 chemicals including 33 priority compounds and 8 other pollutants representing high risk for aquatic fauna and flora and also for human health [2]. The aim of the presented study was to evaluate passive sampling SPMD method [3] with aim to monitor trends in pollutants concentration in surface water, applied for the river Danube. For priority pollutants that are poorly soluble in water, eg. polycyclic aromatic hydrocarbons (PAHs), the laboratory methods of direct analysis of water samples are not sensitive enough to determine these substances at the trace levels of stated environmental quality standards. The passive sampling SPMD devices work as integrative samplers and allow the measurement of time-weighted average concentration of pollutant in water for a period of up to several weeks. The study was conducted in Danube river at 4 sampling sites in Austria and Slovakia, with deployment of SPMD samplers for 14-day exposure. The content of PAHs after isolation from samplers was determined by gas chromatography coupled with mass spectrometry. The concentration of 16 PAHs in the water were low, in the order of ng.l<sup>-1</sup>. Concentrations of the PAHs decreased with increasing water temperature in the whole region, which reflects the seasonality in PAH emissions to water, most likely via atmospheric deposition. The observed seasonal oscillation of PAH concentration has an implication for the design of future monitoring programs aimed at assessment of long term trends.

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## Collection and analysis of polar pesticides from surface water using polar organic chemical integrative samplers

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The EU directive 2008/105/EU [1] based on the the Stockholm treaty on POPs and the EU Water framework directive states the limits of concentrations (environmental quality standards) in surface waters for 41 chemicals including 33 priority compounds and 8 other pollutants representing high risk for aquatic fauna and flora and also for human health, including pesticides [2]. Conventional analytical methods used for monitoring by spot sampling measure the total concentration and often fail to detect trace amounts, in comparison with the passive samplers, which allow to estimate the time-weighted average concentration of dissolved fraction of analytes over a certain period of time at a very low level. This dissolved fraction is directly related to chemical activity in water and describes the contaminant behavior in the environment. Passive samplers of the polar organic chemical integrative sampler type (POCIS) are used to monitor the hydrophilic contaminants, such as pesticides, pharmaceuticals, steroid hormones or antibiotics. The sampler consists of Oasis HLB adsorbent compressed between two microporous polyethersulfonic membranes. The sampler works on time integrative principle. The presented study is aimed at the determination of selected polar pesticides in the river Bosna in Bosnia and Herzegovina. Passive samplers were deployed at 10 sampling profiles in the river from its spring upstream the city of Sarajevo down to the confluence of Bosna with Sava. POCIS passive samplers were exposed to river water for 26 to 43 days. Following exposure samplers were analysed for content of polar pesticides by LC-ESI-MS/MS technique. The determined concentrations of the 14 target pesticides in water were low, in the order of units of ng.l<sup>-1</sup>.

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## **Uklanjanje pesticida iz industrijskih otpadnih voda nedisperzivnom tečno-tečnom ekstrakcijom u membranskom kontaktoru**

### **Removal of the pesticides from the industrial wastewater by nondispersive liquid-liquid extraction in the membrane contactor**

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Čista voda predstavlja vitalan resurs u savremenom društvu koji je pod uticajem porasta stanovništva i povećanim zagađenjem industrijskim produktima, pa je od velike važnosti uklanjanje štetnih materija iz industrijskih otpadnih voda. Među štetnim supstancama prisutnim u vodama, pesticidi zauzimaju jedno od centralnih mesta.

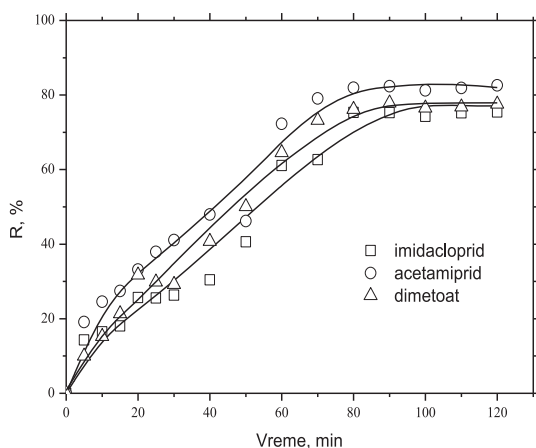
Membranska ekstrakcija je nedisperzivna tečno-tečna ekstrakcija u kojoj dolazi do razmene mase između dve nemešljive tečnosti razdvojene mikroporoznom membranom [1]. U poređenju sa klasičnim tečno-tečnim ekstraktorima, membranski ekstraktori imaju nekoliko prednosti: velika kontaktna površina po zapremini, moguća je ekstrakcija sa veoma malim zapreminama organske faze, nema curenja iz jedne faze u drugu što se reguliše protokom faza, ceo postupak je lako automatizovati i cena ekstrakcije je manja u odnosu na klasičnu.

Cilj ovog rada bio je uklanjanje pesticida (imidakloprida, acetamiprida i dimetoata) iz industrijskih otpadnih voda primenom trofazne (polazni rastvor, ekstragens, rastvor za reekstrakciju), kontinualne membranske ekstrakcije u kontaktoru na bazi mikroporoznih kapilara sa recirkulacijom polaznog rastvora.

Membranski kontaktor se sastojao od staklene cevi u čijoj unutrašnjosti se nalazi 50 paralelno postavljenih polipropilenskih hidrofobnih kapilara (efektivna dužina kapilare 12,5 cm, unutrašnji prečnik 280  $\mu\text{m}$ , debljina zida 190  $\mu\text{m}$ , poroznost 28%). Polazni, vodeni rastvor za ekstrakciju (rastvor pesticida u dejonizovanoj vodi ili rastvor komercijalne formulacije pesticida u česmenskoj vodi, koncentracija pojedinačnog pesticida 20  $\text{mg dm}^{-3}$ ) pumpan je pomoću peristaltičke pumpe kroz lumen kapilara u režimu rada sa recirkulacijom. Ekstragens (5% TOPO u di-n-heksiletru) se nalazio u porama membrana. Rastvor za reekstrakciju (2  $\text{mol dm}^{-3}$  HCl) se nalazio sa spoljašnje strane kapilara i bio je stacionaran. Koncentracija pesticida je određivana tečnom hromatografijom (HPLC-UV Dionex-0650) sa reversno faznom kolonom Eclipse XDB-C18 (Agilent).

Stepen uklanjanja pesticida iz polaznog rastvora ekstrakcije u rezervoaru,  $R$ , predstavlja realno stanje u ekstrakciji i opisuje količinu ispitivanog pesticida koja je uklonjena iz celokupne zapremine polazne vodene faze. Imidakloprid, acetamiprid i dimetoat imaju nizak koeficijent raspodele (vrednosti  $\log D$  u sistemu oktanol-voda su za imidakloprid 0,46; za acetamiprid 1,55 i za dimetoat 1,37), i u klasičnoj tečno-tečnoj ekstrakciji maksimalno se iz vodenog rastvora ukloni 10% ovih pesticida.

Na slici 1 prikazan je uticaj vremena ekstrakcije na ukupni stepen uklanjanja pesticida iz polaznog rastvora (rastvor komercijalnih formulacija pesticida u česmenskoj vodi). Stepenn uklanjanja ispitivanih pesticida u rezervoaru vodene faze raste sa proticanjem vremena ekstrakcije, i teži graničnoj vrednosti koja se za ispitivane pesticide postiže posle 70 minuta. Uslovi ekstrakcije hemijski čistih pesticida i uzoraka otpadne industrijske vode bili su isti. Stepenn uklanjanja ispitivanih pesticida iz komercijalnih formulacija su vrlo slični rezultatima koji su dobijeni iz rastvora hemijski čistih pesticida što ukazuje na to da komponente koje su dodate u komercijalni preparat pesticida ne utiču na njihovu ekstrakciju.



**Slika 1.** Vremenska zavisnost uklanjanja pesticida iz otpadne industrijske vode primenom membranske ekstrakcije (protok 1,1 cm<sup>3</sup> min<sup>-1</sup>).

Ispitivan je i uticaj protoka vodene faze koja je recirkulisala između kontaktora i rezervoara u opsegu od 0,5 do 1,8 cm<sup>3</sup> min<sup>-1</sup>. Povećanjem protoka stepenn uklanjanja pesticida raste i dostiže oko 80% pri najvećem protoku.

Na osnovu eksperimentalnih rezultata membranske ekstrakcije ispitivanih pesticida koji imaju nizak koeficijent raspodele, u sistemu sa recirkulacijom polaznog rastvora za ekstrakciju, može se zaključiti da ova metoda daje značajno bolje rezultate u poređenju sa klačnom tečno-tečnom ekstrakcijom i predstavlja novu mogućnost za prečišćavanje industrijskih otpadnih voda.

### Zahvalnica

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## **Jonska tečnost kao ekstragens u tečno-tečnoj mikroekstrakciji za pripremu uzorka pre HPLC analize pesticida**

### **Ionic liquid based liquid-liquid microextraction for sample preparation before HPLC analysis of pesticides**

Tatjana Trtić-Petrović, Aleksandra Dimitrijević

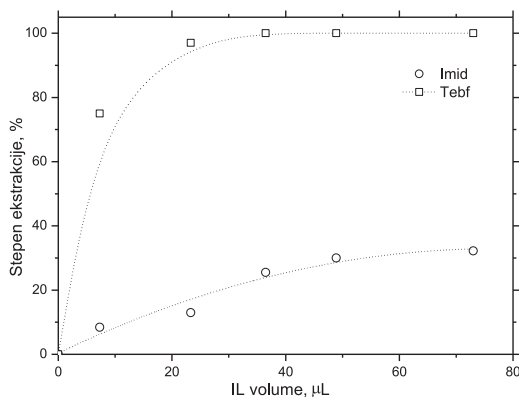
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Jonske tečnosti (IL) sa jedinstvenim osobinama kao što su niska zapaljivost i napon pare, mogućnost rada u širokom opsegu temperatura, visoka jonska konduktivnost, visoka solvaciona mogućnost, hemijska stabilnost i selektivnost, visoka ekstrahibilnost za neorganske, organske i biomolekule, kao i niska štetnost za okolinu, predstavljaju alternativu za klasične organske rastvarače u tečno-tečnoj ekstrakciji [1, 2]. Jonske tečnosti se sastoje od organskog katjona (obično heterocikli koji sadrže azot kao što su imidazol, piridin, itd.) i organskog ili neorganskog anjona. Važna karakteristika IL je da kombinacijom anjona i katjona moguće menjati i podešavati njihove fizikohemijske osobine. Cilj ovog rada je primena jonske tečnosti kao ekstragensa u mikroekstrakciji u fazi pripreme uzorka pre HPLC analize pesticida. Optimizovani su parametri koji utiču na ekstrakciju: zapremina IL i vodene faze, vreme ekstrakcije i centrifugiranja, kao i jonska jačina rastvora. Metoda je validirana i primenjena za određivanje izabranih pesticida u uzorcima industrijske otpadne vode.

Za mikroekstrakciju su izabrana dva pesticida: imidakloprid (Imid) i tebufenozid (Tebf). Koeficijenti raspodele u sistemu oktanol/voda za Imid i Tebf su 0,46 i 4,38, redom. Pesticidi su ekstrahovani dodatkom jonske tečnosti [ $C_6MIM$ ] [ $(CF_3SO_2)_2N$ ] (1-heksil-3-metilimidazolium bis(trifluorometilsulfonil) imida) u vodeni rastvor (dejonizovana ili otpadna industrijska voda), nakon intenzivnog mućkanja (Vortex, 2500 rpm), faze su odvojene centrifugiranjem (2min na 2000 rpm). Vodena faza se odvoji dekantovanjem od IL, koja ostaje na dnu epruvete (gustina korišćene IL je  $1,38 \text{ g mL}^{-1}$ ). Koncentracija pesticida u IL je određivana tečnom hromatografijom (Agilent 1100 HPLC) sa reversno faznom kolonom Ecclipse XDB-C18 i UV-detektorom na talasnoj dužini 254nm.

Na slici 1 prikazan je uticaj zapremine IL na stepen ekstrakcije Imid i Tebf. Povećanjem zapremine IL, stepen ekstrakcije pesticida raste, i dostiže 100% za Tebf sa  $20 \mu\text{L}$  ekstragensa, dok je maksimalni stepen ekstrakcije Imid (30%) postignut sa  $75 \mu\text{L}$  ekstragensa. Faktor koncentrovanja koji zavisi od stepena ekstrakcije, ali i od odnosa zapremine vodene faze i IL, opada sa povećanjem zapremine IL. S obzirom da je cilj rada bio analiza niskih koncentracija pesticida,  $40 \mu\text{L}$  je određeno kao optimalna zapremina IL za mikroekstrakciju ispitivanih pesticida.

U daljem radu utvrđeni su parametri za optimalnu ekstrakciju ispitivanih pesticida: vreme potrebno za ekstrakciju 2 min uz snažno mućkanje (2500 rpm), odvajanje IL i vodene faze centrifugiranjem na 2000 rpm, 2 min, i dodatak NaCl ( $0.5 \text{ mol L}^{-1}$ ) povećava stepen ekstrakcije Imid, a ne utiče na ekstrakciju Tebf.



**Slika 1.** Uticaj zapremine IL na stepen ekstrakcije Imid i Tebf

Kalibracione prave ispitivanih pesticida su određene pod optimalnim uslovima mikroekstrakcije sa IL kao ekstragensom (Tabela 1). Dobijeni su visoki koeficijenti korelacije za oba ispitivana pesticida. Niži limit detekcije je dobijen za Tebf. Primenom optimizovane mikroekstrakcione metode za pripremu uzorka određene su koncentracije Imid i Tebf u uzorcima industrijske otpadne vode. Relativna standardna devijacija za određene koncentracije u odnosu na nominalne vrednosti je bila manja od 10%.

**Tabela 1.** Parametri kalibracionih prava Tebf i Imid

Pesticid	Imid	Tebf
Odsečak na Y osi	$1.04 \times 10^6$	$-2.55 \times 10^6$
Nagib prave	$1.14 \times 10^8$	$5.04 \times 10^8$
Koeficijent korelacije $r^2$	0.9999	0.9999
Limit detekcije, $\mu\text{g L}^{-1}$	8.6	1.8
Limit kvantifikacije, $\mu\text{g L}^{-1}$	28.0	6.0

Mikroekstrakcija sa jonskom tečnošću kao ekstragensom predstavlja brzu, jednostavnu metodu sa malom potrošnjom IL, efikasnom ekstrakcijom za jedinjenja različite polarnosti, kompatibilna za direktnu analizu tečnom hromatografijom, i bez štetnog efekta po okolinu. Prikazani rezultati pokazuju da mikroekstrakcija sa jonskim tečnostima predstavlja alternativu za druge ekstrakcione tehnike koje se koriste kao metode za pripremu uzorka u analizi pesticida u prirodnim i otpadnim vodama.

### Zahvalnica

*Finansijska podrška za ovo istraživanje dobijena je od Ministarstva za prosvetu i nauku Republike Srbije kroz projekte III 45006.*

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## **Uklanjanje teških metala iz vode adsorpcijom na sirovoj i modifikovanoj interstratifikovanoj montmorionit/kaolinit glini**

### **Removal of heavy metals from aqueous solutions by adsorption on raw and modified interstratified montmorillonite/kaolinite clay**

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#### **Uvod**

Prisustvo teških metala u životnoj sredini, čak i u niskim koncentracijama, negativno utiče na zdravlje ljudi, biljnog i životinjskog sveta. Konvencionalni postupci za uklanjanje teških metala iz otpadnih voda uključuju: precipitaciju, koagulaciju/flokulaciju, sorpciju, jonsku izmenu i membransku filtraciju [1]. Adsorpcija predstavlja jednostavan, efikasan i ekonomičan način prečišćavanja vode [2], pa je veliki broj aktuelnih istraživanja okrenut ka pronalaženju novih, lako dostupnih i jeftinih adsorbenasa za uklanjanje teških metala.

Cilj ovog rada je ispitivanje uticaja pH vodenog rastvora na efikasnost uklanjanja teških metala (Pb, Cd, Cu, Zn) primenom lokalno dostupne sirove i mehaničkim mlevenjem modifikovane gline, određivanje adsorpcionog kapaciteta gline i mogućnosti njene primene u sistemima za prečišćavanje otpadnih voda.

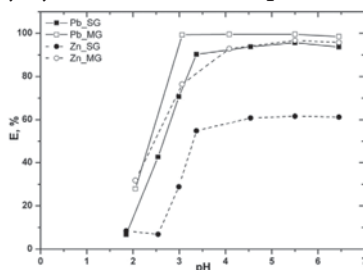
#### **Rezultati i diskusija**

Prirodna glina korišćena kao adsorbens u eksperimentima šaržne adsorpcije dobijena je iz rudnika Bogovina, Srbija. Glina je modifikovana mehaničkim mlevenjem u planetarnom Turbula Type 2 TC Mixer mlinu pri odnosu mase kuglica prema masi uzorka 4:1 u trajanju od 19 sati. Karakterizacija gline urađena je rendgenostrukturnom analizom (Siemens Kristallflex D-500) i laserskom metodom za određivanje veličine čestica (Malvern 2000SM Mastersizer). Rendgenostrukturna analiza je pokazala da se ispitivana glina sastoji od ~ 60% montmorionita i ~ 40% montmorionit/kaolinit kompozita. Srednja veličina čestica sirove gline je 27 µm, a mlevene gline 17,1 µm.

Adsorpcioni eksperimenti izvođeni su na temperaturi od 25°C u šaržnom sistemu pri sledećim uslovima: vreme kontakta 60 min, koncentracija gline 2 g/L, ukupna polazna koncentracija metala 50 mg/L, pH 2-6,5 i brzina mućkanja 200 rpm. Koncentracija Pb(II), Cd(II), Cu(II) i Zn(II) u vodi pre i nakon adsorpcije određivana je voltametrij-ski (Metrohm). U zavisnosti od pH vodenog rastvora određena je efikasnost uklanjanja



teških metala iz vode,  $E$ , i adsorpcioni kapacitet gline,  $q_e$ . Na slici 1 predstavljena je zavisnost efikasnosti uklanjanja Pb(II) i Zn(II) od pH rastvora.



**Slika 1.** Zavisnost efikasnosti uklanjanja,  $E$ , Pb(II) i Zn(II) od pH vode primenom sirove (SG) i mlevene (MG) gline kao adsorbensa

**Tabela 1.** Adsorpcioni kapaciteti,  $q_e$ , sirove i mlevene gline pri pH vrednosti vodenog rastora 4-6,5

Adsorbens	$q_e$ (Pb), mg/g	$q_e$ (Cu), mg/g	$q_e$ (Zn), mg/g	$q_e$ (Cd), mg/g
SG	6,0	5,4	3,8	3,7
MG	6,2	6,2	6,2	6,2

Sa slike 1 jasno se vidi da pH rastvora značajno utiče na  $E$  metala iz rastvora. Adsorpcija Pb(II) i Zn(II) raste od ~7% do ~95% i od ~8% do ~61%, respektivno, u opsegu pH 1,9-4,0 nakon čega  $E$  ostaje konstantno. Slična zavisnost dobijena je i za Cu(II) i Cd(II). Ovo se objašnjava činjenicom da su pri niskim pH rastvora aktivna mesta na glini više protonovana i stoga manje dostupna za vezivanje teških metala. Sa povećanjem pH rastvora aktivna mesta postaju dostupnija za adsorpciju pozitivno naelektrisanih jona kroz elektrostatičke sile privlačenja, što ima za rezultat povećanje  $E$  metala iz rastvora. Takođe, vidi se da mlevenjem modifikovana glina ima veću efikasnost uklanjanja metala u celom opsegu pH. U tabeli 1 predstavljeni su adsorpcioni kapaciteti ispitivanih metala na sirovoj i mlevenoj glini u intervalu pH 4-6,5, u kojem je efikasnost uklanjanja metala najveća. Mehaničkim mlevenjem gline smanjuje se veličina čestica gline tj. povećava se specifična površina za adsorpciju tako da se adsorpcioni kapacitet za sve metalne jone povećava.

Na osnovu dobijenih rezultata može se zaključiti da je interstratifikovana montmorionit/kaolinit glina iz rudnika Bogovina veoma efikasan adsorbens za uklanjanje teških metala iz rastvora ( $E > 97\%$ ) i može se smatrati potencijalno primenljivom za prečišćavanje otpadnih voda kontaminiranih teškim metalima.

## Zahvalnica

Finansijska podrška za ovo istraživanje dobijena je od Ministarstva za prosvetu i nauku Republike Srbije kroz projekte III 45006 i III 45012.

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## Seasonal variations of natural organic matter adsorption onto activated carbons

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Naturally-occurring organic matter (NOM) in dissolved, colloidal, or particulate forms is ubiquitous in natural waters [1]. The dissolved form, the fraction that passes through a 0.45 µm filter, constitutes the major components of NOM in natural waters. The quantity and characteristics of natural organic matter are significantly different for different waters, caused by biogeochemical cycles in the environment. Moreover, the amount of organic components in the composition of same location NOM may vary seasonally due to different weather conditions such as rain, floods, droughts and others. NOM is composed of very small molecules of hydrophilic acids, proteins and amino acids to very large molecules such as humic and fulvic acids. The aim of this study was to compare the adsorption of DOC from surface and groundwater using powdered activated carbons (PAC) in different seasons. Surface water sample was the Danube River while groundwater was from 400 m depth in the region of Backi Petrovac (average values of duplicate measurements results given for quality parameters in Table 1).

**Table 1.** Characteristics of surface- and groundwater

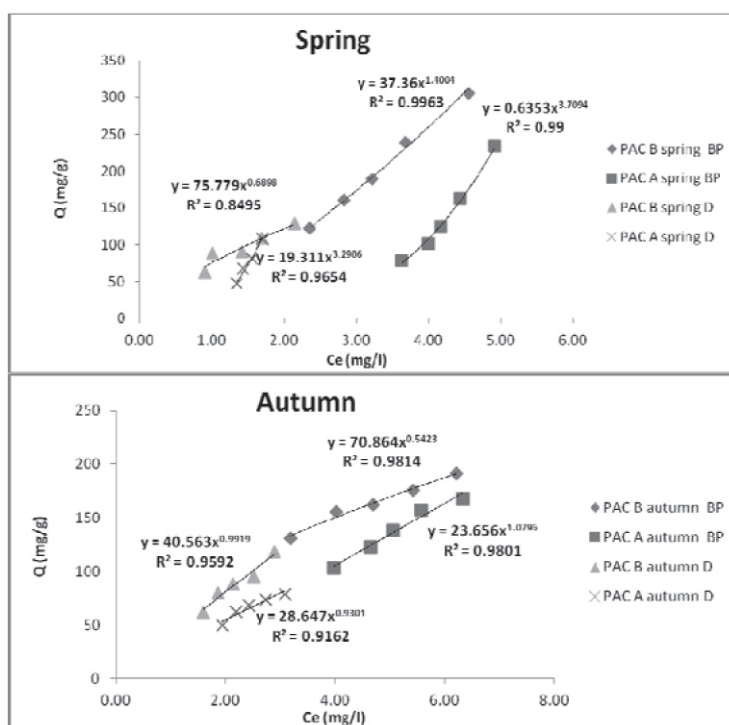
Parameter	Unit	Surface water-Danube (D)		Ground water- Backi Petrovac (BP)	
		spring	autumn	spring	autumn
Temperature	°C	24	21	24,1	20.5
pH	/	7,1	7.3	8,1	8.4
Conductivity	µS/cm	387	392	345	368
TOC	mg/l	2.85	3.60	6.97	7.35
DOC	mg/l	2.80	3.50	6.10	7.20

Two carbons were selected as adsorbents. The characteristics were determined from N<sub>2</sub> isotherm data collected at 77K (Autosorb-1-MP, Quantachrome USA) (Table 2). PAC adsorption experiments were conducted in a glass bottles containing 100 ml of filtrated water and 5, 10, 15, 20 and 30 mg/l of adsorbent. The solutions were mixed for 5h. Samples were filtrated through glass-fiber filters and analyzed on DOC content by Liquid TOCII Elementar, Germany. The adsorption parameters were calculated by Freundlich isotherm (average values of duplicate measurements are given in Figure 1. Higer loads at same equilibrium concentrations are observed for PAC B which might be due to higher specific surface area

for both seasons. More favourable adsorption is present in autumn in most cases. This result indicate possibility of structural change of DOC in different seasons which may affect adsorption efficiency.

**Table 2.** PACs characteristics

Carbons	BET surface area (m <sup>2</sup> /g)	Pore radius (Å)	Total pore volume (cm <sup>3</sup> /g)
PAC A	950	18.10	0.50
PAC B	1150	18.17	1.26



**Figure 1.** Adsorption isotherms and their parameters in spring and autumn

### Acknowledgement

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## Prirodna radiaktivnost voda za piće u Srbiji

### Natural radioactivity of drinking water in Serbia

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Hemijski sastav podzemnih voda zavisi od hemijskog sastava stena akvifera, uslova toka i vremena njihovog zadržavanja u vodonosnom sloju. Prirodna radi-oaktivnost u podzemnim vodama uglavnom potiče od prisutnihi radioaktivnih elemenata u Zemljinoj kori koji se mogu isprati iz geoloških slojeva kroz koje pro-laze ove vode i fizičko-hemijskih uslova pod kojima se one nalaze. Cilj ovog rada bio je da se primenom multivarijantne statističke analize omogući bolje razume-vanje hidrogeohemijskih procesa koji kontrolišu hemijski i radioaktivni sadržaj analiziranih voda za piće.

Šest regionalnih geotektonskih jedinica (Panonski basen, Zapadnosrbijanski Dinaridi, Vardarska zona (šumadijsko-kopaoničko-kosovska jedinica), Srpsko-makedonski masiv, Karpatobalkanidi istočne Srbije i Dakijski basen) značajno se razlikuju prema količini i kvaliteta podzemne vode [1]. Uzorci pijaće vode (n=43) sakupljeni su u 5 geotektonskih zona i analizirani na fizičko hemijske parametre (temperaturu, pH, elektroljovodljivost, mineralni ostatak, sadržaj bikarbonata, hlorida, sulfata, klacijuma, magnezijuma, natraijuma, kalijuma, silikata) i radio-aktivnost (ukupnu alfa i ukupnu beta aktivnost, aktivnost <sup>40</sup>K, <sup>137</sup>Cs, <sup>134</sup>Cs, <sup>226</sup>Ra, <sup>228</sup>Ra, <sup>238</sup>U). Ukupna alfa i beta aktivnost odredjena je prema standardnim meto-dama za tanke slojeve ISO9696[2] i ISO9697 [3] sa efikasnošću za alfa zračenje 31% i za beta zračenje 44%. Gama spektrometerske analize su radjene prema već opisanom postupku [4].

Analizirane pijaće vode imaju širok raspon temperatura (5,8 – 29,5 °C), pH vrednosti (6,4 - 11,4), električne provodljivosti (40 – 946 μS/cm) i ukupnog sadr-žaja rastvorenih mineralnih materija (9,6 - 825,7 mg/l) koje su kategorizovane kao vode sa niskim sadržajem rastvorivih mineralnih materija (suvi ostatak na 180 °C do 500 mg /l) i srednjim sadržajem rastvorivih mineralnih materija (suvi ostatak između 500 i 1500 mg /l). Većina voda priprada Ca–HCO<sub>3</sub> tipu, a po obilnosti slede Na–Ca–HCO<sub>3</sub> i Ca–Mg–HCO<sub>3</sub> tip.

Ukupna alfa aktivnost je u rasponu od 0,01 do 0,052 Bq/l. Ove vrednosti su niže od 0,5 Bq/l, koja je predložena kao granična vrednost za izloženost radijaci-ji za vodu za piće od strane Medjunarodne zdravstvene organizacije [5]. Ukupna beta aktivnost varirala je između 0,010 i 0,336 Bq/l, što je takodje ispod grani-ce od 1Bq/l preporučene kao ciljane vrijednosti [5] za radne uslove postojećih

sistema za vodo snabdevanje. Gama aktivnost izmerena za radijum ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ), uran ( $^{238}\text{U}$ ) i kalijum ( $^{40}\text{K}$ ) je niska. Vrednosti za kalijum su najviše i predstavljaju većinski udeo u beta-aktivnosti u uzorku vode. Ustanovljena umerena korelacija ( $r=0,58$ ,  $n=43$ ) između ukupne beta aktivnosti i  $^{40}\text{K}$  aktivnosti može poticati i od primenjene metode za analizu ukupne beta aktivnosti koja uključuje i doprinos  $^{40}\text{K}$ . Vrednosti aktivnosti koncentracije  $^{226}\text{Ra}$  ( $\alpha$  emiter,  $t_{1/2}=1600$  godina), koji nastaje pri raspadu  $^{238}\text{U}$ , a prati metabolizam kalcijuma u ljudskom telu s eventualnim taloženjem u kostima i  $^{228}\text{Ra}$  ( $\beta$  emiter,  $t_{1/2}=5,77$  godina) su niže od 260 mBq/l, odnosno 320 mBq/l. Najveća vrednost odnosa aktivnosti  $^{226}\text{Ra}/^{228}\text{Ra}$  od 13,3 u jednom uzorku vode ukazuje na određenu vrstu stena u tom akviferu. Maksimalne izmerene aktivnosti za  $^{137}\text{C}$  ( $t_{1/2}=30$  godina) i  $^{134}\text{C}$  ( $t_{1/2}=2$  godina) su bile 9 mBq/l, odnosno 6 mBq/l.

Izračunata je ukupno primljena godišnja doza pri ingestiji vode za piće računata kao zbir doza svakog pojedinog nukleida ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  i  $^{238}\text{U}$ ) uz pretpostavku da odrasla osoba, u proseku, troši 2 l vode dnevno [5] uzimajući u obzir faktore doze prema direktivama Međunarodne komisije za zaštitu od zračenja [6].

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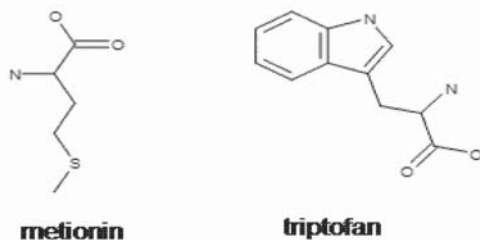
## Inhibitorski efekat triptofana i metionina na koroziono ponašanje mesinga u rastvoru natrijum-tetraborata

### Inhibitory effect of tryptophane and methionine on brass corrosion behaviour in sodium tetraborate solution

Milan Radovanović<sup>1</sup>, Marija Petrović<sup>1</sup>, Ana Simonović<sup>1</sup>,  
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Mesing odlikuju pre svega dobre korozione osobine koje omogućavaju njegovu primenu u agresivnim sredinama kakve su morska voda, zatim sredine u kojima su prisutni hloridni i sulfatni joni. Upotrebom mesinga u takvim sredinama vremenom ipak dolazi do oksidacije. Kako bi se smanjili negativni efekti eksploatacije mesinga u ovakvim sredinama već godinama se iznalaze načini za usporavanje oksidacije mesinga. Jedna od najefikasnijih metoda je upotreba organskih jedinjenja kao inhibitora korozije mesinga [1,2]. Nažalost, većina ispitanih inhibitora su toksična jedinjenja koja mogu imati negativne posledice na životnu sredinu. Poslednjih godina se ulažu napor i iznalaze jedinjenja iz grupe „zelenih inhibitora” koji nemaju štetno dejstvo po životnu sredinu.. U takva jedinjenja spadaju amino kiseline [3-5] koje su ispitivane i pokazale dobre rezultate kao inhibitori korozije bakra [6] i mesinga [7]. U ovom radu ispitivane su dve esencijalne amino kiseline L-triptofan (Trp) i L-metionin (Met) kao inhibitori korozije mesinga u rastvoru natrijum-tetraborata. Struktura ispitivanih amino kiselina prikazana je na slici 1.

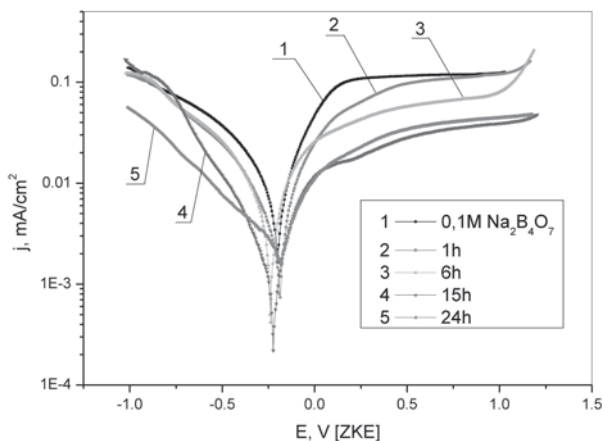


Slika 1. Struktura metionina i triptofana

Procedura se sastojala u uranjanju i držanju elektrode u 0,01M rastvoru triptofana i metionina u različitom vremenskom periodu, nakon čega su merenja vršena u 0,1M rastvoru natrijum-tetraborata (pH~9). Primenjene su elektrohemijske metode ispitivanja.

U alkalnim rastvorima tokom anodne polarizacije najpre dolazi do rastvaranja cinka kao elektronegativnijeg elementa, dok na višim potencijalima dolazi do oksidacije bakra do Cu<sup>+</sup> i Cu<sup>2+</sup> jona i građenja oksida i hidroksida [8]. Elektrohemijska

ispitivanja su pokazala da metionin i triptofan utiču na elektrohemijsko rastvaranje mesinga, značajno ga umanjujući.



**Slika 2.** Polarizacione krive mesinga snimljene u 0,1M  $\text{Na}_2\text{B}_4\text{O}_7$  (1) nakon stajanja u 0,01M Trp 1h (2), 6h (3), 15h (4) i 24h (5).  $v=10\text{mVs}^{-1}$

Dobre inhibitorske osobine metionina i naročito triptofana mogu se pripisati adsorpciji molekula na površini mesinga pri čemu zbog svoje veličine triptofan pokriva veliki deo površine elektrode ostvarujući interakciju sa mesingom preko indolnog prstena [9], što može omogućiti formiranje kompleksa  $[\text{Cu-Trp}_n]_{\text{ads}}^+$  koji štiti površinu legure od daljeg rastvaranja [10], dok se adsorpcija metionina na površinu mesinga odvija preko S atoma [6].

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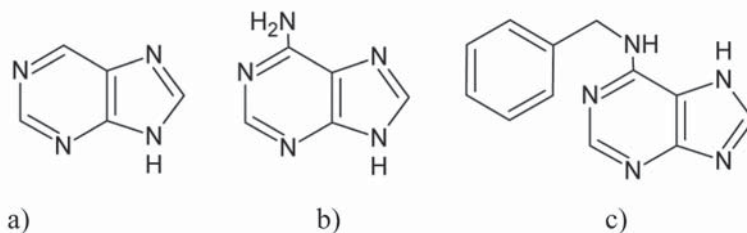
## Purin i njegovi derivati kao "zeleni inhibitori" korozije bakra

### Purine and its derivatives as "green inhibitors" of copper corrosion

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Proizvodi na bazi bakra imaju izuzetan značaj u današnjem društvu, kao jednostavan primer može se navesti da se bakarne cevi mogu naći kako u sistemima distribucije pijaće vode [1], tako i u industrijskim postrojenjima, kao što su na primer sistemi za desalinizaciju [2], gde tokom upotrebe može doći do pojave korozije. Koroziono ponašanje bakra zavisi od različitih faktora, a jedan od njih mogu biti i prisutni hloridni joni [3,4]. Važan je i način pristupanja ovom problemu jer je većina komercijalnih inhibitora korozije toksična. Jedna od alternativa je korišćenje takozvanih "zelenih inhibitora", a purin i njegovi derivati spadaju u ovu grupu jedinjenja. Na Slici 1 prikazane su strukture purina (PU), adenina (AD) i 6-benzilaminopurina (BAP), gde se može videti da su svi oni ciklična jedinjenja koja u molekulima sadrže i atome azota, što je poznato da povoljno utiče na njihovu interakciju sa bakrom [5].

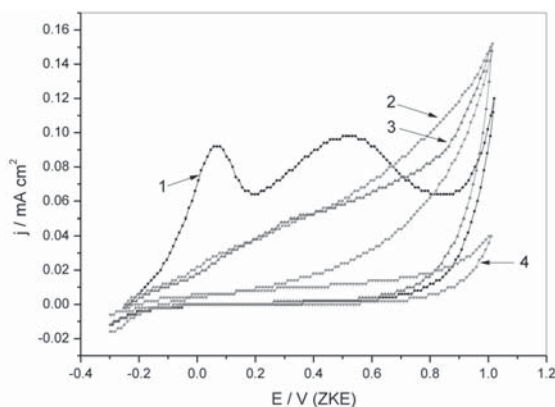


**Slika 1.** Struktura a) purina, b) adenina i c) 6-benzilaminopurina

Više istraživanja pokazalo je da se mogu koristiti kao inhibitori korozije metala [6-10], a ovom prilikom posmatran je njihov uticaj na elektrohemijsko ponašanje bakra u alkalnim hloridnim rastvorima. Elektrohemijsko ponašanje bakra u alkalnim rastvorima karakteriše oksidacija bakra do stanja Cu(I) i Cu(II), pri čemu na taj proces utiču i hloridni joni prisutni u rastvoru [11]. Uopšteno mehanizam dejstva organskih inhibitora korozije može podrazumevati adsorpciju na površini metala, koja može biti fizičke ili hemijske prirode, ali i formiranje kompleksa sa metalom. U pH oblasti koja je proučavana u ovom istraživanju, dominantna forma PU je neutralan molekul [6], a kada su u pitanju AD i BAP moguće je da se nađu i u anjonskom obliku [9,12]. Tako da se uticaj inhibitora na rastvaranje bakra može pripisati adsorpciji neutralnog molekula ili anjonske forme na površini bakra. Kao



što se može videti na osnovu grafika prikazanih na Slici 2, sva ispitivana jedinjenja pokazala su inhibitori uticaj na koroziju bakra, s tim što se sa udaljavanjem od korozionog potencijala uočava značajnija razlika u njihovoj efikasnosti.



**Slika 2.** Krive dobijene u prvom ciklusu ciklične potenciodinamičke polarizacije bakra u rastvoru sastava 0,1M boraks, 0,05M NaCl (1) i sa dodatkom  $1 \cdot 10^{-3}$  M purina (2), adenina (3) i 6- benzilaminopurina (3), pri brzini promene potencijala  $10 \text{ mVs}^{-1}$

Svakako kao najefikasniji pokazao se 6-benzilaminopurin, što se i očekivalo na osnovu strukture i veličine njegovog molekula. Koncentracija inhibitora prisutna u rastvoru takođe je faktor koji utiče na stepen efikasnosti inhibicije korozionih procesa. Inače, sva korišćena organska jedinjenja utiču i na katodni proces redukcije kiseonika, a još u značajnijoj meri na anodni proces oksidacije bakra.

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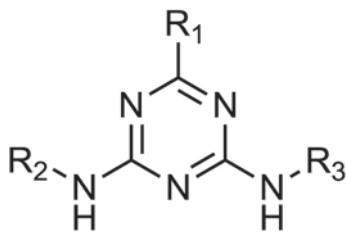
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## Reversed-Phase Liquid Chromatography Retention Data as Predictors of the Biological Properties of Some *s*-Triazine Pesticides

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*s*-Triazines (1,3,5-triazines) are organic heterocyclic compounds of considerable interest in agricultural chemistry. Their derivatives are widely used as herbicides, as well as pharmaceutical compounds [1,2]. Higher concentrations of *s*-triazine derivatives could express toxic activity in the human body [3,4]. Detoxification and degradation of *s*-triazine molecules are usually very slow. In the present paper, *in silico* oral absorption, expressed as Caco-2 cells permeability (Caco-2), and *in silico* skin permeability (SP) of twelve *s*-triazine derivatives (desethyldeisopropylatrazine, desisopropyl-atrazine, desethylatrazine, simatrazine, atrazine, sebuthylatrazine, propazine, terbuthylazine, desmetryn, ametryn, prometryn and terbutryn) were predicted according to their retention times ( $\log t_R$ ) obtained by reversed-phase high-performance liquid chromatography (RP HPLC) [5]. *In silico* absorption parameters were calculated by using *PreADMET* software [6]. The basic structure of studied compounds is presented in Figure 1.



**Figure 1.** The basic structure of the compounds studied.

The connection between the chromatographic behaviour of the analyzed *s*-triazine derivatives and their absorption in the human body could be assumed due to the influence of their lipophilicity, which is a dominant molecular factor in RP chromatography [7,8] as well as in skin and oral absorption.

As a result of this study, the two linear mathematical models for prediction of SP and Caco-2 parameters of the mentioned *s*-triazine derivatives, characterized by the standard statistical measures (correlation coefficient - *r*, Fisher's value - *F*, standard deviation - *s*) and *cross-validation* parameters (*cross-validated* determination coefficient -  $r^2_{CV}$ , *adjusted* determination coefficient -

$r^2_{\text{adj}}$ , predicted residual sum of squares - PRESS, total sum of squares - TSS) were constructed:

$$\text{SP} = 1.648 \log t_R + 4.496 \quad \text{Eq. 1}$$

$$(r = 0.9774, F = 214.30, s = 0.1295, r^2_{\text{CV}} = 0.9152, r^2_{\text{adj}} = 0.9510, \text{PRESS} = 0.3190, \text{TSS} = 3.7632)$$

$$\text{Caco-2} = 4.852 \log t_R + 16.374 \quad \text{Eq. 2}$$

$$(r = 0.9451, F = 87.73, s = 0.6101, r^2_{\text{CV}} = 0.8403, r^2_{\text{adj}} = 0.8826, \text{PRESS} = 5.5719, \text{TSS} = 34.8874)$$

On the basis of the obtained mathematical models it can be concluded that retention parameters ( $\log t_R$ ) of studied *s*-triazines could be successfully used as predictors of their oral and skin absorption in the human body. The optimal values of the cross-validation parameters confirm the significant predictive ability of the estimated equations 1-2.

### Acknowledgement

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## Proučavanje efikasnosti različitih viših procesa oksidacije pri razgradnji odabranih neonikotinoidnih insekticida

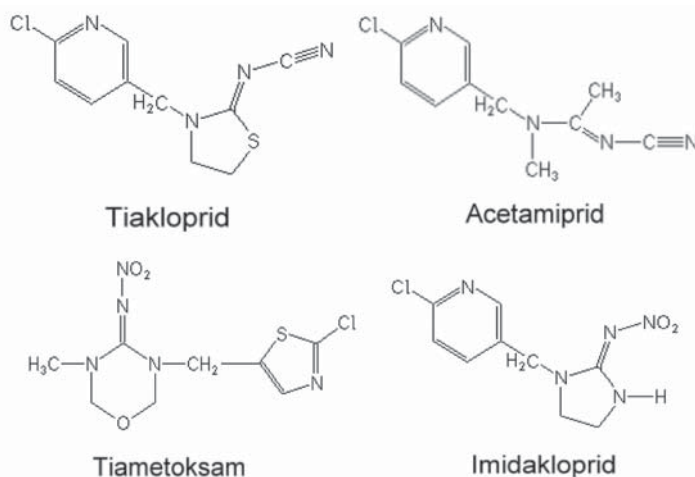
### Study of efficiency of different advanced oxidation processes for degradation of selected neonicotinoid insecticides

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Od uvođenja sintetičkih piretroida pa do danas neonikotinoidi predstavljaju najvažniju klasu insekticida [1]. Fizičko-hemijske osobine petočlanih i šestočlanih prstenastih sistema i necikličnih neonikotinoida su igrale važnu ulogu za njihov uspešan razvoj u moderne insekticide [2]. U ovom kontekstu fotostabilnost je značajna osobina neonikotinoidnih insekticida. Iz literaturnih podataka je poznato da se energetski procep funkcionalnih grupa neonikotinoida  $[=X-Y]$  za prelaz iz osnovnog stanja u pobuđeno singletno stanje povećava sledećim redosledom  $[=CH-NO_2] < [=N-NO_2] < [=N-CN]$  [3,4]. Strukture proučavanih neonikotinoida u ovoj studiji date su na Slici 1.



**Slika 1.** Nazivi i strukturne formule proučavanih neonikotinoida

U cilju smanjenja rizika od zagađenja pesticidima, radi se na razvoju novih tehnologija koje bi omogućile efikasnu razgradnju ovih biorezistentnih organskih jedinjenja [5]. Moguće rešenje je primena viših oksidacionih procesa (AOP) koji su u stanju da proizvedu hidroksi-radikale pod blagim eksperimentalnim uslovima [6,7].

U radu je upoređena kinetika fotorazgradnje četiri standarda neonikotinoida sa odgovarajućim komercijalnim formulacijama (imidakloprid – Confidor® 70-WG, tiametoksam – Actara® 25-WG, acetamiprid – Mospilan® 20-SP i tiakloprid – Calypso® 480-SC) primenom različitih AOP (fotoliza,  $\text{H}_2\text{O}_2/\text{UV}$  i  $7,2\%\text{Fe}/\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ ). Fotorazgradnja insekticida je praćena primenom HPLC–DAD. Eksperimenti su vršeni u šaržnom fotohemijском reaktoru uz primenu živine lampe (125 W, emisioni maksimumi u UV oblasti na 304, 314, 335 i 366 nm, sa najintenzivnijim emisionim maksimumom na 366 nm) čija je energija iznosila  $3,57 \text{ mW}/\text{cm}^2$ . Tokom eksperimenata uveden je kiseonik pri protoku od  $4,98 \text{ cm}^3/\text{min}$ , a pH vrednost rastvora je podešena na 2,8. Za poređenje efikasnosti fotorazgradnje korišćeni su rezultati dobijeni nakon 180 min ozračivanja.

Pri fotoličkoj razgradnji  $0,38 \text{ mmol}/\text{dm}^3$  rastvora standarda neonikotinoida utvrđeno je da je efikasnost fotorazgradnje tiametoksama i imidakloprida približno ista, dok tiakloprid i acetamiprid ne podležu fotolizi. Pri proučavanju efikasnosti fotolize neonikotinoida u komercijalnim formulacijama pri istim eksperimentalnim uslovima uočeno je da u slučaju tiametoksama dolazi do smanjenja brzine fotolize.

U prisustvu  $45 \text{ mmol}/\text{dm}^3 \text{ H}_2\text{O}_2$ , odnosno primenom  $\text{H}_2\text{O}_2/\text{UV}$  sistema, utvrđena je približno jednaka efikasnost razgradnje imidakloprida i acetamiprida kako u standardnim rastvorima, tako i komercijalnih formulacija. Međutim, u slučaju tiakloprida i tiametoksama zapažen je uticaj matriksa na brzinu fotorazgradnje.

Heterogeni fotokatalitički sistem  $7,2\%\text{Fe}/\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$  se pokazao kao najefikasniji u fotorazgradnji ispitivanih neonikotinoida, pri čemu nije zapažen značajniji uticaj ni strukture supstrata, ni matriksa komercijalnih formulacija.

## Zahvalnica

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## Uticaj pH na uklanjanje stroncijuma iz vodenih rastvora pomoću aLVB sorbenta

### The effect of pH on strontium removal from aqueous solutions using aLVB sorbent

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Kontaminacija životne sredine radioaktivnim materijalima postala je jedan od značajnih problema savremene civilizacije. Stroncijum (<sup>90</sup>Sr), je β-emiter sa vremenom poluraspada 28,6 godina, koji u velikoj količini nastaje pri nuklearnoj eksploziji [1]. Zbog visoke rastvorljivosti i biotoksičnosti, odvajanje i izolovanje stroncijuma zahteva posebnu pažnju. Tokom poslednjih decenija, istraživači ulažu velike napore za separaciju radioaktivnih jona iz otpadnih voda [2]. Među mnogim metodama, sorpcija je jedna od visoko ekonomičnih i najefikasnijih metoda.

Cilj ovog rada je da ispita uticaj pH na uklanjanje Sr(II) jona iz vodenih rastvora pomoću *Lagenaria vulgaris* (aLVB) sorbenta.

Kao “low cost” i lako dostupan sorbent koristila se kora biljke roda *Lagenaria vulgaris*. Ova biljka je uzgajana na području jugoistočne Srbije, na nadmorskoj visini od 700 m, bez prskanja i đubrenja. Radni rastvori su pripremani rastvaranjem Sr(NO<sub>3</sub>)<sub>2</sub> u dejonizovanoj vodi. Adsorpcija je proučavana u “batch” sistemu: mešanjem 0.8 g aLVB sa 200 cm<sup>3</sup> rastvora Sr(NO<sub>3</sub>)<sub>2</sub>. Početna koncentracija Sr(II) jona bila je 50 mgL<sup>-1</sup>, a eksperimenti su izvođeni na pH vrednostima od 2 do 10. Uzorci su sakupljeni nakon 0, 1, 4, 10, 40, 90 i 240 minuta. Svi sakupljeni uzorci su analizirani na ICP-AES (Perkin-Elmer 400).

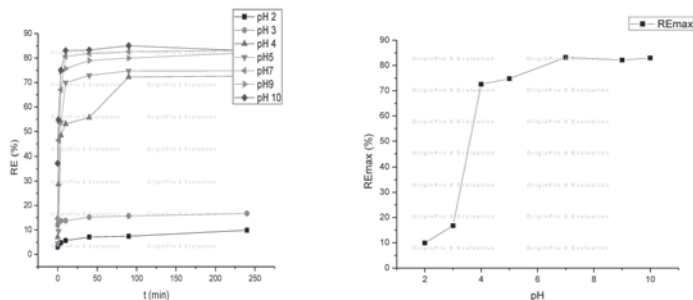
Efikasnost uklanjanja (RE) jona metala biosorbentom, je izračunata prema sledećoj jednačini:

$$RE = \frac{c_0 - c_t}{c_0} \times 100$$

gde su:

RE-efikasnost uklanjanja,  $c_0$ -početna koncentracija Sr(II) jona,  $c_t$ -rezidualna koncentracija Sr(II) jona.

Jedan od najznačajnijih parametara koji utiče na proces adsorpcije je pH rastvora, jer utiče na naelektrisanje na površini sorbenta i na oblik u kome se joni nalaze u rastvoru [3].



**Slika 1.** (a) Efikasnost uklanjanja-vreme, (b) Maksimalna efikasnost uklanjanja-pH

Na osnovu dobijenih rezultata uočava se da sa porastom pH vrednosti, raste i efikasnost uklanjanja, sve do pH 7, nakon čega dolazi do zasićenja (slika 1). Glavni mehanizam ovog procesa je jonska izmena, uslovljena prisustvom karboksilne, karbonilne, hidroksilne i fenil grupe. Na pH vrednostima nižim od 4, koncentracija  $H^+$  jona je visoka, pa samim tim dolazi do takmičenja sa  $Sr(II)$  jonima za okupaciju aktivnih mesta na površini sorbenta, što rezultuje smanjenom adsorpcijom [4]. Na pH od 4 do 7 dolazi do značajnijeg porasta efikasnosti uklanjanja, zbog deprotonacije površinskih grupa, a samim tim i do jače interakcije između jona i površine. Najveća efikasnost uklanjanja (83,22%) je na pH 7. Na višim vrednostima pH (9 i 10) efikasnost se smanjuje, a glavni uzrok je precipitacija [5].

Ovo istraživanje pokazuje da pH rastvora ima veliki uticaj na proces sorpcije i da je najveća efikasnost uklanjanje  $Sr(II)$  jona iz vodenih rastvora pomoću aLVB sorbenta na pH 7.

### Zahvalnica

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**Stabilnost i toksičnost  
heksil 2-[4-(dietilamino)-2-hidroksibenzoil]benzoata  
i njegova sudbina u životnoj sredini**

**Stability and toxicity of  
hexyl 2-[4-(diethylamino)-2-hydroxybenzoil]benzoate  
and its environmental fate**

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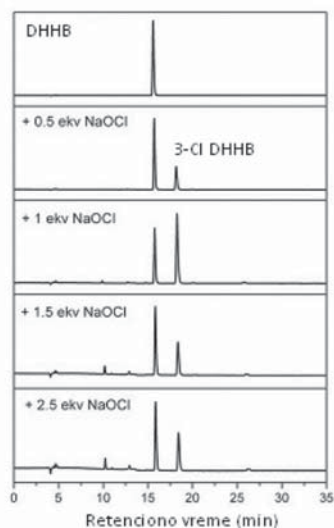
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Izlaganje ultraljubičastom (UV) zračenju, čiji je prirodni izvor Sunce, ima različite štetne uticaje na čovečiju kožu, kao što su opekotine, prevremeno starenje ili rak kože. Sve veća zabrinutost zbog nepovoljnog uticaja UV zračenja po ljudsko zdravlje, povećala je upotrebu preparata za zaštitu od sunca. Ovi preparati pružaju zaštitu od štetnih UV zraka budući da sadrže UV filtere, supstance sposobne da apsorbuju, reflektuju i/ili raspršuju fotone svetlosti. Prisustvo UV filtera u vodenim sredinama, a posebno u bazenskim vodama, povećalo je, međutim, brigu o njihovom uticaju na životnu sredinu [1]. Iako su ova jedinjenja uglavnom stabilna pod dejstvom UV zračenja, pod određenim uslovima ipak može doći do njihove razgradnje, ili se neretko dešava da reaguju sa sredstvima na bazi hlora, kakva se obično koriste za dezinfekciju bazenskih voda [2]. Iako je poznato da proizvodi ovih reakcija mogu da budu toksični, podaci o njihovoj sudbini nakon što dospeju u životnu sredinu su veoma ograničeni.

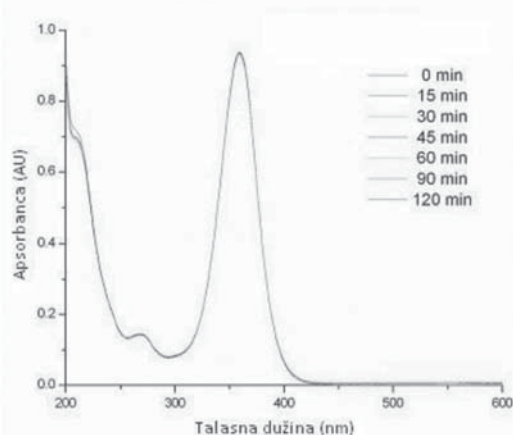
U okviru ovog istraživanja, ispitivana je stabilnost i toksičnost relativno novog UV filtera, heksil 2-[4-(dietilamino)-2-hidroksibenzoil]benzoata (DHHB), koji je razvio BASF pod trgovinskim nazivom Uvinul A Plus. Simulirani su dezinfekcioni uslovi i ispitivano je ponašanje DHHB-a u prisustvu natrijum hipohlorita (NaOCl). Proizvodi hloriranja određeni su tačno-hromatografskom metodom visoke performanse sa detektorom sa nizom dioda (HPLC-DAD) na osnovu poređenja retacionih vremena sa nezavisno sintetisanim standardima. Pored toga, stabilnost DHHB-a i njegovih hloriranih proizvoda određivana je pod dejstvom UV zračenja u fotoreaktoru sa šest živinih fluorescentnih lampi niskog pritiska koje emituju UV-A (355 nm) zračenje. Rastvori testiranih jedinjenja ozračivani su po 120 minuta, alikvoti su periodično uzimani i analizirani na UV-Vis spektrofotometru i HPLC-DAD. Proučavan je i toksični efekat DHHB-a i njegovih proizvoda na luminescentnu bakteriju *Vibrio fischeri*. Krajnje tačke toksičnosti su određivane merenjem smanjenja luminescencije bakterija nakon inkubacije sa testiranim jedinjenjima.



Obzirom da molekul DHHB-a sadrži snažne elektron-donorske grupe, ( $-\text{OH}$ ,  $-\text{NEt}_2$ ) koje imaju jak afinitet prema elektrofilnim reagensima, kakav je hlor, uočena je gotovo trenutna reakcija DHHB-a sa hipohloritom. Glavni proizvod koji nastaje je 3-Cl DHHB (slika 1). Rezultati ispitivanja fotostabilnosti pokazuju da su DHHB i njegov 3-hloro produkt stabilni pod dejstvom UV-A zračenja (primer na slici 2).



**Slika 1.** HPLC-DAD  
hromatogrami rastvora



**Slika 2.** UV-Vis apsorpcioni spektri DHHB-a  
DHHB sa različitim koncentracijama NaOCl  
tokom 120 min UV-A zračenja.

Što se tiče toksičnosti, u slučaju DHHB-a rezultati pokazuju 20% inhibicije luminescencije nakon 30 minuta ekspozicije za koncentraciju  $0,96 \text{ mg L}^{-1}$  ( $\text{EC}_{20} = 0,96 \text{ mg L}^{-1}$ ), a vrednost  $\text{EC}_{20}$  za 30 minuta ekspozicije za 3-Cl DHHB iznosi  $0,85 \text{ mg L}^{-1}$ . Ovi rezultati ukazuju na potencijalnu opasnost ovih jedinjenja po živi svet, zbog čega je potrebna dalja procena toksičnosti na još nekim vodenim organizmima. Ona će pokazati koliko su zabrinjavajuće transformacije do kojih dolazi u životnoj sredini ili je pak, zbog slabe rastvorljivosti ovih jedinjenja u vodi, opasnija mogućnost njihove bioakumulacije.

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## **ESI-MS ispitivanje interakcije hroma(III) i benzoeeve, salicilne i ftalne kiseline kao markera oksidativnog stresa**

### **ESI-MS Investigation of Interaction between Chromium(III) and Benzoic, Salicylic and Phthalic Acids as oxidative stress markers**

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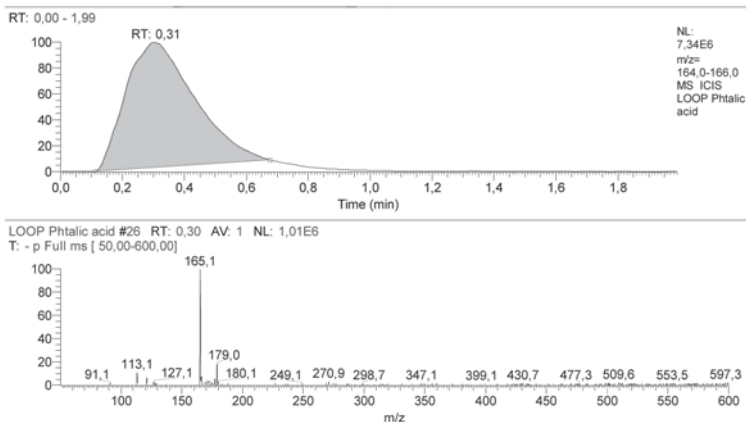
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U radu je izvršeno ispitivanje interakcija koje hrom(III) može da ostvari sa prirodnim organskim supstancama, benzoevom (BA), salicilnom (SA) i ftalnom kiselinom (PA), koje stvarajući slobodne radikale, utiču na pojavu oksidativnog stresa. Ispitivanje ostvarenih interakcija je izvršeno elektrosprej-jonizacionom masenom spektrometrijom (ESI-MS).

Oksidativni stres je stanje u organizmu koje se javlja kada slobodni radikali nadvladaju mehanizme antioksidativne zaštite organizma. Ovakvo stanje može da se javi i pri izlaganju živog organizma većim koncentracijama teških metala[1]. Tako i Cr(III) kao teški metal može da izazove pojavu markera oksidativnog stresa. Cr(III) gradi komplekse sa anjonima datih organskih kiselina vezujući se preko O-donor atoma. ESI-MS dozvoljava akviziciju masenih spektara direktno iz tačnog uzorka, na taj način analizirajući sve ravnotežne vrste u nativnoj fazi. Blagi uslovi jonizacije ESI izvora minimiziraju fragmentaciju, ostavljajući prisutne molekulske i jonske vrste uglavnom u neizmenjenim obliku[2,3].

Za ESI-MS ispitivanja korišćen je instrument LCQ Deca, sa *quadrupole ion trap* masenim analizatorom, Thermo Finnigan (USA) i pratećom opremom. Odabran je negativan mod instrumenta, jer ispitivane kiseline u uslovima ESI izvora grade deprotonizovani molekulski jon  $[M-H]^-$ . Analizom ESI-MS spektara određen je osnovni jon  $BA m/z 121$  (rel. int. 100%). Optimizacija radnih uslova instrumenta je izvršena prema benzoatnom jonu  $m/z 121$  (monitoring jon). Analogno tome je izvršena optimizacija radnih uslova za SA i PA, kod kojih su osnovni joni  $m/z 137$  i  $m/z 165$ , respektivno. ESI-MS LOOP kvantitativna analiza monokomponentnih sistema BA, SA i PA, je izvršena injektiranjem tačnih zapremina rastvora (20  $\mu$ L) primenom LOOP aparata. ESI-MS LOOP-hromatogrami su pokazali dobar oblik i integritet pika, kako za TIC, tako i za traženi opseg  $m/z 120-122$  za BA,  $m/z 136-138$  za SA,  $m/z 164-166$  za PA (Slika 1).



**Slika 1.** ESI-MS LOOP-hromatogram ftalne kiseline (bez prisustva hroma);  $c = 8.575 \mu\text{mol/L}$  u  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  50:50, negativan joniz. mod,  $\text{flow rate} = 100 \mu\text{L/min}$ .

Izračunate su površine LOOP-hromatogram pikova za date opsege algoritmom ICIS (EXALIBURE<sup>®</sup> program), za različite koncentracije BA, SA i PAi različite koncentracije rastvora Cr(III) i BA, Cr(III) i SA, Cr(III)i PA. Površina očitana sa dijagrama za BA u prisustvu Cr(III) je 4.819% manja od analogne površine za BA bez prisustva Cr(III), odnosno 54.53% manja od analogne površine za SA bez prisustva hroma, i 63.72% manja od analogne površine za PA bez prisustva hroma, što ukazuje na značajnu interakciju PA i Cr(III), koja je najveća u grupi ispitivanih sistema. Razlike u površinama ispod pikova LOOP hromatograma su rezultat koordinacione interakcije Cr(III) i datih kiselina, a dobijeni rezultati za ispitivane sisteme su pokazali da jenjen intenzitet u skladu sa strukturom liganda.

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## Investigation of interaction of lead(II) with salicylic acid as oxidative stress compound by ESI-MS

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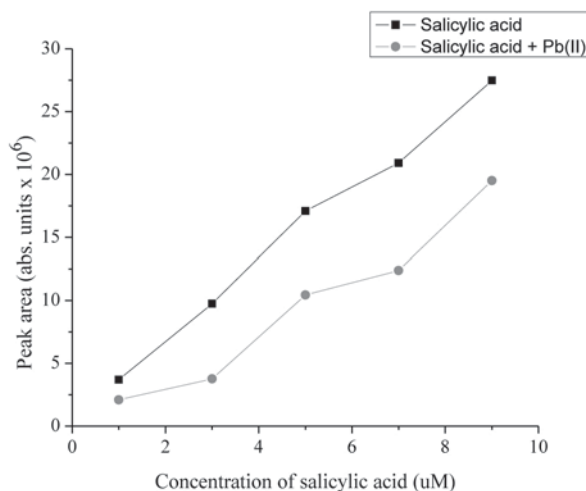
Lead (Pb) is a strong environmental pollutant with high toxicity to animals and plants. Lead can induce the production of reactive oxygen species including the  $O_2^-$  and  $H_2O_2$  causing oxidative stress and damaging health effects. Oxidative stress plays a role in pathogenesis of many disease and toxicities. Earlier investigations have shown the role of salicylic acid in plant responses to a wide range of oxidative stresses. Salicylic acid induces resistance to water deficit and reduction of damaging effects of heavy metals. One of the mechanisms involved in salicylic acid effect on biotic stress is the regulation of  $H_2O_2$ . [1]

All investigated solutions were made by dilution of concentrated stock solutions with the solvent methanol/water (80/20 v/v). Solutions of salicylic acid were analyzed by ESI-MS immediately after preparation. Mixed solutions of salicylic acid and lead(II) ion were analyzed after 24 hours. ICISmodul of Xcalibur™ 1.3 software is used for calculating the areas of each ESI-MS total ion current chromatogram of 5  $\mu$ L loop injection for the defined mass range of pure solutions of salicylic acid and mixed solutions of salicylic acid and Pb(II). (Table and Figure). [2]

The quantification is based on the fact that all areas of obtained chromatograms are in direct function of the peak intensities. In systems with interaction between salicylic acid and Pb(II), the intensity of the observed characteristic ion is reduced. [3]

**Table 1.** Values of peak area of salicylic acid without and with presence of lead(II) ion

Concentration of salicylic acid ( $\mu$ M)	Peak area in mass range of salicylate ion (abs. units $\times 10^6$ )	
	Without presence of Pb(II)	With presence of Pb(II)
1	3.70	2.09
3	9.75	3.77
5	17.09	10.45
7	20.90	12.39
9	27.48	19.51



**Figure 1.** Concentration of salicylic acid versus peak area, for systems without and with presence of Pb(II).

This decrease is caused by coordination bonding or other interactions between salicylic acid and Pb(II). In systems of salicylic acid and Pb(II), for identical salicylic acid concentration, proportionally smaller area of chromatographic peak is obtained, and the relative decrease in area can be related to the strength of the interaction of Pb(II).

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## **Poređenje koncentracija elemenata dobijenih BCR ekstrakcijom korišćenjem tri različite tehnike**

### **Comparison of element concentrations obtained by BCR extraction using three different techniques**

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Cilj ovoga rada je poređenje srednjih vrednosti koncentracija elemenata dobijenih nakon sekvencijalne ekstrakcije uzoraka sedimenata i muljeva iz otpadnog kanala industrijske zone Pančeva i okoline, metodom analize varijanse. Primjenjene su tri tehnike ekstrahovanja za prva tri koraka standardizovane BCR sekvencijalne ekstrakcije i to: mućkanje uzoraka na rotacionoj mućkalici u trajanju od šesnaest sati u okviru konvencionalne sekvencijalne ekstrakcije (KSE); dvominutno izlaganje uzoraka mikrotalasima snage 90 W u okviru mikrotalasne sekvencijalne ekstrakcije (MTSE); i tridesetominutno izlaganje uzoraka ultrazvučnim talasima u okviru ultrazvučne sekvencijalne ekstrakcije (UZSE). Četvrti korak u primeni sve tri tehnike je bio isti, kuvanje uzoraka sa carskom vodom na vodenom kupatilu [1]. Nakon svih primenjenih ekstrakcionih koraka, u rastvorima je određivan sadržaj Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sn, Sr, V, Ti, Zn, As, Se i Hg metodom induktivno spregnute plazme sa optičkom emisijom spektrometrijom (ICP/OES).

Na osnovu ANOVA testa srednjih vrednosti ekstrahovanih količina elemenata dobijenih nakon prve faze BCR ekstrakcije trima tehnikama ekstrahovanja za većinu ispitivanih elemenata ne postoji značajna razlika između srednjih vrednosti dobijenih trima tehnikama ekstrahovanja ( $P > 0,05$ ). Aluminijum, Ca, Mg, Mn, Si, Sr i V nemaju značajnu razliku u srednjim vrednostima koncentracija dobijenih nakon primene brzih tehnika ekstrahovanja (MTSE i UZSE). U slučaju Al i V niže koncentracije su dobijene nakon KSE dok su veće dobijene nakon MTSE i UZSE. Odsustvo značajne razlike u srednjim vrednostima dobijenih nakon ekstrakcije brzim tehnikama za Ca, Mg, Mn, Si i Sr je zbog značajno nižih vrednosti značajnije dobijenih nakon KSE.

Ne postoji značajna razlika u srednjim vrednostima koncentracija za Al, Ba, Ca, Co, Cr, Fe, Ni, Si, Sn, Sr, V i As dobijenih brzim tehnikama ekstrakcije (MTSE i UZSE) nakon druge BCR faze (Tabela 1). U slučaju Ca i Sr niže srednje vrednosti koncentracija su dobijene nakon KSE dok su se veće i slične dobijene nakon MTSE i UZSE. Drugačiji je odnos kod ostalih elemenata, tako na primer najveće vrednosti ekstrahovanih koncentracija su dobijene nakon KSE, dok manje a slične srednje vrednosti su dobijene nakon MTSE i UZSE.

**Tabela 1.** One way ANOVA srednjih vredosti ekstrahovanih koncentracija elemenata nakon druge faze BCR ekstrakcije primenom tri tehnike ekstrakcije

Al-KSE-II	$P = 3,55 \cdot 10^{-7}$	Ba-KSE-II	$P = 0,0343$	Ca-KSE-II	$P = 0,0002$	Co-KSE-II	$P = 0,0230$
Al-MTSE-II		Ba-MTSE-II		Ca-MTSE-II		Co-MTSE-II	
Al-UZSE-II		Ba-UZSE-II		Ca-UZSE-II		Co-UZSE-II	
Al-MTSE-II	$P = 0,2564$	Ba-MTSE-II	$P = 0,5666$	Ca-MTSE-II	$P = 0,1019$	Co-MTSE-II	$P = 0,5298$
Al-UZSE-II		Ba-UZSE-II		Ca-UZSE-II		Co-UZSE-II	
Cr-KSE-II	$P = 0,0343$	Fe-KSE-II	$P = 3,27 \cdot 10^{-11}$	Ni-KSE-II	$P = 3,1 \cdot 10^{-5}$	Si-KSE-II	$P = 7,61 \cdot 10^{-9}$
Cr-MTSE-II		Fe-MTSE-II		Ni-MTSE-II		Si-MTSE-II	
Cr-UZSE-II		Fe-UZSE-II		Ni-UZSE-II		Si-UZSE-II	
Cr-MTSE-II	$P = 0,4978$	Fe-MTSE-II	$P = 0,0678$	Ni-MTSE-II	$P = 0,9390$	Si-MTSE-II	$P = 0,0710$
Cr-UZSE-II		Fe-UZSE-II		Ni-UZSE-II		Si-UZSE-II	
Sn-KSE-II	$P = 1,01 \cdot 10^{-8}$	Sr-KSE-II	$P = 0,0459$	V-KSE-II	$P = 6,33 \cdot 10^{-6}$	As-KSE-II	$P = 0,0004$
Sn-MTSE-II		Sr-MTSE-II		V-MTSE-II		As-MTSE-II	
Sn-UZSE-II		Sr-UZSE-II		V-UZSE-II		As-UZSE-II	
Sn-MTSE-II	$P = 0,0863$	Sr-MTSE-II	$P = 0,2922$	V-MTSE-II	$P = 0,2800$	As-MTSE-II	$P = 0,3888$
Sn-UZSE-II		Sr-UZSE-II		V-UZSE-II		As-UZSE-II	

Za ekstrahovane koncentracije Ca, Co, K, Na, Ni, Si i Sr nakon treće faze BCR sekvencijalne ekstrakcije ne postoji značajna razlika u koncentracijama dobijenim nakon primene brzih tehnika ekstrahovanja (MTSE i UZSE). U slučaju Ca i Sr niže srednje vrednosti koncentracija su dobijene nakon KSE dok su veće i slične vrednosti dobijene nakon MTSE i UZSE. Kod ostalih elemenata, najveće vrednosti ekstrahovanih sadržaja dobijene su nakon KSE, dok manje a slične srednje vrednosti su dobijene nakon MTSE i UZSE. Dobijeni rezultat može se objasniti pretpostavkom da brze tehnike ekstrahovanja u prethodna dva BCR koraka nisu u dovoljnoj meri rastvorile karbonate u uzorcima i da se ta nerastvorena količina karbonata dalje rastvara, primenom mikrotalasa i ultrazvučnih talasa u trećem koraku BCR ekstrakcije.

Za pseudo ukupne količine Ca, Co, Mg, Na i Se postoje značajne razlike u uzorcima koji su u prethodnim trima fazama BCR ekstrakcije bili tretirani pomoću KSE, MTSE i UZSE. Za sve elemente najveća srednja ekstrahovana vrednost koncentracije je nakon MTSE.

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## **Mogućnosti primene i efikasnost elektrokoagulacije u tretmanu otpadnog ofset razvijača**

### **The application and efficiency of electrocoagulation in the treatment of waste offset developer**

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Grafička industrija obuhvata širok spektar tehnologija koje predstavljaju potencijalne izvore zagađenja s' obzirom na to da koriste čvrste materijale i hemikalije, kao i da proizvode otpad. Bilo u segmentu proizvodnje grafičkih materijala, ili kao sam štamparski proces, relativno malim troškovima može se značajno uticati na okolinu odgovornim zbrinjavanjem otpada koji se proizvodi.

Postupkom ofset štampe se danas može proizvesti cela paleta štampanih proizvoda visokog kvaliteta. Ofset štampa je najznačajniji postupak ravne štampe i pokriva 85% štamparske delatnosti u celom svetu, pa je samim tim i najštetnija po okolinu najviše zbog pristustva boja i rastvarača koji sadrže štetne supstance. Proces ofset štampe može se podeliti u tri koraka: 1. priprema za štampu (pre-press), 2. štampa (press) i 3. završna grafička obrada (postpress) [1]. U segmentu pripreme ofset ploče za štampu koristi se razvijač. Naime, dejstvom ofset razvijača se uklanjaju neočvrsljeni elementi (štamapjući ili neštamapjući, zavisno od vrste osvetljavanja), pod uticajem sledećih analognih veličina: temperature, koncentracije, trajanja i hidrodinamičkih faktora. Nakon razvijanja otpadni razvijač sadrži osnovne komponente (silikate, karbonate i sulfite natrijuma, silikate, bromide i hidrokside kalijuma, D-sorbitol, metol i hidrohinom ) ali i komponente koje sa površine tretirane ofset ploče tokom procesa razvijanja prelaze u ofset razvijač (fotosenzitivna jedinjenja, polimerna veziva, teški metali, novolak i drugi). Tretiranje otpadnog ofset razvijača je neophodno pre odlaganja u životnu sredinu.

Elektrohemijske tehnike su privukle enormnu pažnju zbog svoje svestranosti, bezbednosti, selektivnosti, podložnosti automatizaciji i ekološke kompatibilnosti. Elektrokoagulacija (EK) se pojavljuje kao jedan od najefikasnijih elektrohemijskih procesa. Proces EK uključuje mnogo hemijskih i fizičkih fenomena koji koriste elektrode za izvor jona u tok otpadne vode. U EK joni se proizvode „in situ“ i proces uključuje tri koraka: 1. formiranje koagulanata elektrolitičkom oksidacijom površina elektroda, 2. destabilizaciju kontaminanata, suspenziju čestica i razbijanje emulzije i 3. agregaciju destabilizovanih faza u formu flokula [2]. EK proces je okarakterisan jednostavnim radom, smanjenom produkcijom mulja i time da nije potrebna upotreba hemikalija [3, 4].

Eksperimentalnim istraživanjem u laboratorijskim uslovima ispitivana je mogućnost primene i efikasnost elektrokoagulacije u tretmanu otpadnog ofset razvijača praćenjem sledećih faktora: prirode elektroda, međuelektrodnog rastojanja,



optimalnog vremena i gustine struje. Efikasnost elektrokoagulacione tehnike je procenjena na osnovu smanjivanja mutnoće, sadržaja organske materije sa aspekta  $UV_{326}$  apsorbanse i sadržaja bakra pri navedenim faktorima optimizacije EK procesa.

Kao stacionarni reaktor, korišćena je staklena čaša zapremine 250 ml, dok su kao elektrode upotrebljene 4 aluminijumske ili gvozdene ploče, dimenzija 10 x 5 x 0,2 cm. Ujednačeno mešanje otpadnog ofset razvijača postignuto je upotrebom magnetne mešalice. Uzorci su sakupljeni u određenim vremenskim intervalima (1, 5, 10, 20, 40, 60 minuta) EK procesa. Analiza koncentracije bakra vršena je primenom Atomskog apsorpcionog spektrometra (PerkinElmer, AAnalyst 700) plamena tehnika u skladu sa USEPA 7000b metodom. Sadržaj organske supstance određen je UV/VIS spektrometrom (UV-1800 SHIMADZU) na 326 nm. Mutnoća je merena turbidimetrom (HI 93703, HANNA Instruments, Portugal).

Rezultati dobijeni u toku istraživanja ukazuju da veliku efikasnost uklanjanja polutanata podjednako pokazuju i aluminijumske i elektrode od gvožđa. Dobijeni rezultati nakon procesa pokazuju dobru efikasnost elektrokoagulacije sa primenom veće gustine struje. Za gustine struje 2, 4, 8 mA/cm<sup>2</sup> više od 90% bakra se ukloni za 5, 10 i 20 minuta, respektivno. Efikasnost uklanjanja mutnoće nakon 60 minuta je 92,1%, a sadržaja organske materije 80,2% pri 2 mA/cm<sup>2</sup>. Pri većim gustinama struje efikasnosti uklanjanja navedenih polutanata se povećavaju. Negativna strana veće gustine struje je povećanje gubitka električne energije i zagrevanje samog otpadnog razvijača koji se prečišćava. Promena rastojanja između elektroda utiče na protok struje u rastvoru i na stvaranje koagulanata. Stopa efikasnosti uklanjanja mutnoće, sadržaja organske materije i sadržaja bakra iz otpadnog ofset razvijača je veoma velika (iznad 96%) pri međuelektrodnom rastojanju od 1,5 cm.

## Zahvalnica

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## Acute toxicity of petroleum benzene

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Petroleum hydrocarbons are the primary constituents in oil, gasoline, diesel, and a variety of solvents and penetrating oils. As such, petroleum hydrocarbons are a primary focus of many site and product risk assessments. Because petroleum hydrocarbon products are complex mixtures of chemicals, risk assessments for these products generally focus on specific toxic constituents. The petroleum constituents of primary interest to human health have been the aromatic hydrocarbons (i.e., benzene, ethylbenzene, toluene, and xylenes), polynuclear aromatic hydrocarbons (PAHs), gasoline additives (e.g., MTBE, TBA), and combustion emissions from fuels (e.g., carbon monoxide, benzene, acetaldehyde, formaldehyde, diesel particulates) [1].

The term "hazardous" is usually used to indicate potential hazard of chemical. In principle, being "hazardous" is a consequence of one or more intrinsic properties of a substance. It may derive from physicochemical property of a substance, toxicity to human health or toxicity to the environment (aquatic/soil organisms, flora, fauna etc) [2].

The aim of this work was to research and compare the acute toxicity of benzene to aquatic (*Tetrahymena pyriformis* (IGC<sub>50</sub>)) and terrestrial (oral Rat and Mouse (LD<sub>50</sub>)) species.

Toxicity value of benzene to *Tetrahymena pyriformis* was obtained from the literature [3] and the experimental data for rat and mouse (oral LD<sub>50</sub> values) were collected from the literature [4].

In this study several models were used for non-polar compounds to aquatic [3] and terrestrial species [5, 6] to determine the acute toxicity of benzene (Table).

**Table 1.** Experimental and predicted values of acute toxicity of benzene to aquatic and terrestrial species

Name of compound	logP	Exp. T. <i>pyriformis</i> log(1/IGC <sub>50</sub> ), mmol/l	Pred. T. <i>pyriformis</i> log(1/IGC <sub>50</sub> ), mmol/l /TR	Exp. oral Rat LD <sub>50</sub> mmol/kg	Pred. Oral Rat LD <sub>50</sub> mmol/kg / TR	Exp. oral Mouse LD <sub>50</sub> mmol/kg	Pred. oral Mouse LD <sub>50</sub> mmol/kg /TR
Benzene	2.13	-0.12	-0.36/0.24	11.90	45.16/3.79	60.17	4.27/ 0.07

The acute toxicity (aquatic and terrestrial species) of benzene is shown differences in their excess toxicity. The possible reasons may be different.

Aquatic toxicity is one of endpoints used in environmental risk assessment to determine the safe use and disposal of organic chemicals. The endpoints are a result of different routes of exposure in various species. The effect of a chemical is dependent on the species, route of exposure, and dose.

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## Persistence, bioaccumulation and toxicity of petroleum benzene

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Chemicals that are persistent in the environment, bioaccumulate in people and/or wildlife, and are toxic are called PBTs. Because of these features, as long as they remain in commerce and may therefore be released into the environment, they will threaten the health of humans and wildlife. The nature of the risk will depend on their specific toxic properties, the size of the exposed population or ecosystem, and the extent and duration of exposure. But, because of their persistence and ability to bioaccumulate, once exposure levels are sufficient to cause adverse effects in humans, domestic animals, or wildlife, their impacts are not easily reversed. Then, even if their production and use are discontinued, many years may pass before their concentrations have sufficiently declined so that they no longer pose risks [1].

The aim of this work is to study the persistence, bioaccumulation and toxicity (chronic) of benzene in the environment.

The PBT Profiler is a screening-level tool that provides estimates of the persistence, bioaccumulation, and chronic fish toxicity potential of chemical compounds. It is designed to be used when no data are available. In order to help interested parties make informed decision on a chemical's PBT characteristics, the PBT profiler automatically identifies chemicals that may persist in the environment and bioaccumulate in the food chain. These chemicals are identified using thresholds published by the EPA [2].

Chemicals that are persistent, bioaccumulative, and toxic have the potential to concentrate to levels that may cause significant adverse impact on human health and the environment. The results of estimation of benzene for persistence, bioaccumulation and toxicity are presented in Table.

**Table 1.** PBT profiler estimate of benzene

Name of compound	Persistence		Bioaccumulation	Fish ChV (mg/l)
	Media (water, soil, sediment, air) Half-life (days)	Percent in Each Medium	BCF	
Benzene	38; 75; 340; 13	40%; 26%; 0%; 34%	12	6.4

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## Possible hepatotoxic action of petroleum benzene

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




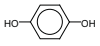
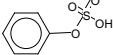

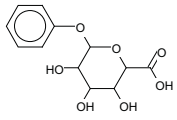

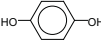



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The aromatic hydrocarbons are identified as chemicals of interest for health risk assessments at most petroleum-contaminated sites and for sites affected by petroleum solvent. Benzene is the only aromatic hydrocarbon classified by the U.S. Environmental Protection Agency and other health and environmental agencies as a "known human carcinogen," and therefore, is the primary focus of many petroleum hydrocarbon risk assessments. Exponent has conducted hundreds of site risk assessments where benzene was a chemical of concern. The potential exposure to benzene at a petroleum-contaminated site depends on the concentrations of benzene in the soil, water, and air, and the frequency and duration of expected human contact with the contaminated media. Benzene and the other aromatic hydrocarbons are taken up through the skin, lung, and digestive system, so all three routes of exposure (dermal uptake, inhalation, and incidental ingestion) need to be considered in assessing health risks [1].

The aim of this work is to predict the possible metabolites of benzene by a specialized software (OECD (Q)SAR Application Toolbox [2]) which can cause hepatotoxic action.

The results of the probable metabolic activation in liver (observed and predicted) of benzene are presented in the Table.

**Table 1.** Probable metabolic activation of benzene by (Q)SAR Application Toolbox

Observed liver metabolism by Toolbox; DNA and Protein binding		Liver metabolism simulator by Toolbox; DNA and Protein binding	
7 metabolites;		7 metabolites;	
	Protein and DNA binding – No binding.		Protein binding – Nucleophilic heterocycle ring opening; <u>DNA</u> <u>binding</u> – Aliphatic epoxides, Aziridines and Epoxyethers.
	Protein binding -Michael-type nucleophilic addition; Nucleophilic cycloaddition to diketones; <u>DNA binding</u> – No binding.		Protein and DNA binding – No binding.
	Protein and DNA binding – No binding.		Protein and DNA binding – No binding.
	Protein and DNA binding – No binding.		Protein binding -Michael-type nucleophilic addition; <u>DNA binding</u> – No binding.
	Protein and DNA binding – No binding.		Protein and DNA binding – No binding.
	Protein and DNA binding – No binding.		Protein binding -Michael-type nucleophilic addition; Nucleophilic cycloaddition to diketones; <u>DNA binding</u> – No binding.
	Protein binding -Michael-type nucleophilic addition; <u>DNA binding</u> – No binding.		Protein and DNA binding – No binding.

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## **Određivanje humanih, životinjskih i biljnih sterola i hormona u rečnim sedimentima**

### **Determination of human, animal and plant sterols and hormones in river sediments**

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Humani i životinjski steroli se mogu koristiti kao indikatori fekalnog zagađenja životne sredine, ali i za razlikovanje izvora kontaminacije na osnovu njihovih odnosa [1]. Povišene koncentracije biljnih sterola i hormona mogu prouzrokovati brojne neželjene efekte na ljudski organizam [2-4]. Tragovi ovih novih zagađujućih materija se mogu detektovati u površinskoj i podzemnoj vodi, a zbog akumulacije i u sedimentima [3]. Cilj ovog rada je razvoj i optimizacija metode ekstrakcije uzorka rečnog sedimenta za određivanje tragova humanih, životinjskih i biljnih sterola i hormona. Tokom optimizacije izvršen je izbor rastvarača za ekstrakciju, mase sedimenta, kao i vreme ultrazvučne ekstrakcije. Za kvantitativnu analizu dobijenih ekstrakata razvijen je postupak hromatografskog razdvajanja dvadeset sterola i hormona tačnom hromatografijom, uz korišćenje jonskog trapa kao masenog detektora (LC-MS/MS, engl. Liquid Chromatography-Tandem Mass Spectrometry) i hemijske jonizacije na atmosferskom pritisku.

Za ekstrakciju analita iz sedimenta ispitano je šest rastvarača različite polarnosti: metanol, aceton, etil-acetat, acetonitril, dihlormetan i heksan. Masa uzorka rečnog sedimenta je optimizovana sa ciljem da faktor predkoncentrovanja bude što veći, a količina ekstrahovanih nečistoća što manja. Radi skraćenja vremena pripreme uzorka testirana su i različita vremena ultrazvučne ekstrakcije.

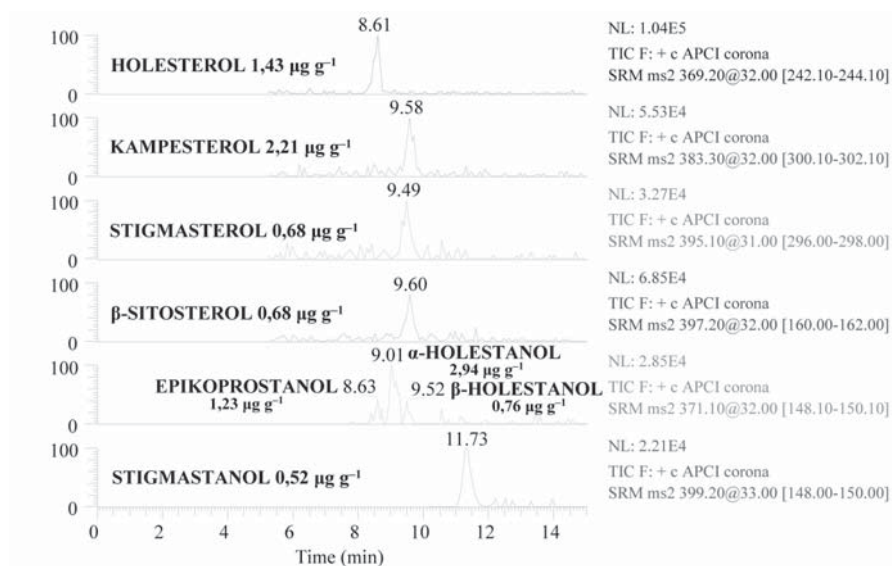
U konačno razvijenoj i optimizovanoj proceduri pripreme uzorka, sediment je ekstrahovan u ultrazvučnom kupatilu u trajanju od 10 min. Uzorak je potom centrifugiran i odvojen je supernatant. Postupak ekstrakcije je ponovljen još dva puta, a dobijeni supernatanti su spojeni. Ekstrakt je uparen i kvantitativno prenet na kolonu za prečišćavanje, pakovanu silika-gelom i anhidrovanim Na<sub>2</sub>SO<sub>4</sub>. Nakon nanošenja uzorka, izvršeno je eluiranje smešom metanol/etil-acetat u odnosu 1:1. Dobijeni prečišćeni ekstrakt je uparen do suva, a zatim rekonstituisan u metanolu, filtriran i analiziran.

U razvijenoj LC-MS/MS metodi, mobilna faza se sastojala od metanola i dejonizovane vode. Utvrđeno je da je za optimalno hromatografsko razdvajanje dvadeset odabranih sterola i hormona potrebno razviti dve metode, jer nije bilo moguće razdvojiti značajan broj analita, posebno hormona. Takođe je pokazano da



17 $\alpha$ - i 17 $\beta$ -estradiol, zatim estron i estriol, kao i epikoprostanol,  $\alpha$ - i  $\beta$ -holestanol imaju identične MS<sup>n</sup> reakcije fragmentacije, ali ih je moguće hromatografski razdvojiti odgovarajućim gradijentom mobilne faze. Na osnovu rezultata MS<sup>n</sup> analize, izabrane su karakteristične reakcije fragmentacije za kvantitativno određivanje i potvrdu prisustva svakog analita u razvijenim LC–MS/MS metodama.

Vrednosti prinosa optimizovane metode su bile visoke (81–120%), sa relativnom standardnom devijacijom manjom od 22%. Metoda pripreme uzorka je uspešno primenjena u analizi uzorka sedimenta reke Morave u kojem su detektovani tragovi humanih, životinjskih i biljnih sterola (slika 1).



**Slika 1.** Hromatogram uzorka sedimenta reke Morave sa količinama detektovanih sterola.

### Zahvalnica

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## Određivanje anizomicina u životinjskim tkivima

### Determination of anisomycin in animal tissues

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Anizomicin je antibiotik izolovan iz bakterijske vrste *Streptomyces griseolus* za koji je nekoliko studija pokazalo da je citotoksičan prema ćelijama malignog tumora, tj. da može suzbiti njihov rast [1]. Cilj ovog rada bio je razvoj i optimizacija metode ekstrakcije ovog antibiotika iz životinjskih tkiva, kao što su srce i jetra. Ispitivani su različiti rastvarači za ekstrakciju, kao i metode prečišćavanja dobijenog ekstrakta. Ekstrakt je analiziran metodom tečne hromatografije sa tandem masenom spektrometrijom (LC–MS/MS, engl. liquid chromatography–tandem mass spectrometry).

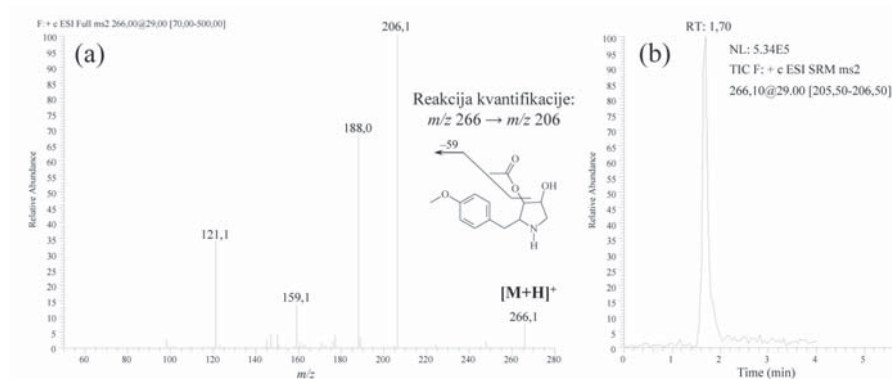
Kao rastvarači za ekstrakciju anizomicina iz tkiva ispitivani su metanol i acetonitril. S obzirom na to da antibiotici strukturno slični anizomicinu pokazuju afinitet prema proteinima, posebna pažnja je posvećena deproteinizaciji u cilju povećanja ekstrakcije analita iz matrice, što se postiže upotrebom trihlorsirćetne kiseline (TCA, engl. trichloroacetic acid) [2]. Dodatni problem prilikom ekstrakcije iz tkiva kao kompleksne matrice predstavlja masnoća, koja se može ukloniti upotrebom heksana [3].

U optimizovanoj metodi ekstrakcije na prethodno homogenizovan uzorak tkiva dodat je metanol i vršena je sonikacija 30 min. Uzorak je zatim centrifugiran i odvojen je supernatant. Postupak ekstrakcije metanolom je ponovljen, a dobijeni supernatanti su spojeni i preneti u levak za razdvajanje, gde je dodat heksan radi odmašćivanja. Nakon razdvajanja faza, odliven je donji sloj metanola i uparen do suva u struji azota u vodenom kupatilu na 30 °C. Ostatak je suspendovan u 5% rastvoru TCA. Dobijeni ekstrakt je potrebno prečistiti, a prisutan anizomicin izolovati i koncentrovati, za šta se koristi metoda ekstrakcije na čvrstoj fazi (SPE, engl. solid-phase extraction). Dobijeni uzorak je nanošen na OASIS HLB (HLB, engl. hydrophilic-lipophilic balance) SPE kolonu, prethodno kondicioniranu metanolom i dejonizovanom vodom. Po nanošenju uzorka, kolona je sušena na vakuumu oko 10 min. i eluirana sa metanolom. Eluat je uparen do suva u struji azota u vodenom kupatilu na 30 °C, a zatim rekonstituisan sa 1 ml metanola. Dobijen ekstrakt je propušten kroz filter veličine pora 0,45 µm i analiziran.

Za razvijenu i optimizovanu metodu dobijeni su visoki prinosi, u opsegu 73–114% (za tkivo srca) i 81–104% (za tkivo jetre). Za kvantitativno određivanje korišćeni su standardi koji odgovaraju matrici uzorka. Naime, utvrđeno je da matrica uzorka umanjuje jonizaciju analita za 53–78%, zbog čega je potrebno

koristiti odgovarajuće standarde koji se pripremaju za svaku vrstu tkiva dodatkom određene zapremine standardnog rastvora anizomicina u krajnji ekstrakt dobijen nakon SPE procedure.

Za LC-MS analizu korišćen je Surveyor LC sistem (Thermo Fisher Scientific, SAD) i Zorbax Eclipse® XDB-C18 kolona (Agilent Technologies, SAD), dimenzija 4,6 mm x 75 mm x 3,5 µm. Mobilna faza sastojala se od metanola, dejonizovane vode i 10% sirćetne kiseline. Maseni spektri dobijeni su korišćenjem LCQ Advantage (Thermo Fisher Scientific) jonskog trapa, kao masenog spektrometra uz elektrosprej jonizacionu tehniku. Za kvantifikaciju i potvrdu prisustva anizomicina odabrane su reakcije fragmentacije protonovanog molekula analita u najintenzivnije fragmentne jone (slika 1).



**Slika 1.** (a) MS/MS spektar anizomicina sa reakcijom odabranom za kvantifikaciju; (b) hromatogram odabrane reakcije kvantifikacije anizomicina.

Granica detekcije metode, izračunata kao koncentracija pri kojoj je vrednost odnosa signala i šuma 3:1, iznosi 1,5 ng g<sup>-1</sup>, a granica kvantitativnog određivanja, koja odgovara koncentraciji pri kojoj je vrednost odnosa signala i šuma 10:1, iznosi 5,0 ng g<sup>-1</sup>. Dobijeni parametri pokazuju da je razvijena metoda osetljiva i pouzdana za određivanje tragova anizomicina u tkivu.

### Zahvalnica

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## Greenhouse gas emissions modeling using artificial neural networks approach

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Greenhouse gas (GHG) emissions have become major concern due to their impact on global warming [1]. European greenhouse gas emissions can be broken down by the economic activities that lead to their production: Energy supply and use (60% of Europe's GHG emissions), Transportation (20% of Europe's GHG emissions), Agriculture (10% of Europe's GHG emissions), Industrial processes (7% Europe's greenhouse gas emissions) and Waste (3% of of Europe's GHG emissions) [2].

In this paper, a development of an Artificial Neural Networks (ANNs) model for the prediction of GHG emission for European countries is presented. ANNs are a data processing system consisting of a large number of simple, highly interconnected processing elements inspired by the biological system and designed to simulate the neurological processing ability of the human brain [3].

In order to create a suitable ANN prediction model, the selected input variables need to cover all GHG emission sectors. Therefore, the following sustainability, economical and industrial indicators have been used as inputs: Gross domestic product (GDP), GDP in agriculture and industry, Gross inland energy consumption, Share of renewable energy in gross final energy consumption, Electricity generated from renewable sources, Number of motor vehicles, Age of the passenger cars, Air transport of goods and passengers, Area under organic farming, Roundwood removals and production, Organisations and sites with EMAS registration, Municipal waste generation and Waste deposit onto or into land. The inputs and GHG data are obtained from the Eurostat [4], United Nations Economic Commission for Europe (UNECE) [5] and World Bank [6] database. The model was trained, validated and tested with the data for 28 European countries for the period from 2004 to 2010.

The ANN architecture used in this study is the General Regression Neural Network (GRNN) [7], which has already demonstrated good results in environmental modelling [8,9]. GRNN is a one-pass learning network consisting of four layers. The number of neurons is defined by the number of input/output variables and the number of training cases used for model training (details in [8]). Other architectural and training parameters were varied during the GRNN creation, in order to investigate the particular influence of every of these parameters on the performance of GRNN for GHG emission forecasting. Therefore, 24 GRNN models with

different architecture and training parameter sets were created and analysed using multiple performance indicators. The GRNN model with the best performance (the relative error for test set of 4%) was the model that has random validation data selection, linear scale function, Euclidian distance metrics and genetic algorithm for the determination of smoothing factor. A comparison of GRNN results with multi-linear regression model (MLR) created and tested using the same dataset showed that GRNN model has demonstrated much better forecast performance, since the MLR model has the relative error of 15% for the test set.

The model is able to provide a prediction for GHG emissions for 2011, since the GRNN model inputs values were available for the studied European countries (GHG emissions for 2011 were not available on Eurostat). Results show that in the year 2011, a 1.6% reduction of GHG emissions in comparison to 2010 can be expected in the studied countries. The biggest decrease of GHG emissions can be expected in Finland, while the biggest increase of 4% is expected in Slovenia. Only in the case of Austria the results suggest that GHG emissions will stay the same as in 2010.

The presented GRNN model can be used not only for GHG emissions forecasting, but also for simulating various scenarios of GHG emission by changing the values of the input variables, e.g. to simulate possible consequences of regulatory actions on GHG emissions. The obtained results can be used by regulatory bodies and governments to support the development of GHG reduction strategies at national level.

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## **Primena jonske hromatografije za određivanje fluora u uglju posle sagorevanja u kiseoničnoj bombi**

### **Application of ion chromatography for fluorine determination in coal after oxygen bomb combustion**

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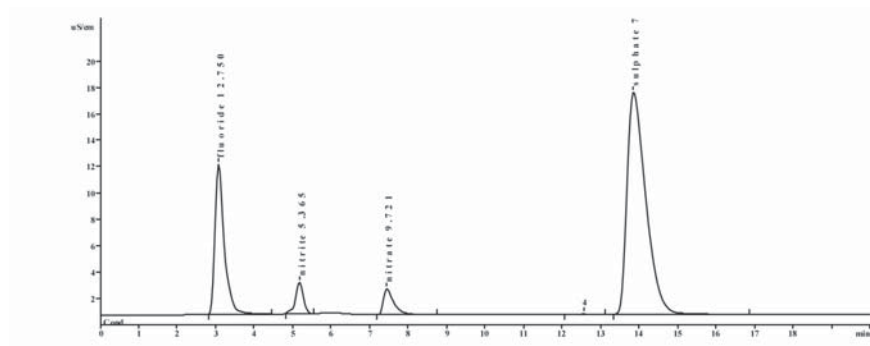
Halogeni elementi u uglju se nalaze na nivou tragova, ali zbog gasovitih jedinjenja koja nastaju tokom sagorevanja uglja, a koja izazivaju niz ekoloških problema privlače sve veću pažnju [1]. Određivanje fluora u uglju je sprega adekvatnog izdvajanja ovog elemenata iz kompleksne čvrste matrice u vodeni rastvor i merenja jonske koncentracije.

U ovom radu ugalj je sagorevan u kiseoničnoj bombi (1108 Oxygen Combustion bomb, Parr) u cilju ekstrakcije fluora u obliku gasovitih jedinjenja. Izdvojena gasovita jedinjenja su apsorbovana u vodi ili vodenom rastvoru NaOH, koncentracije 1 mol/L. Sadržaj fluorid-jona u rastvoru je ispitivan metodama visoke osetljivosti kao što su direktna potenciometrija sa jon-selektivnom elektrodom (JSE) i jonska hromatografija (IC).

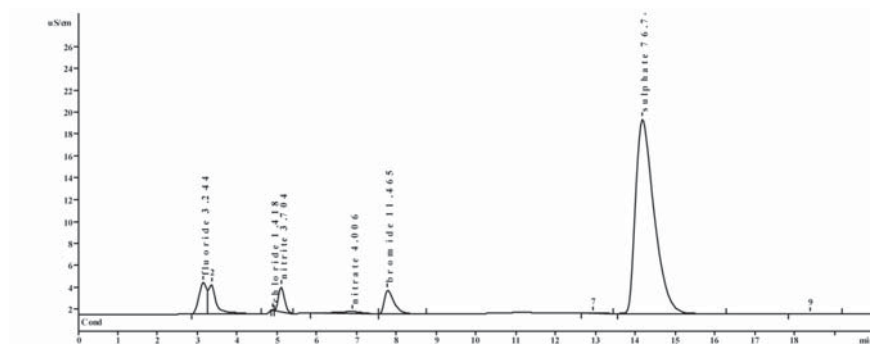
Hromatografska određivanja su vršena pomoću Metrohm, 761 Compact IC hromatografa. Korišćena je separaciona anjonska kolona Metrosep A supp 1-250, uz pretkolonu Anion Supersep 1. Kao mobilna faza korišćen je rastvor natrijum-karbonata koncentracije 3 mmol/L. Protok mobilne faze je bio 1 mL/min, vreme analize 20 minuta, a injektirana zapremina 20 µL. Rastvori uzoraka i standarda su pre snimanja hromatograma filtrirani kroz membranski filter od 0,45 µm. Direktna potenciometrijska merenja rađena su na pH-jon metru (C860, Consort) fluorid-selektivnom elektrodom (ISE27B, Consort) uz odgovarajući mešoviti pufer (eng.-tisab).

Na slici 1 prikazan je hromatogram uzorka, gde je kao rastvor za apsorpciju izdvojenih gasovitih jedinjenja korišćen rastvor NaOH. Sa slike 1 se uočava da je koncentracija fluorid-jona visoka, iznad očekivane i veća od one koja je određena pomoću JSE. Jedan od razloga je što se tokom sagorevanja uzorka u kiseoničnoj bombi, izdvajaju mali organski molekuli koji u apsorpcionom rastvoru disosuju. Ovi organski anjoni iz kolone eluiraju istovremeno ili u bliskom vremenskom periodu sa fluorid-jonom. Iz tog razloga pik na hromatogramu za fluorid-jon je veći nego što odgovara njegovoj realnoj koncentraciji u rastvoru, pošto se preklapa sa pikom organskih anjona. Zbog toga rezultati određivanja

fluorid-jona jonskom hromatografijom mogu biti veći od stvarnih vrednosti. Iako se kolona koja je korišćena za hromatografsko razdvajanje može primeniti u širokoj oblasti pH, izvršena je neutralizacija adsorpcionog rastvora pomoću IC-H filtera za neutralizaciju baznih uzoraka. Hromatogram neutralizovanog rastvora prikazan je na slici 2. Poređenjem hromatograma adsorpcionog rastvora pre i posle neutralizacije primetno je bolje razdvajanje fluorid-jona i organskih anjona koji eluiraju uz fluorid-jon.



Slika 1. Hromatogram baznog apsorpcionog rastvora



Slika 2. Hromatogram apsorpcionog rastvora nakon neutralizacije

Poređenjem rezultata dobijenih direktnom potenciometrijom i metodom IC, uočava se da postoje znatna odstupanja u određivanju koncentracije fluorid-jona u apsorpcionom rastvoru ovim dvema metodama. To znači da se neutralizacijom baznih rastvora postiže bolje razdvajanje fluorid-jona i anjona organskih kiselina, ali nedovoljno za pouzdano i tačno određivanje njegove koncentracije u apsorpcionom rastvoru. Takođe, i u slučaju kada se za apsorpciju produkata sagorevanja uglja koristi voda metodom IC dobijaju se povećane koncentracije fluorida i hromatogram sličan prikazanom na slici 2.

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## Ispitivanje sadržaja Pb, Cd i Cr u prstenovima prirasta platana (*Platanus acerifolia* Ait.)

### Determination of Pb, Cd and Cr in plane (*Platanus acerifolia* Ait.) tree-rings

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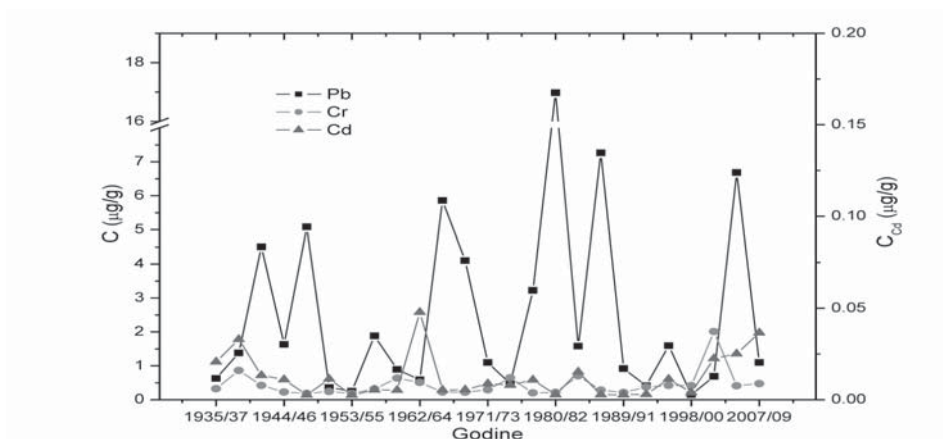
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Kao bioindikator stanja zagađenosti životne sredine mogu se koristiti listovi biljaka, lišajevi, mahovine kao i prstenovi prirasta (godovi). Drveće u umerenoj zoni formira prsten prirasta svake godine koji mogu biti tačno datovani. Prilikom opredeljivanja za izbor prstenova prirasta, kao bioindikatora presudno je uticala činjenica da analizom sadržaja ispitivanih elemenata u njima dobijamo i periode njihovih akumulacija. Na osnovu tih rezultata otvaraju se mogućnosti analize promena stanja zagađenosti životne sredine u proteklom periodu [1, 2, 3]. Kolutovi platani kao i odgovarajući uzorci zemljišta na dve dubine (0-20 i 20-40 cm) su uzorkovani 2010. godine na lokaciji Bulevar kralja Aleksandra u Beogradu, u toku njegove rekonstrukcije. Uzorci su pripremani odvajanjem po tri prstena prirasta počevši od 1935. do 2009. godine. Mikrotalasnom digestijom (ETHOS 1, Milestone, Italy) su uzorci prevodjeni u rastvor. Merenje koncentracija Pb, Cd i Cr u prstenovima prirasta je vršeno na ICP-OES (Thermo Scientific iCAP 6500 Duo ICP spectrometra) spektrometru.

Srednje trogodišnje vrednosti koncentracija Pb, Cd i Cr u prstenovima prirasta platana (*Platanus acerifolia* Ait.) u periodu od 1935. do 2009. godine sa odabrane lokacije su prikazane na Slici 1. Dobijeni rezultati jasno ukazuju da su koncentracije Pb u prstenovima prirasta veće za oko jedan do dva reda veličine od odgovarajućih koncentracija dobijenih za Cr i Cd. Ovi rezultati su očekivani za ovu lokaciju na kojoj je svakodnevno izražena dinamična saobraćajna aktivnost. Uočljivo je takođe da se koncentracija Pb u analiziranim uzorcima u periodu od 1989. pa do 2009. godine u proseku niže nego u periodu od 1935. do 1989. godine. Takav trend promena koncentracija nije izražen i uočljiv u slučaju Cd i Cr. U slučaju Cd i Cr se dobija vrednost Pearson-ovog korelacionog koeficijenta od 0,39, što predstavlja slabu pozitivnu korelaciju, dok u svim ostalim slučajevima nema korelacije.

Srednje vrednosti koncentracija Pb, Cd i Cr u prstenovima prstima platana u celokupnom periodu ispitivanja 1935-2009. su upoređivane sa dva perioda: od 1989. do 2009. godine i od 1935. do 1989. godine. U Tabeli 1. su prikazani rezultati srednjih vrednosti koncentracija Pb, Cd i Cr u prstenovima prirasta u navedenim periodima, % njihovog povećanja ili smanjenja u odnosu na ceo period kao i koncentracije u zemljištu na dve dubine.





**Slika 1.** Srednje trogodišnje vrednosti koncentracija Pb, Cr i Cd u prstenovima prirasta platana

**Tabela 1.** Srednje vrednosti koncentracija Pb, Cr, Cd ( $\mu\text{g/g}$ ) u prstenovima prirasta platana i zemljištu i % njihovog smanjenja/povećanja koncentracija u periodima od 1935-1989 i 1989-2009

Elementi	Pb	Cd	Cr
Srednje vrednost za ceo period 1935-2009.	2,77	0,013	0,44
Srednje vrednosti za period 1935-1989.	3,21	0,012	0,37
Srednje vrednosti za period 1989-2009.	1,65	0,015	0,61
% smanjenja, povećanja konc. od 1989-2009 u odnosu na ceo period 1935-2009.	-40,4	15,4	38,6
Zemljište 0-20cm	65,91	2,63	104,51
Zemljište 20-40cm	71,45	1,71	60,94

Dobijeni rezultati prikazani u Tabeli 1. ukazuju na smanjenje samo koncentracija Pb u periodu od 1989-2009. godine u odnosu na ceo period ispitivanja za 40,4%. Ovi rezultati se mogu dovesti u vezu sa krizom iz 90-tih godina kao i početkom korišćenja automobila na bezolovni benzin.

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## **Akumulacija Cu, Ni i Zn u prstenovima prirasta platana (*Platanus acerifolia* Ait.)**

### **Accumulation of Cu, Ni and Zn in plane (*Platanus acerifolia* Ait.) tree-rings**

Ivana R. Milošević<sup>1</sup>, Dragan M. Marković<sup>2</sup>,  
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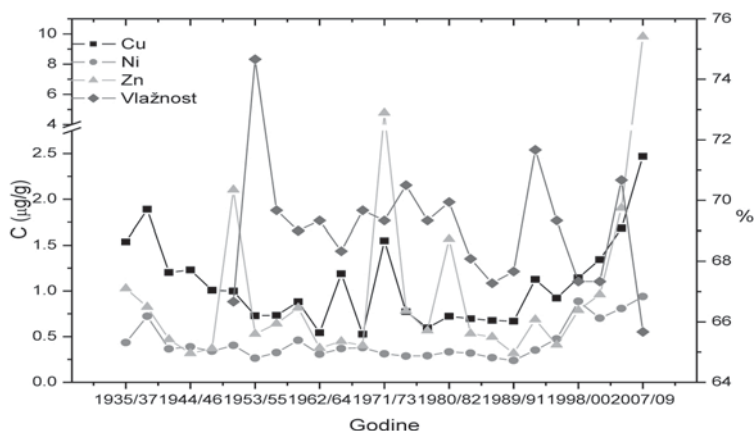
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Analizom sadržaja metala u bioindikatorima kao što su lišajevi, mahovine, pa-  
prati, lišće itd. može se uočiti samo ukupni odgovor korišćenih bioindikatora na  
nivo zagađenja životne sredine. Oni nam ne mogu prikazati periode veće ili manje  
zagađenosti kroz koji prolaze tj. da li su efekti zagađenja isti svake godine ili posto-  
je periodi većeg zagađenja. Prstenovi prirasta sa druge strane nam omogućavaju  
vraćanje u određene periode i razumevanje trendova akumulacija metala [1,2]. Za  
određivanje koncentracije Cu, Ni i Zn u prstenovima prirasta platana korišćena je  
ICP-OES metoda. Merenja su izvršena korišćenjem Thermo Scientific iCAP 6500  
Duo ICP spectrometra. Digestija je izvršena mikrotalasnim digestorom ETHOS  
1, Milestone, Italy. Uzorkovanje prstenova prirasta je izvršeno 2010. godine na lo-  
kaciji Bulevara kralja Aleksandra u Beogradu. Te godine je vršena rekonstrukcija  
bulevara i drveće platana je tada posećeno. Uzorci su pripremani od segmenata po  
tri prstena prirasta (na svake tri godine) počevši od 1935 do 2009. Uzorci zemlji-  
šta su uzorkovani na dve dubine (0-20 i 20-40 cm).

Na Slici 1. prikazane su srednje vrednosti koncentracija Cu, Ni i Zn u prsteno-  
vima prirasta platana (*Platanus acerifolia* Ait.) kao i relativna vlažnost vazduha  
( $R_h$ ) sa lokacije Bulevar Kralja Aleksandra (Beograd) u periodu od 1935 do 2009.  
Sa Slike 1. uočava se sličan trend promena koncentracija Cu, Ni i Zn u prstenovi-  
ma prirasta, dok se taj trend promena razlikuje za slučaj relativne vlažnosti vaz-  
duha. Izračunavanjem Pearson-ovih korelacionih koeficijenta dobijene su sledeće  
vrednosti: Ni-Zn (0.49); Cu-Zn (0.70); Cu-Ni (0.74); Ni- $R_h$  (-0.40); Zn- $R_h$  (-0.38) i  
Cu- $R_h$  (-0.33). Dobijeni rezultati ukazuju na postojanje jakih pozitivnih korelacija  
između Cu i Ni i između Cu i Zn, dok se u slučaju Ni i Zn uočava slaba pozitivna  
korelacija. U svim slučajevima relativna vlažnost vazduha je u slaboj negativnoj  
korelaciji sa Cu, Ni i Zn. Sličan trend porasta koncentracija ispitivanih eleme-  
nata (Slika 1.) se može primetiti u periodu od 1989. do 2009. godine. Upoređujući  
odnose srednjih vrednosti koncentracija Cu, Ni i Zn u prstenovima prirasta pla-  
tana u periodima od 1989. do 2009. i od 1935. do 1988. dobijene su sledeće vred-  
nosti: 1.4, 1.7 i 2.2, redom. Ovi rezultati ukazuju na povećan sadržaj Cu, Ni i Zn u  
zadnjih dvadeset godina vegetacionog perioda platana.



**Slika 1.** Srednje trogodišnje vrednosti koncentracija Cu, Ni i Zn ( $\mu\text{g/g}$ ) u prstenovima prirasta platana i relativna vlažnost vazduha- $R_h$  (%)

U Tabeli 1. prikazane su srednje vrednosti koncentracija Cu, Ni i Zn u prstenovima prirasta i zemljištu. Iz prikazanih tabelarnih vrednosti srednjih koncentracija prstenova prirasta platana uočava se da su najmanje vrednosti dobijene za Ni, a potom za Cu i Zn. Takodje se može zapaziti da se koncentracije Cu, Ni i Zn u zemljištu smanjuju sa njegovom dubinom. Samo je u slučaju Ni izmerena veća koncentracija u zemljištu od dozvoljene, a koja iznosi 50 mg/kg [3].

**Tabela 1.** Srednje vrednosti koncentracija Cu, Ni i Zn ( $\mu\text{g/g}$ ) u prstenovima prirasta i zemljištu

Elementi		Cu	Ni	Zn
Prstenovi-prirasta		1.07	0.44	1.28
Zemljište	0-20 cm	59.86	128.64	172.73
	20-40 cm	24.52	72.49	101.39

Dominantni izvor Cu, Ni i Zn na ispitivanoj lokaciji je automobilska saobraćajna aktivnost, koja se iz godine u godinu povećava. U zadnjem dvadesetogodišnjem ispitivanom periodu zapažen je porast koncentracija Cu, Ni i Zn koje izražene u procentima iznose: 25.5, 43.2 i 66.4.

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## **Geološke i geohemijske karakteristike sedimentnih stena Kremanskog basena (Srbija)**

### **Geological and geochemical characteristics of Kremna basin sedimentary rocks (Serbia)**

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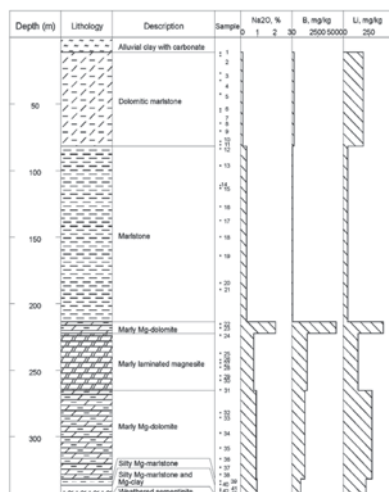
Kremanski basen koji spada u jezerske basene Zlatiborskog kompleksa, lociran na jugozapadu Srbije, još uvek je nedovoljno istražen. Starost jezerskih sedimentata Kremanskog basena određena je kao Donji miocen, a njegova površina iznosi oko 15 km<sup>2</sup> [1]. Za ispitivanje sedimentata uzeta su 43 uzorka iz bušotine Zlatibor-2 (ZLT-2) sa različitih dubina (0-343 m), što je prikazano na Slici 1. Rendgenskom analizom određen je mineraloški sastav sedimentata, a sadržaj makro- i mikroelemenata kao i retkih zemalja emisionom i masenom spektrometrijom (ICP-ES i ICP-MS).

Na osnovu dobivenih rezultata izdvojeno je nekoliko litoloških tipova: laporoviti magnezit, laporoviti Mg-dolomit, alevritski Mg-laporci, laporoviti dolomit, dolomitski laporac, laporac, Mg-glina i dolomitski alevrit.

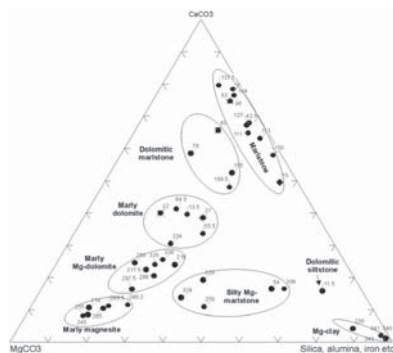
U sastavu sedimentata Kremanskog basena dominira dolomit, praćen promenljivim količinama kvarca, kalcita, magnezita i glina.

U višim delovima sedimentne serije (do dubine od oko 210 m) dominiraju kalcit i dolomit, a u dubljim delovima dolomit i magnezit. Sadržaj minerala glina u laporcima i dolomitskim laporcima je mali, što ukazuje na relativno slabo hemijsko raspadanje stena u obodu basena. Na aridne uslove sedimentacije u dubljem delu basena (marginalno-jezerska facija) ukazuje prisustvo sirlezita i glip-tomorfoze od evaporita. Na takve uslove ukazuje i povećan sadržaj natrijuma u sedimentima marginalno-jezerske facije.

Povećani odnosi Mg/Ca i Sr/Ca pokazuju periode hemijskog taloženja karbonata [2]. Odnosi Ca/Al, Sr/Al and Ba/Al takođe su karakteristični za periode velikog taloženja karbonata. U nekim slučajevima pokazuju nešto manje vrednosti zbog izuzetno niske koncentracije aluminijuma.



**Slika 1.** Litološki stub bušotine ZLT-2 sa raspodelom uzoraka.



**Slika 2.** Triangularni dijagram odnosa  $\text{MgCO}_3$ ,  $\text{CaCO}_3$  i drugih komponenti [3], sa aspekta ispitivanih uzoraka.

Odnos Sr/Ca je najveći u magnezitima, što ukazuje na pojavu aragonita kao prekursora karbonatnih minerala u blago evaporitskim uslovima. Visoka produktivnost je obeležena povećanim sadržajem organskog ugljenika, što je tipično za veći deo basena bogatog laporcima. Anoksični uslovi su definisani povećanim U/Th odnosom, koji maksimalne vrednosti dostiže u magnezitima.

Ova istraživanja su pomogla detaljnijoj proceni evolucije ispitivanog jezerskog basena.

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## Odraz pritisaka sa kopnenih površina na geohemijska svojstva vode karstnog vrela

### Repercussion of the pressure from the surface area to the geochemical properties of water of karst spring

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Cilj ovog rada je da se proceni uticaj pritisaka sa kopnenih površina sliva, na geohemijska svojstva voda kaptiranih izvora-izvorišnog horizonta „Mareza“. Karstno vrelo „Mareza“ je razbijeno u nizu povremenih i stalnih izvora, koji izbijaju na kotama od 26.0mm do 33.11mm. U višegodišnjem proseku procenjena količina vode je u opsegu od 2 do 10 m<sup>3</sup>/s. Na potezu od oko 1km dužine, javlja se preko 30 stalnih izvora, od kojih su četiri kaptirani za vodosnabdevanje, a ostala količina vode formira vodotok Trešnice [1]. Sama izvorišna zona „Mareze“ je na kontaktu vodopropusnih gornjokrednih slojevitih do bankovitih krečnjaka i kvartarnih glaciofluvijalnih sedimenata, u bazisu prostranog sliva Skadarskog jezera, tako da su izvori kontaktno-prelivni do uzlazni. Zone sanitarne zaštite zahvaćene vode nisu pouzdano definisane, jer ni sliv nije bliže određen po položaju i veličini, kao što nije poznato poreklo vode [1].



Slika 1. Geografski položaj izvorišta "Mareza"

Primenjeni metodološki pristup oslonjen je zato na istraživanja geohemijskih svojstava voda. U hemiji karbonatnih podzemnih voda regionalne razlike postoje, a za definisanje stepena tih promena usled upliva zagađivača korišćeni su kao

indikatori, vrednosti limitirajućih pokazatelja kvaliteta vode i mol.odnos Ca/Mg,  $\text{evqSO}_4/\text{Cl}$ . Podaci su poređeni sa dobijenim u ranijem periodu, kao i sa svojstvima karstnih voda drugih područja [2]. Hidrogeološkim izviđanjima utvrđeni su brojni „rasuti“ izvori zagađenja, (slika 1) čiji se sastojci posredno ili neposredno, preko površinskih karstnih oblika (muzge, škrape, ponori, itd.), nagomilavaju u uže slivno područje izvorišta. Poređenjem podataka (tabela 1), zavisno od perioda istraživanja, uočavaju se razlike jer su gotovo svi osnovni konstituenti vode u porastu. Temperatura vode u prethodnom periodu varirala je od 9.0-10.0°C, dok je u zadnjem periodu utvrđeni raspon od 9.6-11.2°C, pri indeksu zasićenosti kiseonikom od 66-75%. Evidentirana su odstupanja od normalnih vrednosti za sastojke karstne vode [2]. To se ogleda i u vrednostima mol odnosa Ca/Mg kao i  $\text{evq SO}_4/\text{Cl}$ , koji pored ostalog ukazuju na prodor fekalija i sastojaka đubriva. U prilog tome, je porast nitrata i fosfata za oko 10 puta i visok procenat >68% mikrobiološke neispravnosti sirove pijaće vode [3].

**Tabela 1.** Ekstremne, srednje i vrednosti međuodnosa nekih sastojaka vode izvorišta

Parametri		pH	EC	°dH	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca/Mg	SO <sub>4</sub> /Cl
1968/78	Min	7.20	126	6.3	26.8	5.5	122.0	2.0	4.5	1.27	0.47
	Xsr	7.40	171	8.6	45.6	9.6	173.8	6.7	14.9	3.08	1.59
	Max	8.00	217	10.9	56.0	15.4	213.5	10.0	35.8	5.10	6.42
2011/12	Min	7.00	230	8.9	36.8	9.6	179.0	9.8	8.7	1.27	0.34
	Xsr	7.72	325	8.9	50.0	12.3	199.0	12.7	15.1	2.63	0.91
	Max	8.30	438	10.6	60.3	17.6	213.0	16.5	24.2	3.81	2.41

Preporučuje se monitoring sirove vode, kao preduslov upravljanja kvalitetom vode, i time zaštita ovog dragocenog izvorišta.

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## **Validacija imunoenzimskih testova za detekciju aflatoksina prisutnih u hrani**

### **Validation of immunoenzymatic tests for the detection of aflatoxin present in food**

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#### **Uvod**

Mikotoksini su toksični sekundarni metaboliti većeg broja saprofitskih plesni. Unošenjem toksina gljivica u organizam ljudi i životinja nastaju mikotoksikoze [3].

Nacionalna zakonska regulativa u našoj zemlji propisala je maksimalno dozvoljene koncentracije (MDK) aflatoksina od 2-15 µg/kg u hrani i 10-50 µg/kg u hrani za životinje.

Ciljevi istraživanja su potvrđivanje zahteva za karakteristike izvođenja, tehničke kompetentnosti i nezavisnosti primene ELISA testa, koji se zasniva na selektivnoj reakciji antigen-antitelo, pri detekciji aflatoksina i aflatoksina B1. Verifikacija se bazira na upotrebi referentnih materijala, kontaminiranih uzoraka, učestvovanju u međulaboratorijskim ispitivanjima na različitim matriksima, od strane različitih izvršioca i laboratorija.

Parametri ispitivanja baziraju se na Odluci Evropske komisije EC/657/2002, AOAC priručniku [1] i zahtevima za karakteristike izvođenja zadatih od strane proizvođača.

#### **Materijal i metode**

- **Princip:** Karakteristika ELISA testova je antitelo antigen reakcija. Sadržaj antigena u uzorku može se proceniti na osnovu njihove sposobnosti vezivanja za antitela koja su prethodno fizički apsorbovana za zidove bunarčića plastične ploče za mikrotitraciju.
- **ELISA testovi:** Celer Afla total-Tecna, Italy i Celer Afla B1-Tecna, Italy.
- **Kontaminirani uzorci brašna:** LOD-2ppb, N<sub>1</sub>-5ppb, N<sub>2</sub>-10ppb, N<sub>3</sub>-20ppb.
- **Referentni materijali:** Kikiriki 3.6 µg/kg i proteinska smeša 9.9 µg/kg.
- **Uzorci međunarodnih međulaboratorijskih ispitivanja i koncentracije aflatoksina B1:** Progetto Trieste 2011 kukuruz 9.67 µg/kg i 2.71 µg/kg i FAPAS MT Round 2012 kukuruz 9.32 µg/kg [4].

#### **Rezultati i zaključak**

Zadati limit detekcije za ukupne aflatoksine iznosi 2 µg/kg, za aflatoksin B1 1 µg/kg. Tačnost iznosi 134±19 % za ukupne aflatoksine i 124 ± 22 za aflatoksin B1. Laboratorijsku preciznost koju treba dokazati kreće se u intervalu od 10-20% [1].



Ekspirimen se ogledao ispitivanjem uzorka bliskom limitu detekcije (LoD) u šest uzastopnih merenja, i ispitivanjem drugih uzoraka u duplikatu, od strane dva izvršioca u najmanje tri različita vremenska intervala [2]. Statističkom obradom dobijenih eksperimentalnih rezultata u programu ValHemMet dobijeni su verifikacioni podaci (Tabela 1.).

**Tabela 1.** Prikaz rezultata za sve parametre ispitivanja i poređenje sa zadatim vrednostima

Parametar	Rezultati	Opseg (µg/kg)	LoD /LoQ (µg/kg)	Tačnost (Recovery %)	Preciznost (CV%)
Ukupni aflatoksini	Zadati:	2-20	2	134±19	11.6 ± 3.5
	Dobijeni:	Potvrđen ispitivanim koncentracijama	1,1	100-114	4
				92-128	9.5
				99-108	5.2
				87-119	9.4
Afla B1	Zadati:	1- 40	1	124 ± 22	20
	Dobijeni:	Potvrđen ispitivanim koncentracijama	Z =  0.86 – 1.05		

Rezultati verifikacije i rezultati međulaboratorijskih poređenja pokazali su da je značaj imunoenzimskih testova pri detekciji mikotoksina u hrani veliki. Ogleda se u specifičnoj, preciznoj i tačnoj kvantitativnoj detekciji aflatoksina, aflatoksina B1 u hrani.

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## Heterogena fotokatalitička razgradnja alprazolama

### Photocatalytic degradation of alprazolam

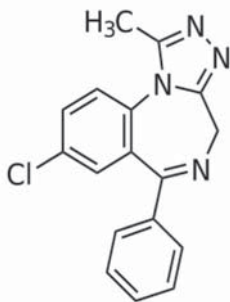
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Lekovi su raznovrsna grupa hemikalija koja se koristi u velikim količinama širom sveta i kao takvi kontinualno se unose u okolinu izazivajući njeno zagađenje. Prisutni su u okruženju u opsegu  $\text{ng/dm}^3$ – $\mu\text{g/dm}^3$ . U okolini su detektovane različite grupe lekova: analgetici, antibiotici, antiepileptici,  $\beta$ -blokatori, antidepresanti, anksiolitici, sedativi itd. [1]

Benzodiazepini pripadaju grupi supstanci koje deluju na centralni nervni sistem i imaju anksiolitičko, sedativno i hipnotičko dejstvo i oni su jedni od najčešće prepisivanih lekova na svetu. Alprazolam, diazepam, lorazepam i oksazepam su glavni predstavnici ove grupe lekova. [2] Calisto i dr. su ispitivali fotostabilnost benzodiazepina pod uticajem simuliranog sunčevog zračenja i pokazalo se da je brzina direktne fotolize lorazepama velika (vreme polu-života raspada je manje od jednog sunčanog dana), dok su oksazepam, diazepam i alprazolam pokazali mnogo veću stabilnost na fotorazgradnju sa vremenom polu-života od 4, 7, odnosno 228 sunčanih dana. [2]

Alprazolam (8-hlor-1-metil-6-fenil-4*H*-[1,2,4]-triazol[4,3- $\alpha$ ]-[1,4]-benzodiazepin,  $\text{C}_{17}\text{H}_{13}\text{ClN}_4$ ,  $M_r = 308,765$ , CAS No 28981-97-7, Slika 1) je dobijen iz 1,4-benzodiazepina nove generacije. Zbog svog antidepresivnog efekta, sinergičkog efekta kao anksiolitik u kombinaciji sa antidepresantima kod pacijenata sa uznapređovalim kancerom, kao i u lečenju patoloških oboljenja koja uključuju hronične bolesti anksioznosti, kao što je socijalna fobija, alprazolam je vrlo često prepisivan lek. [3-5]



**Slika 1.** Strukturna formula alprazolama [5]

Heterogena fotokataliza primenom  $\text{TiO}_2$  Degussa P25 kao katalizatora se pokazala kao efikasna metoda za uklanjanje brojnih organskih polutanata iz vode. Cilj ovog rada je ispitivanje uticaja različitih faktora na efikasnost fotokatalitičke razgradnje alprazolama primenom UV zračenja u prisustvu  $\text{TiO}_2$  Degussa P25 kao katalizatora.

Kao izvor veštačkog zračenja primenjena je živina lamp (emisioni maksimumi u UV oblasti na 304, 314, 335 i 366 nm, sa najintenzivnijim emisionim maksimumom na 366 nm) uz upotrebu odgovarajućeg konkavnog ogledala. Za praćenje kinetike razgradnje, pored HPLC–DAD, korišćena je i potenciometrija za praćenje promene pH-vrednosti rastvora tokom razgradnje.

Pored ispitivanja uticaja masene koncentracije katalizatora, ispitan je i uticaj početne pH-vrednosti suspenzije i utvrđeno je da nema značajniji uticaj na efikasnost fotokatalitičke razgradnje alprazolama. S obzirom da fotokatalitička razgradnja može da uključi reakciju između supstrata i hidroksil-radikala adsorbovanih na površini, kao i direktnu reakciju sa šupljinama, primenom alkohola, koji su poznati kao dobri hvatači radikala, ispitano je na koji od ova dva načina se odvija razgradnja alprazolama. U tu svrhu primenjeni su metanol i etanol. Budući da u prisustvu alkohola dolazi do značajne inhibicije fotokatalitičke razgradnje zaključeno je da se proces razgradnje odvija uglavnom preko hidroksil-radikala, dok reakcija sa šupljinama ima sporednu ulogu. U cilju ispitivanja uticaja prisustva elektron-akceptora, koji sprečavaju rekombinaciju parova elektron-šupljina primenjeni su vodonik-peroksid i kalijum-bromat. Na osnovu dobijenih rezultata može se zaključiti da se u prisustvu oba elektron-akceptora povećava brzina fotokatalitičke razgradnje, pri čemu je uticaj kalijum-bromata izrazitiji.

### Zahvalnica

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## **Association of modified humic acids from peat with organic toxic substances**

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The protection of wood and cellulose-containing materials from the harmful effects is provided by the use of fungicides that are organic toxic substances leading to pollution of the environment (soil, various reservoirs) [1]. The detoxification of pollutants can be made of natural physiologically active substances. They are humic acids. The ability of humic acids to capture and retain the substances of different nature is provided by the functional groups and the aromatic fragments in their macromolecules [2].

The necessity of using humic acids as detoxifying agents in the remediation of contaminated environments requires the development of more effective humic substances modified their functional composition and physico-chemical properties. One solution to this problem is the mechanochemical activation of humic sources [3].

It was shown that mechanical activation of peat destroys the structure, greatly increases the yield of humic acids, reduces the value of the average molecular weight, changes the structural-group composition. The mechanical activation of peat in the presence of an alkaline agent increases the number of oxygen-containing functional groups and the acidic properties of the carboxyl groups of hydrocarbon fragments are reduced.

The constants of biocides' association (cyproconazole, tebuconazole) with the initial and modified humic acids were determined. The binding of humic acids with tebuconazole is higher than with cyproconazole. In this case, the structural modification of peat humic acids provides the more efficient interaction with biocides. The modification of natural peat acids without reagent increases the association constant by 2.5 times for cyproconazole, and modification of humic acids in the presence of alkali is by 3.6 times for tebuconazole. The interaction of biocides with humic substances and their toxicity is weakened and depends on the strength of the formed complex.

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## **Sorpciono ponašanje hidrofobnih organskih jedinjenja na organskoj materiji sedimenta**

### **Sorption behaviour of hydrophobic organic compounds onto sediment organic matter**

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Za ispitivanje sorpcije i desorpcije organskih jedinjenja na čvrstim fazama najčešće se koriste dve tehnike eksperimenata: statički i dinamički. Statički eksperimenti podrazumevaju sorpciju u ravnotežnim uslovima, dok dinamički eksperimenti podrazumevaju sorpciju u neravnotežnim uslovima. U ovom radu ispitano je ponašanje hidrofobnih organskih jedinjenja (1,2,3-trihlorbenzena, 1,2,4-trihlorbenzena, naftalena, fenantrena, pirena i fluorantena) u neravnotežnim i ravnotežnim uslovima na sedimentu Dunava u cilju poređenja sorpcionog ponašanja hidrofobnih organskih jedinjenja u različitim uslovima.

Sorpcione izoterme su postavljene na sedeći način: u zavisnosti od ispitivanog organskog jedinjenja u vijale je odmerena određena masa sedimenta, a zatim dodata dejonizovana voda koja je sadržala 0,01%  $\text{CaCl}_2$  i 100 mg/l  $\text{NaN}_3$  (osnovni rastvor). Potom je u svaki vijal dodata određena zapremina osnovnog metanolnog rastvora organskog jedinjenja koncentracije ~1000  $\mu\text{g/ml}$ . Početne koncentracije u zavisnosti od jedinjenja bile su u opsegu od 50-1000  $\mu\text{g/l}$ , a koncentracija dodatog metanola u konačnom rastvoru bila je <0,1% (v/v). Vijali su zatim podvrgnuti kontinualnom mešanju tokom 7 dana. Količina sedimenta u svakom eksperimentu je podešena tako da dobijeni odnos sediment/rastvor rezultuje sorpcijom organskog jedinjenja u opsegu od 20-80%. Nakon završenog uravnotežavanja, sadržaj vijala je centrifugiran nakon čega su uzimani uzorci bistrog supernatanta određene zapremine za analizu organskih jedinjenja.

Dinamički eksperimenti izvedeni su upotrebom kolona od nerđajućeg čelika na sledeći način: određena masa predhodno osušenog i usitnjenog sedimenta Dunava punjena je u kolonu s gornje strane, dok je osnovni rastvor (navedi sastav) ulazio u kolonu odozdo pomoću peristaltičke pumpe. Hidrodinamičke osobine pakovane kolone su određene propuštanjem tiouree kao nesorbujuće supstance. Nakon toga su propuštani pojedinačni rastvori odabranih organskih jedinjenja koncentracije ~60  $\mu\text{g/l}$  pri protoku od oko 1,2 ml/min. Eluati su sakupljeni u određenim vremenskim intervalima tokom 96 h, a potom analizirani na sadržaj organskih jedinjenja.

Analiza organskih jedinjenja podrazumevala je primenu tačno-tečne ekstrakcije heksanom, nakon čega su ekstrakti analizirani primenom gasne hromatografije sa

masenom spektrometrijom (GC/MS, Agilent 7890A/5975C) ili sa detektorom sa zahvatom elektrona (Agilent Technologies 6890 sa  $^{63}\text{Ni}$   $\mu\text{ECD}$ ).

Freundlich-ov model za sorpcione izoterme dao je zadovoljavajuće koeficijente korelacije ( $R^2=0,988-0,996$ ) za sve sorbate na ispitivanom sorbentu. Ispitivani sorbent dao je nelinearne izoterme za sva ispitivana jedinjenja, što znači da afinitet za sorpciju opada sa porastom koncentracije sorbata. S obzirom da direktno poređenje sorpcionih koeficijenata nije moguće zbog njihovih različitih jedinica, a koje su posledica nelinearnosti sorpcionih izoterma, koeficijenti raspodele normalizovani na sadržaj organskog ugljenika ( $\log K_{OC}$ ) izračunati su za tri odabrane ravnotežne koncentracije ( $C_e = 1\%, 5\%$  i  $50\%$  rastvorljivosti u vodi). U slučaju dinamičkih eksperimenata potrebno je napomenuti da za ispitivana jedinjenja nije bilo moguće postići potpunu krivu proboja čak ni posle 96h, koliko su eksperimenti trajali. Stoga je za izražavanje rezultata korišćen odnos koncentracije jedinjenja u eluatu nakon 96 h i početne koncentracije jedinjenja u influentu ( $C/C_0$ ). Tako, što su vrednosti  $C/C_0$  više kraće je vreme zadržavanja datog jedinjenja na koloni i obrnuto.

$K_{OC}$  vrednosti, dobijene u ravnotežnim uslovima rastu u sledećem nizu: naftalen < 1,2,4-trihlorbenzen < 1,2,3-trihlorbenzen < fenantren < piren < fluoranten. Primenom dinamičkih eksperimenata, vrednosti  $C/C_0$  rastu u sledećem nizu: fluoranten < pirena < fenantren < 1,2,4-trihlorbenzen < 1,2,3-trihlorbenzen < naftalen. Poređenjem  $C/C_0$  vrednosti dobijene iz kolonskih eksperimenata sa  $\log K_{OC}$  vrednostima dobijenim u ravnotežnim uslovima može se uočiti sledeće: vreme zadržavanja na koloni za ispitivana jedinjenja u skladu je sa afinitetom za sorpciju dobijenim iz statičkih eksperimenata. Tako su najniže vrednosti  $C/C_0$  dobijene za fenantren, piren i fluoranten, 15, 5 i 8%, redom, što je u skladu sa većim afinitetom za sorpciju dobijenim iz statičkih eksperimenata  $\log K_{OC}=4,81, 5,28$  i  $5,43$ , redom. Dodatno, za trihlorbenzene i naftalen više vrednosti  $C/C_0$  (38-58%) posledica su manjeg zadržavanja na koloni i manjeg afiniteta sorpcije u statičkim eksperimentima ( $\log K_{OC}=3,00-3,50$ ).

Parametri sorpcije, afinitet za sorpciju i vreme zadržavanja na koloni, pokazuju pozitivnu korelaciju sa  $\log K_{OW}$ . Dobijeni koeficijenti korelacije između afiniteta sorpcije i hidrofobnosti molekula, vremena zadržavanja i hidrofobnosti molekula na koloni bili su  $R^2=0,914$  i  $R^2=0,926$ , redom. Pozitivna korelacija pokazuje da sa povećanjem hidrofobnosti molekula raste i afinitet sorpcije odnosno vreme zadržavanja na koloni, što ukazuje da hidrofobnost molekula kontroliše sorpciju datih jedinjenja na ispitivanom sorbentu.

## Aknowledgment

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## **Perzistentna organska jedinjenja u sedimentu reke Tise**

### **Persistent organic pollutants in river Tisza sediments, Serbia**

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U radu su prikazani rezultati ispitivanja prisustva perzistentnih organskih jedinjenja (POPs) u 10 uzoraka sedimenta reke Tise. Ispitano je prisustvo 17 jedinjenja iz grupe organo-hlornih pesticida i njihovih metabolita, kao i prisustvo 16 jedinjenja iz grupe policikličnih aromatičnih ugljovodonika (PAH).

Uzorkovanje sedimenta je izvedeno duž toka reke Tise u Srbiji, tokom septembra 2010. godine. Sediment je uzet plastičnim uzorkivačem, pakovan u polietilenske vreće i transportovan u laboratoriju. Nakon sušenja na vazduhu uzorci su samleveni i prosejani kroz sito.

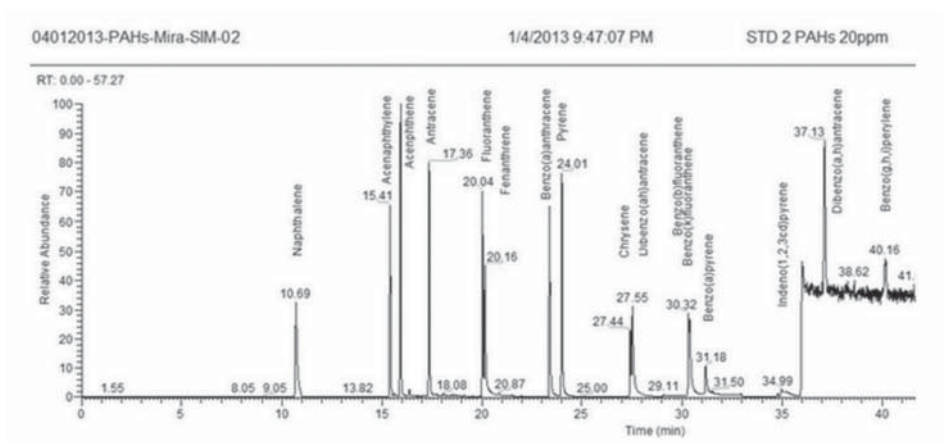
Policiklični aromatični ugljovodonici i pesticidi ekstrahovani su primenom Sokslet ekstrakcije (US EPA 3540C) uz prečišćavanje ekstrakta na koloni silika gela (US EPA 3630C). Analiza dobijenih ekstrakata urađena je gasnom hromatografijom sa masenom detekcijom GC/MS, na uređaju Thermo Focus DSQII sa TriPlus autosemplerom (US EPA 8100 and US EPA 8081A).

Rezultati istraživanja pokazuju da koncentracije lindana i njegovih metabolita, heptahlor-epoksida, aldrina, endrina,  $\alpha$ -endosulfana, DDT-a, DDE-a i DDD-a u sedimentu reke Tise prelaze maksimalno dozvoljene vrednosti prema Uredbi o graničnim vrednostima zagađujućih materija u površinskim i podzemnim vodama i sedimentu i rokovima za njihovo dostizanje. Nađene koncentracije ostataka pesticida i metabolita se kreću u opsegu od 5  $\mu\text{g/kg}$  a.s.s.\* do 278  $\mu\text{g/kg}$  a.s.s. Pesticidi su detektovani u 92 % slučajeva. Nije nađen ni jedan uzorak sedimenta sa koncentracijom pesticida većom od remedijacione vrednosti od 4000  $\mu\text{g/kg}$ .

Koncentracije pojedinačnih jedinjenja iz grupe policikličnih aromatičnih ugljovodonika se kreću od 0,01  $\text{mg/kg}$  a.s.s. do 6,11  $\text{mg/kg}$  a.s.s. i ispod su maksimalno dozvoljenih vrednosti, prema istoj Uredbi za većinu ispitanih analita. Izuzetak je jedino antracen koji je u 5 uzoraka sedimenata, premašio MDK vrednost. Nađeni ukupan sadržaj 16 jedinjenja iz grupe PAH-ova se u ispitanim sedimentima kreće od 1,14  $\text{mg/kg}$  a.s.s. do 1,99  $\text{mg/kg}$  a.s.s. (Slika 1).

Dobijene visoke koncentracije ostataka pesticida i metabolita u sedimentima su očekivane zbog blizine poljoprivrednih površina sa dugim istorijatom primene sredstava za zaštitu bilja.





\*a.s. apsolutno suvi sediment.

Slika 1. Raspodela STD 2 PAHs 20 ppm.

## **Metali u sedimentu i jetri četiri različite vrste riba iz reke Tise**

### **Metals in the sediment and liver of four fish species from Tisza river, Serbia**

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Metali predstavljaju prirodne komponente akvatičnih ekosistema u kojima je njihov sadržaj uslovljen, sa jedne strane, hemijskim sastavom sedimenta, a sa druge, antropogenim unosom. Različiti način ishrane, tip staništa, pokretljivost riba i druge karakteristike koje su u vezi sa ponašanjem uslovljavaju razlike u bioakumulaciji metala kod različitih vrsta.

Sprovedeno istraživanje obuhvatilo je analizu Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr i Zn u sedimentu i jetri četiri ekosistemski različite vrste riba: štuki (*Esox lucius* L.) kao piscivornoj vrsti, kečigi (*Acipenser ruthenus* L.) i deverici (*Brama brama* L.) kao bentivornim vrstama i šaranu (*Cyprinus carpio* L.) kao omnivornoj vrsti.

Uzorkovanje riba i sedimenta vršeno je celom dužinom toka reke Tise kroz Srbiju. Savremeni sedimenti uzeti su sa 20 lokaliteta tokom tri vremenska perioda 15.9., 24.9. i 12.11.2010. godine. Ukupno je uzeto 30 uzoraka, od čega su 27 uzoraka sedimenta uzeta direktno iz reke Tise, a 3 iz pritoka (jedan iz rečice Jegričke, a dva iz korita reke Begej). Četiri uzorka su uzeta iz bušotina u blizini korita reke Tise. Ukupno 160 jedinki riba sakupljano je tokom oktobra 2010. godine od lokalnih ribara na 4 lokaliteta: na ulazu same reke u Republiku Srbiju kod Kanjiže (153. km rečnog toka), pre i posle brane kod Novog Bečeja (58. odnosno 72. km rečnog toka) i na ušću reke Tise u Dunav (3. km rečnog toka). Multielementarna analiza uzoraka sedimenata rađena je u komercijalnoj laboratoriji Acme Analytical Laboratories (Vancouver) Ltd, dok je određivanje sadržaja metala u jetri riba vršeno indukovanim kuplovanom plazmom sa optičkim emisijom spektrofotometrom (ICP/OES, Thermo Scientific iCAP 6500 Duo instrumentu, Thermo Fisher Scientific, Cambridge, UK) na Hemijskom fakultetu Univerziteta u Beogradu.

U uzorcima sedimenta na svim lokalitetima utvrđene su povećane koncentracije za Cd, Cr, Cu, Ni i Zn. Međutim, jedino su koncentracije Ni iznad maksimalno

dozvoljenih vrednosti prema Uredbi o graničnim vrednostima zagađujućih materija u površinskim i podzemnim vodama i sedimentu i rokovima za njihovo dostizanje ("Sl. glasnik RS", br. 50/2012).

U ukupnim prosečnim vrednostim Al, As, Cr, Hg, Ni i Pb akumuliraju se najviše u kečigi, Cd, Co, Cu, Fe i Zn u šaranu, Mn, Se i Sr u deverici. Koncentracije Pb i Cd u jetri šarana i kečige su iznad maksimalnih dozvoljenih vrednosti prema Pravilniku o količinama pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama ("Sl. list SRJ", br. 5/92, 11/92 – ispr. i 32/2002 i "Sl. glasnik RS", br. 25/2010 – dr. pravilnik i 28/2011 – dr. pravilnik). Sprovedenim istraživanjem utvrđeno je da omnivorne i bentivorne vrste riba akumuliraju više metala u odnosu na piscivorne vrste.

## Determination of platinum concentration in deciduous tree leaves

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The increase in the number of cars and vehicles fitted with catalytic converters has contributed to the traffic-related PGE pollution in the environment. The automobile catalyst converters, used in car industry, reduce the emission of pollutants, such as carbon monoxide, nitrogen oxides and unburned hydrocarbons. During the utilisation of converters, as a result of abrasion of the catalyst surface, platinum is released into environment and deposited along roadways, on adjacent vegetation and soil and in water resources [1]. Catalyst converter emitting Pt, may undergo rapid transformations in the environment, and subsequently behave similarly to soluble Pt salts [2], which rise a concern for its bioavailability to plants and possibility of this element entering the food chain. Platinum available to plants is indication of pollutant potential hazard to the ecosystem, especially to man and livestock, who consume plants growing on contaminated soils [3].

The main objective of this work was to develop a method for determination of platinum in deciduous tree leaf samples by using inductively coupled plasma mass spectrometry (ICP-MS). The determination of low Pt concentrations in complex environmental sample matrices (i.e. plant material), with interfering effects from matrix elements requires the application of appropriate preparation steps. Nevertheless, a mathematical correction is usually sufficient for the detection of Pt in plant samples [4]. The leaf samples of horse chestnut (*Aesculus hippocastanum*) were collected at the end of vegetation cycle, in September, during the years 2009 and 2012, from the Karađorđev park, situated in a heavy traffic area. Half of the leaf samples were briefly rinsed with bidistilled water before further preparation, while the other half was left unwashed. Approximately 0.7 g of leaves (dry weight) was digested with 5 ml of 65% HNO<sub>3</sub> and 3 ml of 30% H<sub>2</sub>O<sub>2</sub> in a microwave oven. After digestion, the solution was diluted with bidistilled water to a total volume of 25 ml. The concentration of platinum was determined by ICP MS. To eliminate the effect of the matrix, the "matrix-matched" standards were included in the analysis. The "matrix-matched" standards were prepared with the lichen reference material (IAEA-336) and spiked with Pt.

The aim of this preliminary study was to obtain an information about the anthropogenic platinum content in deciduous tree leaves from the urban area of Belgrade. The surveys of traffic-related heavy metals, especially lead, based on

tree leaf samples in Belgrade have been carried out during previous years [5, 6]. It has been noted that, along with the reduced use of leaded gasoline in Belgrade, the concentration of lead in the leaves had a decreasing trend. That observation is in accordance with an increased number of vehicles using non-leaded gasoline as well as of those equipped with catalytic converters. Therefore, an increase of platinum concentration, originating from catalytic converters, could be expected in environmental samples during the next years.

The method based on microwave digestion and ICP-MS determination can be used for determination of low concentrations ( $\text{ng g}^{-1}$ ) of Pt in leaf samples. The use of "matrix-matched" standards was found to be necessary in the ICP-MS determination of Pt. The concentration of platinum in the samples was in the range  $0.5\text{--}1.67 \text{ ng g}^{-1}$ . The obtained results showed similar or lower concentration of Pt than previously reported for plant materials [7, 8]. Higher concentrations were obtained in unwashed samples, indicating that brief rinsing with bidistilled water has the effect on the concentration of Pt in the samples. According to available literature, this is the first record of platinum concentration in deciduous tree leaf samples in Serbia. Further research is needed and more extensive study of platinum concentration in leaves during a multi-year period of time in order to obtain more informations about anthropogenic, traffic-related Pt emission.

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## Effect of Different Cosolvents on the Sunflower Oil Transesterification Catalyzed by Calcium Oxide

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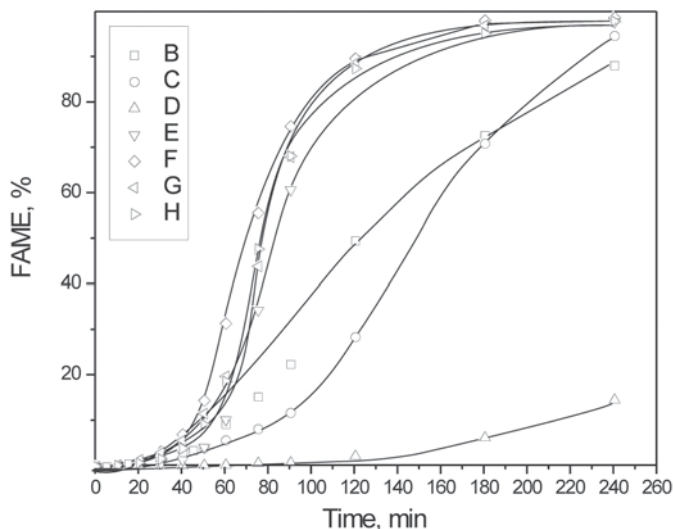
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Transesterification of triglycerides present in edible and non-edible oils produce fatty acid alkyl esters (biodiesel) and glycerol. Due to stringent environmental constraints for the biodiesel production, the conventional homogeneous base catalysed process using several alkali and alkaline metal alkoxides is being replaced by the heterogeneous solid catalysts. In the presence homogeneous base catalyst water and free fatty acids catalysts favours the formation of stable emulsion making separation of methyl ester more difficult. Glycerol is also obtained as an aqueous solution of relatively low purity. The transesterification reaction is very sensitive to the presence of water and free fatty acids [1]. Problems related to water and free fatty acid could be avoided by using the heterogeneous catalyst. In the heterogeneous system, however, the presence of more than two phase causes mixing problems. To overcome mixing problems an appropriate cosolvent can be used.

In this study the kinetics of the transesterification reaction in the presence of different cosolvents (diethylether, dioxane, methyl ethyl ketone, triethanolamine, n-hexane and ethyl acetate) were investigated. The transesterification reaction was carried out in a 0.5 litre batch reactor. The reactor is equipped with a reflux condenser, a cooling water circulation system, temperature sensor, electrically heated jacket and magnetic agitator for proper mixing. The transesterification reaction was carried out at a temperature of 60°C, atmospheric pressure and a maximum speed of mixing magnetic stirrer. Methanolysis of sunflower oil was carried out in 6:1 molar ratio. The amount of CaO catalyst was calculated on the weight of the oil. Then, 20% (calculated on the weight of the oil) cosolvent (n-hexane, ethyl acetate, n-butyl acetate, 1-4 dioxane, methylethyl ketone, propylene carbonate, triethanolamine) was added in the batch reactor. The yield of biodiesel was analysed by HPLC method. In the cosolvent presence the reaction rate is as fast as homogeneous.

The yield of methyl esters, after 4 hours of transesterification reaction is as follows: diethyl ether (88.3%), dioxane (94.8%), methyl ethyl ketone (14.7%), triethanolamine (97.9%), n-hexane (98.8%) and ethyl acetate (97.1%). As can be seen from Fig. 1. if triethanolamine and ethyl acetate were used as cosolvents the transesterification reaction is almost identical as the transesterification occurs without cosolvent. The transesterification in the presence methyl ethyl ketone, dioxane and diethylether as cosolvents is less than when the same reaction occurs without cosolvent. n-hexane slightly improves the transesterification reaction in the presence of activated CaO.



**Figure 1.** The variations of the FAME yields with the progress of sunflower oils methanolysis catalyzed by CaO in the presence of different cosolvents (20% based on the oil weight): no cosolvent–H; methyl ethyl ketone–D; tetrahydrofuran–D; ethyl acetate–G; triethanolamine–E; diethyl ether–B; dioxane–C; and n-hexane – F (reaction conditions: oil, 91.92 g; catalyst, 5%; 60°C; and methanol-to-oil molar ratio, 1:6).

This is contrary to the expectations because all these cosolvents are well known in the literature [2] as good cosolvents for the homogeneous methanolysis if KOH was used as catalyst. It remains unclear why tested cosolvents showed inhibitory effect on the reaction rate with heterogeneous catalysts. Probably their effect is based on blocking the active sites in the crystal structure of CaO, and therefore prevents the formation of calcium methoxide which catalyze methanolysis reaction.

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## **Primena biohemijskog inženjerstva kao način dobijanja toksina koji se mogu upotrebiti kao oružje za masovno uništenje**

### **The application of biochemical engineering as a way to get the toxins that can be used as weapons of mass destruction**

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Konvencija o bioloskom oružju iz 1972.god. uključuje toksine kao biološko oružje, mada biološki agensi obuhvataju žive organizme koji mogu rasti i razmnožavati se, što toksini ne mogu. Toksini su toksični produkti bioloških organizama, često vrlo složene hemijske strukture zbog čega su svrstani u hemijsko oružje. Mnoge zemlje su potpisnice Konvencije o zabrani hemijskog oružja koja je stupila na snagu aprila 1997.god., ali se veruje se da su nastavljena dalja istraživanja koja imaju za cilj sintezu novih toksina kao bojnih otrova.

Brzi razvoj genetskog inženjerstva i biotehnologije izbrisao je strogu granicu između hemijskog i biološkog oružja. Genetičkim inženjerstvom moguće je u bakteriju ili virus ugraditi odgovarajući DNA kako bi se dobili, u dovoljnoj količini, toksični proteini koji su se teško dobijali postupcima hemijske sinteze. Mnogi toksini, dobijeni na ovaj način, imaju nekoliko puta jače dejstvo od nervnih bojnih otrova, tako da se potpuni efekat postiže sa malim količinama tako izmenjenih bakterija. Dejstvo toksina na žive organizme zavisi od vrste toksina, primljene doze i puta ulaska u organizam. (Tabela1.)

**Tabela 1.** Neki najotrovniji toksini i njihovo dejstvo

<b>Toksini</b>	<b>Način unosa u živi organizam</b>	<b>LD<sub>50</sub> (LC<sub>50</sub>)</b>
Botulin [1]	oralno, injekcijom, inhalacijom	1 ng/kg (čovek)
Palitoksin [2]	intravenozno	1 µg/kg (čovek)
	intratracheal	0.054 µg/kg (miš)
	intraperitonealno	>2 µg/kg (miš)
	oralno	<1 µg/kg (miš) 767 µg/kg (miš)
Ricin [3]	intraperitonealno	22 µg/kg(čovek)
	oralno	20-30 mg/kg(čovek)
Saksitoksin [4,5]	oralno, injekcijom, inhalacijom	8,0 µg/kg (miš)
		0,3-1 mg /kg (čovek)
Tetrodotoksini[5]	oralno, , inhalacijom	334 µg/kg (miš)
	injekcijom	25 mg /kg (čovek) 8 µg/kg (čovek)



Jedan od najotrovnijih toksina je botulin toksin, jer u koncentraciji od 1ng/kg može biti smrtonosan. Neki toksini deluju sporo dok drugi veoma brzo. Sak-sitoksin i ricin su navedeni u Popisu 1. (hemikalije sa najvećim rizikom) Aneksa o hemikalijama Konvencije o zabrani hemijskog oružja.

Istraživanja i proračuni pri upotrebi oružja za masovno uništenju američke vojske pokazali su da je za neutralisanje žive sile na km<sup>2</sup> bojišta za klasično konvencionalno oružje potrebno utrošiti 2000\$, za upotrebu nuklearnog oružja 800\$, za hemijsko oružje 600\$, a za upotrebu biološkog oružja samo 1\$.

Toksini kao oružje za masovno uništenje, zbog ekonomičnosti proizvodnje, visoke specifičnosti i selektivnosti delovanja bez oštećenja materijalnih dobara (rat bez razaranja), bez teških ekoloških posledica, koje bi bile kod nuklearnog rata, za nekoliko decenija mogu postati osnovno oružje nacija koje žele dominaciju svetom. Mada su mnoge zemlje potpisnice Konvencija o zabrani hemijskog oružja, ono bi se moglo uništiti u narednih 15god., dok za biološko i nuklearno se ni ne nazire početak uništavanja. Zbog svega toga trebalo bi pojačati kontrolu hemijskih i bioloških agenasa kao i toksina i imati odgovarajuće procedure za njihovu verifikaciju. Neophodno je angažovanje državnih struktura u cilju edukacije stanovništva o opasnosti primene oružja za masovno uništenje (OMU).

### Zahvalnica

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## **Prisustvo i ponašanje pojedinih farmaceutika tokom odvijanja procesa rečne obalske filtracije**

### **Occurrence and behavior of selected pharmaceuticals during river bank filtration**

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Kontaminacija vodnih resursa velikim brojem mikropolutanata je jedan od ključnih problema zaštite životne sredine sa kojima se čovečanstvo suočava. Pošto su mikropolutanti prisutni u vodenoj sredini u veoma niskim koncentracijama, razumevanje uticaja mikropolutanata na slatkovodne resurse i životnu sredinu je primarni korak u proceni rizika izloženosti ispitivanim supstancama [1].

Od posebnog značaja su emergentne supstance (EmS), koje predstavljaju zagađujuće materije koje su novootkrivene u životnoj sredini, a pre svega su aktuelne zbog kontinualnog porasta njihove upotrebe i činjenice da u ranijim studijama nisu smatrane kao značajne zagađujuće materije u životnoj sredini. Relativno novo viđenje i svest o prisutnosti emergentnih supstanci, a posebno farmaceutskih proizvoda (FP) u površinskim i podzemnim vodama i mogući negativan uticaj na životnu sredinu, ogleda se u eksponencijalnom povećanju broja studija koje se bave emergentnim supstancama počevši još od 1990-ih [2].

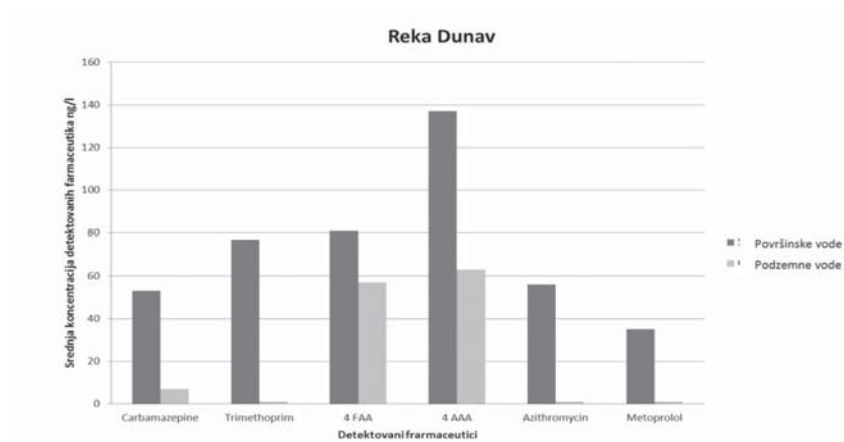
Pošto se u prethodnim studijama pokazalo da se farmaceutici ne uklanjaju potpuno u konvencionalnim postrojenjima za tretman otpadnih voda i činjenici da se u Republici Srbiji tretira samo 15 % otpadne vode [3], postoji veliki broj farmaceutski aktivnih jedinjenja koja dospevaju u površinske vodotokove. Navedena činjenica je veoma značajna pošto u Republici Srbiji veći gradovi i gušće naseljena područja uglavnom koriste vodu za piće koja se zahvata iz aluvijalnih izvorišta podzemne vode. Za analizu prisutnosti farmaceutika u površinskim i podzemnim vodama su odabrani: karbamazepin, trimetoprim, aziromicin, metoprolol, kao i metaboliti metamizola 4 – FAA i 4 – AAA.

Cilj rada je ispitivanje prisustva i ponašanje izabranih farmaceutika i njihovih metabolita tokom prolaska vode kroz korito reke i sediment akvifera.

U okviru sprovedenog istraživanja, kolektovano je 9 uzoraka površinske vode Dunava u blizini Kovina i 18 uzoraka podzemne vode iz drenažnih bunara na potezu drenažne linije Kovin – Dubovac.

Analiza uzoraka na prisustvo ispitivanih farmaceutika realizovana je u laboratoriji Tehnološko – metalurškog fakulteta u Beogradu korišćenjem tehnike ekstrakcije iz čvrste faze (SPE) i tehnike masene hromatografije tandem masene

spektrofotometrije (LC-MC<sup>2</sup>) [4]. Na osnovu dobijenih rezultata analize prikazanih na slici 1, može se uočiti značajno smanjenje nivoa koncentracije prilikom prolaska farmaceutski aktivnih jedinjenja kroz rečno korito i vodonosni sloj akvifera.



**Slika 1.** Srednje koncentracije detektovanih farmaceutika u površinskim i podzemnim vodama

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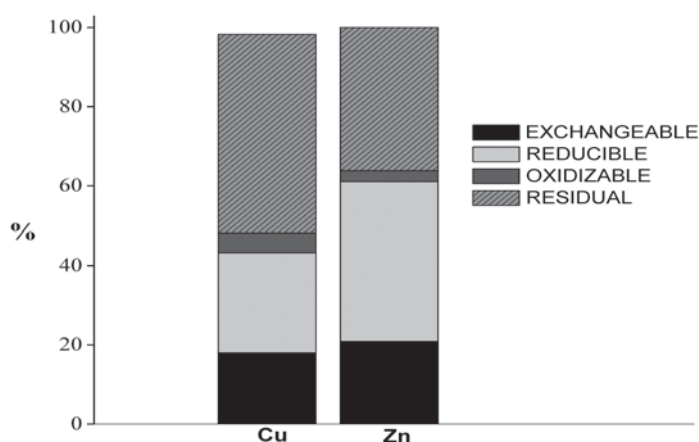
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## Use of fly ash for remediation of Krivaja river sediment polluted with cooper and zinc

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The aim of this study was to determine the possibility of using fly ash (F) for the solidification/stabilization (S/S) of metals polluted sediment (S) from the Krivaja river basin (Serbia). Krivaja sediment contains  $170 \pm 3.91$  mg/kg of Cu and  $832 \pm 29.1$  mg/kg of Zn, and thus belongs to the last quality class in the Serbian sediment classification and needs remediation [1]. Fly ash was used as a stabilising agent because it occurs as a secondary industrial product. Microwave assisted BCR sequential extraction procedure was employed to assess potential of Cu and Zn mobility and risk to the aquatic environment [2]. S/S matrices were prepared according to Dalmacija et al., 2011, [3]. In order to determine the leaching behaviour of the S/S mixtures, two batch leaching tests TCLP and DIN 3841-4 S<sup>4</sup> were performed, with each one having a different sort of leaching fluid. Results are interpreted using national regulation for examining toxicity characteristic of waste intended for disposal, and also for testing parameters of waste and leached liquids for inert, non-hazardous and hazardous waste landfills [4]. The results of BCR sequential extraction are presented in Fig. 1. According to the risk assessment code (RAC), 21 % of zinc and 18% of cooper in carbonate phase comes under the moderately high risk category [5].



**Figure 1.** Distribution of Cu and Zn in sequential extraction fractions of untreated Krivaja sediment sample

The results of TCLP and DIN 3841-4 S<sup>4</sup> tests on treated samples are presented in Table 1. All leached metal concentrations, according to TCLP procedure, were far below the regulatory limits, making all specimens eligible for disposal. Addition of fly ash has an obvious positive effect on metal immobilization.

**Table 1.** Leached concentrations of Cu and Zn in S/S specimens according to DIN 3841-4 S<sup>4</sup> test

S/S matrices	TCLP		S/S matrices	DIN 3841-4 S <sup>4</sup>	
	Zn	Cu		Zn	Cu
	mg/l			mg/kg	
S <sub>99</sub> F <sub>1</sub>	11.1	0.10	S <sub>99</sub> F <sub>1</sub>	5.58	0.45
S <sub>95</sub> F <sub>5</sub>	10.8	0.05	S <sub>95</sub> F <sub>5</sub>	5.44	0.37
S <sub>90</sub> F <sub>10</sub>	9.45	0.05	S <sub>90</sub> F <sub>10</sub>	4.22	0.22
S <sub>80</sub> F <sub>20</sub>	4.32	0.04	S <sub>80</sub> F <sub>20</sub>	2.18	0.20
S <sub>70</sub> F <sub>30</sub>	3.33	0.03	S <sub>70</sub> F <sub>30</sub>	2.10	0.18
TCLP regulatory levels	250	25	A <sup>1</sup>	4	2
			B <sup>2</sup>	50-200	50-100

<sup>1</sup>A-Maximum allowed concentration of accepting waste as inert <sup>2</sup>B-Maximum allowed concentration of accepting waste as non-hazardous

Concerning the DIN 3841-4 S<sup>4</sup> regulations all S/S matrices can be classified as inert waste from the aspect of leached concentrations of cooper. Zinc concentrations in the leachant exceeded this value only in S/S samples with less than 10% of fly ash in content, but again it represents non-hazardous waste. Overall, the tests results indicated that S/S treatment was effective in immobilizing Zn and Cu. In addition, this kind of waste treatment is advantageous from an economic point of view, because in this way metal polluted sediment is immobilized by using fly ash as a binder, which results in managing the disposal of two waste types. "Controlled utilization" of S/S specimens can be considered. These results represent a promising technology in the field of green remediation.

### Acknowledgement

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## Adsorpcija As(III) i As(V) u koloni pomoću bakrom modifikovanog bigra: Bohart-Adams model

### Column adsorption of As(III) and As(V) using copper coated tufa: Bohart- Adams model

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The objective of the study was to examine the applicability of Bohart-Adams model for column adsorption of As(III) and As(V) from water using copper coated tufa. Copper oxide addition to different adsorbents showed its efficiency towards arsenic removal [1,2]. Generally, tufa shows advantages over various materials because of its low cost and good arsenic adsorption capacity [3,4]. Natural tufa samples used in this work were obtained from deposits, collected from region Temska, Pirot, Serbia. The samples were crushed in an agate mortar and washed with distilled water in order to remove the surface dust. After drying crushed material was sieved and fraction with grain size from 0.022 to 0.50 mm was used in further study.

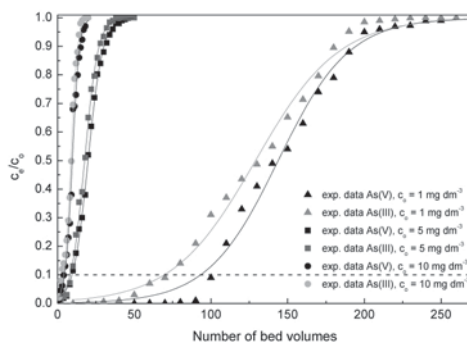
Selected tufa fraction was rinsed with deionised water and dried at 90°C in vacuum oven. Column, diameter 2.0 cm and length 40 cm, with sintered filter and valve was loaded with tufa. Column content is flushed with 100 cm<sup>3</sup> of acetone. After that, 100 cm<sup>3</sup> of 1% solution of CuCl<sub>2</sub> is continuously pumped through the system for 24 h. The copper reduction was performed by addition of 60 cm<sup>3</sup> (1:1) 0.1 M NaBH<sub>4</sub> and 1 M NaOH mixture continuously for 24 hours at 2 cm<sup>3</sup> min<sup>-1</sup>. Prepared adsorbent is then dried at 70°C for 24 hours. Vacuum-filtration of the prepared adsorbents was performed using 0.05 µm pore size polytetrafluoroethylene (PTFE) filter membrane.

The Bohart-Adams model [5] is one of the most widely used in a large variety of cases to describe sorption in dynamic conditions. A simplified version is given by Equation 1:

$$\frac{c}{c_0} = \frac{1}{1 + \exp\left[\frac{k_{BA}}{Q}(q_0 m - c_0 V)\right]} \quad (1)$$

where  $c$  (mol dm<sup>-3</sup>) is the outlet concentration of sorbable species concentration at eluted volume  $V$ ,  $c_0$  (mol dm<sup>-3</sup>) is the inlet concentration,  $m$  (g) is the amount of sorbate in the column,  $k_{BA}$  (dm<sup>3</sup> mol<sup>-1</sup> min<sup>-1</sup>) is the Bohart-Adams rate constant,  $Q$  (cm<sup>3</sup> min<sup>-1</sup>) is the volumetric flow rate and  $q_0$  (mmol g<sup>-1</sup>) is the maximum solid phase concentration of arsenic when it is in equilibrium.

Breakthrough curves for arsenic adsorption on copper coated tufa are shown in Figure 1.



**Figure 1.** Breakthrough curves for initial arsenate concentration of 1, 5 and 10  $\text{mg dm}^{-3}$  at pH 4,  $m_{\text{sorbent}} = 100 \text{ g}$ ,  $Q = 3 \text{ cm}^3 \text{ min}^{-1}$ ,  $\text{EBV} = 250 \text{ cm}^3$ ,  $n = 3$ .

Results of linear and nonlinear fit of experimental data using Bohart-Adams sorption model were presented in Table 1.

**Table 1.** Results of linear and non-linear fitting of experimental data obtained by Bohart-Adams sorption model

	$c_0$ $\text{mg dm}^{-3}$	$k_{\text{BA}}$ $\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$	$q_0$ $\text{mmol g}^{-1}$	$R^2$	$k_{\text{BA}}$ $\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$	$q_0$ $\text{mmol g}^{-1}$	$R^2$
		Linear fit			Nonlinear fit		
As(V)	1	0.207	1.577	0.952	0.130	1.438	0.994
As(III)		0.222	1.207	0.895	0.111	1.290	0.995
As(V)	5	0.0562	2.647	0.686	0.126	0.990	0.999
As(III)		0.0493	2.730	0.685	0.139	0.880	0.998
As(V)	10	0.0608	2.698	0.834	0.133	0.954	0.990
As(III)		0.0520	2.855	0.812	0.144	0.865	0.994

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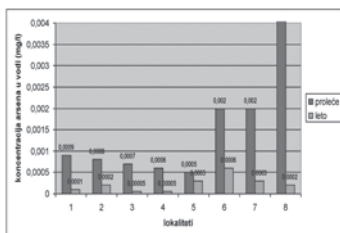
## Arsen u industrijskim otpadnim vodama

### Arsenic in industrial wastewater

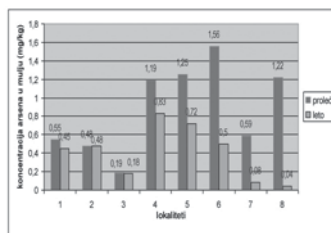
Snežana Aksentijević<sup>1</sup>, Jelena Kiurski<sup>2</sup>

<sup>1</sup>Trg Svetog Save 34, 31000 Užice (sneza.aksentijevic@gmail.com)

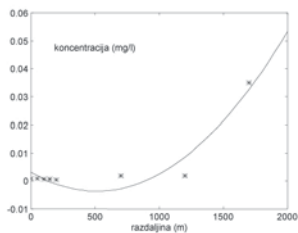
Prisustvo arsena u životnoj sredini, čak i u niskim koncentracijama, ugrožava zdravlje ljudi i životinja. Praćenje ukupnog sadržaja arsena, dobija na značaju, prevažodno zbog njegove toksičnosti. Koncentracije arsena ispitivana je u vodi i sedimentu u Dragića potoku i niz reku Đetinju u koji se izlivaju otpadne vode dva velika metaloprerađivačka sistema koji prerađuju aluminijum, bakar i njihove legure i programskim paketom MATLAB prikazana je njegova distribucija sa rastojanjem. Kontaminacija životne sredine arsenom može biti antropogenog i prirodnog, geološkog, porekla [1]. U podzemnim i u otpadnim vodama, može se naći u obliku organskog i neorganskog oblika [2]. Toksičnost i mobilnost arsena varira u zavisnosti od valentnog stanja i hemijskog oblika [3]. Rukovanje, skladištenje i priprema uzoraka vode izvršena je u skladu sa standardnom metodom EPA 200.7 u plastične posude od 1 litra. Rukovanje, skladištenje i priprema uzoraka sedimenta izvršena je prema standardnoj EPA metodi 3050 B. Uzorci vode i sedimenta analizirani su na ukupan sadržaj arsena tehnikom generisanja hidrida na uređaju ICAP 6500 Duo ICP. Koncentracija arsena u uzorcima sedimenata date su u odnosu na suhu masu sedimenata.



**Slika 1.** Promena koncentracije arsena u vodi-proleće/leto 2009.g

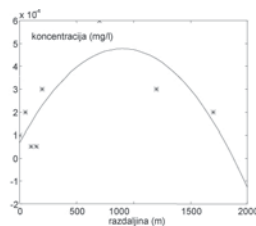


**Slika 2.** Promena koncentracije arsena u mulju - proleće/leto 2009.g



**Slika 3.** Distribucija arsena u vodi sa rastojanjem-proleće

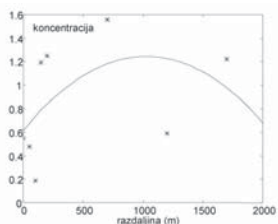
$$y = 2.5616 \times 10^{-8} x^2 - 2.6186 \times 10^{-5} x + 3.0623 \times 10^{-3}$$



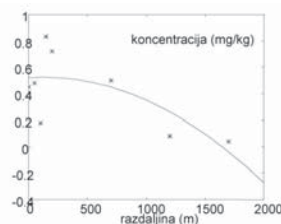
**Slika 4.** Distribucija arsena u vodi sa rastojanjem-leto

$$y = -5.0300 \cdot 10^{-10} x^2 + 9.0842 \cdot 10^{-7} x + 6.7099 \cdot 10^{-5}$$





**Slika 5.** Distribucija arsena u sedimentu sa rastojanjem-proleće  
 $y = -5.9392 \times 10^{-7} x^2 + 1.2206 \times 10^{-3} + 6.1671 \times 10^{-1}$



**Slika 6.** Distribucija arsena u sedimentu sa rastojanjem-leto  
 $y = -2.2579 \cdot 10^{-7} x^2 + 5.6110 \cdot 10^{-5} x + 0.51939$

Izmerene koncentracije arsena u vodi i sedimentu Dragića potoka i niz reku Đetinju ne prelaze vrednosti MDK od 0,05 mg/l [4] i [5] od 25 mg/kg, s obzirom na to da Srbija nema zakonsku regulativu za kvalitet sedimenta. Distribucija sa rastojanju od mesta direktnog izlivanja otpadnih voda iz metaloprerađivačkog sistema, pokazuje da se koncentracije metala smanjuje, osim arsena u vodi uzorkovanog u proleće 2009. godine. Vodostaj u proleće je bio znatno viši nego u letnjem periodu sa vrlo turbulentnim tokom vode i zahvaćeni su i drugi izvori zagađenja sa okolnih poljoprivrednih zemljišta (korišćenje pesticida, veštačkih đubriva). Do sada da nisu poznate koncentracije arsena u području reke Đetinje, a samim tim ni antropogeni doprinos eventualnom porastu koncentracije, i iz toga razloga izvedena su ova ispitivanja po prvi put na ovim lokalitetima. Da bi se unapredio kvalitet već zagađene životne sredine, odnosno da bi se zaštitila još nezagađena sredina, neophodno je mere zaštite zasnivati na metodologiji koja zaštitu od zagađena posmatra u vidu kompleksnog sistema, naročito vode, kao ograničenog i osetljivog prirodnog resursa. Jedan od elemenata tog sistema je praćenje koncentracije arsena i raspodele između tečne i čvrste faze, kao i porediti eksperimentalno dobijene koncentracije sa koncentracionim nivoima propisanim nacionalnim direktivama za vodu i sediment.

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## Merenja i povratne informacije

### Assessment and feedback

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Cilj rada je korišćenje novih tehnika i metoda u nastavi radi podizanja nivoa kvaliteta rada sa posebnim osvrtnom na principe, praksu merenja i povratne informacije. Dobra procena i merenja u svakoj fazi rada doprinose ostvarenju ciljeva, funkcionisanje kriterijuma i standarda što daje priliku za aktivno učenje na svim nivoima nastave počev od obdaništa do univerziteta.

Na taj način podstiče se redovno učenje, pružaju mogućnosti za validne informacije, razvija mehanizam motivisanosti, interakcije, dijaloga, samoocenjivanja, usavršavaju kriterijumi koji će doprineti dobijanju potrebnih znanja primenljiva u praksi, mogućnost za nove ideje, rešavanje najpre lakših zadataka, a zatim težih što stvara uslove za kreativan rad. Angažovanjem studenata i uopšte slušalaca je neophodno stalno povećavati, jer je to najbolji način za sticanje praktičnih znanja i razvoj veština.

Ključne reči: Principi merenja, teorija-praksa, razumevanje potreba studenata, timski rad.

### Neophodni principi merenja

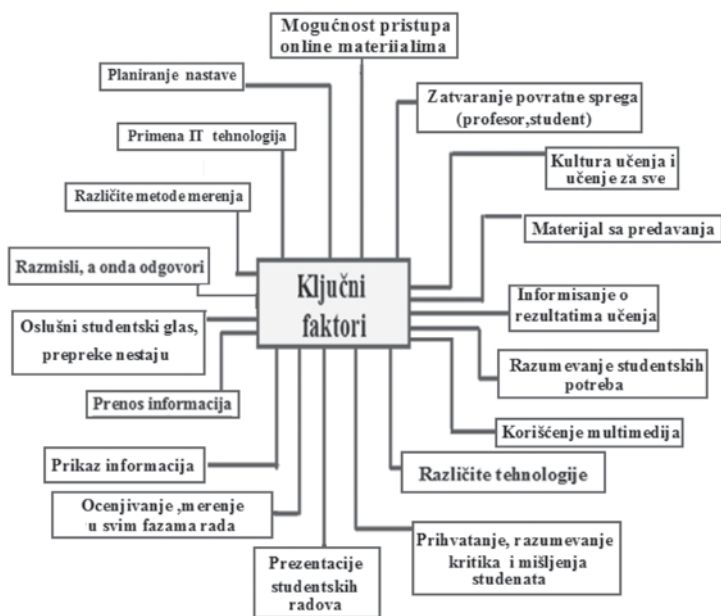
Pre svega treba definisati ciljeve, kriterijume i standarde, a zatim aktivno uključiti studente kako bi transfer znanja bio optimalan. Misija profesora treba da bude u razvoju ključnih praktičnih veština na temu studijskih programa, kao i realizacija novih koncepata i ideja koje su primenljive u praksi za uvođenje kritičkog mišljenja od strane studenata kao i razumevanje njihovih individualnih potreba.

Planiranje predavanja treba da se sastoji iz više jednostavnih koraka: pristupačnost, jasnost, dizajniranje kursa, definisanje veština koje treba razvijati da bi se u što većoj meri pomoglo studentima, kroz povratne informacije saznati šta misle studenti ne samo o sadržaju kursa već i o njihovom zadovoljstvu od učenja, razvijati mentorski sistem, uključivati studente u prezentacije, razvijati motivaciju za korišćenje informacionih i drugih tehnologija za sticanje znanja, truditi se da studenti razumeju gradivo.

Tehnologije nisu magična karta, mada se puno koriste u obrazovanju, nekada i nisu interesantne jer su to novi putevi za prezentaciju starih materijala. Lepo ih je koristiti kada možete nešto da uradite što niste mogli pre toga. Studentima su neophodna iskustvena znanja, a prikupljanje informacija može da se realizuje i van učionice.

Dizajniranje boljih pitanja, organizovanje vremena, procesa rada, optimizacija, diskusija u učionici i laboratoriji je prioritetan zadatak profesora. Diskusije treba organizovati u grupama, sistematski raditi uz uputstva, kreativnost i razmišljanje, što će pomoći realizaciji ideja. Podsticati motivisanost za uspešnost, interakciju i dialog, komentare, a sve to u fazama rada meriti i informisati studente je preduslov za uspešnu nastavu.[1]

Merenja svih rezultata studenata i beleženje povratnih informacija, uvažavanje njegovog mišljenja i želja doprinosi poboljšanju iskustava učenja. Aktivan dijalog u toku predavanja motiviše studente i stvara uslove da osećaju zadovoljstvo pri radu i učenju i realizuju nove koncepte i ideje sa svojim profesorima. Prezentacija primera iz prakse smanjuje barijere učenja. Na sledećoj slici dat je mehanizam podizanja nivoa kvaliteta nastave u Visokoj školi.



**Slika 1.** Ključni faktori za definisanje nivoa kvaliteta predavanja u Visokoj školi

Merenja i povratne informacije u nastavi jesu ključni parametri, koji utiču na ostvarenje misije predavanja i učenja, razvoj veština, motivisanje i ohrabrivanje u diskusiji pri rešavanju zadataka, realizaciju novih koncepata i ideja, razumevanje individualnih potreba studenata i čine bitan jednostavan korak savremene nastave na Visokim školama i fakultetima.

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## **Geospatial support for the monitoring of water pollution loads due to the meat industry facilities effluent discharge in the vicinity of Novi Sad**

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### **Introduction**

The meat industry sector emerges as one of the three significant contributors to the most pressing environmental problems - water pollution [1]. Meat industry is an important industrial segment that represents about 10 percent of all manufacturing industries in Vojvodina. It consumes a significant quantity of water and represents a major contributor of organic loads discharged into the water bodies. Wastewater from meat industry is a complex mixture of water, blood, bone and bone dust, tissue, manure, hair, fat, feathers, with a high content of organic matter. Also detergents, crude oil, pesticides and other substances which are used in operation and maintenance procedures can be found in the effluent water. Within the research, the implementation of geoinformation system for monitoring of water pollution loads due to the meat processing industry effluent discharging in the vicinity of Novi Sad is examined.

### **Emerging and hazardous compounds identified**

Analysis of meat processing industry wastewater samples from Novi Sad area has been conducted on GCMS in SCAN mode, with the goal of possible organic pollutants identification [2]. Organic compounds were extracted by liquid-liquid extraction. Total of 259 compounds and wide variety of compound groups have been identified [1]. Compounds identified during analytical study, and that can be found on NORMAN's list of emerging substances are: industrial chemicals (*p-xylene*), PCPs (*isocineole*, *1,8-cineole*, *carvone*), fragrances (*dl-limonen*), wood preservatives (*p-cresole*) and antifoaming agents (*surfyrol 104A*). A significant number of detected compounds have one or more hazardous characteristics - *2-Octenal*, (*E*)-, (*E,E*)-*2,4-Decadienal*, *o-Guaiacol*, *Diethyladipate*, *2,6-Dimethylphenyl isocyanate*, *Phenol*, *2,6-dimethoxy-4-(2-propenyl)-*, *Ethylallylphthalate*, *Emery*, (*E*)-*Isoeugenol*, *Behenic alcohol*.

### **Geospatial context of obtained data**

Except qualitative identification of the compounds present in wastewater samples, it is necessary to consider additional factors that influence water pollution at the area of interest. Spatial context of meat industry wastewater discharging should

also be consider in order to conduct a successful monitoring programme of water pollution. Accordingly, it is necessary to consider the cumulative effects of same pollutants of separate individual point sources. Furthermore, it is necessary to consider the variables related to the mutual characteristics of each facility (technological process, infrastructure of the facility) that influencing water pollution loads. By bringing described data into spatial relations, and by systematical organization of the database with spatial extension it is possible to create a relationship between all of the above variables. Vector display of meat processing facilities at the territory of Novi Sad, with assigned attribute data about properties of each facility in a tabular form, was created in Quantum GIS. Obtained vector layer in a form of shapefile is imported into previously formed database in PostgreSQL database system with PostGIS spatial extender. Uniquely determined tables with data about all identified hazardous and emerging substances at the investigated locations were created independently and also imported into PostgreSQL.

### Conclusions and future works

Brief inspection of vector layer and associated database search enable us to draw conclusions considering dependence of pollutants occurrence and location-specific factors as well as factors related to the characteristics of each plant. Furthermore, vector layers of groundwater distribution and depth or drinking water sources might be overlaid with existing one which could enable us investigation of additional impacts of meat processing industry onto the recipients. Established geographic information system, also, is a contribution to the creation of pollution map of Novi Sad. It can be concluded that advanced detection methods and spatiotemporal modelling are essential for producing accurate maps of urban pollution [3].

### Acknowledgement

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## Izveštaj o kvalitetu otpadnih voda u industriji Vršca

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Zaštita životne sredine je prioritetan zadatak svakog grada [1], [2] i [3], pa je tako i Vršac među prvima izgradio sekundarni prečištač otpadnih voda.



**Slika 1. i 2.** Sekundarni prečišćivač otpadnih voda u Vršču  
(slika 1 levo – mehanički tretman otpadnih voda,  
slika 2 desno – bazeni za aeraciju otpadnih voda). Foto: U. Božanić.

Otpadne vode industrije Vršca ispuštaju se u gradsku kanalizaciju, što je regulisano i opštinskim propisom (Sl. list opštine Vršac, br. 6/90 i 2/91) [4], odnosno odlukom skupštine opštine Vršac o odvođenju i prečišćavanju otpadnih voda (od 25.12.2005.) [5].

Kao osnova za rad učenika i nastavnika Poljoprivredne škole "Vršac" iz Vršca, u vezi kvaliteta otpadnih voda iz vršačke privrede, poslužio je rad S. Radojković [6]. Uglavnom, praćeni su parametri kao i pre 15 godina, sa manjim izuzecima, jer je u međuvremenu došlo do promene u načinu i broju uzorkovanja otpadnih voda iz pojedinačnih industrijskih postrojenja.

Na ovaj način pokušali smo da steknemo utisak o trendu zagađenja pripodnih recipijenata otpadnim vodama iz industrije Vršca.

Količina zagađujućih materija kontroliše se na osnovu obrađenih rezultata uzorkovanja vode u UPOV "Drugi oktobar" u Vršču. Uzorkovanje i analizu otpadnih voda, kao i predloženi tretman za pojedine vrste zagađenja, vrši Zavod za javno zdravlje "Pomoravlje" iz Čuprije.

Na osnovu podataka dobijenih iz UPOV "Drugi oktobar" iz Vršca, pokušaćemo da utvrdimo kretanje nivoa zagađenja u određenom vremenskom periodu.

Kvalitet otpadnih voda iz industrije u Vršcu posmatran je i analiziran sa nekoliko aspekata:

1. Količina zagađujućih materija iz industrijskih postrojenja,
2. Predloženi tretman za pojedine vrste zagađenja vodotokova,
3. Količina otpadnih voda od privrednih subjekata koji su priključeni na javnu kanalizaciju,
4. Količina otpadnih voda od privrednih subjekata koji nisu priključeni na javnu kanalizaciju.

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## **Distribucija i identifikacija koliformnih bakterija u vodi na lokalitetu Skadarsko jezero, kao indikatora prisustva emergenta u vodi**

### **Distribution and identification of coliform bacteria in the water in the locality Skadar Lake, as an indicator of the presence of emergents in water**

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#### **Uvod**

U prirodnom akvatičnoj sredini desavaju se fizički, hemijski i biološki procesi, koji utiču na sadržaj, transformaciju i kretanje konstituenata u vodi [1]. Veliko broj hemikalija izaziva ogroman pritisak na životnu sredinu, javno zdravlje i naravno biosferu [2]. Pregled vode, posmatran sa aspekta sanitarne bakteriologije i hemije, koji se rutinski radi u gotovo svim laboratorijama, za ocjenu higijensko-epidemiološkog stanja vode, mnogi poistovjećuju sa stvarnim stanjem kvaliteta voda, međutim, površinske vode predstavljaju vodene ekosisteme u kojima vladaju odnosi intrakcija sredine i organizama u njima, pa se samo na osnovu njih može suditi o kvalitetu površinskih voda [3]

#### **Cilj**

Ovaj rad ima za cilj da ukaže na mogućnost uspostavljanja veze između distribucije i identifikacije koliformnih bakterija fekalnog porijekla sa prisustvom policikličnih aromatičnih ugljikovodonika.

#### **Materijal i metode**

Skadarsko jezero se nalazi na krajnjem jugozapadnom dijelu Crne Gore. Napa-ja se vodom sa slivnog područja, površine 5.490 km<sup>2</sup>, od čega je na teritoriji Crne Gore 4.460 km<sup>2</sup>, a na teritoriji Albanije oko 1.030 km<sup>2</sup>. Najvažnije pritoke Skadarskog jezera su: Morača, Karatuna, Bazagurska matica, Crnojevića rijeka, Orahov-štica i Crmnička rijeka. Značajne količine vode jezero dobija preko vodotoka koji dreniraju zbijenu izdan Zetske ravnice (Mala Morača, Plavnica, Zetica, Gostiljska rijeka, Pjavnik, Mala Mrka, Kodrabutanska rijeka, Velika Mrka i Rujela).



## Rezultati i diskusija

U toku istraživanja novembar 2012, u uzorcima vode iz jezera Skadarko jezero, na lokalitetu Skadarsko jezero zapaženo je značajno prisustvo koliformnih bakterija fekalnog porijekla 2300/100 ml i 146/100 ml streptokoka fekalnog porijekla. Identifikovane su bakterije roda *Echerichia* i *Enterobacter*. Sto se tiče prisutva emergenata u vodi izdvajaju se: ostaci nafnih derivata, farmaceutika i sredstava za ličnu higijenu. Emergentne substance, niske doze i pseudo-perzistencija mogu da proizvedu izuzetno jak hemijski i eko-stres, koji može sasvim da promjeni odnose u životnoj sredini, prvenstveno, zbog ne poznavanja i ne razumijevanja toksikoloških implikacija. Značaj se naglašen na niske doze kojima emergentne substance (hormonski uznemiravajuće substance) u koncentracijama pikomolarnog i nanomolarnog ranga, mimikrujući prave hormone i imitiraju njihove funkcije i cikluse. U svojoj doktorskoj disertaciji [4] izvor, nalaženje i sudbinu farmaceutika u površinskim vodama, dovodi u vezu sa nalaženjem koliformnih bakterija u vodi. [5] prisustvo bakterija u vodi prikazuju kao dokaz organskih influenata na kvalitet izvorišta Stand i ujedno obavezuju na njegovu sanitarnu zaštitu.

## Zaključak

Identifikovanje koliformnih bakterija u vodi ukazuje na sanitarnu ugroženost voda kao i na prisustvo emergenata u vodi ili njihovih jedinjenja koja su nastala u procesima transformacije jedinjenja u vodi. U vodi se svakodnevno odvijaju transformacioni procesi kao što su biorazgradnja, fotoliza-apsorpcija, hidroliza-oksidacija i redukcija-oksidacija, što dovodi do otpuštanja i primanja elektrona, što utiče na njihove osobine i toksična svojstva [2]. Kod emergenata koji su organske komponente, kao i za ostale organske komponente u vodi, skoro sve značajne redoks reakcije potpomažu mikroorganizama.

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## Adsorption of Cr(VI) from aqueous solutions on organofunctionalized fully-acid activated sepiolite

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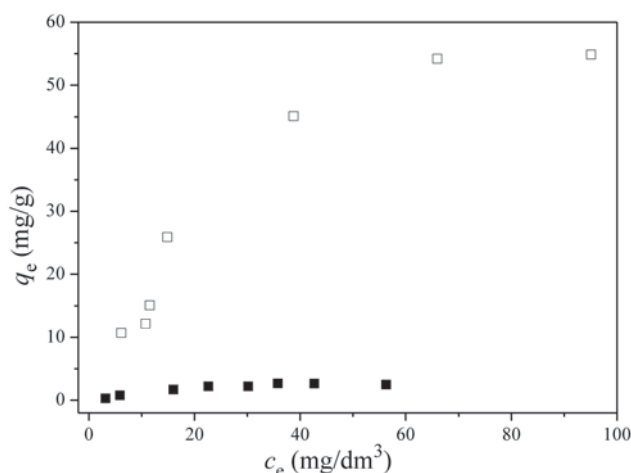
Chromium is found in nature primarily in the form of trivalent species, Cr(III). The hexavalent chromium, Cr(VI) occurs naturally in rocks but it is found in nature mainly as a result of the industrial processes. Due to toxic, carcinogenic and mutagenic features of Cr(VI), its removal from the environment is necessary. The objective of this study was to investigate the removal of Cr(VI) using fully-acid activated sepiolite functionalized with organosilane.

Sorbents for the removal of Cr(VI) anions species from aqueous solutions was obtained by functionalization of fully-acid activated sepiolite with organosilane: (3-mercaptopropyl)trimethoxysilane or mercaptosilane,  $(\text{HS}-(\text{CH}_2)_3-\text{Si}-(\text{OCH}_3)_3)$  and [3-(2-aminoethylamino)propyl]trimethoxysilane or aminesilane,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ . Functionalization is done by condensation between the silanol groups of fully-acid activated sepiolite and silanol groups of organosilane, which are formed during hydrolysis of methoxy groups of organosilane.

The results of characterization show that better functionalization of the fully-acid activated sepiolite was achieved by using aminesilane than mercaptosilane. Based on the results of scanning electron microscopy of sepiolites, it was observed that the functionalized sepiolites retained the fibre morphology of the parent material. Also, the results of X-ray diffraction analysis showed that functionalized materials retained the structure of the starting sepiolite. The change in FT-IR spectra of the starting sepiolite after functionalization indicated that molecules of organosilanes bind to the surface of sepiolite by chemical bonds. It was shown that textural characteristics of aminesilane functionalized sample was significantly different compared to mercaptosilane functionalized sample. The values of specific surface area, pore size and volume of aminesilane functionalized sepiolite show a drastic reduction, primarily, in microporosity compared to the starting sepiolite. Textural characteristics of mercaptosilane functionalized sepiolite are similar to the characteristics of the starting sepiolite. The results of determining of the point of zero charge of sepiolites showed a much larger change in acid-base properties of the starting sepiolite after aminesilane functionalization than after mercaptosilane functionalization. The functionalization with aminesilane increases the basic character of the sepiolite surface, while after functionalization with mercaptosilane, acid-base properties of sepiolite does not change significantly.

In the sorption experiments, the initial concentration of Cr(VI)-solutions were less than  $1 \text{ g/dm}^3$ , and during equilibration with the sorbents the pH value of the solutions changed from initial values of  $(2.0 \leq \text{pH}_{\text{initial}} \leq 4.5)$  to equilibrium values in the range of  $(2.2 \leq \text{pH}_{\text{final}} \leq 9.9)$ . In such conditions, the main forms of Cr(VI)

in solution are  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ . By lowering the pH value of the solution, the concentration of  $\text{HCrO}_4^-$  increases, while the concentration of  $\text{CrO}_4^{2-}$  decreases. Based on the results of Cr(VI) sorption on functionalized sepiolite it was observed that the sorption capacity of aminesilane functionalized sepiolite is significantly higher than the sorption capacity of mercaptosilane functionalized sepiolite at all investigated initial pH of Cr(VI)-solutions, and in particular at the very low initial pH (2.0) (Figure 1).



**Figure 1.** The adsorption isotherms of Cr(VI): on mercaptosilane functionalized fully-acid activated sepiolite at initial pH 2.0 (■); on aminesilane functionalized fully-acid activated sepiolite at initial pH 2.0 (□).

The mechanisms of sorption of Cr(VI)-anions on the mercaptosilane functionalized sepiolite are nonspecific electrostatic interactions between Cr(VI)-anions and protonated mercapto ( $-\text{SH}_2^+$ ) groups, as well as, the reduction of Cr(VI)-anions to  $\text{Cr}^{3+}$ -ions with mercapto ( $-\text{SH}$ ) groups, followed by electrostatic attraction between the ions  $\text{Cr}^{3+}$ -ions and sulphonate ( $-\text{SO}_2\text{O}^-$ ) groups formed by oxidation of mercapto groups. The mechanisms of sorption of Cr(VI)-anions on aminesilane functionalized sepiolite are nonspecific electrostatic interactions between Cr(VI)-anions and protonated amine ( $-\text{NH}_2^+$  and  $-\text{NH}_3^+$ ) groups, at low pH values of the solution, as well as, formation of hydrogen bonding between  $\text{CrO}_4^{2-}$ -ions and nonprotonated amine ( $-\text{NH}-$  and  $-\text{NH}_2$ ) groups, at the higher pH values of the solution.

## Comparason of Arithmetic Mean and Median as the Measures for Central Tendencies of Selected Eco-Chemical Parameters of the Serbian Rivers

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The monitoring program of The Public Water Management Company Srbijavode produced, over many decades, huge data base which consists of monthly measurements for the most important eco-chemical parameters. For our analysis we have chosen 17 the most important eco-chemical parameters which were observed at the River Danube and its tributaries between 1992 and 2006 [1][2].

The arithmetic mean is one of the simplest statistical tools for expressing central tendency of the analysed data set, but its application has some drawbacks. Any extreme value will strongly affect arithmetic mean, so it may become totally misrepresentative for realistic expression of the central tendency. The Grubbs test and the Q test are the most often used for the identification of the outliers but their power can be seriously deteriorated if there is more than one outlier present (Q test) or data is heavily skewed. Skewness affects the Grubbs test twofold, by moving the value of arithmetic mean ( ) toward the value of the outlier and by increasing the value of standard deviation (SD), which altogether may decrease value of the G below the critical level (Equation 1).

$$G = \frac{|x_{\text{suspected value}} - \bar{X}|}{SD} \quad (1)$$

Median (M), arithmetic mean and standard deviation were compared before and after exclusion of outliers. Percent difference was calculated by formula:

$$\%D = \frac{x_b - x_a}{x_b} * 100 \quad (2)$$

%D is percent difference between M, or SD calculated before ( $x_b$ ) and after ( $x_a$ ) outlier exclusion.

Based on their variability i.e. tendency to possess outliers in data set, eco-chemical parameters were divided into 2 groups. In the first group there are parameters which had only one outlier per approximately 30 measurements, and their arithmetic mean changes on average less than 5% after outlier exclusion: biological oxygen demand (BOD-5), chemical oxygen demand (COD), UV extinction at 254 nm, dissolved oxygen (DO), oxygen saturation (O%), total dissolved solids (TDS), electrical conductivity (EC), temperature, tot. and m-2p alkalinity, CO<sub>2</sub> and pH. In the second group there are: suspended matter (SM), tot. P, PO<sub>4</sub><sup>-3</sup>, NO<sub>3</sub><sup>-</sup> and ammonia. Increased occurrence of outliers among these parameter values is evident and average change of arithmetic mean ranges between 12% (NO<sub>3</sub><sup>-</sup>) and 30% (ammonia).

Based on a thorough quantitative analysis of the data, several conclusion can be drawn:

- Exclusion of outliers had strongest effect on change of SD, while median remained the least affected or unchanged at all. The percent change of SD is generally few times greater than the change of arithmetic mean. Also, the change of arithmetic mean is few times greater than change of median.
- For 12 out of 17 parameters the difference between arithmetic mean and median wasnot significant since it was less than 5%.
- In cases where larger number of outliers was discarded, difference between median and arithmetic mean diminished significantly.

Parameter	%D before and after outlier exclusion
SM	from 34.0% to 22.7%
Tot. P	from 21.6% to 6.5%
PO <sub>4</sub> <sup>-3</sup>	from 15.3% to 3.4%
NO <sub>3</sub> <sup>-</sup>	from 14.0% to 4.7%
Ammonia	from 41.4% to 24.7%

- Several examples shown in the table below are the best illustration of the resilience of M to the influence of the outliers compared to the :

Parameter	Sampling location	N	No. of excluded outliers	%D for median	%D for
Ammonia	Sm	159	11	0.0	44.1
SM	V	136	5	0.0	31.2
SM	Z	168	14	0.0	28.7
Nitrates	P	134	9	0.0	21.1
Phosphates	VM	158	4	0.0	17.4
Tot. P	Z	115	5	0.0	12.7

Decrease in difference between M and ,after exclusion of the outliers,can be solely attributedto the change of which in the best way illustrates the superiority of median as the most appropriate mean for the expression of the central tendencies of the data sets. This analysis offers strong, quantitative evidences in order to unanimously resolve this very fundamental question.

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## Uklanjanje pesticida iz vodenih rastvora karbonizovanim otpadnim vlaknima konoplje

### Carbonized waste hemp fiber for pesticide removal from water

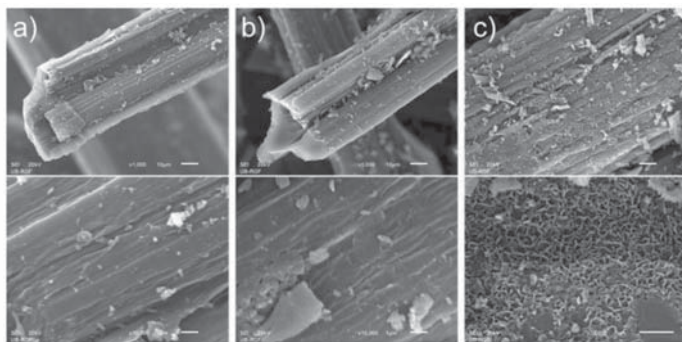
Marija Vukčević<sup>1</sup>, Ana Kalijadis<sup>2</sup>, Tatjana Vasiljević<sup>1</sup>,  
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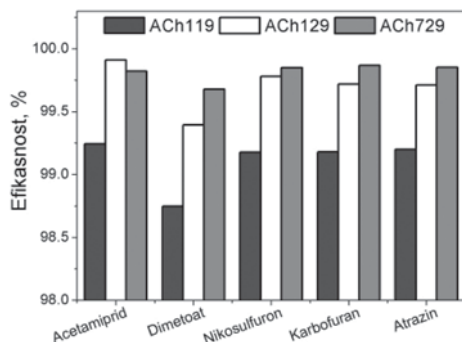
Poslednjih godina sve više pažnje se poklanja korišćenju jeftinih i lako dostupnih materijala kao polaznih sirovina u proizvodnji sorpcionih ugljeničnih materijala. Kratka vlakna konoplje, koja predstavljaju otpad pri preradi konoplje u tekstilnoj industriji, sa ekonomskog i ekološkog stanovišta predstavljaju primamljivu sirovinu za dobijanje aktiviranog ugljeničnog materijala [1].

U ovom radu će biti ispitana mogućnost korišćenja karbonizovanih otpadnih vlakana konoplje u adsorpciji pesticida. Aktivirana vlakna konoplje dobijena su karbonizacijom otpadnih vlakana konoplje na 700°C (ACh729) i 1000°C (ACh119 i ACh129), i naknadnom aktivacijom karbonizovanog materijala na 900°C, korišćenjem KOH, kao aktivirajućeg agensa, u različitim odnosima KOH:karbonizovani materijal (1:1 – ACh119, 2:1 – ACh129 i ACh729). Površina dobijenih materijala okarakterisana je određivanjem specifične površine, prečnika i zapremine pora, kao i količine površinskih grupa. Morfološke karakteristike određene su skenirajućom elektronskom mikroskopijom (Slika 1). Adsorpcija je vršena iz rastvora smeše pet pesticida: acetamiprida, dimetoata, nikosulfurona, karbofurana i atrazina. Koncentracija pesticida tokom vremena adsorpcije određivana je metodom HPLC-MS<sup>2</sup> [2].



**Slika 1.** SEM fotografije aktiviranih vlakana konoplje pri uvećanju od 1000 i 10000 (20000) puta: a) ACh119, b) ACh129 i c) ACh729

Efikasnost uzoraka aktiviranih vlakana konoplje u uklanjanju pesticida iz rastvora, u kom je početna koncentracija svakog pesticida iz smeše bila  $50 \text{ mg/dm}^3$ , prikazana je grafički na Slici 2. Po postizanju ravnotežne adsorpcije, efikasnost uklanjanja pesticida veća je od 98 % kod svih ispitivanih uzoraka.



**Slika 2.** Efikasnost uklanjanja pesticida iz rastvora smeše pesticida

U cilju sticanja uvida u kinetiku procesa adsorpcije, na rezultate dobijene u ovom eksperimentu, primenjena su tri modela: jednačina pseudo-prvog reda, jednačina pseudo-drugog reda i model intračestične difuzije. Adsorpcija pesticida iz vodenog rastvora smeše pesticida prati kinetiku pseudo-drugog reda i odvija se kroz: brzu površinsku adsorpciju, intračestičnu difuziju i finalni ravnotežni stupanj, pri čemu intračestična difuzija nije jedini proces koji kontroliše brzinu adsorpcije. Brzina izdvajanja pesticida najveća je na uzorku ACh729, a najveću efikasnost u uklanjanju pesticida pokazuju ACh129 i ACh729. Analizom ravnotežnih podataka pokazano je slaganje sa Lengmirovom adsorpcionom izotermom, kao i da se karbonizacijom na  $1000^\circ\text{C}$  i aktivacijom uz dva udela KOH do  $900^\circ\text{C}$ , dobija materijal homogenije raspodele aktivnih mesta za adsorpciju pesticida.

Na osnovu dobijenih vrednosti adsorpcionih kapaciteta, kao i na osnovu efikasnosti sorpcije, može se zaključiti da aktivirana vlakna konoplje pokazuju dobre sorpcione karakteristike prema pesticidima i da se kao takva mogu koristiti kao filteri za uklanjanje pesticida iz vode.

### Zahvalnica

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## **Uklanjanje organskih zagađujućih materija iz vodenih rastvora korišćenjem hidrotermalnog ugljenika kao sorbenta i nosača katalizatora**

### **The removal of organic pollutants from aqueous solutions using hydrothermal carbon as sorbent and catalyst carrier**

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Zoran Laušević<sup>1</sup>, Mila D. Laušević<sup>2</sup>

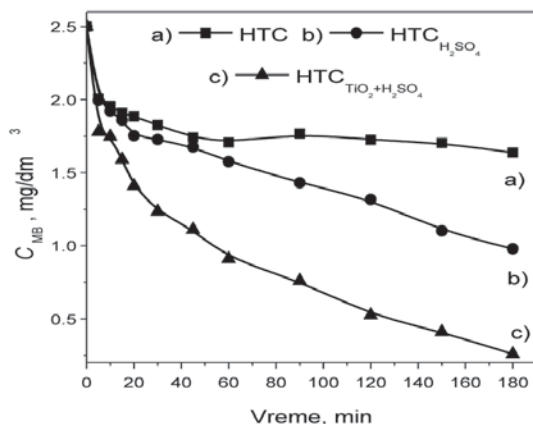
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Poslednjih godina velika pažnja se poklanja uklanjanju organskih zagađujućih materija, koje se mogu naći u otpadnim vodama savremene industrije i predstavljaju izvor značajnog zagađenja. Pored standardnih metoda prečišćavanja (hemijsko taloženje i koagulacija ili adsorpcija na organskim i neorganskim materijalima), u cilju što efikasnijeg uklanjanja organskih zagađujućih materija sve češće se koriste fotokatalitički procesi. Proces prečišćavanja ovako zagađene vode često podrazumevaju korišćenje ugljeničnih materijala, ili kao sorbenta u procesima adsorpcije ili kao nosača katalizatora u procesima fotokatalitičke razgradnje. Poslednjih godina razvijen je postupak hidrotermalne karbonizacije kao novi postupak dobijanja ugljeničnih materijala. Hidrotermalna karbonizacija se izvodi u autoklavu pod visokim pritiskom, pa se hidrotermalni ugljenik (HTC) [1-3] dobija na temperaturama znatno nižim od standardnih temperatura karbonizacije, što sa ekonomskog i ekološkog aspekta čini ovaj proces isplativijim od klasičnog postupka karbonizacije.

U ovom radu ispitivana je mogućnost korišćenja HTC-a u procesima uklanjanja organskih zagađujućih materija iz vodenih rastvora i to kao sorbenta u metodi adsorpcije i kao nosača katalizatora u fotokatalitičkim procesima. HTC korišćen u ovom radu dobijen je hidrotermalnom karbonizacijom na temperaturi od 220°C, uz maksimalni generisani pritisak od 32 bar, a kao ugljenični prekursor korišćen je rastvor glukoze koncentracije 2,3 mol/dm<sup>3</sup>. Primena HTC-a kao sorbenta testirana je na modelu adsorpcije metilensko-plavog (eng. methylene blue – MB) iz vodenog rastvora. U cilju ispitivanja mogućnosti primene HTC-a kao nosača katalizatora u fotokatalitičkim procesima razgradnje organskih polutanata, površina HTC-a impregnirana je titan-dioksidom kao katalizatorom. Impregnacija površine HTC-a titan dioksidom postignuta je adsorpcijom titana iz kiselog rastvora, i naknadnim odgrevanjem materijala u cilju potpune oksidacije adsorbovanog Ti do TiO<sub>2</sub>. Fotokatalitička aktivnost HTC-a impregnisanog titan-dioksidom ispitana je u procesu fotokatalitičke razgradnje MB. U cilju ispitivanja udela adsorpcije u ovom procesu uklanjanja MB, kao sorbent je korišćen HTC modifikovan sumpornom kiselinom.





**Slika 1.** Adsorpcija MB na površini HTC-a (a) i modifikovanog HTC-a (b) i fotokatalitička razgradnja MB korišćenjem HTC-a kao nosača katalizatora (c)

Adsorpcijom MB na površini HTC-a dolazi do smanjenja početne koncentracije MB za oko 34%, a ravnotežna adsorpcija se postiže nakon 60 minuta (Slika 1a). Modifikacija površine HTC-a sumpornom kiselinom dovodi do značajnog povećanja efikasnosti adsorpcije, ali i do produženja vremena potrebnog za postizanje ravnotežne adsorpcije (Slika 1b). Tretiranje površine HTC-a sumpornom kiselinom dovodi do oksidacije površine i povećanja količine površinskih kiseoničnih grupa [4]. Obzirom da površinske grupe predstavljaju aktivna mesta za adsorpciju, povećanje njihove količine dovodi do poboljšanja sorpcionih svojstava HTC-a, pa se HTC modifikovan sumpornom kiselinom može uspešno koristiti kao sorbent u procesima uklanjanja MB iz vode. Rezultati dobijeni ispitivanjem fotokatalitičke aktivnosti HTC-a impregnisanog titan-dioksidom (Slika 1c), pokazuju da se upravo primenom HTC-a kao nosača katalizatora u procesu fotokatalitičke razgradnje MB, postiže najveća efikasnost u prečišćavanju vode zagađene ovim polutantom.

### Zahvalnica

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## Adsorption and photocatalytic degradation of methylene blue on carbon monolith with TiO<sub>2</sub> coating

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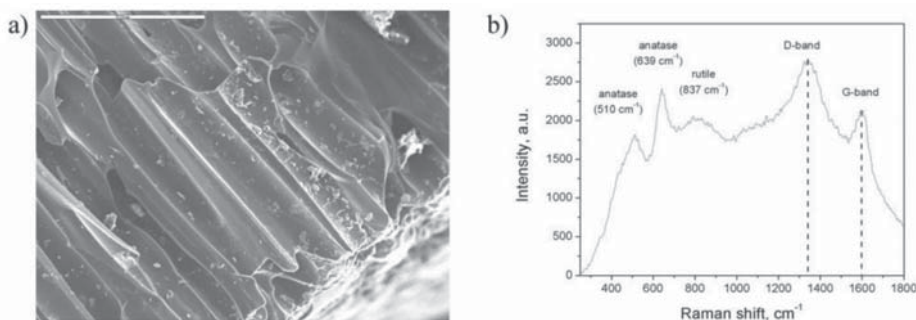
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Recently, more attention has been paid to photocatalytic degradation as an effective method for removal of organic pollutants from the environment, especially from water. Titanium dioxide (TiO<sub>2</sub>) has been proven to be a good photocatalyst due to good stability, high activity, little harmfulness to humans, easy availability and low cost [1,2]. Nowadays, different materials can be used as catalytic carrier for TiO<sub>2</sub> in the photocatalytic degradation process.

We have used cheap and simple methods for loading TiO<sub>2</sub> particles on carbon monolith (CM) carrier. Photocatalysts were prepared by impregnation of CM with TiO<sub>2</sub> using titanium solution. Additionally, the CM composite photocatalysts were obtained by dip-coating method which implies the use of different binders [1].

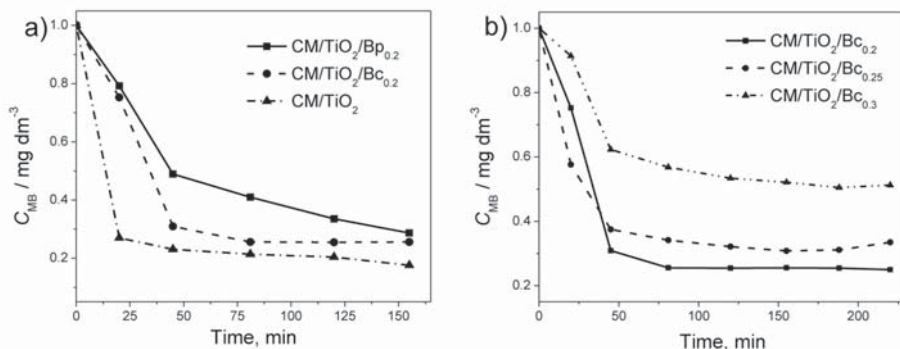
CM is composite carbon material containing activated carbon on the inner capillary walls [3], which is good sorbent for methylene blue (MB) [4]. The amount of surface oxygen groups and specific surface area, obtained by temperature-programmed desorption and BET method, respectively, as well the adsorption test, showed that the high level of MB adsorption on CM elevates the photocatalytic activity of TiO<sub>2</sub> [2]. The presence of TiO<sub>2</sub> on CM carrier was determined by Raman spectroscopy and scanning electron microscopy (Fig. 1).



**Figure 1.** SEM photograph (a) and Raman spectrum (b) of carbon monolith loaded with TiO<sub>2</sub> particles

Photocatalytic degradation of MB on CM impregnated with TiO<sub>2</sub> was investigated in the presence UV irradiation. It was found that CM discs thickness and

the binder mass fraction in the composite photocatalysts affect the photocatalytic activity. The best photocatalytic activity of CM composite photocatalysts was achieved in the presence of a small mass fraction of binder and with increased CM disc thickness (Fig. 2).



**Figure 2.** Degradation of methylene blue in the presence of TiO<sub>2</sub> with a) Teflon (Bp<sub>0.2</sub>), Sodium carboxymethyl cellulose (Bc<sub>0.2</sub>) and without binder; and b) different mass fraction of Bc

In order to investigate the influence of incident angle between UV rays and CM cross section on the photocatalytic activity, photocatalytic experiments were performed using different angles value: 90° and 82°. For the thinner sample (2mm), angle alternation has no major impact on photocatalytic activity. On the other hand, for the thicker CM disc (5mm), changes in the incident angle of UV rays leads to reflection from the walls of the CM capillary column. Consequently, the probability of collision between UV rays and TiO<sub>2</sub> particles increases, and therefore improve the photocatalytic activity of CM photocatalysts.

### Acknowledgments

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**POSTER PREZENTACIJE**  
**Sekcija 2**

*POSTER PRESENTATIONS*  
*Section 2*

## Effect of catalyst on mesotrione degradation in DBD reactor

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A large number of pesticide active ingredients have been registered and marketed for pest control purposes around the world. [1] Because the population growth will increase, need for food and consequently agricultural activities will become more and more acute. Use of chemicals for higher yields of agricultural crops will be still effective in the near future. Their elimination from wastewater effluents is the subject of considerable concern of environmental remediation and has attracted many researchers in recent years. [2] Mesotrione is a newer member of the triketone group of herbicides which is chemically derived from a natural phytotoxin produced by the bottlebrush plant *Callistemon citrinus*. [3] It was developed by Syngenta Crop Protection and marketed under the commercial name Callisto®. [3, 4] It is a selective pre- and post-emergence herbicide that controls most broadleaf and some grass weeds in maize crops. [5] Mesotrione has acidic properties (pKa of around 3), which are determinant for his environmental behaviour as well as for the analytical method development. [6]

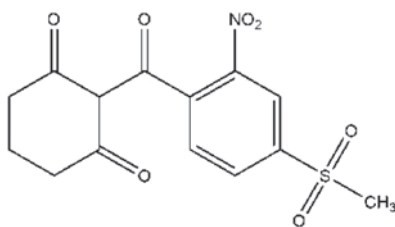


Figure 1. Mesotrione

DBD reactor was used for degradation of mesotrione. It is a nonthermal plasma reactor, which is based on coaxial dielectric barrier discharge. DBD can produce UV light and many reactive species such as free electrons, negative ions, positive ions, uncharged short-lived radicals, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>. The •OH radical is known to play most important role since its oxidation potential is higher than that of atomic oxygen and ozone. [7] DBD in combination with catalyst generates higher concentration of hydroxyl radicals and process is more efficient.

The aim of this work was to investigate degradation of mesotrione in DBD reactor with addition of manganese and hydrogen peroxide as catalyst. Manganese concentration was 5 mM; hydrogen peroxide was used in concentration of 20 mM. In each series of experiments, the treatment was started with 2 L of pesticide solution (concentration of 200 ppm). Pesticide solution was circulated ten times through reactor. Energy density of 45 kJ/L, by one pass, was introduced in the solution. The introduced energy density was increased using multiple passes through the reactor. Degradation products were identified by high performance liquid chromatography (HPLC-DAD) and UHPLC–Orbitrap–MS analyses. There were differences in degradation products for just DBD, DBD with addition of manganese, and DBD with addition of peroxide, suggesting different mechanisms of degradation. Chromatograms show that degradation process is faster with manganese and peroxide in DBD reactor. Based on results a mechanism governing catalytic oxidation reactions of mesotrione was proposed. Addition of manganese and peroxide can successfully improve mesotrione degradation in DBD reactor.

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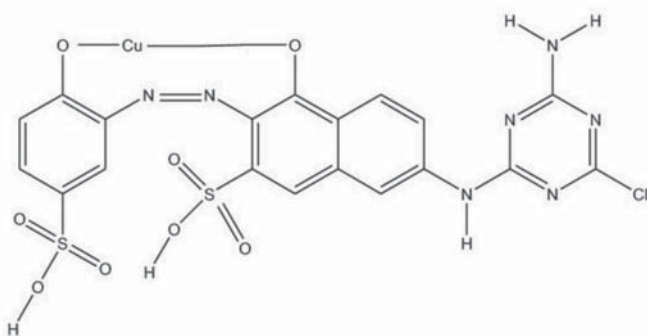
## Electrochemical degradation of Reactive Blue 52 using palladium, graphite and cobalt electrode

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Textile industry is rated as one of the most polluting sector among the different human activities. [1] Approximately, one million tons of dyes are produce every year all around the world. Up to 50% of the dyes are lost after the dyeing process and disposed out in the effluents. Colour is usually the first contaminant to be recognized in effluents. Very small amount of dyes in water (10 – 20 mg/l) is highly visible and affects water transparency and gas solubility of lakes, rivers and other water bodies. [2, 3] Dyes contained in textile effluents retain their colour and structural integrity under diverse weather conditions due to their design to persist under oxidizing and reducing conditions, washing and light exposure. [1] Reactive dyes are one of the most significant technological innovations of the 20th century in the dyes field. [4] They are generally water soluble and used for dyeing cellulosic fiber, such as cotton and rayon, but are also used for silk, wool, nylon, and leather. [5] Reactive azo dyes have one or more azo groups (R1–N=N–R2) and aromatic rings mostly substituted by sulfonate groups. Their complex structure is responsible for their intensive colour, high water solubility; resist fading on exposure to sweat, soap, water, light. [3, 6] They are considered as recalcitrant xenobiotic compounds. [7]



**Figure 1.** C.I. Reactive Blue 52, Drimaren blue X-3LR  
CAS No.: 12225-63-7  $\lambda_{\text{max}} = 615 \text{ nm}$

In recent years, great attention is given to electrochemical methods for the degradation of the dye molecules. In these methods, the main reagent is electron, which induces redox reactions that lead to the transformation and destruction of molecules.



A limited number of papers have been published dealing with the direct electrodegradation of dyes in aqueous solution on suitable cathodes. As Reactive Blue 52 contains azo groups in the chromophore, the direct cathodic reduction to the corresponding amines could be an interesting process for the decolourization of highly coloured concentrated dyestuff solutions. Electrochemical degradation of Reactive Blue 52 was done using different cathodes: palladium, graphite and cobalt. Experiment was carried out in undivided electrochemical cell in the presence of 0.1 M sodium sulphate as supporting electrolyte. Sodium sulphate is already present in actual effluents from textile industry at considerable concentration. Dye concentration selected for electrolytic experiments was 60 ppm. This value is included in the range of real dye concentration found in textile effluents. [4] The volume of solution to be treated was 340 mL and the effective cathode area was 180.74 mm<sup>2</sup>. Fisher platinum electrode was employed as anode. The homogeneous nature of the medium during the electrolyses was maintained using magnetic stirrer. Decolourization rate, influence of pH and applied voltage (3; 4.5; 6 and 12 V) were examined at different cathodes. Products of electrochemical degradation were monitored by HPLC-DAD.

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## Interakcija između poli(vinilpirolidona) i $\text{Pb}^{2+}$ -jona

### Interaction between polyvinylpyrrolidone and $\text{Pb}^{2+}$ ion

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Uklanjanje olova iz zagađenih voda je ispitivano na mnogim komercijalnim i sintetisanim adsorbensima. Među ove materijale spadaju: treset, hidratizovano gvožđe, aluminijum oksidi, granulirani gvožđe oksid, biopolimeri, veštačke anjonske gline, prirodni i modifikovani zeoliti. Olovo se u česmenskoj vodi retko javlja u koncentracijama većim od 5  $\mu\text{g/l}$ , izmerene koncentracije olova u prirodnim vodama se kreću u opsegu 0,4 do 0,8  $\text{mg/l}$ , a lokalna zagađenja potiču od rudarskih kopova, odnosno industrijskih izvora.

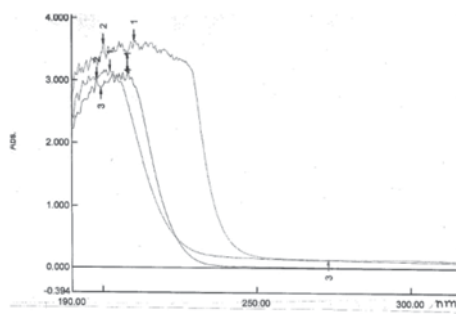
Poli(vinilpirolidon), (PVP) je visoko polaran, amfoterni polimer, koji se sintetiše lančanom polimerizacijom preko slobodnih radikala, polazeći od monomera N-vinilpirolidona. Molarna masa PVP se obično izražava preko K-vrednosti, zasnovane na kinematičkom viskozitetu i računate prema Fikentscher-ovoj jednačini. PVP nalazi primenu u mnogim granama industrije zbog dobre rastvorljivosti, i to ne samo u vodi nego i u velikom broju organskih rastvarača niske toksičnosti, kao i visoke sposobnosti kompleksiranja i građenja filmova.

PVP korišćen za analize komercijalnog naziva K30, usrednjene molarne mase,  $M_w = 55\,000\text{ g/mol}$  nabavljen je od kompanije Sigma-Aldrich. Rastvori komercijalnog PVP K30 koncentracije od 1  $\text{g/l}$  pripremani su u dejonizovanoj vodi. U 50 ml rastvora polimera dodat je olovo(II)-nitrat tako da je koncentracija olova bila od 1  $\text{mg/l}$  do 10  $\text{mg/l}$ . Ovako pripremljeni rastvori su energično mešani u zatvornim posudama na mućkalici u vremenskom periodu od 1 sata na sobnoj temperaturi (25°C). Nakon mućkanja rastvori su ostavljeni preko noći do uspostavljanja ravnoteže. Zapremina od 50 ml ovog rastvora je ekstrahovana sa metilen-hloridom, i to tri puta sa po 15 ml. Nakon ekstrakcije organski sloj je uparen do suva na vodenom kupatilu, na temperaturi od 40°C, a ostatak nakon uparavanja, koji je sadržao kompleks PVP- $\text{Pb}^{2+}$ , rastvoren je u 50 ml vode. Ravnotežne koncentracije olova određene su primenom optičke emisije spektrometrije sa indukovano spregnutom plazmom. Količina adsorbovanog olova na PVP je određena na osnovu razlike početne i ravnotežne koncentracije jona olova(II). Rastvor PVP i rastvor kompleksa nastao vezivanjem jona olova(II) za PVP je određen spektrofotometrijski (Slika1).

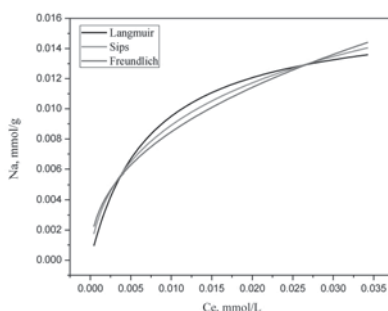
Interakcija između  $\text{Pb}^{2+}$ -jona i polimera može se objasniti preko elektrostatičke sile i građenja koordinativnih veza. Uticaji koji mogu imati efekat na interakciju polimer-metal, a suštinski zavise od polimera su: priroda atoma u osnovnom

nizu, funkcionalne grupe vezane za osnovni niz, struktura polimera, molekulska masa i polidisperznost, rastojanja između funkcionalnih grupa i osnovnog niza, itd. Ostali uticaji izuzev osobina polimera su: pH, jonska jačina, priroda i naelektrisanje jona metala i temperatura. Rađeno je pri pH vrednosti rastvora PVP i jona olova(II) u osegu od 4,62 do 5,30.

Interakcija između adsorbensa i adsorbata opisana je izotermama, i to najčešće korišćenim modelima po Langmuir-u i Freudlich-u. Takođe, količina adsorbovanog jona olova po gramu PVP, ( $N_a$ , mmol/g) u funkciji ravnotežne koncentracije, ( $C_e$ , mmol/l) predstavljena je i sve više korišćenim Langmuir-Freundlich, takozvanim Sips, modelom (Slika 2). Parametri i adsorpcione konstante izoterme su prikazani u Tabeli 1.



Slika 1. Spektri PVP i kompleksa sa  $Pb^{2+}$



Slika 2. Sorpcione izoterme

Tabela 1. Parametri i konstante adsorpcionih izoterme

Freundlichova jednačina	
$S_m$ / mmol g <sup>-1</sup>	-
$K_F$ / (mmol g <sup>-1</sup> ) (mmol <sup>-1</sup> dm <sup>3</sup> ) <sup>n</sup>	0,06182
n	0,43169
R <sup>2</sup>	0,99088
Langmirova jednačina	
$S_m$ / mmol g <sup>-1</sup>	0,01651
$K_L$ / (mmol <sup>-1</sup> dm <sup>3</sup> )	135,74523
n	-
R <sup>2</sup>	0,98065
Sipsova jednačina	
$S_m$ / mmol g <sup>-1</sup>	0,02745
$K$ / (mmol <sup>-1</sup> dm <sup>3</sup> ) <sup>n</sup>	8,8815
n	0,36662
R <sup>2</sup>	0,99794

$S_m$  -maksimalna adsorbovana količina,  $K$ -koeficijent izoterme,  $n$ -konstanta izoterme,  $R^2$ -korelacioni koeficijent

## **Studija adsorpcije herbicida iz grupe sulfonilurea na aktivnom uglju**

### **Study of the adsorption of sulfonilurea herbicide on activated carbon**

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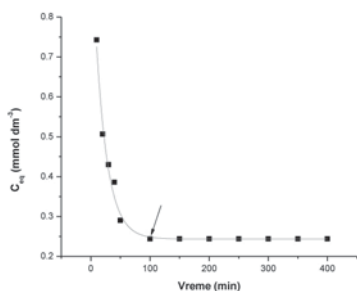
Ponašanje nikosulfurona, molekulske formule  $C_{15}H_{18}N_6O_6S$ , herbicida iz grupe sulfonilurea u životnoj sredini nije poznato. Relativno visoka rastvorljivost u vodi ( $>100 \text{ mg l}^{-1}$ ) može dovesti do brze migracije u akvifer kao i potencijalne kontaminacije plitkih podzemnih voda.

U ovom istraživanju proučavana je adsorpcija nikosulfurona na aktivnom uglju. Dobijene adsorpcione izoterme su interpretirane korišćenjem Langmirove, Frojndlihove i Sipsove jednačine.

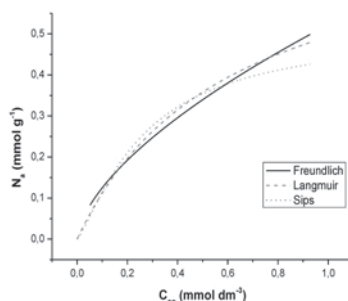
Visoko-performansna tečna hromatografija (HPLC) primenjena je za kvantifikaciju nikosulfurona u pripremljenim uzorcima. Izvršen je razvoj HPLC metode pri čemu su sledeći parametri pokazali najbolje rezultate: razdvajanje je izvršeno na Bischoff C18 ACE (250 x 4 mm) koloni uz eluent 30% acetonitril/70% voda (pH 2,5,  $H_3PO_4$ ). Jedinjenje se detektuje UV detektorom na 245 nm, vreme analize 8 min., protok 1,5 ml/min. Injektovano je 20  $\mu\text{l}$  rastvora uzorka. Kolona je termostatirana na temperaturi od 25 °C. Na sobnoj temperaturi (25 °C), nakon upotrebe 100 mg adsorbensa i 40  $\text{cm}^3$  rastvora nikosulfurona različitih početnih koncentracija, mešanjem u vremenskom periodu od 10, 20, 30, 40, 50, 100, 150, 200, 250, 300, 350 i 400 minuta dobijena je kriva ravnotežnih koncentracija (Slika 1). Adsorbovana količina nikosulfurona određena je iz razlike početne koncentracije i koncentracije nakon adsorpcije.

Rezultati (Slika 2.) su prikazani u obliku adsorpcionih izotermi ( $N_a$  – broj molekula adsorbovan po gramu adsorbensa u funkciji ravnotežnih koncentracija,  $C_{eq}$ ). Langmirova izoterma pokazuje dobro slaganje sa promenom početnih koncentracija nikosulfurona. Frojndlihova izoterma (eksperimentalni model koji može da se primeni kao neidealna adsorpcija na heterogenim mestima i kao višelsojna adsorpcija) pokazuje bolje slaganje sa eksperimentalnim rezultatima.

Izoterma Langmir – Frojndlihovog tipa, takozvana Sipsova [1], uz pretpostavke vezane za heterogenost površine i za definisanje broja aktivnih mesta gde jedan molekul adsorbata inteeaguje sa jednim aktivnim mestom na površini, se u najbolje slaže sa eksperimentalnim podacima adsorpcije nikosulfurona. Na ovaj način dokazano je da se adsorpcija odigrava bez interakcije između molekula adsorbata. Konstante i parametri izotermi adsorpcije nikosulfurona na aktivnom uglju prikazani su u Tabeli 1.



**Slika 1.** Promena koncentracije nikosulfurona sa vremenom



**Slika 2.** Profili izračunatih izoterma dobijenih korišćenjem Langmirovog, Frojndlihovog, Sipsovog modela

**Tabela 1.** Parametri i konstante adsorpcionih izoterma

Frojndlihova jednačina	
$S_m / \text{mmol g}^{-1}$	-
$K_F / (\text{mmol g}^{-1}) (\text{mmol}^{-1} \text{dm}^3)^n$	0,52216
$n$	0,62126
$R^2$	0,97945
Langmirova jednačina	
$S_m / \text{mmol g}^{-1}$	0,79183
$K_L / (\text{mmol}^{-1} \text{dm}^3)$	1,65005
$n$	-
$R^2$	0,95156
Sipsova jednačina	
$S_m / \text{mmol g}^{-1}$	0,5116
$K / (\text{mmol}^{-1} \text{dm}^3)^n$	5,45744
$N$	0,28193
$R^2$	0,98583

$S_m$  - maksimalna adsorbovana količina na adosorbensu kada je oformljen monosloj ( $\text{mmol g}^{-1}$ ),  $K$  - koeficijent izoterme,  $n$  konstanta izoterme,  $R^2$  - korelacioni koeficijent

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## **Detekcija organofosfornih usporivača gorenja u zemljištu u Pančevu, Srbija**

### **Detection of organophosphate flame retardants in soil in Pančevo, Serbia**

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Usporivači gorenja su hemikalije koje se koriste u različitim materijalima i opremi (nameštaj, plastika, elektronska oprema, tekstil, poliuretanske pene, premazi itd.) zbog svoje sposobnosti sprečavanja širenja vatre. Ograničenja u korišćenju polibromovanih difenil etara (PBDE) dovela su do povećane upotrebe alternativnih hemikalija, kao što su organofosforni usporivači gorenja (OFR) [1]. Nekoliko hlorovanih OFR je uključeno u Izveštaj EU o proceni rizika: tris (2-hloretil) fosfat (TCEP), tris (2-hlorizopropil) fosfat (TCPP) i tris (1,3-dihlor-2-propil)fosfat (TDCP) [2,3,4]. Pokazano je da TCEP ima kancerogeni i teratogeni efekat na organizme. OFR su detektovani u površinskoj vodi, podzemnoj vodi i kišnici, u snegu, u vazduhu i prašini, kao i u sedimentu [5,6,7]. Međutim, pojava, izvori i putevi degradacije OFR u zemljištu nisu još uvek detaljno ispitani.

U ovom radu su predstavljeni rezultati detekcije OFR u zemljištu u blizini reke Tamiš u Vojvodini, Srbija, kao i u uzorcima površinske vode reke Tamiš u cilju ispitivanja uticaja poplava na koncentracije OFR u zemljištu. Uzorci zemljišta su prikupljeni u blizini reke Tamiš ispred i iza nasipa. Nakon liofilizacije uzorci zemljišta su ekstrahovani 12 h sa 150 mL toluena u Twisselmann ekstratoru, ekstrakti su upareni do suva, rastvoreni u smeši metanol-voda (14:1) i 60 min tretirani u ultrazvučnom kupatilu. Ekstrakti su filtrirani kroz celuloza acetatni membranski filter papir sa porama veličine 0,2 µm. 7 mL ekstrakta je zatim analizirano koristeći mikroekstrakciju čvrste faze (SPME) u kombinaciji sa gasnom hromatografijom-masenom spektrometrijom (GC-MS).

GC 6890N sistem (Agilent Technologies, Santa Clara, CA) je opremljen sa 30 metara HP-5MS kapilarnom kolonom prečnika 250 µm i debljine filma 0,25 µm. Korišćen je GC temperaturni program: početna temperatura 50 °C u trajanju od 2 min, zatim zagrevanje brzinom 5 °C min<sup>-1</sup> do 250 °C, i 15 °C min<sup>-1</sup> od 250 °C do 300 °C, i zadržavanje temperature od 300 °C u trajanju od 1 minut. Detekcija šest organofosfatnih usporivača gorenja, TCPP; TDCP, TCEP, tri (n-butil) fosfata - TnBP, tris (2-butoksietil) fosfata - TBEP, trifenil fosfata - TPP je urađena pomoću elektronske jonizacije i SIM režima rada na MS5973 (Agilent Technologies) [8].

Ukupan organski ugljenik (TOC) je određen na TOC analizatoru (Vario TOC cube, Elementar, Hanau, Nemačka). TOC sadržaj bio je u opsegu od 1.5 do 2.1 %. Koncentracije OFR (srednja vrednost (standardna devijacija) ng g<sup>-1</sup>)

u uzorcima zemljišta bile su 1.0 (0.1)ngg<sup>-1</sup> za TCEP, 0.8 (0.2)ngg<sup>-1</sup> za TCPP i 1.0 (0.2)ngg<sup>-1</sup> za TBEP. Koncentracije TnBP, TPP i TDCP su bile ispod granice detekcije u svim uzorcima zemljišta. S obzirom na to da su OFR detektovani u istim opsezima u uzorcima zemljišta ispred i iza nasipa i da su koncentracije OFR u uzorcima površinske vode reke Tamiš bile ispod granica detekcije, može se zaključiti da plavljenje zemljišta nema uticaja na koncentracije OFR u zemljištu. Rezultati pokazuju da se procesi atmosferske depozicije moraju uzeti u obzir u proceni rizika prisustva OFR u zemljištu, naročito za hlorovane OFR, TCEP i TCPP. Proces suve depozicije OFR u gasovitoj fazi mogu biti značajan izvor TCEP u zemljištu.

Dobijeni rezultati predstavljaju prve podatke analize OFR u zemljištu u Srbiji. Ostali podaci o pojavi OFR u zemljištu prikupljeni iz različitih oblasti (urbanih, ruralnih, udaljenih oblasti) suneophodni za procenu izvora OFR u zemljištu i ispitivanje procesa distribucije OFR između različitih medijuma životne sredine.

### Zahvalnica

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## **Screening and target analysis of endocrine disrupter BPA in the Danube surface water in Novi Sad locality, Serbia**

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Endocrine disrupters (EDs) are xenobiotics, that occur in food and environment and can interfere with specific bioactivity and biochemical species in biosynthesis, metabolism and hormone activities [1,2]. In the last decade, particular attention focuses on bisphenol A (BPA) as an emerging issue of concern in the field of environmental protection.

BPA as industrial chemical is mostly used in the production of polycarbonate plastics and epoxy resins, unsaturated polyester-styrene resins and flame retardants and is widespread in everyday life in a vast range of products such as reusable baby bottles and toys, metallic food and drink cans, electronic equipment, sports safety equipment, dental sealants, etc [2,3,4]. It is noticed that fertility problems (decrease in sperm production), obesity, endocrine dysfunction and increasing carcinogenic risk are the main adverse effects of BPA presence in the environment on human health [1]. The resulting effects of exposure to BPA can be cumulative, irreversible and particularly harmful to fetus and young children due to the lack of feedback hormones regulation [2].

Bisphenol A is on the NORMAN list of the emerging substances and is also on the list of substances for further investigation of their endocrine adverse effects and possible identification as priority or priority hazardous substances according to the European Commission in the field of water policy [5,6]. As part of a screening analysis on water quality of the Danube section near Novi Sad, Serbia a particular attention was focused on BPA in order to evaluate the risk of population to the endocrine disrupter contamination. Generally, there is a lack of the information on the levels and the conditions of EDs in the countries of the Western Balkan region, especially in the surface water.

The Danube surface water samples in Novi Sad surroundings were collected during the period 2011-2012 and analysed by GC-MS. Bisphenol A (BPA) was detected in all surface water samples during the screening and target analysis and this should be of great concern because there is a link between the environmentally relevant low concentrations of EDs and the disease prevalence. High frequency of the detection and presence of BPA in the Danube surface water confirmed the significant anthropogenic impact and pollution of the Danube in the Novi Sad locality, Serbia. Such contamination of the Danube could affect the security of the drinking water supply, since the Drinking Water Treatment Plant of Novi Sad is very close to the river bank. Accordingly, the future investigations will be focused



on seasonal variations of BPA concentrations along the specific sites of the Danube, with the quantitative structure-activity relationships (QSARs) analysis, in order to evaluate the ecotoxicological risk and pollution impact on human health and the environment.

### Acknowledgement

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## Uticaj pH vrednosti na uklanjanje arsena koagulacijom podzemne vode

### Effects of pH on arsenic removal during groundwater coagulation

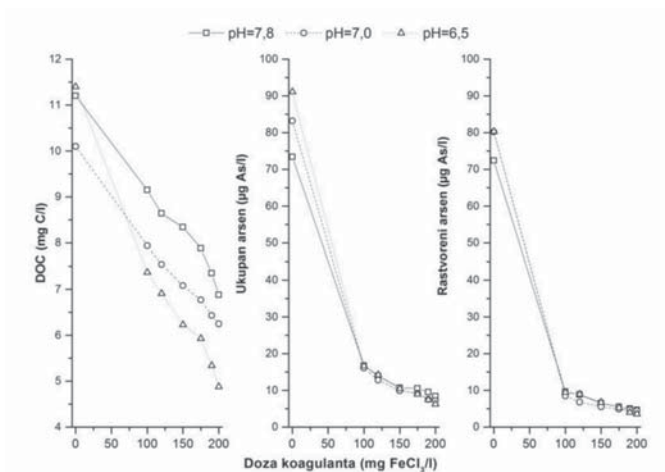
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Arsen je značajan kontaminant različitih medijuma životne sredine i zbog svoje visoke toksičnosti jedan od najvećih problema današnjice. Kontaminacija prirodnih voda arsenom rezultat je kako geohemijskih procesa, tako i antropogenih aktivnosti, a konzumiranje vode za piće glavni put ekspozicije arsenu [1,2]. Toksičnost arsena je uslovljena oblikom u kojem je arsen prisutan, pri čemu su neorganski oblici arsena ( $\text{As}^{\text{III}}$  i  $\text{As}^{\text{V}}$ ) znatno toksičniji od organskih. Arsen je mobilan pri pH vrednostima koje su karakteristične za površinske i podzemne vode (pH 6,5-8,5) i pod oksidacionim i pod redukcionim uslovima [3]. Zbog izrazite mobilnosti i konsekvantne toksičnosti, maksimalno dozvoljena koncentracija arsena u vodi za piće je regulisana na 10  $\mu\text{g/l}$  [4]. Kao odgovor na sve oštrije kriterijume kvaliteta vode za piće, poslednjih godina su istraživanja intenzivirana u cilju poboljšavanja postojećih i razvoja novih tehnologija za što efikasnije uklanjanje arsena. Proces koagulacije identifikovan je kao jedna od najboljih dostupnih tehnologija za uklanjanje arsena u tretmanu vode za piće [5]. Cilj ovog rada bio je da se ispita uticaj pH vrednosti na uklanjanje arsena iz podzemne vode bogate prirodnim organskim materijama tokom procesa koagulacije.

Ispitivanja su sprovedena na podzemnoj vodi sa teritorije srednjeg Banata, koju karakteriše visok sadržaj prirodnih organskih materija, POM ( $10,9 \pm 0,7 \text{ mg/l DOC}$ ) i ukupnog arsena ( $87,2 \pm 5,6 \mu\text{g/l}$ ). Specijacijom u sirovoj vodi rastvorenog arsena ( $76,3 \pm 5,5 \mu\text{g/l}$ ) utvrđeno je prisustvo neorganskih formi ( $38,4 \pm 0,6 \mu\text{g/l As}^{\text{III}}$  i  $24,2 \pm 6,7 \mu\text{g/l As}^{\text{V}}$ ), ali i organski vezanih oblika arsena ( $11,7 \pm 2,1 \mu\text{g/l}$ ). Voda je u laboratorijskim uslovima (*jar test*) koagulisana primenom 100-200 mg  $\text{FeCl}_3/\text{l}$ . Ispitivanja su sprovedena pri različitim pH vrednostima vode (pH=7,8; 7,0 i 6,5). Na slici 1 date su vrednosti sadržaja POM i arsena u vodi koagulisanoj sa  $\text{FeCl}_3$ , u zavisnosti od primenjene doze koagulanta i pH vrednosti. Utvrđeno je da sa porastom doze koagulanta i sniženjem pH vrednosti vode opada sadržaj prirodnih organskih materija (za 18-57% DOC), pri čemu su najbolji rezultati postignuti pri maksimalnoj dozi koagulanta (200 mg/l  $\text{FeCl}_3$ ) i pH vrednosti od 6,5 (rezidualni DOC je iznosio 4,88 mg/l). Dobijeni rezultati u skladu su sa zapažanjima drugih autora [6]. Ukupan sadržaj arsena u koagulisanoj vodi niži je u odnosu na sadržaj u sirovoj vodi za 77-89% (pH=7,8), 81-91% (pH=7,0) i 82-93% (pH=6,5), u zavisnosti od primenjene doze koagulanta. Visoka efikasnost uklanjanja arsena (naročito pri pH=6,5), može se objasniti njegovom interakcijom sa POM i koprecipitacijom sa  $\text{FeCl}_3$ . Rezidualni sadržaj rastvorenog arsena

u koagulisanjoj vodi (3,56-9,63  $\mu\text{g As/l}$ ) niži je od definisanih 10  $\mu\text{g As/l}$  [4], pri svim ispitivanim dozama koagulantata i pH vrednostima. Koagulacijom vode pri pH=6,5 i dozi koagulantata od 200 mg  $\text{FeCl}_3/\text{l}$ , maksimalno je postignuto uklanjanje  $\text{As}^{\text{V}}$  (>99% u odnosu na sadržaj u sirovoj vodi), dok je smanjenje sadržaja  $\text{As}^{\text{III}}$  i organski vezanog arsena iznosilo 66% i 92%, redom.



**Slika 1.** Sadržaj DOC i arsena (ukupnog i rastvorenog) u  $\text{FeCl}_3$  koagulisanjoj vodi u zavisnosti od primenjene doze koagulantata i pH vrednosti

Snižavanjem pH vrednosti vode pre njenog tretmana, poboljšavaju se efekti koagulacije u smanjenju sadržaja POM uz istovremenu koprecipitaciju arsena. Za efikasnije uklanjanje rezidualnog trovalentnog arsena iz vode, potrebno je pre procesa koagulacije primeniti oksidacioni tretman npr. ozonom, hlorom ili nekim drugim oksidacionim sredstvom.

### Zahvalnost

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## Characterization of dissolved organic matter from the Danube river before and after ozone oxidation

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The presence of organic matter can have a great influence on the behaviour of other constituents in water, as well as on treatment efficacy. These molecules can act as proton donors or acceptors and can affect the transport and degradation of various pollutants. Dissolved and suspended organic matter affects the availability of nutrients and serves as a substrate for microbial growth [1]. Most contaminants show different mobilities in aqueous systems, because they interact with organic matter, resulting in greater migration of hydrophobic substances than expected, based on the relationship between their structure and mobility in the aquatic environment [1, 2, 3].

Organic matter can be removed from water using various treatments. Ozonation is often used in combination with other processes, in order to improve their efficiency in the removal of different contaminants and organic matter from water. Ozone reacts mainly with double bonds and aromatic structures. In that way ozone changes the structure of organic matter and enables its efficient removal in water treatment [4, 5].

Data on elemental composition, size and distribution of organic matter, functional groups, hydrophilicity and hydrophobicity, are of great importance when considering the possible interactions between organic matter and other water constituents, as well as for planning appropriate treatments. This data can be obtained using different methods, and one of them is chemical fractionation using resins [6]. This work describes the results of ozonation on the character of dissolved organic matter (DOM) present in Danube river water (Figure 1). For this purpose, resin fractionation using DAX-8 and XAD-4 was employed. The XAD-8 resin favours the isolation of hydrophobics (HPO-A), while XAD-4 resin adsorbs the hydrophilic acid fraction (HPI-A). The hydrophilic non acid fraction (HPI-NA) passes through the resins [7].

Danube river water was sampled during May 2012, and the measured dissolved organic carbon (DOC) content was  $3.66 \pm 0.20$  mg/L. Results show that the DOM present in the Danube river water is mainly of hydrophilic character, with a hydrophilic fraction content of 78% of the total DOC. The hydrophobic fraction accounts for 23% of the total DOC. Ozonation ( $1.5 \text{ mg O}_3 / \text{mg DOC}$ ) removed 22% of the DOM content relative to the raw water. In addition, the DOC structure changed, with increasing polarity and hydrophilic character, and a slight HPO-A content decrease, compared to the raw water.



**Figure 1.** Characterization of DOM from the Danube:  
(a) before and (b) after ozonation

The results are consistent with findings of other authors [8], who reported that as a result of the reaction with ozone, organic matter changes structure, which is reflected in reductions in molecular weight, increasing the number of acidic functional groups and creating more polar compounds.

In future work the influence of ozone oxidation on interactions of organic matter and other constituents of Danube river water will be investigated.

### Acknowledgments

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## Uticaj oksidacije ozonom na promenu sadržaja prirodnih organskih materija u podzemnoj vodi

### Effects of oxidation by ozone on the changes in the natural organic mater content from groundwater

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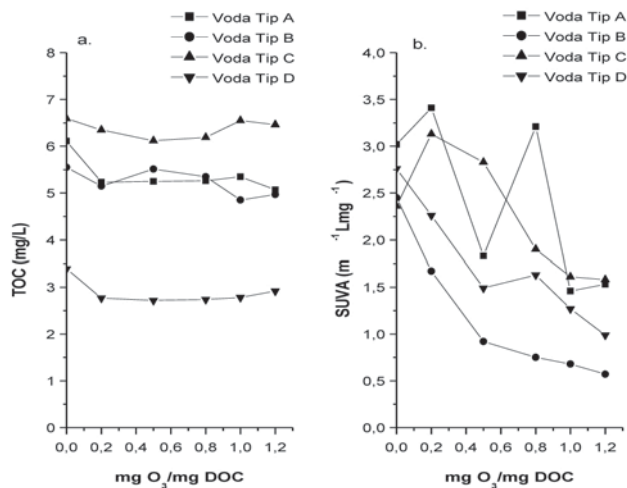
Prirodne organske materije (POM) karakteriše veliki diverzitet organskih molekula huminske i ne-huminske prirode. Hemijske karakteristike prirodnih organskih materija su uslovljene prirodom materijala i biogeochemijskim procesima koji su uključeni u ciklus ugljenika u akvatičnim sistemima, te je njihova struktura specifična za svaki lokalitet [1]. Prisustvo prirodnih organskih materija u vodi može da uzrokuje niz neželjenih problema vezanih za kvalitet vode za piće, a neki od najznačajnijih su: uticaj na organoleptički kvalitet vode, povećanje potrebe za koagulantom i dezinfekcionim sredstvom, što rezultuje povećanjem produkcije otpadnog mulja i formiranjem toksičnih dezinfekcionih nusprodukata, povećanje stepena kompleksiranja metala (npr. arsen) itd.

Veliki problem na teritoriji AP Vojvodine i jedan od najčešćih razloga neprihvatljivog kvaliteta vode za piće jeste prisustvo visokog sadržaja POM u podzemnoj vodi koja se koristi kao resurs vode za piće u ovom regionu. Shodno navedenom problemu, cilj ovog istraživanja bio da se ispituju karakteristike POM podzemne vode sa odabranih lokaliteta u Vojvodini, kao i da se ispita uticaj oksidacije ozonom, kao često primenjivanog oksidanta u tretmanu vode za piće, na promenu sadržaja POM u vodi. Ispitivana je podzemna voda sa teritorije Bačkog Petrovca (Tip A), Kulpina (Tip B), Maglića (Tip C) i Gložana (Tip D).

Sirova voda je ozonirana u laboratorijskim uslovima u staklenoj koloni zapremine 2L, primenom generatora ozona *Argentox* (kapaciteta 1 g/h). Primenjivane su doze ozona u opsegu od 0,2-1,2 mg O<sub>3</sub>/mg DOC. Sadržaj ukupnog i rastvorenog organskog ugljenika (TOC i DOC, redom) analiziran je na aparatu Elementar LiquiTOCII. Sadržaj organskih materija koje apsorbuju UV zračenje na 254 nm određivan je merenjem na UV-1800 Shimadzu spektrofotometru i računata je specifična UV apsorbanција (SUVA).

Rezultati ispitivanja uticaja različitih doza ozona na promenu sadržaja i karakteristike POM, izraženo preko vrednosti TOC i SUVA prikazani su na slici 1. Ispitivane vode međusobno se razlikuju po sadržaju POM, pri čemu vode Tip A-C imaju približno isti sadržaj ukupnog organskog ugljenika (5,55-6,60 mg/L) u odnosu na vodu Tip D (3,39 mg/L). SUVA vrednost (2,37-3,03 L·mg<sup>-1</sup>·m<sup>-1</sup>) ukazuje da je u svim ispitivanim vodama zastupljena smeša i hidrofobnih i hidrofilnih struktura POM. Stepem smanjenja

sadržaja TOC varira u zavisnosti od primenjene doze ozona i tipa vode i iznosi 1-20%, pri čemu je najveća efikasnost procesa pri svim dozama ozona zabeležena za vodu sa najmanjim sadržajem POM (Tip D). Primena ozonizacije je uticala na strukturu i prirodu rezidualnih POM, izraženu preko vrednosti  $UV_{254}$  i SUVA. Sa povećanjem doze ozona u opsegu od 0,20-1,20 mg  $O_3$ /mg DOC mogu se zapaziti skokovite promene SUVA vrednosti, kao posledica naizmeničnog raskidanja dvostrukih veza aromatičnih molekula usled oksidativnog dejstva ozona na molekule POM i formiranja novih struktura koje apsorbuju UV zračenje na ovoj talasnoj dužini. Generalno se može reći da je smanjenje SUVA vrednosti tokom ozonizacije (do 61%) posledica oksidativne transformacije hidrofobne u polarniju hidrofilnu frakciju POM.



**Slika 1.** Uticaj oksidacije ozonom na promenu sadržaja a. TOC i b. SUVA u podzemnoj vodi sa različitih lokaliteta u AP Vojvodini

Na osnovu dobijenih rezultata može se zaključiti da se u zavisnosti od tipa vode razlikuju doze ozona koje je potrebno primeniti za optimalno smanjenje sadržaja POM u vodi. U cilju optimalnog uklanjanja POM i postizanja kvaliteta zdravstveno bezbedne vode za piće, ozonizaciju je kao oksidacioni predtretman neophodno kombinovati sa drugim tehnologijama, kao što su npr. koagulacija/flokulacija i adsorpcija na aktivnom uglju.

### Zahvalnost

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## **Analitička strategija za određivanje niskih koncentracija olova u prisustvu natrijum-hlorita HG-ICP-OES metodom**

## **An analytical strategy for the determination of low level of lead in the presence of sodium chloride by HG-ICP-OES**

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Kako zahtevi analiza postaju sve rigorozniji, vrlo često je neophodno odrediti tragove i ultratragove ciljanih elemenata, a kad je olovo u pitanju, to je često neophodno i od velike važnosti posebno u biološkim i uzorcima životne sredine. Kako bi se rešio problem detekcije olova u tragovima i ultratragovima u različitim uzorcima detekcijom na ICP-OES, pristupljeno je razvijanju metode hidridnog generisanja plumbana,  $PbH_4$ . Ova metoda (HG-ICP-OES) bi pružala veću stopu unošenja analita u sistem, što bi uslovljalo veću osetljivost i tačnost samog merenja, a sa druge strane bi se eliminisale spektralne i matriks interference čiji se uticaj i posledice ogledaju u relativno lošim detekcionim limitima za olovo. Na osnovu dosadašnjih ispitivanja i uz određenu dozu rezerve, određivanje olova na ICP-OES prilikom direktne analize, uvođenjem uzorka klasičnim sistemom koji uključuje koncentrični nebulajzer, daje pouzdane i tačne rezultate pri koncentracijama iznad 20  $\mu g/L$  Pb. Ova tvrdnja se zasniva na gruboj i uopštenoj proceni na osnovu iskustva, jer sam detekcioni limit metode zavisi od matriksa uzorka. Problem predstavlja tačno i precizno detektovati koncentracije ispod te vrednosti.

Poznato je da je prisustvo oksidacionog sredstva ( $K_2Cr_2O_7$ ,  $H_2O_2$ ,  $(NH_4)_2S_2O_8$ ,  $KMnO_4$ ,  $Ce(SO_4)_2$ ,  $KBrO_3$  i  $K_3Fe(CN)_6$ ) u reakcionom sistemu od kritične važnosti kako bi se omogućilo efikasno i brzo generisanje plumbana [1,2]. U odsustvu oksidacionog sredstva pokušaji da se generiše plumban iz Pb(II) vodili su pojavi Pb(0) kao glavnom proizvodu i isuviše niskim prinosima plumbana. [3] Stoga, kao najprihvatljivije rešenje predlagana je njegova oksidacija u Pb(IV) iz kog se najlakše generiše plumban. Međutim, kako je teško održati metastabilni Pb(IV) u rastvoru, dodatak kompleksirajućih sredstava može da pomogne. Detaljnim pregledom literature, kao najefikasniji reagens pokazao se kalijum-heksacijanoferat(III) [4], što je i u praktičnom delu ovog rada dokazano. Ostvareni su jako niski detekcioni limit i ostvarena je široka linearnost kalibracione prave. Pored svojih prednosti jedini nedostatak, ali i najznačajniji je potencijalna toksičnost ovog reagensa kao i njegova kontaminacija tragovima olova koji se pre korišćenje ovog reagensa moraju ukloniti što zahteva dodatne operacije.

U cilju pronalaženja alternativnog sredstva, ispitana je mogućnost primene natrijum-hlorita kao pogodnog reagensa. Nakon optimizacije HG-ICP-OES metoda je primenjena na realnim uzorcima vode kao i na sertifikovanom referentnom uzorku podzemne vode BCR-610. Dobijeni rezultati su upoređeni sa rezultati-



ma dobijenim dvema metodama: DPASV i ICP-MS. Ovaj reagens se pokazao kao efikasniji i sa njim su ostvareni još niži detekcioni limiti olova nego sa do sada uobičajeno primenjivanim  $K_3Fe(CN)_6$ . Prednost natrijum-hlorita u odnosu na  $K_3Fe(CN)_6$  je ta što je reagens mnogo čistiji u smislu kontaminacije olovom i ne zahteva dodatno prečišćavanje. Ovaj reagens se inače upotrebljava kao dezinfekci-ono sredstvo u procesu prečišćavanja voda pa je sa ekološke tačke gledišta mnogo prihvatljiviji od potencijalno toksičnog kalijum-heksacijanoferata(III).

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## Investigation of trace elements in forest soils by BCR sequential extraction method and its transfer to *Macrolepiota procera*

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In this study, soil samples were collected from Kruševac and Trstenik, Serbia in autumn and subjected to the modified Community Bureau of Reference (BCR) sequential extraction procedure in order to investigate the chemical partitioning of metals in soils and to predict heavy metals uptake by mushrooms which grown at the same soils. The soil samples were subjected to a three stage extraction procedure proposed by the BCR. The three phases that were separated out in the following order:

**Table 1.** Modified BCR three stage sequential extraction procedure

Step	Solid phase	Extraction reagents
1	Exchangeable and weak acid soluble fraction	1g of soil sample, 40 ml of 0.11 mol/L CH <sub>3</sub> COOH, shake 16 h, room temperature
2	Reducible fraction	40 ml of 0.5M NH <sub>2</sub> OH·HCl (pH 1.5), shake 16h, room temperature
3	Oxidisable fraction	10 ml of 8.8 H <sub>2</sub> O <sub>2</sub> (pH 2), shake 1 h at 85°C, cool, add 50 ml of 1 M CH <sub>3</sub> COONH <sub>4</sub> (pH 2), shake 16 h room temperature

The analytical accuracy of the method was evaluated by using the Standard Reference Materials (CRM 684 River Sediment Extractable Phosphorus, from Po River, Italy). The mushrooms samples were prepared to analysis using microwave acid digestion procedure. Metal concentrations of soil fractions and mushrooms samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). The following elements were analyzed: As, Al, Ag, Cd, Cu, Cr, Co, Ba, Bi, Mn, Ni, Fe, Se, Pb, Zn, Tl, Ti and Sr. The analytical accuracy of the method was evaluated by using the Standard Reference Materials (TORT-2, lobster hepatopancreas reference material for trace metals). The pseudo-total concentrations of metals in soil were determined after aqua regia digestion. The sum of the metal contents obtained from the modified BCR sequential extraction procedure [1] and pseudo-total metal contents for soil samples were used to calculate recovery values. In order to evaluate the bioavailability of metals, the relationships between the mushrooms metal and soil-extractable metal concentrations were compared.

In this study, the bioaccumulation factor (BAF) was used to estimate the bio-availability of (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, and Pb) in the mushrooms. The bioaccumulation factor is a competent technique developed to assess the level of the metal in the plant as a fraction of the soils total. Also bioaccumulation factors are considered a simple tool to estimate the bioaccumulation of contaminants in a particular organism in a specific medium. It was calculated as the ratio of the element concentration in in the mushrooms (in mg g<sup>-1</sup> dry wt) to the total soil element content (in mg g<sup>-1</sup> dry wt). Also translocation factor was culculated for stalk and cups. Translocation is the process leading to the redistribution of a chemical substance, once it has been deposited on the aerial parts of a plant, to the other parts that have not been contaminated directly. Translocation is important in predicting the contamination of edible parts of those plants that are not consumed whole.

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## Trace and major elements pollution originating from coal ash suspension and transport processes

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In this paper, we have investigated trace and major elements leaching during and immediately after coal ash transport to the dump of the „Kolubara“ power plant in Lazarevac, Serbia. Coal combustion in power plants generates large amounts of ash that is marginally used or, in most cases, stored more or less unprotected in the environment where it can represent a significant source of heavy metals, PAHs and other pollutants [1]. „Kolubara“ power plant is producing  $6-8 \times 10^9$  kg of coal ash annually. Coal ash obtained by combustion in the „Kolubara“ power plant is mixed with water and transported to the dump. Storage of wet coal ash usually protects from wind spreading but decreases the time necessary for leaching of various elements [2]. In order to assess pollution caused by leaching of major and minor elements during ash transport through the pipeline and its storage, samples were subjected to modified sequential extraction.

The total of 60 samples of filter ash as well as the ash from active, currently filled and passive, previously filled cassettes of Kolubara“ power plant were studied. Samples were extracted consecutively with distilled water, 1M ammonium acetate, 0.2 M ammonium oxalate/0.2 M oxalic acid, acidic solution of  $H_2O_2$  and a 6 M solution of HCl. Concentrations of the elements in the extracts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Correlation analysis and two multivariate analysis methods (principal component analysis and cluster analysis) were carried out in order to provide better understanding of the nature of associations of trace elements with substrates. Principal component analysis (PCA) have been performed by the means of PLS ToolBox, v.6.2.1, for MATLAB 7.12.0 (R2011a). PCA was carried out as an exploratory data analysis by using a singular value decomposition algorithm (SVD) and a 0.95 confidence level for Q and T2 Hotelling limits for outliers. Using only a limited number of principal components (PCs), the dimensionality of the retention data space was reduced, further analysis simplified, and the parameters were grouped according to similarities. Descriptive statistics and Kruskal Wallis one-way analysis of variance by ranks test have been performed by the means of a demo version of NCSS statistical software. All data were pre-treated (mean centered and scaled to the unit standard deviation) before any statistical operations in order to prevent highly abundant components to dominate in the final result over the components present in much smaller quantities.

First phase of the extraction is characterized with high amount of Mg, especially in active cassette. Samples from passive cassettes have a higher content of Mg compared to samples from filter fly ash. Magnesium is also extracted in

fifth phase in similar amount, but with a highest content in samples from filter fly ash. First phase is specific by high amount of Ni extracted from samples in active cassettes. In all other extraction procedures Ni is present only in a very small amount in samples from passive cassettes. Calcium is extracted only in fifth phase, with high amount in samples from filter fly ash and active cassettes. The highest content of Al is detected after third extraction, in equal amount in samples from all cassettes. Significant amount of this element is also found after fifth extraction, especially in samples from filter fly ash and active cassettes, after fourth extraction, in all extracts and after second extraction, in samples from passive cassette, especially from first depth. Also, it was found a significant amount of As in samples from active cassettes after first three extraction procedures, particularly after third extraction.

It can be concluded that zinc, nickel and chromium are released during the ash transport and arsenic is released continuously. On the contrary, these elements, as well as chromium, become concentrated during coal ash transport. Adsorbed portions of calcium, Mg and K are also leaching during coal ash transport.

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## **Uklanjanje olova i kadmijuma iz otpadnih voda pomoću višeslojnih ugljeničnih nanocevi modifikovanih amino-polietilen glikolom**

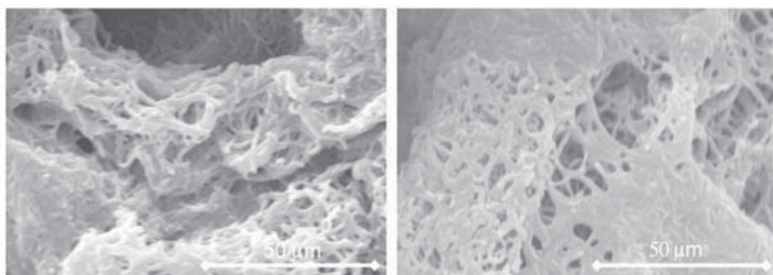
### **Removal of lead and cadmium from wastewater by amino polyethylene glycol modified multi-walled carbon nanotubes**

Zlate S. Veličković<sup>1</sup>, Zoran J. Bajić, Aleksandar D. Marinković,  
Radovan Karkalić, Dalibor Jovanović, Ljubomir Gigović

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Zagađenje vode teškim metalima se javlja kao posledica prirodnih procesa i ljudskih aktivnosti. Sagorevanje fosilnih goriva, topljenje ruda, ispusti gradske kanalizacije i industrijskih otpadnih voda, rudarske aktivnosti, deponije i prirodni geohemijski procesi predstavljaju izvore zagađujućih materija [1, 2]. Bez obzira na poreklo izvora teški metali se lako šire u vodenom sistemu i teže da se akumuliraju u živim organizmima, usled čega dolazi do raznih oboljenja kod čoveka i poremećaja u ekosistemu [1].

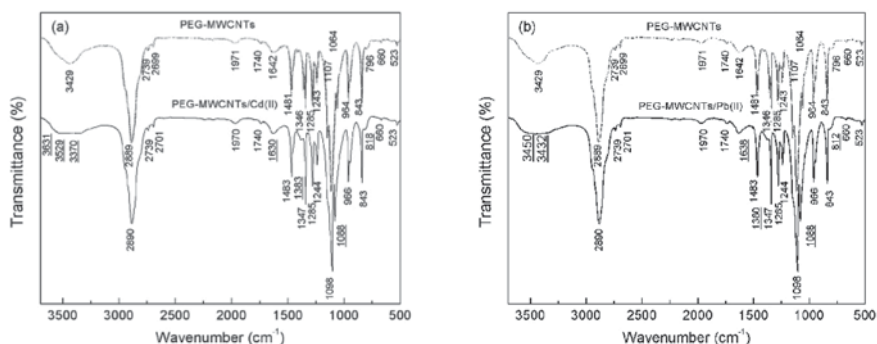
U toku ovog istraživanja izvršena je funkcionalizacija višeslojnih ugljeničnih nanocevi (MWCNTs) pomoću 6-amino-polietilenglikola (PEG) po objavljenom postupku [2] i ispitana je mogućnost novog, sintetisanog adsorbenta (MWCNTs-PEG) za uklanjanje Cd(II) i Pb(II) iz vodenih rastvora. Sintetisani adsorbent je okarakterisan tehnikama: SEM (Slika 1.), FTIR (Slika 2.), TGA i ispitana su njegova fizička svojstva (BET površina, Zeta potencijal, tačka nultog naelektrisanja).



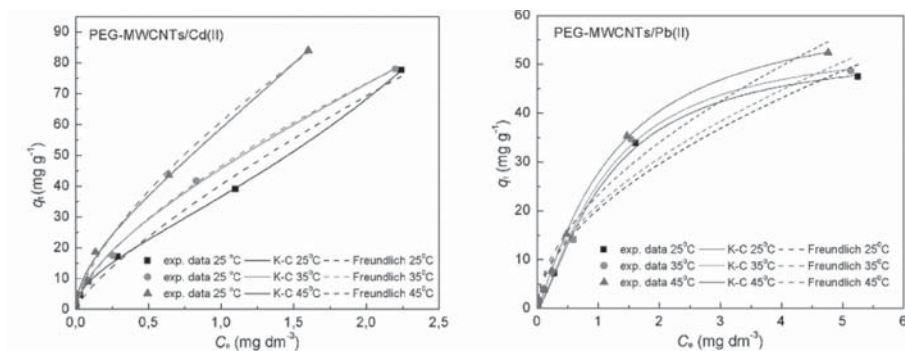
**Slika 1.** SEM fotografije PEG-MWCNTs.

Ispitivanje je vršeno u šaržnom sistemu, serijama eksperimenata gde je ispitivan: uticaj vremena kontakta, pH vrednosti, koncentracije metala u rastvoru i temperature na adsorpciju jona metala na PEG-MWCNTs.

Adsorpcija Cd(II) i Pb(II) na PEG-MWCNTs pokazuje jaku zavisnost od pH vrednosti rastvora. Zavisnost adsorpcije od vremena kontakta može se opisati Weber-Morisovim kinetičkim modelom, dok adsorpcija pokazuje najbolje slaganje sa modelom Koble-Koriganove izoterme (Slika 3.).



**Slika 2.** FTIR spektar PEG-MWCNTs, pre i posle adsorpcije Cd(II) i Pb(II) ( $m/v = 100 \text{ mg dm}^{-3}$ ,  $T = 25^\circ\text{C}$ ,  $C_0 = 10 \text{ mg dm}^{-3}$  na pH 8 (Cd) i pH 6 (Pb).



**Slika 3.** Adsorpcione izoterme (Freundlichova i Koble-Corriganova ) za Cd(II) i Pb(II) na PEG-MWCNTs, na 25, 35 i 45 °C. ( $C_0 = 0,10, 0,20, 0,50, 1,0, 2,0, 5,0$  i  $10,0 \text{ mg dm}^{-3}$ ,  $m/V = 100 \text{ mg dm}^{-3}$ , pH=8 za Cd i pH=6 za Pb ).

Termodinamički parametri pokazali su da je adsorpcija Cd(II) i Pb(II) spontana i endotermna. Maksimalni adsorpcioni kapacitet PEG-MWCNTs pri početnoj koncentraciji od  $10 \text{ mg dm}^{-3}$ , ( $T = 25^\circ\text{C}$ , pH = 8 za Cd(II) i pH=6 za Pb(II)) je  $77,6 \text{ mg g}^{-1}$  za kadmijuma i  $47,5 \text{ mg g}^{-1}$  za olovo, što ukazuje da se ovaj adsorbent može koristiti za uklanjanje ovih jona iz otpadnih voda.

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## Degradacija trihloretilena hidrodinamičkom kavitacijom

### Degradation of trichloroethylene by hydrodynamic cavitation

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Kavitacija je formiranje, rast i implozivni kolaps gasom ili parom ispunjenih mehurova u tečnom medijumu [1].

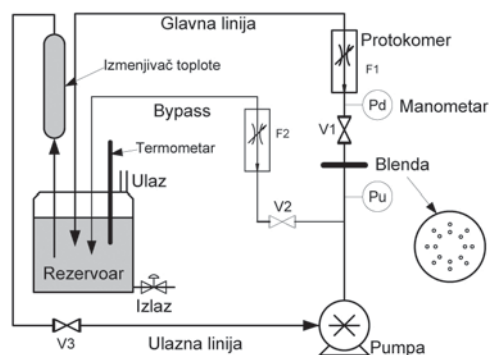
Kolaps mehurova generiše ekstremnu energiju (temperature od oko 10000 °C i pritiske od 50 do 100 MPa unutar mehurova [2]) za hemijske i mehaničke efekte.

Ugljentetrahlorid, hloroform i trihloroetilen su među najrasprostranjenijim zagađujućim materijama u površinskim i podzemnim vodama.

Imajući to u vidu, u ovom radu ispitana je mogućnost degradacije trihloroetilena u vodenim rastvorima koncentracije od 0,1 do 4,0 mmol/L postupkom hidrodinamičke kavitacije.

Degradacija vodenih rastvora trihloroetilena vršena je na hidrodinamičkim kavitatorima sa otvorima [3].

Na slici 1 prikazana je šema hidrodinamičkog kavitatora sa otvorima.



Slika 1. Šema hidrodinamičkog kavitatora

Ispitan je uticaj: ulaznog pritiska rastvora trihloroetilena, polazne koncentracije rastvora ( $C_0$ ), temperature rastvora i vreme interakcije na stepen degradacije trihloretilena i sadržaj hlorida u dobijenom rastvoru.

Koncentracije trihloroetilena u polaznim i dobijenim rastvorima određivan je gasno hromatografskom metodom (headspace, HP 5890 series II, FID). Koncentracija  $Cl^-$  jona u rastvoru određivana je spektrofotometrijski (UV mini 1240, Shimadzu).



Na osnovu dobijenih rezultata utvrđeno je da:

- a) Hidrodinamička kavitacije efikasno, u roku od 20 minuta, u potpunosti degradiše trihloroetilen iz vodenih rastvora.
- b) Koncentracije trihloroetilen u rastvoru, na konstantnoj temperaturi, eksponencijalno opada sa produženjem trajanja kavitacije.
- c) Koncentracije  $Cl^-$ , na konstantnoj temperaturi, linearно raste sa porastom vremena kavitacije.
- d) Brzina degradacije, na određenoj  $C_0$ , raste sa povećanjem temperature rastvora.
- e) Brzina degradacije, na određenoj temperaturi, raste sa povećanjem  $C_0$ .
- f) Postoji optimalan ulazni pritisak rastvora u kavitator za postizanje maksimalnog stepena degradacije na određenoj temperaturi.

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## **Target analysis of priority WFD and emerging contaminants in the Danube River near Novi Sad**

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As second largest Europe's river, Danube River and related groundwater aquifers represent an important source of drinking water for about twenty million people from ten European countries. On the other hand, discharging of municipal and industrial wastewater, in some cases without any water treatment, directly into the Danube is not uncommon. Since previous studies conducted by International Commission for the Protection of the Danube River (ICPDR) have established the presence of numerous toxic chemicals including detergents, pharmaceuticals, pesticide residues, perfluorinated substances, personal care products chemicals, heavy metals and microbial pollution in the Serbian part of the Danube River, the urgent need of precise monitoring of the Danube surface water is emphasized [1].

In order to assess the quality of drinking water in Novi Sad, the Danube surface water was analyzed in detail. The water samples were collected during the two campaigns in July and September 2012 covering summer and autumn periods at five different localities. The location of sample points were selected to cover most factors that could influence Danube water contamination, such as site Ribarac (upstream of the city Novi Sad) to monitor incoming pollutants, sites Beogradski kej (situated in the urban area) and Ratno Ostrvo to monitor municipal contaminants and pollutants coming from industrial zone where oil refinery is situated, and finally, sites 100 m after each discharges to monitor effects of dilution and overall contamination of surface water. The sampling at all selected localities has been conducted under equal hydrometeorological conditions. Compounds for target analysis were selected based on the previous screening analysis [2, 3] and polyaromatic hydrocarbons (PAHs), organic pesticides, polychlorinated biphenyls (PCBs) and phenol derivatives have been included in the list.

Organic pesticides (p, p'-DDE, p,p'-DDD and dieldrin) were detected only in the samples collected in June, due to the households, farms and extensive agricultural activities in the beginning of the summer season. Increased concentration of p,p'-DDD could be the consequence of uncontrolled usage of this chemical as pesticide in East European countries. It should be noticed that the results for concentration levels of DDT and its metabolites in surface water of Danube corresponds with the previously obtained results of the surface water quality (Serbian Environmental Agency, 2011).

Identified PCBs in the surface water at sampling site Ratno ostro could originate either from oil refinery or from thermal-power plant TE-TO situated in its vicinity. However, the results of the surface water quality published by the Serbian Environmental Agency in 2011 show that PCBs were detected in sediments of the Danube in the vicinity of Novi Sad. Therefore, it can be concluded that detected PCBs were desorbed from sediments.

Detection of di-(ethylhexyl)-phthalate and 1,2-benzothiazole at the sampling point Ribarac indicates incoming pollution from other European countries. Di-(ethylhexyl)-phthalate belongs to the most common phthalate plasticizers, due to its suitable properties and low cost. It is widely used in manufacturing of products made of PVC. It is also applied as hydraulic fluid and as a dielectric fluid in capacitors, as solvent in glow sticks and as plasticizer in medical devices. 1,2-benzothiazole enter the environment from a number of sources such as the leaching of rubber products, fine particles of automobile tires, and antifreeze, and also it is gaining in popularity in the wood and leather industries.

Increased concentrations of PAHs (fluorine, phenanthrene, anthracene, chrysene), phthalates, and phenol compounds were detected in the samples collected at site Beogradski kej. PAHs are primary generated from combustion processes and could be transported by the wind from the thermal and power plant. In general, fluoranthene is an indicator of less efficient or lower-temperature combustion, since non-alternant PAHs are less preferred in formation than alternant PAHs. Detection of anthracene indicates presence of phenanthrene as its common impurity. The source of anthracene could be small house appliances waste, since it is used as semiconductor, wood preservative, coating material and insecticide.

Considering the samples collected 100 meters downstream of discharges, the dilution effect was observed, however the content of some phenol compounds was still above the Predicted No Effect Concentrations, and could cause adverse effects.

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## Photocatalytic degradation of Rhodamine B using pure and Fe-doped TiO<sub>2</sub> nanoparticles

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Jadranka Kuljanin-Jakovljević, Mirjana Čomor

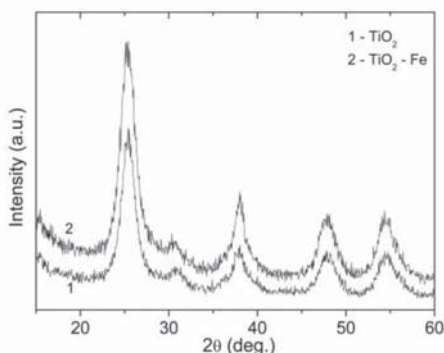
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Titanium-dioxide, as biological and chemically stable, non-toxic, highly efficient and non-expensive photocatalyst has been widely used for water and air purification. However, since its band-gap energy value is high (3.0 for rutile and 3.2 eV for anatase) UV light must be used for its activation. UV light makes just 5% of sun-light, so it is necessary to manipulate with band-gap of TiO<sub>2</sub> in such a way to move its spectral response towards vis part of the spectra. Established way for achieving this goal is doping of TiO<sub>2</sub> host with metal ions. Since ionic radius of Fe<sup>3+</sup> ion (0.64Å) is very similar to that of Ti<sup>4+</sup> ion (0.68Å) [1], it can be expected that this ion will be easily incorporated in TiO<sub>2</sub> matrix. Additionally, doping TiO<sub>2</sub> with Fe<sup>3+</sup> is an effective approach to reduce electron-hole recombination rate and increase photocatalytic efficiency in terms of its semi-full electronic configuration [2]. Nevertheless, ability of preventing charge recombination strongly depends on Fe<sup>3+</sup> ion concentration, since above certain amount, dopant ions, become recombination centers. It is necessary to evaluate optimal percentage of Fe<sup>3+</sup> ions that must be incorporated in TiO<sub>2</sub> host in order to achieve both positive effects.

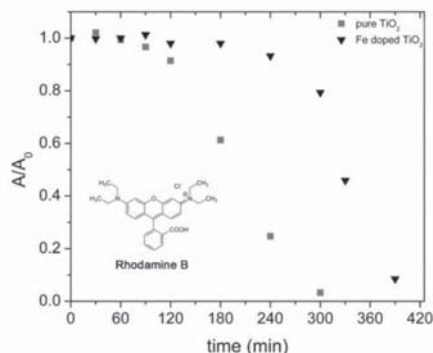
Here, we present our preliminary results in estimation of this value. We have used slightly modified synthetic procedure previously established by Wang et al. [3]. Both, pure and Fe - doped (2.5 wt.%) samples are synthesized and their structure is characterized by X-ray diffraction (Fig. 1.). Both samples have predominantly anatase crystal structure with small additional content of brookite phase (shoulder at 30.8°). XRD of doped sample have shown that there are no traces of iron oxide or ilmenite, or some other iron-containing impurity.

Reflectance spectra (not presented) have confirmed that spectral response of doped sample is moved towards visible spectral region. By applying Kubelka-Munk method on obtained spectra, it was estimated that band – gap energy on undoped sample is about 3.0 eV, while that of Fe-doped is about 2.3 eV.

In order to examine photocatalytic activity of obtained samples, we have tracked photocatalytic degradation of organic dye Rhodamine B (RB) (inset in Fig. 2.) in the presence of pure and doped TiO<sub>2</sub>. In a typical procedure, 20mg of catalyst was suspended in 20ml of RB water solution (5x10<sup>-5</sup> M).



**Figure 1.** XRD patterns of pure and Fe-doped  $\text{TiO}_2$



**Figure 2.** Kinetic plots of the degradation of RB in the presence of pure and doped  $\text{TiO}_2$  nanoparticles.

The suspension was constantly purged with  $\text{O}_2$  and magnetically stirred for one hour to establish the adsorption-desorption equilibrium of the dye on the catalyst surface, and then irradiated using visible-light lamp. Aliquots (1ml) were periodically collected during 270 min (pure  $\text{TiO}_2$ ) or 390 min ( $\text{Fe-TiO}_2$ ) and then were centrifuged in order to separate photocatalyst from supernatant. Subsequently, absorbance spectra of obtained samples were measured. Absorbance intensity ratios  $A/A_0$ , (where  $A_0$  is absorbance at zero time and  $A$  is absorbance at a time  $t$  of irradiation, at 549 nm which is absorption maximum wavelength of Rhodamine B) were plotted as a function of irradiation time (Fig. 2). It was estimated that undoped  $\text{TiO}_2$  has higher photocatalytic activity then doped one.

As we have mentioned earlier, reason could be too high content of Fe ions, which can serve as recombination centers for photogenerated carriers. Our future work will be directed towards estimation of proper content of Fe-ions in  $\text{TiO}_2$  host, by which balance between activity in visible part of the spectra and prevention of charge-carrier recombination can be achieved.

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## **Rezidue DDT, DDD i DDE u uzorcima humanog mleka i krvi pupčanika na teritoriji pokrajine Vojvodine**

### **DDT, DDD and DDE residues in human milk and umbilical cord blood in Vojvodina region**

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Kontrolisana i nekontrolisana upotreba i upravljanje organohlornim pesticidima (OCP) rezultirala je značajnim stepenom kontaminacije velikog broja biotskih i abiotskih matriksa u životnom okruženju. OCP predstavljaju sintetizovanu grupu ubikvitarnih toksičnih jedinjenja čije rezidue imaju negativan uticaj na zdravstveni status živih organizama. DDT i njegovi metaboliti spadaju u grupu OC insekticida sa vremenom poluživota u zemljištu od 22 dana do 30 godina, zavisno od sastava zemljišta, prisustva mikrobioloških vrsta, klimatskih uslova i drugih faktora. Molekuli date grupe jedinjenja donekle mogu da „imitiraju” estrogene, pokazujući afinitet za pojedine hormonske receptore i na taj način narušavaju hormonsku ravnotežu organizma. Iz navedenih razloga ukupni DDT se svrstava u supstance koje remete rad endokrinog sistema. Usled izražene postojanost, hemijske stabilnosti, lipofilnosti, niskog stepena biotransformacije i degradacije u svim medijumima živote sredine, OCP deluju na reprodukciju i razvoj biote (smanjenje fertiliteta), imaju imunotoksične (imunosupresivno dejstvo i razvoj autoimunih bolesti) i karcinogene efekte. Posebno su osetljivi fetus, čija je ekspozicija u materici, i dojena odojčadi koji su izloženi relativno visokim nivoima organohlornih pesticida tokom kritičnog perioda organogeneze i razvoja.

Najčešći izvor ekspozicije čoveka organohlornim pesticidima su vazduh, hrana i voda. Humano mleko predstavlja visoko lipofilnu biološku tečnost koja sadrži komponente prisutne i u masnom tkivu, te su koncentracije OCP u humanom mleku reprezentativni pokazatelji njihovih nivoa u plazmi, lipidnom serumu i masnom tkivu. Iz tog razloga koncentracioni nivoi kontaminiranog mleka reflektuju opterećenje i toksikološki status čitavog organizma i mogu se uzeti kao indikatori globalne izloženosti humane populacije [1]. Uzorkovanje humanog mleka i krvi pupčanika ne predstavlja invazivnu metodu što joj daje izuzetnu prednost nad ostalim metodama uzorkovanja humanog materijala, neophodnim za ocenu sveobuhvatne humane ekspozicije. Kontinualni monitoring pre- i postnatalne izloženosti novorođenčadi, kao biološki najosetljivijih na delovanje OC jedinjenja, na području grada Novog Sada i Vojvodine do sada nije rađen.

Tokom istraživanja prikazanog u radu, u periodu od jula do oktobra 2012. godine, paralelno su prikupljeni uzorci krvi iz pupčanika i ranog humanog mleka (kolostruma) od 20 zdravih trudnica starosti između 20 i 39 godina, sa teritorije Vojvodine. Uzorci krvi uzeti su za vreme porođaja, dok je kolostrum prikupljen tokom prvih par dana laktacije. Svi uzorci su analizirani na sadržaj DDT, DDD i DDE gasnim hromatografom VARIAN CP-3380 (Varian, Australija), sa detektorom elektronskog zahvata (ECD 63Ni) na kapilarnoj koloni ZB-1 (Phenomenex, USA) 30 m dužine, promera 0,25 mm i veličinom čestica filma od 0,25  $\mu$ m.

Ukupni koncentracioni nivoi DDT i metabolita u uzorcima humanog mleka kretali su se u opsegu od 50 do 302 ng/g<sub>lipidne faze</sub> (mediana: 92.5, aritmetička sredina $\pm$ standardna devijacija: 110.8 $\pm$ 58.13288). U svim analiziranim uzorcima krvi iz pupčanika, ukupne koncentracije DDT i njegovih metabolita bile su ispod limita detekcije (<0.5 ng/g<sub>lipidne faze</sub>). Dominantan doprinos toksikološkom opterećenju humanog mleka, u svim prikupljenim uzorcima, primarno je imao DDE metabolit, sa koncentracijama od 50 do 279 ng/g<sub>lipidne faze</sub> (mediana: 92.5, aritmetička sredina $\pm$ standardna devijacija: 108.15 $\pm$ 54.01391). Rezidue DDD metabolita kvantifikovane su u 50% analiziranog humanog materijala, sa koncentracijama 20 do 40 puta manjim od koncentracija DDE u istim uzorcima. Sam DDT detektovan je samo u jednom uzorku humanog mleka, sa nivoom od 15 ng/g<sub>lipidne faze</sub>. Analizom dobijenih rezultata, utvrđeno je da stepen kontaminacije humanog mleka raste sa godinama starosti majki donora, i opada tokom perioda hospitalizacije. Značajna korelacija između težine bebe na porođaju i stepena kontaminacije humanog mleka nije utvrđena.

Rezultati sprovedenih simultanih istraživanja kontaminacije humanog mleka i krvi iz pupčane vrpce primenom visoko-sofisticiranih metoda, jedinih na teritoriji Novog Sada/Vojvodine/Srbije, koja su odobrena od strane Etičkog odbora Kliničkog centra Vojvodine, ukazuju na kontaminaciju humanog mleka organohlornim kontaminantima, što zahteva dalja sistematska i kontinualna istraživanja prisustva navedene grupe kancerogenih, mutagenih i teratogenih jedinjenja u humanom materijalu.

### Zahvalnica

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## Environmental situation-actual and required bonitet of the river Ibar

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### Abstract

Monitoring of the environmental pollution inevitably encompasses monitoring and water resources quality classification. Quality control of the surface waters with actual national regulation implies the enforcement of the Regulation on Watercourse Categorization. Water resources are classified into four categories and required classes of water quality are defined at given watercourse segments. Surface water, according to threshold values of quality indicators, is classified into class I, II, IIA, IIB, III, IV and NC (not classified). Categorization is done based on the following indicators: dissolved oxygen, percentage of oxygen saturation, BOD-5, HPK, degree of saprobity, the most possible number of coliform bacteria, suspended matter, dry residue of filtered water, pH, visible waste matter, color and odor [1].

River Ibar springs under the mountain Hajla in Montenegro, 20 km downstream from Rozaje enters to the territory of the Republic of Serbia and flows to Kraljevo where flows into the West Morava. Ibar, with a total length of 276 km, is the largest and the most important tributary of the West Morava, with natural surrounding drainage area of 8060 km<sup>2</sup> [2]. This paper presents comparatively analysis of actual and required bonitet class along watercourse of the river Ibar using monitoring results of water quality from the Republic Hydrometeorological Service of Serbia (RHSS) for year 2011 [3]. Defined quality of the river Ibar watercourse is I, IIB, IIB, IIA and IIA class of bonitet at five profiles: Batrage, Rudnica, Raska, Usce and Kraljevo, respectively. Determined disproportion between actual and required class of water quality is the real evaluation of environmental condition.

Analysis of parameters, water quality indicators at all profiles shows that the values of suspended matter corresponded to II, IV and NC, while measured pH value belonged to III and IV class. Increased values of nitrite nitrogen in certain series at measuring stations Rudnica, Raska, Usce and Kraljevo determine II/IV class; presence of harmful and dangerous substances is registered at profile Raska with values of phenol index within III/IV class. Saprobiotic testing of phytobenthos show that watercourse is burdened by moderate organic pollution and bio-indicators of  $\beta$  and  $\alpha$ -mesosaprobic zone prevail. According to the categorization, the obtained values for of saprobity index correspond to class II of water quality. Concentrations of primary nutrients in the water at the profile Batrage corresponded to class II water qua-



lity, except concentrations of total phosphorus which exceeded the threshold values of class II. Table 1 shows belonging of parameters to relevant water class according to results of monitoring of water quality of the river Ibar at determined measuring stations. In such way, environmental situation is expressed in real time and space according to degree of pollution of water resource as its important segment.

**Table 1.** Bonitet class of water quality along watercourse of the river Ibar

Number	Measuring station	River	Dissolved oxygen	Percent of oxygen saturation	BOD-5	HPK	Degree of saprobic	The most probable num. of coli bacteria	Suspended solids	Dry residue filtered water	pH	Visible waste materials	Color	Odor	The actual class	The required class
1.	Batrage	Ibar	I	II	II	I	II	II	VK	I	IV	I	I	I	II/III	I
2.	Rudnica	Ibar	I	II	II	I	II	III	III	II	IV	I	I	I	III/IV	IIB
3.	Raska	Ibar	II	II	II	I	II	IV	IV	II	-	I	III	I	III	IIB
4.	Usce	Ibar	I	II	II	I	II	III	IV	II	IV	I	I	I	III	IIA
5.	Kraljevo	Ibar	I	II	II	I	II	II	IV	I	III	I	I	I	III	IIA

Preservation of bonitet class stipulated by law, as environmental performance of watercourse, is reliable indicator of natural environment protection. Determined water quality at monitored measuring stations is: Batrage-II/III, Rudnica-III/IV, Raska-III, Usce-III and Kraljevo-III bonitet class, therefore the actual water quality deviates from required bonitet of the river Ibar and indicates the environmental pollution.

## Keywords

Environment, bonitet, the river Ibar

## Acknowledgement

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## **Polybrominated diphenyl ethers as a new group of environmental pollutants**

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In recent years considerable attention is paid to the group of brominated flame retardants (BFRs), which show an inhibitory effect on the ignition of combustible organic materials. Many different BFRs have been developed and several of them have been produced synthetically [1]. The most important compounds of this type are polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and brominated cyclic hydrocarbons. BFRs have been used for a long time - pentaBDE (which is not manufactured anymore) as the first BFR was commercialized in the 1950s. The environmental importance of these compounds is caused by the fact that they could be released from the consumer products during their normal use, together with their toxicity, environmental persistence and ability of bioaccumulation [2-4].

In this study the pollution of small ecosystem by brominated flame retardants was addressed. The breeding ponds near the village Záhlinice in Central Moravia (Czech Republic) were selected as model locality. The main goal was the evaluation of the level of contamination in fish and birds as two consecutive segments of food chain. 17 pieces of small and larger fish (10 species) and 14 birds (4 species) were caught and the levels of BDEs in individual tissues were analysed after homogenization with anhydrous Na<sub>2</sub>SO<sub>4</sub> using pressurized solvent extraction. The extracts were cleaned-up by column chromatography on florisil and alumina treated by concentrated sulphuric acid and analysed by GC-ECD. Ten various PBDEs (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-118, BDE-153, BDE-154, BDE-183) were targeted.

The highest level of sum of 10 PBDEs was found in skin of catfish (57.6 µg.kg<sup>-1</sup>) and in its muscle tissue (84.7 µg.kg<sup>-1</sup>) the lowest levels showed pike (12.3 µg.kg<sup>-1</sup> of muscle tissue) and crucian carp (11.3 µg.kg<sup>-1</sup> of skin). The content of PBDEs in fish tissues was found to be greatly influenced by various factors like fat content, fish age and food composition. BDE-47 and BDE-28 were most often found in highest levels.

The levels in bird tissues were highly variable. Cormorant showed the lowest level of contamination (sum of 10 PBDEs was between 38.2 and 77.7 µg.kg<sup>-1</sup>). These levels were detected only in tissues of 3 out of 5 individuals. This low level contamination could be caused by the high mobility of this species. Substantially higher levels were found in tissues of heron (from 52.4 to 501.2 µg.kg<sup>-1</sup> in liver, from 31.3 to 549.3 µg.kg<sup>-1</sup> in muscles, from 71.9 to 289.2 µg.kg<sup>-1</sup> in heart and kidney tissue). Each of congeners No. 3, 47, 100, 153 and 154 contributed at least

by 14%, BDEs 28 and 118 were not detected in any sample. Quite high levels of PBDEs were also found in tissues of Rough-legged buzzard (183.9  $\mu\text{g.kg}^{-1}$  in liver tissue, 132.2  $\mu\text{g.kg}^{-1}$  in muscle) and in Common buzzard (from 66 to 285.9  $\mu\text{g.kg}^{-1}$  in liver tissue, from 51.1 to 66  $\mu\text{g.kg}^{-1}$  in muscle, from 45.1 to 308.9  $\mu\text{g.kg}^{-1}$  in heart and kidney tissue).

The obtained results confirmed the assumption that with increasing trophic level the contamination by PBDEs increases due to biomagnification processes.

As the probable source of contamination two industrial facilities close to the model locality were assessed. The first one is the Fatra Company, which is one of the biggest processors of plastics (PVC, PE, PP and PET) in Central Europe and holds a significant share in the plastics industry in the Czech Republic (in 2011, the company's turnover amounted to nearly  $2.7 \times 10^9$  CZK). The second possible source is the Metalšrot Company in Tlumacov, dealing with scrap iron and non-ferrous metals, their processing and subsequent sale of treated scrap and non-ferrous metals.

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## Environmental problems connected with fire-fighting

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Nowadays, a variety of new materials making human life more comfortable is currently being developed and put into use. These materials often show high flammability, and many toxic products like PAHs, PCDDs, PCDFs, CO etc. are released during their combustion in case of fire. Moreover, extinguishing by water is usually ineffective in these cases, as well as in the case of crude oil based products which are also widely transported and used. The above mentioned facts are the reasons of increasing use of foam extinguishing agents.

The first aim of our study was application of ecotoxicological tests for estimation of environmental risk caused by the waste after the fire was extinguished. The second aim was evaluation of the ecotoxicological impact of foam based fire extinguishing agents. Matrices from the fire places sampled by firemen were tested using the methods defined in the Czech legislation concerning waste management. Ecotoxicity (one of the hazardous waste properties labelled H-14) of solid waste is determined on the basis of ecotoxicological values obtained by testing aqueous leachates on followed organisms: water flea *Daphnia magna* (crustaceans), white mustard *Sinapis alba*, Rosopsida freshwater fish *Brachydanio rerio* Hamilton-Buchanan (Teleostei, Cyprinidae), freshwater algae *Desmodesmus subspicatus* and *Pseudokirchneriella subcapitata*. Limit value of LC (EC, IC)50 for declaration of ecotoxicity properties is  $\leq 10 \text{ ml} \cdot \text{L}^{-1}$  for the most sensitive of above mentioned organisms [1,2]. Thus the water leachates of samples from fire places were prepared and subjected to ecotoxicological testing. The two standard and three alternative tests were conducted on some terrestrial and aquatic organisms (dicotyledon terrestrial plant *Sinapis alba*, monocotyledon aquatic plant *Lemna* sp., freshwater crustacean *Daphnia magna*, *Thamnocephalus platyurus* and *Artemia salina*). The other testing organism was monocotyledon terrestrial plant *Allium cepa*. Samples which were ecotoxicologically evaluated came from following fire place; I-Illegal dump, II Wooden garden building, IIIA Textil market, IIIB-textil market sampled up from the hard watertight asphalt surface, IV- Garden building. In fact all tested matrices indicated small ecotoxicity for aquatic ecosystem. It wasn't possible to evaluate ecotoxicological values of LC, EC, IC 50 for most of the sample (except IIIB and IV). Only sample IIIB exhibit dangerous property H-14 ecotoxicity. Value of 48hEC50 calculated for *Daphnia magna* was  $1.88 \text{ ml L}^{-1}$ . This sample was taken from the watertight asphalt surface. The water leachate of this sample fumed – the residual amount of extinguishing agent could be the explanation of higher ecotoxicity of this sample.

Within the second objective of our work we at first tried to find out some ecotoxicological information concerning foam extinguishing agents. Following the

Regulation REACH till 2020 it should be ensured that within the territory of the European Community only chemical substances and preparations with known hazardous properties will be produced and imported and that their production, use and elimination will be safe. In fact information about hazard of the modern foam extinguishing agents to the environment (ecotoxicity) which should be a part of safety data sheet of these agents is rare or is completely absent.

Concentrates of foam extinguishing agents which are most often applied in cases of fire in the Czech Republic were obtained from Fire Rescue Unit in South Moravian region as follows: Sthamex F-15, Expyrol F-15, Mousol APS F-15, Finiflam F-15 and Pyrocool B. In our study 3-5% solution in water as effective working concentration of extinguishing agent were tested. Since surfactants have a negative impact mainly on aquatic ecosystem predominantly the ecotoxicity on aquatic organisms was tested using following organisms: *Thamnocephalus platyurus*, *Daphnia magna*, *Lemna minor*. As the sole representative of terrestrial plant *Sinapis alba* (white mustard) was used. Based on the results of the ecotoxicological tests the values of LC50, EC50 and IC50 for the tested preparations were calculated and their ecotoxicities were compared. All tested surfactants which are part of extinguishing foaming agent exhibit high ecotoxicity. Ecotoxicological values for all foam extinguishing agents were from  $\mu\text{L.L}^{-1}$  (Pyrocool B) to  $\text{mL.L}^{-1}$  (Mousol APS F-15). Comparing sensitivity of testing organisms all water organisms were much more sensitive to all tested foam extinguishing agents than *Sinapis alba*. In fact that these agents are often applied at terrestrial ecosystem one screening test in contact arrangement with seeds of terrestrial plant organism *Lactuca sativa* was also conducted [3] and obtained results were compared with those of aquatic tests.

### Acknowledgement

*This study was supported from the project No. FCH-S-13-2087.*

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## Određivanje ekoloških parametara u vodama Save i Dunava

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Cilj ovog istraživanja je određivanje nivoa zagađenosti u vodama Save i Dunava. Zagađenje vode može da potiče iz mnogobrojnih izvora: bioloških, prirodnih izvora, uzrokovano ljudskom aktivnošću i sl. Ključni izvori zagađenja reka u Srbiji su neprečišćene industrijske i komunalne otpadne vode. Oko **50%** zagađenja ispuštenog u reke dolazi od industrijskih postrojenja, a samo **13%** komunalnih otpadnih voda se tretira pre ispuštanja.

Toksične materije na vodene biocenoze deluju: smanjenjem kiseonika, mehanički i toksično. Razgradnja otpadnih materija veoma je usporena, pa je količina kiseonika potrebnog živim bićima u njoj višestruko smanjena. Najveću opasnost za vodene biocenoze predstavljaju otpaci hemijske industrije, jer se sastoje od baza, kiselina, fenola i drugih štetnih, jedinjenja.

Voda je uzorkovana u januaru 2013. godine na pet različitih lokacija (tri sa reke Save i dve sa reke Dunav).



**Slika 1.** Lokacije na Savi – Kapetanija, Makiš i Zabran



**Slika 2.** Lokacije na Dunavu – Batajnica i Vinča

Merenje toksičnosti uzoraka vršeno je na aparatu LUMIstox 300 Vibrio-Fischeri testom. Vibrio-Fischeri je standardni test za merenje toksičnosti zagađenih voda. Zasniva se na merenju smanjenja bioluminescencije bakterije vrste *Vibrio Fischeri*, koja je direktno srazmerna smanjenju koncentracije bakterija usled toksičnog dejstva zagađivača. *Vibrio Fischeri* je Gram-negativna, slanovodna bakterija koja ima bioluminiscentne osobine.

Takođe je vršeno i određivanje ukupnog organskog ugljenika (TOC). Ova analitička metoda se često koristi kao nespecifični pokazatelj kvaliteta voda i predstavlja količinu ugljenika koja je vezana u obliku organskih jedinjenja. Tipična TOC analiza, pored organskog, meri i neorganski ugljenik, ali i sadržaj ugljen-dioksida i soli ugljene kiseline.

Pored merenja toksičnosti i određivanja ukupnog organskog ugljenika u vodama Save i Dunava, rađena je i detekcija na prisustvo pesticida HPLC metodom. Od pesticida vršena su ispitivanja prisustva četiri nove grupe insekticida koji spadaju u nikotinoide: imidakloprid, tiakloprid, tiametoksan i klotianidin.

## **Case studies of student projects - Enhanced analytical investigations on the pollution state of Sava and Danube river**

### **Nova Gorica: Quantitative target analyses of selected organic pollutants**

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#### **Abstract**

We collected water samples from the Danube and Sava rivers from five different locations (Sava - Kapetanija, Sava - Zabran, Sava - Makiš, Danube - Batajnica, Danube - Vinča). From each location it was collected 2.5 L sample of water and on the site was measured pH. Water was kept in dark glass bottles and protected from further impacts. There are a number of organic pollutants in various ways due to the river and include pesticides, oil, grease, oils and detergents. Key sources of pollution are industrial effluents and municipal wastewater.



**Figure 1.** Sampling locations on Sava river: Kapetanija, Makiš and Zabran



**Figure 2.** Sampling locations on Danube river: Batajnica and Vinča



Tests were performed on HPLC (pesticides), the TOC (total organic carbon) and the LUMISTOX (luminescent bacteria). HPLC-was determined in the presence of pesticides. The analysis is reduced to 4 neonikotinoid insecticides (thiametoxam, imidacloprid, acetamiprid and thiacloprid). These four insecticides were detected with retention times of (4.4, 5.7, 6.5, and 8.5 min). Neonicotinoid insecticides are a relatively new group of active ingredients with novel modes of action. They act as antagonists by binding to postsynaptic nicotinic receptors in the insects central nervous system.

Lumistox 300 is an instrument for the analysis of toxicity in accordance with ISO 11348 with uminescent bacteria (*Vibrio fischeri*) and other luminescent methods. *Vibrio fischeri* is a standard test for measuring the toxicity of contaminated waters. It is based on measuring the decrease in bioluminescence bacteria of the species *Vibrio fischeri*, which is directly proportional to the reduction in the concentrations of bacteria due to the toxic effects of pollutants. *Vibrio fischeri* is a gram-negative bacterium that has a saltwater bioluminescent properties.

TOC (total organic carbon) This parameter is used to measure the expression level of pollution, waste water. It is used for several years and is a more accurate measure of the organic matter content of HPK and BPK of his procedure determination is reduced to its present complete oxidation of C to CO<sub>2</sub> and its titrimetric determination after absorption of NaCl. Today TOC quickly determine in special device - carbon analyzer, which is done in the catalytic oxidation of organic matter to CO<sub>2</sub> and H<sub>2</sub>O, which are then separated condensation, after which the CO<sub>2</sub> infrared analyzer determines in this way a certain amount of CO<sub>2</sub> is directly proportional to the initial sample C. TOC value is expressed in mg C / L.

## **Određivanje koncentracije toksičnih metala u zimzelenom drveću Beograda i okoline**

### **Determination of toxic metal concentrations in conifers from Belgrade and surrounding area**

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Biomonitoring može da posluži kao sredstvo za procenu zagađenosti životne sredine. U ovom istraživanju za procenu zagađenosti Beograda i okoline toksičnim metalima korišćene su iglice i grančice tri roda četinarara: bora (lat. *Pinus*), jele (lat. *Abies*) i tise (lat. *Taxus*). Cilj istraživanja je ispitivanje zagađenja metalima na prostoru na kome biljka raste na osnovu koncentracija metala u iglicama i grančicama i objašnjenje odakle zagađenje potiče ukoliko se utvrdi da ono postoji.

Prikupljeno je ukupno 32 uzorka – 26 sa teritorije Beograda, 5 iz Pančeva i 1 iz Banatskog Brestovca u toku meseca aprila i maja 2012. godine. Beograd i Pančevo odabrani su zbog toga što predstavljaju urbane sredine pod velikim uticajem zagađenja od saobraćaja i od ostalih urbanih izvora, a Banatski Brestovac zbog toga što predstavlja prirodnu sredinu koja je mnogo manje izložena istom tipu zagađenja. Uzorkovane su grančice sa iglicama starim oko godinu dana i grančice izdanaka stare nekoliko nedelja. Ispitivane su iglice četinarara jer koncentracija metala u njima predstavlja zbir količine metala koja potiče iz zemljišta i količine metala iz atmosferske depozicije. Analiza iglica različite starosti treba da pokaže gde je koncentrovanje metala veće, a analizom grančica treba da se utvrdi kakvo je koncentrovanje u tom delu biljke u odnosu na iglice.

Mineralizacija proba izvršena je putem mikrotalasne digestije. Koncentracije metala Pb, Zn, Co i Ni određene su metodom plamene atomske apsorpcione spektrometrije (FAAS), a metodom indukovano kuplovane plazme sa optičkom emisionom spektrometrijom (ICP-OES) određeni su pored navedenih i sledeći metali: Ag, Al, Ba, Bi, Ca, Cd, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na i Sr.

U tabeli su prikazani rezultati ICP-OES metode za koncentracije 8 toksičnih metala u izdancima i starijim četinama sva tri roda četinarara sa zagađenih i nezgađenih područja. Koncentracije olova u uzorcima bile su povišene na lokacijama u blizini prometnih saobraćajnica, dok su u uzorcima udaljenim od uticaja saobraćaja bile ispod granice detekcionog limita ili ispod granice. Na osnovu analize iglica bora zaključuje se da olova ima više u starijim četinama nego u mlađim, a u grančicama u većim koncentracijama nego u iglicama. Koncentracije Zn u svim uzorcima nalaze se u granicama normalnih koncentracija za biljke. Za razliku od Pb, stepen akumulacije Zn uglavnom je veći u iglicama izdanaka nego u starijim četinama. Koncentracije Zn u grančicama veće su od koncentracije u iglicama u slučaju jele, a manje u slučaju bora i tise. Koncentracije Co i Ni kretale su se u

okviru dozvoljenih koncentracija za biljke – bile su na granici detekcionog limita ili ispod granice, sem u slučaju Co čije su povišene koncentracije detektovane u uzorcima sa nekoliko lokacija izloženijim zagađenju koje potiče od saobraćaja. Istraživanje je takođe pokazalo da je jela najbolji akumulator za Zn i Pb među analiziranim rodovima četinarara. Koncentracije Ag, Bi, Cd, Cr, Ga, In i Li bile su ispod detekcionog limita u svim probama. Rezultati za Ba, Fe i Sr pokazali su da se ovi metali koncentruju više u starijim četinama nego u izdancima. Njihova koncentracija u okviru je prirodnih vrednosti za biljke i nije u skladu sa nivoom zagađenosti. Koncentracije Cu prelaze dozvoljene granice samo u nekoliko uzoraka jele sa lokacija izloženim zagađenju, dok se Mn nalazi u okviru normalnih granica. Koncentracije Ba, Cu i Fe veće su u grančicama nego u odgovarajućim iglicama četinarara, što nije slučaj i sa Mn i Sr.

metal		Pb [ppm]	Zn [ppm]	Co [ppm]	Ba [ppm]	Cu [ppm]	Mn [ppm]	Fe [ppm]	Sr [ppm]
jela	I-Z	< DL	39,82	2,26	12,98	6,88	26,88	33,59	10,51
	Č-Z	13,86	50,13	8,34	73,86	31,51	36,18	259,12	76,46
	I-N	< DL	17,77	4,93	< DL	< DL	21,77	48,06	1,70
	Č-N	< DL	5,47	< DL	11,02	< DL	16,15	113,59	12,35
bor	I-Z	< DL	39,11	< DL	< DL	6,17	12,18	37,57	1,01
	Č-Z	4,39	31,69	2,15	2,92	6,78	12,51	132,88	8,82
	I-N	< DL	32,64	5,78	< DL	5,29	19,31	31,78	1,69
	Č-N	5,14	8,94	4,29	< DL	< DL	25,49	195,66	9,02
tisa	I-Z	7,51	45,46	< DL	< DL	5,38	50,62	37,08	11,58
	Č-Z	< DL	19,87	6,47	6,89	< DL	144,56	179,16	28,90
	I-N	< DL	63,98	< DL	< DL	12,76	153,39	85,03	16,20
	Č-N	2,16	26,40	6,90	10,78	10,71	413,48	340,54	35,42

*I-Z – izdanci sa zagađenog područja, I-N – izdanci sa nezagađenog područja, Č-Z – starije četine sa zagađenog područja, Č-N – starije četine sa nezagađenog područja*

Kada se uporede vrednosti koncentracija Zn dobijene pomoću navedene dve metode, pokazuje se da su koncentracije sa ICP-OES neznatno niže (u proseku za 8%) u odnosu na koncentracije sa FAAS metode.

Na osnovu analize koncentracija Pb, Co i Cu u iglicama četinarara zaključuje se da zagađenje koje potiče od saobraćaja ima znatnog uticaja i na zagađenje u samoj biljci. Budući da su se Zn, Ba, Fe, Sr i Mn nalazili u normalnim koncentracijama za biljke, može se reći da zagađenje ovim metalima ne postoji. Četinari jesu pogodni za praćenje zagađenosti životne sredine toksičnim metalima, sa izuzetkom onih čije su koncentracije u iglicama bile izuzetno niske čak i u zagađenom sredi-nama (Ag, Bi, Cd, Co, Cr, Ga, In, Li, Ni).

## Non-target screening of organic pollutants in the Danube and Sava rivers, Serbia

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Rivers represent complex ecosystems. The presence of many organic compounds with various chemical properties is coming from both anthropogenic and biogenic sources. Contamination is caused by low-molecular weight organic compounds, like pesticides, plasticizers, ingredients of personal care products, pharmaceuticals etc. The present study is focussed on non-target screening analyses of two rivers in Serbia: the Danube and the Sava rivers. The main aim of this investigation is to identify organic contaminants in these two rivers and to obtain an overview on emission sources affecting the rivers.

Samples were collected in January 2013 from five locations (two from the Danube and three from the Sava river, see Fig. 1)). Sequential liquid/liquid extraction was applied on 1L water samples and the identification of organic pollutants in the extracts was performed by using gas chromatography/mass spectrometry (GC/MS) techniques.

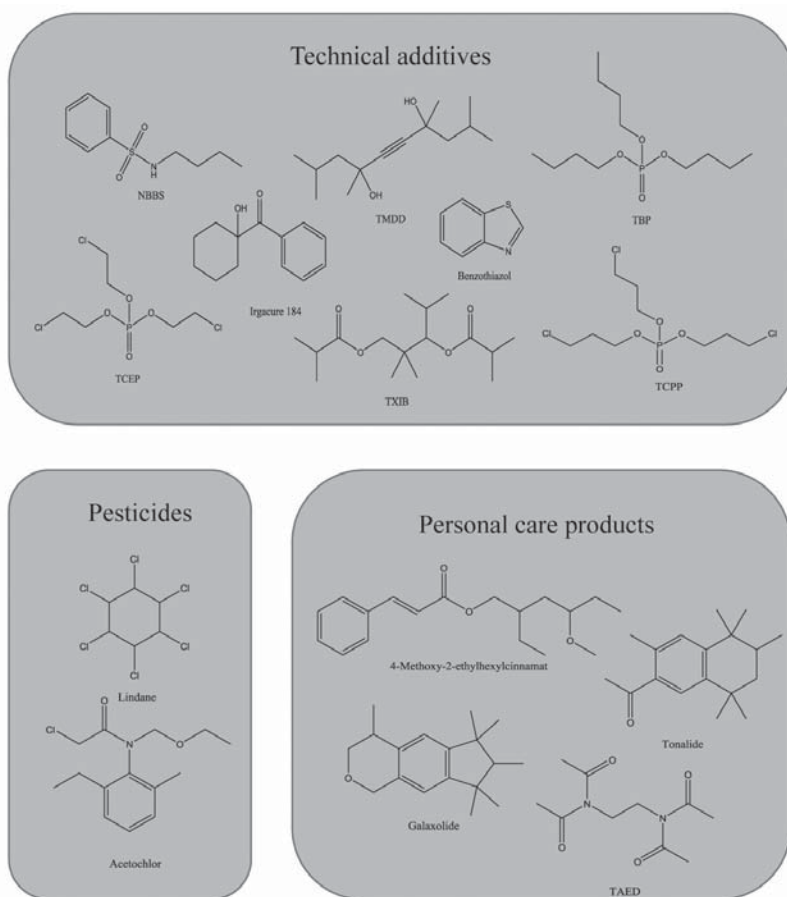


Figure 1. Sampling locations

Non-target screening of the Danube and the Sava rivers revealed a high diversity of the chemical composition. Identified substances can be classified in several groups: pharmaceutical (carbamazepine), personal care products (e.g., TAED, galaxolidetonalide, methylhydrojasmonate, lilial), technical additives (e.g., NBBS, TCPP, TCEP, TBP), pesticides (e.g., lindane, acetochlor), food constituents (caffeine, vitamin E), natural products (dipropyldisulphide, dipropyltrisulphide) and non-specific compounds (e.g., 2-nitro-4-methylphenol, 2-nitrophenol, 2-phenoxyethanol, 2,6-di-*tert*-butyl-4-nitrophenol).

Although it has been reported that the application of some compounds has been banned or restricted, this investigation has shown that they can still be found in the environment, in this case, in waters (TCEP, TCPP, lindane, acetochlor).

This non-target screening is a significant base for monitoring purposes, which can be supported by screening analyses. Further analyses are planned to examine the quantity of these compounds in these rivers.



**Figure 2.** Xenobiotics identified in Danube and Sava river water

## **PAHs in gas and particle-bound phase in indoor/outdoor school environment**

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Polycyclic aromatic hydrocarbons (PAHs) are large group of organic compounds with two or more fused aromatic rings. They are formed by incomplete combustion processes of organic material such as biomass and fossil combustion, vehicular emissions, industrial processes etc. The PAHs may be nontoxic and very toxic and further carcinogenic that is highly structurally dependent. The list of priority PAHs varies in different countries, but US EPA list of 16 priority PAHs is almost used.

The aim of this work was to investigate the seasonal variation of PAHs and their partition between the gas and particulate phases in the indoor (I) and outdoor (O) air.

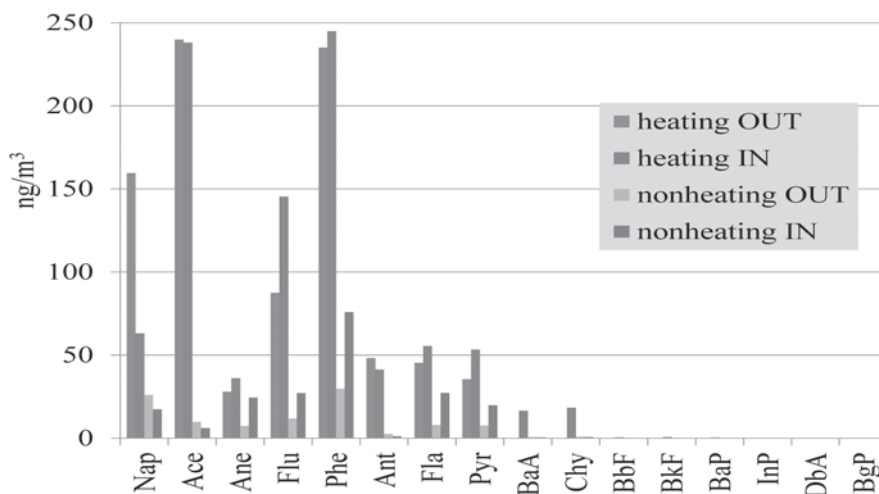
Indoor and outdoor samples were collected in the school environment during both seasons, heating and non-heating (one week, heating- January 2012 and non-heating- May 2012). The school is located next to highly dense traffic street in the central zone of the town in the eastern part of Serbia. Nearby school there is mixed residential-commercial area with number of local heating boilers as sources of air pollution.

Samples were collected using low volume sampler (LVS) for 24h period. PAHs were collected, prepared and analyzed according to Compendium Method TO-13A. The air was drawn by LVS reference sampler (Lackel) through a quartz filter to collect total suspended particles (TSP) and then through polyurethane foam (PUF) to collect gas phase of pollutants. PAHs were analyzed by gas chromatography coupled with mass spectrometry (GC-MS).

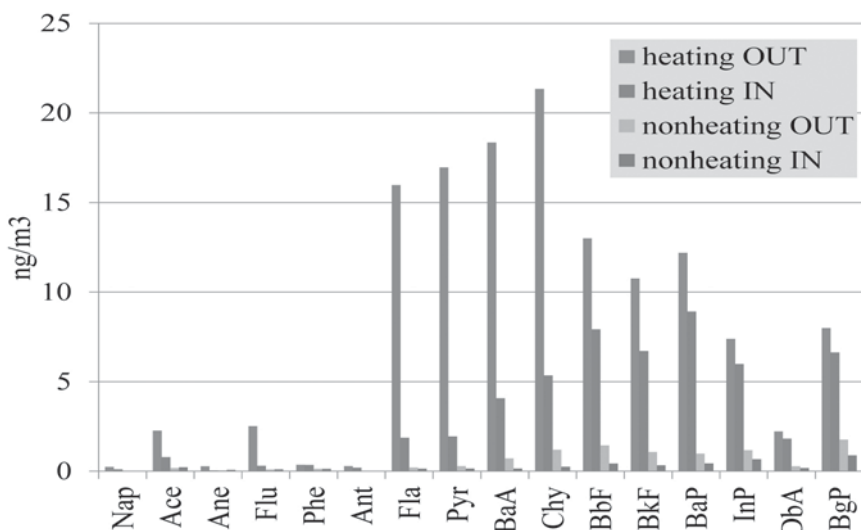
As shown in Fig. 1 and Fig. 2, PAH values were significantly higher in heating period than in non-heating period. Levels were higher for lower-molecular-weight PAHs (three rings) in the gas phase (Ace, Ane, Flu, Phe), where multi-ringed PAHs (BaP, InP, DbA, BgP; five or more rings) were dominantly in particle bounded phase. The phase distribution of the PAHs depends on the vapor pressure, the atmospheric temperature, the PAH concentration and the affinity for suspended particles.

The indoor/outdoor ratios for PAHs were different and I/O ratios were higher for lower-molecular-weight PAHs, especially for PAHs in the gas phase (Ane, Flu, Phe, Fla, Pyr) during heating period.

Multi-ringed PAHs in indoor air were predominantly transported from the outdoor air, and their concentrations were significantly higher in heating period, probably because of influences of road traffic and domestic heating.



**Figure 1.** Average contribution of PAHs in indoor and outdoor air in gas phase during heating and non-heating seasons.



**Figure 2.** Average contribution of PAHs in indoor and outdoor air in particle phase during heating and non-heating seasons.



## Linear synthetic aromatic substances in wastewaters

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Synthetic musk compounds are a group of organic compounds used in perfumes and detergents. The first musk compound was synthesized by German chemist Albert Baur accidentally as a result of his effort to prepare more potent explosive than trinitrotoluene (TNT) in 1888 [1].

Large group of synthetic musk compounds can be divided into four groups: nitromusks, polycyclic musks, macrocyclic musks and linear musks. The presence of musk compounds in the environment (mainly in aquatic systems) has been confirmed in many studies (USA, Japanese, China, Austria, Netherlands, Czech Republic etc.) [2].

Linear musks are quite new group so we know very little about their toxicity, metabolism etc. In the Czech Republic aromatic substances industry existed more than a century ago. Initially, it consisted of small companies and operations. In 1946, small companies were nationalized and Aroma enterprise was gradually built-up. Synthetic aromatic substances, which are subject of this study, come from production of AROMA Praha a.s., which specializes on production of individual fragrances and perfume compositions [3, 4].

This study is focused on the issue of 9 selected linear musk compounds; 2-cyclohexylethanol, citronellol, frescomenthe and isobornylacetate were analysed in influents and effluents from waste water treatment plant at University of Veterinary and Pharmaceutical Science in the town of Brno. This WWTP processes about 1 640 m<sup>3</sup> of waste water per month; technological delay between inlet and outlet is 2 days. The other linear musk compounds, aroacet, aroflorone, isoamyl salicylate, lilial and linalool 925, were sampled at Brno-Modřice sewage treatment plant; 24-hour mixed samples, together with individual samples taken each 2 hours were obtained. Samples were taken at both inlet and outlet. Technological delay between inlet and comparable outlet in Brno WWTP is 24 hours.

For isolation of analytes solid phase microextraction (SPME) was successfully applied. The identification and quantification was carried out by GC-MS using instrument Agilent 6890N/5973N. At inflow and outflow of the Brno-Modřice municipal sewage treatment plant all five targeted analytes were found at the inlet; linalool 925 showed the highest level. Concentration ranges for particular analytes at inflow were as follows: linalool 925: 92.00 - 90.81 ng.mL<sup>-1</sup>; aroacet: 0.473 - 4.406 ng.mL<sup>-1</sup>; aroflorone: 0.369 - 5.336 ng.mL<sup>-1</sup>; lilial: 0.110 - 1.222 ng.mL<sup>-1</sup> and isoamyl salicylate: 0.121 - 0.975 ng.mL<sup>-1</sup>. At the sewage treatment plant outflow



the only analyte detected in all samples was lilial, which occurred in concentrations of 0.017-0.065 ng.mL<sup>-1</sup>. On the other hand, aroacet was not detected in any sample. Aroflorone and isoamyl salicylate were identified only in some samples, but they couldn't be quantified, because their concentrations were between LOD and LOQ values. Linalool 925 was detected in 6 samples of the outflow, but it could be quantified only in three cases. On the basis of data acquired, efficiency of removal of selected linear musk compounds from the wastewater during wastewater cleaning process was evaluated. All analytes under study, excluding lilial, showed high removal efficiencies, which were above 99 %. In the case of lilial this value varied between 78.68 - 96.13 %.

The concentration of four selected linear musk compounds was also evaluated in wastewater samples in influent and effluent from the WWTP at University of Veterinary and Pharmaceutical Science, Brno. 2-cyclohexylethanol wasn't detected in any sample analysed. Fresco menthe was detected in influent at level of 739.5 ng.L<sup>-1</sup>, citronellol concentration was 8601.4 ng.L<sup>-1</sup> and isobornyl acetate was at 1105.5 ng.L<sup>-1</sup>. In effluent the most important linear musk was citronellol at concentration of 499.1 ng.L<sup>-1</sup>, second one was fresco menthe at 26.3 ng.L<sup>-1</sup> and last one was isobornyl acetate at 14.9 ng.L<sup>-1</sup>. The values of the limit of detection (LOD) and limit of quantification (LOQ) were obtained from the calibration function. The overall removal efficiency of linear synthetic musk from wastewater ranged from 91.22 to 96.43 %. Deviation of the results (RSD) from five repetitions ranged from 5.79 to 8.58 %, indicating good repeatability of the analytical method.

### Acknowledgement

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## Concentrations trend of NO, NO<sub>2</sub> and O<sub>3</sub> during the 2011 in Belgrade urban area

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Many problems originated by the air pollution in urban and industrial areas are related to photochemical oxidants [1]. Among them, O<sub>3</sub> and NO<sub>2</sub> can have adverse effects on the environment and human health [2]. Therefore, monitoring and analysis of their behavior in urban environment is very important. In this study we present the results of preliminary analysis of concentrations time series of NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> in Belgrade urban area during the 2011 at two different types of monitoring stations (urban-background: Novi Beograd (NB), Stari Grad (SG) and Vračar (V), as well as urban-traffic Mostar (M)).

Data were obtained from the Air pollution measurement network which operates under the supervision of the Serbian Environmental Protection Agency. Concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> were measured using the chemiluminescence technique and ozone concentrations were measured using Ultra-Violet Photometric ozone analyzer.

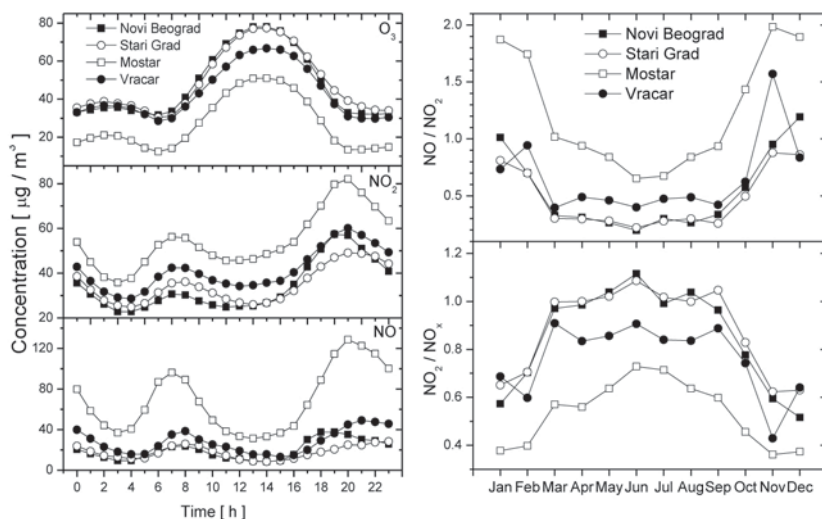
Statistical parameters for 1-h averaged concentrations for all compounds and monitoring stations are shown in Table 1. According to the air quality guidelines set by the World Health Organization, annual mean concentrations of NO<sub>2</sub> at Mostar and Vračar monitoring stations were higher than maximum allowed values (40 µg m<sup>-3</sup>) [2].

**Table 1.** Statistical parameters for 1-h averaged NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> concentrations [µg m<sup>-3</sup>] for all monitoring stations

	NO				NO <sub>2</sub>				NO <sub>x</sub>				O <sub>3</sub>			
	NB	SG	M	V	NB	SG	M	V	NB	SG	M	V	NB	SG	M	V
Av.	19.8	17.7	69.2	27.9	34.1	34.6	54.8	41.4	44.2	42.3	110.6	57.7	47.8	48.8	27.1	43.3
Med	4.9	5.0	29.9	9.1	26.5	27.7	49.1	33.0	24.5	25.3	69.2	33.0	42.0	44.2	16.8	38.4
Min	0.0	0.0	0.2	0.0	3.4	3.4	0.0	0.0	1.4	1.2	0.5	1.0	3.4	3.4	3.4	3.4
Max	924	624	1121	1408	223	178.4	227.3	259.6	1099	751.6	1314	1478	215.8	239.8	183.0	198.4
St.Dev.	51.4	40.0	105.6	60.6	25.8	24.6	29.8	29.5	66.1	53.3	125.2	76.5	35.8	35.1	27.7	32.0
95 <sup>th</sup> Perc	96.6	79.9	273.1	124.4	87.3	83.3	111.3	100.1	153.4	132.6	350.9	190.6	113.9	111.4	83.9	100
10 <sup>th</sup> Perc	0.9	1.5	4.9	2.4	10.3	11.1	23.9	14.9	8.4	9.6	24.1	13.8	3.4	3.4	3.4	3.4

Figure 1 (left) shows diurnal variations of the NO, NO<sub>2</sub> and O<sub>3</sub> concentrations at four monitoring sites. Nitrogen oxide belongs to the primary pollutants, mainly originating from traffic, as indicated by the two rush hour concentration peaks at all stations. Ozone and NO<sub>2</sub> are classified as secondary pollutants. Small delay of NO<sub>2</sub> concentration peaks, as compared to NO, can be explained with the time needed for the production of the secondary NO<sub>2</sub> in reaction of NO and O<sub>3</sub>. On

the other hand, photochemical degradation of  $\text{NO}_2$  leads to formation of  $\text{NO}$  and  $\text{O}_3$ . Concentrations of  $\text{O}_3$  show rapid increase at all locations after 7 h, reaching the maximum value around 13 h. That is in consent with photochemical origin of  $\text{O}_3$  which requires presence of solar radiation. Furthermore,  $\text{O}_3$  concentrations are much higher at the background stations, than at Mostar, where  $\text{NO}$  predominates and  $\text{O}_3$  is consumed through reaction with  $\text{NO}$ .



**Figure 1.** Diurnal variations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$  concentrations (left) and monthly mean of  $\text{NO}/\text{NO}_2$  and  $\text{NO}_2/\text{NO}_x$  ratios (right)

Figure 1 (right) shows variations of the monthly mean  $\text{NO}/\text{NO}_2$  and  $\text{NO}_2/\text{NO}_x$  concentration ratios at all stations. The first ratio reflects intensity of  $\text{NO}$  sources emissions (traffic, heating plants) [1] showing that they were more intensive in winter. Monthly variations of  $\text{NO}_2/\text{NO}_x$  ratio (increases with the distance from the source of  $\text{NO}$ ) indicate that Vracar was affected by stronger  $\text{NO}$  emission than the two other background stations. Together with exceeded maximum allowed concentration of  $\text{NO}_2$ , this can be related to the higher traffic density at this station, particularly during the warmer part of the year.

### Acknowledgment

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## Soil heavy metals content in Belgrade urban parks

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Heavy metals are naturally present in soil, but their increasing emissions in environment result in elevated concentrations and adverse effect on human health, especially in urban areas. Thus, it is important to determine the level of heavy metals in urban parks soil. X-ray fluorescence (XRF) spectrometry is a standard method for elemental analysis of soil [1] and it is nondestructive, requires little sample preparation and allows multielemental analysis. Here we present the results of the analysis of soil samples collected from four public parks in the Belgrade urban area in spring of 2011.

The topsoil samples (0-10 cm) were taken from several locations in each of the four parks (Fig. 1) using steel corer. After drying, sieving and milling, 5 g of each soil sample was pressed into a pellet at the pressure of 30 tons for 60 s (without binder). In this study, a MiniPal 4 XRF spectrometer was used for elemental analysis. It is equipped with 9 W Rh tube and silicon drift detector, with resolution FWHM of 145 eV at 5.9 keV <sup>55</sup>Fe. The live time of each spectrum was 1800 s. The calibration of the instrument was performed using six reference materials (soils and lake sediment). The following heavy metals have been measured: Cr, Cu, Mn, Ni and Zn. In order to test our calibration method, we analyzed soil reference material (NIST2711) as unknown sample prior to analysis of soil samples from a city park and the measured concentrations were in good agreement with certified values.



**Figure 1.** Sampling locations: Karadordev Park - KP, Students Park - SP, Zemun Park - ZP, and Botanic Garden - BG

Concentrations of Cr, Cu, Mn, Ni and Zn in soil obtained in this study were generally in agreement with those previously reported for Belgrade area [2, 3]. The concentration values together with the corresponding maximum allowed concentrations - MAC [4], are given in Table 1.

**Table 1.** Concentrations of Cr, Cu, Mn, Ni and Zn in Belgrade urban parks soil

Element	Concentration [ppm]				
	KP	SP	ZP	BG	MAC
Cr	100	98	120	90	100
Cu	27	86	40	24	100
Mn	769	669	692	612	/
Ni	57	55	82	53	50
Zn	106	164	122	95	300

According to the National legislation [4], in all studied public park soils, Ni concentrations were higher, while concentrations of Cr were close or higher than the corresponding MAC. Concentrations of Cu and Zn were within the prescribed values. Elevated concentration of Cu in Students Park in comparison with the other sampling locations is in agreement with previous research [5]. Manganese is not regulated with the National legislation, but its concentrations were significantly higher than those from several other cities over the world as presented by Marjanović et al. [2].

The results of this study show that the content of heavy metals in Belgrade parks soil does not considerably exceed the maximum allowed concentrations. However, attention should be paid to Mn as its concentration is considerably higher than in other urban areas over the world.

### Acknowledgement

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## **Praćenje kvaliteta otpadnih voda na ispustu u Dunav u Novom Sadu, Srbija**

### **Monitoring of the quality of wastewater discharge into the Danube in Novi Sad, Serbia**

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Utvrđivanje sastava i praćenje količine voda u cilju smanjenja nivoa rizika od negativnog uticaja ima izuzetan značaj za celokupno unapređenje statusa životne sredine. Usled nepovoljne tehničko-ekonomske situacije koja onemogućava modernizaciju tehničko-tehnoloških sistema, prirodni vodeni tokovi postaju kolektori otpadnih voda, koji su u pogledu mogućnosti prihvatanja zagađenja ograničeni. Na području Novog Sada kanalizacionom mrežom obuhvaćeno je oko tri četvrtine stanovništva grada. Sva otpadna voda se postojećim kanalizacionim sistemima izliva u Dunav. Prethodnim istraživanjima ustanovljeno je da se u crpne stanice GC1 i GC2 izliva najveća količina otpadnih voda, koje imaju najveći uticaj na varijacije količine ispuštene otpadne vode. Cilj istraživanja je praćenje kvaliteta otpadnih voda u periodu od 12 meseci, na ispustu GC2 (19° 51' 25,139" E, 45° 15' 44,581" N) postojećeg kanalizacionog sistema kao jednog od najopterećenijih ispusta. Crpna stanica GC2 predstavlja izliv kanalizacije severnog sliva grada Novog Sada koji se nalazi u neposrednoj blizini drumsko železničkog mosta i prihvata otpadne vode severnog dela grada.

U okviru istraživanja, po prvi put na teritoriji grada Novog Sada, uveden je kontinualni on-line monitoring voda pomoću optičkog sistema, Spectrolyser uređaja, proizvođača opreme S.:CAN (Austrija, Beč) za in situ merenje, čime je omogućeno kontinualno merenje osnovnih fizičko-hemijskih karakteristika otpadnih voda (BPK<sub>5</sub>, HPK, NO<sub>3</sub>-N, TSS) u svakom vremenskom trenutku. Podaci dobijeni ovim putem su dopunjeni laboratorijskom analizom pomoću akreditovanih, standardnih metoda ispitivanja, a u cilju sveobuhvatnijeg prikaza realnog statusa vode na selektovanom lokalitetu. On-line oprema obezbeđuje (skoro) kontinualno praćenje promene kvaliteta otpadnih voda, za razliku od standardnih procedura sakupljanja i obrade uzoraka sa ograničenim brojem merenja u određenom periodu vremena [1, 2, 3].

U toku mernih kampanja on-line uzorkovanja u zimskom periodu 2012/13 (decembar, januar, februar) uzorci su sakupljeni tri puta dnevno u periodu od 24 h. Analiza osnovnih fizičko hemijskih parametara (temperature, pH, elektroprovodljivosti, koncentracije rastvorenog kiseonika, utroška permanganata, BPK<sub>5</sub>, HPK, NO<sub>3</sub>-N, NO<sub>2</sub>-N, NH<sub>3</sub>-N, ukupnog fosfora, sulfata), kao i koncentracija metala (Pb, Fe, Cd, Cr, Ni, Zn) urađena je standardnim EPA metodama u akreditovanoj laboratoriji za monitoring deponija, otpadnih voda i vazduha, Fakulteta tehničkih nauka, Univerziteta u Novom Sadu.

Rezultati merenja BPK<sub>5</sub> i HPK ukazuju na dobro slaganje rezultata dobijenih on-line merenjem i rezultata laboratorijskih analiza uzoraka standardnim metodama, sa  $R^2 > 0.83$  čime je potvrđena efikasnost kontinualnog merenja Spectrolyser uređaja. NO<sub>3</sub>-N je bio ispod granica detekcije u svim analiziranim uzorcima, kao i rezultatima dobijenim kontinualnim merenjem. Koncentracije metala Cr, Ni i Cd su takođe bile ispod granice detekcije u svim analiziranim uzorcima. U kampanji merenja sprovedenoj krajem februara uočene su niže koncentracije merenih analita u poređenju sa prethodnim kampanjama u decembru i januaru kao posledica efekta razblaženja usled topljenja snega.

Naredne kampanje monitoringa kvaliteta vode na ispustu GC2 obuhvatiće i mikrobilošku analizu u okviru koje će posebna pažnja biti posvećena prisutnim grupama bakterija, kao najviše proučavanim grupama u otpadnim vodama. Podaci o prisutnim mikroorganizmima su od velikog značaja jer prisustvo karakterističnih grupa mikroorganizama direktno određuje pravac i mogućnosti procesa autopurifikacije vodenih sistema. Uzevši u obzir činjenicu da su površinske vode ekosistemi u kojima interaguju sredina i organizmi u njima, samo na osnovu tih odnosa se može definitivno suditi o kvalitetu posmatrane vode.

Dobijeni rezultati ukazuju na potrebu nastavka kontinualnog monitoringa u cilju procene uticaja sezonskih varijacija na sastav voda i formiranja baze podataka, koja će poslužiti kao osnov za dobijanje informacija o ekstremnim i stresnim periodima. Podaci o sastavu generisanih i ispuštenih otpadnih voda, dobijeni ovakvom kampanjom monitoringa su od posebnog značaja, s obzirom da su raspoloživi podaci izuzetno skromni.

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## Sezonske varijacije nivoa koncentracije HCB u ambijentalnom vazduhu Fruške gore

### Seasonal variations of HCB concentration levels in the ambient air of Fruška gora mountain

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Heksahlorbenzen (HCB) je pesticid koji je Stokholmskom konvencijom inicijalno definisan kao jedan od dvanaest dugotrajnih organskih zagađujućih supstanci (eng. persistent organic pollutants – POPs) i ima svojstva postojanosti, bioakumulacije, toksičnosti i transporta kroz životnu sredinu na velike udaljenosti. HCB je izuzetno stabilan, globalno distribuiran i spada u najotpornije dugotrajne organske zagađujuće supstance [1]. HCB dospeva u životnu sredinu iz industrije i poljoprivrede, ali se nalazi i kao kontaminant u tragovima u nekoliko pesticida i namenjen je nusprodukt u industrijskoj proizvodnji i pri procesima sagorevanja [2].

Upotreba HCB je zabranjena u Republici Srbiji od 1980. godine, pa se smatra da je ispuštanje HCB u životnu sredinu najčešće iz zaliha nastalih ranije, dozvoljenom proizvodnjom. Emisija HCB u vazduh u Republici Srbiji potiče uglavnom od korišćenja pesticida sa primesama HCB i iz industrije metala (obojena metalurgija), a u manjoj meri iz hemijske industrije i sagorevanja u domaćinstvima [3]. U radu su prikazani i diskutovani nivoi koncentracije heksahlorbenzena detektovani u ambijentalnom vazduhu Fruške gore, u periodu od aprila 2009. do maja 2011. godine.

U okviru Projekta *Monitoring of POPs in the CEE counties and other regions (MONET Europe)*, sprovodi se, od 2006. godine, kontinualni monitoring kvaliteta ambijentalnog vazduha na lokalitetu Fruške gore primenom pasivne metode uzorkovanja. Kao medijum za uzorkovanje ambijentalnog vazduha koriste se poliuretanski (*polyurethane foam, PUF*) diskovi prečnika 14cm, debljine 1,5 cm i gustine 0,03 g cm<sup>-3</sup> (tip N3038; Gumotex Breclav, Republika Češka) smešteni unutar dve kalote uzorkivača. Pre izlaganja, svi PUF diskovi su ekstrahovani Sokshlet ekstraktorom 8 sati u acetonu i 8 sati u dihlormetanu, umotani u dva sloja aluminijumske folije, spakovani u polietilenske kesice sa zip zatvaračem i čuvani u zamrzivaču [4].

Nakon uzorkovanja, uzorci vazduha su ekstrahovani dihlormetanom u automatskom ekstraktoru Buchi System B-811. Sa svakim setom od deset uzoraka, analizirana je po jedna slepa proba i po jedan prazan terenski filter. U svaki filter, neposredno pre ekstrakcije, dodat je surogat standard (PCB 30 i PCB 185). Kao interni standard korišćen je PCB 121. Uzorci su analizirani GC-MS sistemom (HP 6890 - HP 5972) opremljenim sa autosemplerom i kolonom DB-5MS. Kompletna procedura analitičkog postupka, stepen pouzdanosti i kontrola kvaliteta primenjenih metoda detaljno su opisani u literaturi [5].



Heksahlorobenzen je detektovan u svim uzorcima ambijentalnog vazduha, u svakom periodu godine. Izmereni nivoi koncentracije HCB su najviši u poređenju sa ostalim detektovanim pesticidima. Koncentracija heksahlorbenzena u ambijentalnom vazduhu Fruške gore je, u toku dve ispitivane godine, iznosila  $76,44 \pm 21,74 \text{ pg/m}^3$  (srednja vrednost  $\pm$  standardna devijacija), a najveća koncentracija od preko  $100 \text{ pg/m}^3$  izmerena je u periodu ranog proleća, odnosno u martu 2010. i 2011. godine. Najniže koncentracije HCB uočene su u letnjem periodu, što je u skladu sa literaturnim podacima [6][7]. Detekcija heksahlorbenzena u svim uzorcima ambijentalnog vazduha ukazuje na njegovu postojanost u životnoj sredini. Uprkos zabrani upotrebe u Republici Srbiji, HCB i dalje dospeva u ambijentalni vazduh procesima primarne i sekundarne emisije.

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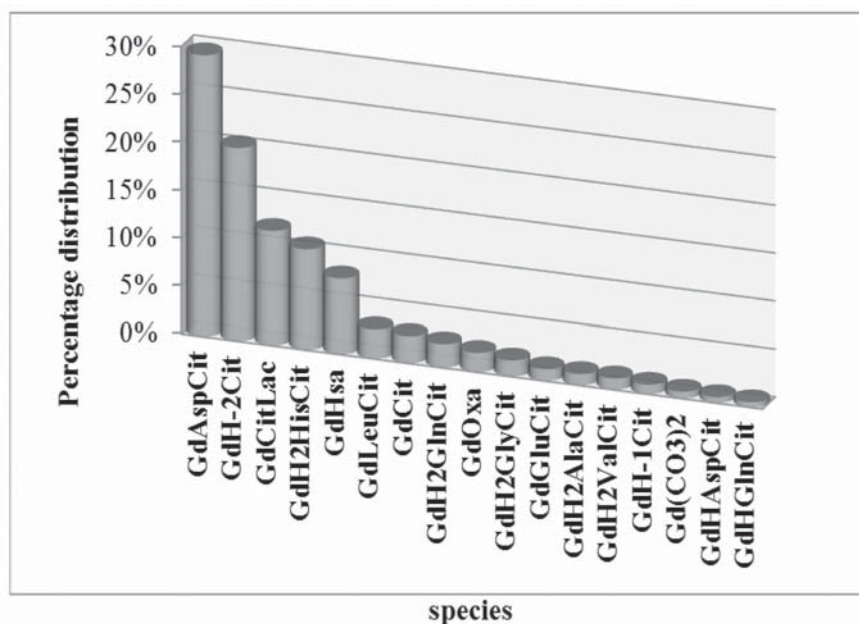
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# Study on Speciation of Gd(III) in Human Blood Plasma by Computer Simulation

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Speciation of Gd(III) in human blood plasma has been investigated by computer simulation using the program Hyss2009[1]. We improved May's et al model[2] by taking into account insoluble species of Gd(III). Binding of Gd(III) to serum albumin was also considered. In our model more than 40 low-molecular-weight serum ligands and 9 metals (Ca(II), Mg(II), Mn(II), Fe(III), Fe(II), Pb(II), Cu(II), Zn(II) and Gd(III)) were included. The model contained over 6000 complexes. About 131 Gd-complexes with blood plasma ligands as well as insoluble species  $Gd_2(CO_3)_3$  and  $Gd(PO_4)_3$  were included. The distribution of the Gd(III)-ion with in plasma complexes has been calculated with different total Gd(III)-ion concentration ranging from  $1.2 \times 10^{-9}$  to  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . The results obtained with Hyss calculation are shown in Figure 1.



**Figure 1.** The species distribution of Gd(III) in human serum at pH=7.40

Main soluble complexes in blood plasma appears to be the mixed ternary complex GdAspCit (Asp=aspartate, Cit=citrate). Binding to albumin levels to about 7.5% of total gadolinium concentration. Increasing of the concentration of Gd(III) leads to decrease of the dominant complex concentration favoring

the appearance of insoluble species. Dominant Gd(III) complexes in serum calculated by Hyss at different concentrations of Gd(III) are shown in **Table 1**.

**Table 1.** Dominant Gd(III)-complexes in serum at different concentrations of gadolinium

Species	Total Gd (molL <sup>-1</sup> )	1.2E-9	1.0E-8	1.0E-7	1.0E-6	1.0E-5	1.0E-4	1.0E-3	1.0E-2
Gd <sub>2</sub> (CO <sub>3</sub> ) <sub>2(s)</sub>		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	69.0%	96.2%
GdPO <sub>4(s)</sub>		0.0%	75.7%	97.6%	99.7%	99.9%	100.0%	31.0%	3.8%
Soluble species		100.0%	24.3%	2.4%	0.3%	0.1%	0.0%	0.0%	0.0%

From **Table 1** it can be seen that increasing the total concentration of gadolinium leads to appearance of insoluble species. The GdPO<sub>4</sub> becomes the dominant species at total Gd(III) concentration of  $1 \times 10^{-4}$  molL<sup>-1</sup>. At concentration of Gd(III)  $1 \times 10^{-3}$  the insoluble species becomes the dominant. Thus GdPO<sub>4</sub> and Gd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> are the dominant species in a wide range Gd(III)-ion concentration consistent with the tendency lanthanides to form insoluble complexes with phosphates.

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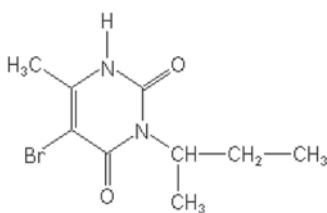
## Development of kinetic-spectrophotometric method for determination herbicide bromacil

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Bromacil is one of a group compounds called substituted uracils. This herbicide is the most frequently applied for weed control in citrus orchards. This herbicide can be applied alone or, in mixtures, to control a broad spectrum of weeds. It is an herbicide use for weed and brush control on road shoulders and non-cropland, as well as for selective weed control on a limited number crops, such as citrus fruit and pineapple[1].

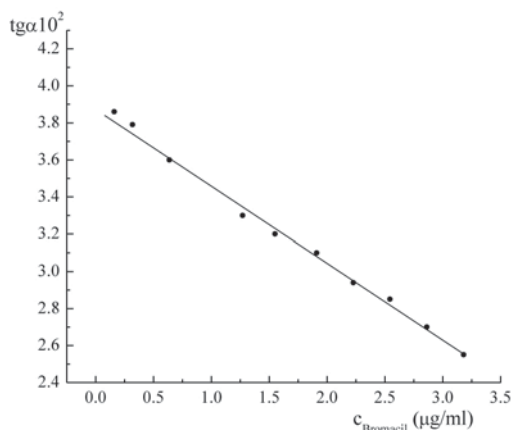
Bromacil determination was reported by different authors using a HPLC and GC method [2-5]. There is one kinetic-spectrophotometric method for bromacil determination in the interval 2.70-16.20 µg/ml [6].



**Figure 1.** Chemical structure of bromacil

The aim of this work was to develop a new kinetic-spectrophotometric method for determination of bromacil. The method is based on inhibited effect of bromacil on oxidation reaction of Sulfanilic acid (SA) by  $\text{H}_2\text{O}_2$  in presence of  $\text{Co}^{2+}$ . Bromacil was determined with linear calibration graph in the interval from 0.160 to 3.180 µg/ml (Fig.1).

The optimized conditions yielded a theoretical detection limit of 0,138 µg/ml based on the  $3S_b$  criterion. The RSD is 5.72-0.34 % for the concentration interval of bromacil 0.160-3.18 µg/ml. The reaction was followed spectrophotometrically at 370 nm. The kinetic parameters of the reaction are reported, and the rate equations are suggested. The tangent method was used for processing of the kinetic data. In order to determine the lowest possible determinable concentration of bromacil, the working conditions required optimization. Therefore, the dependence of the rate of reactions on the concentration of each of the reactants was determined (pH,  $\text{H}_2\text{O}_2$ , SA,  $\text{Co}^{2+}$ ).



**Figure 2.** Calibration curve at temperature of 25.0°C

Figure 2. shows the calibration curve at the temperature of 25.0°C, which can be used for the determination of the bromacil concentration in the interval 0.160-3.180 µg/ml.

**Table 1.** Accuracy and precision of the bromacil determination

Taken (µg/ml)	Found <sup>a)</sup> $\bar{x} \pm \text{SD}$ (µg/ml)	n	RSD (%) <sup>b)</sup>	G (%)	$\frac{\bar{x} - \mu}{\mu} \cdot 100$ (%) <sup>c)</sup>
0.160	0.157±0.02	5	5.72	6.12	2.50
1.550	1.574±0.01		2.74	3.25	1.60
3.180	3.185±0.03		0.34	1.20	0.16

<sup>a)</sup>Mean and standard deviation of five determinations at the 95 % confidence level; <sup>b)</sup>relative standard deviation; G- relative error; <sup>c)</sup>accuracy of the method

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## A comparative study on degradation textile reactive dye by advanced oxidation processes

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Textile production results in high levels of pollution due to the high volume of effluents produced. The composition of the effluent varies. It has high chemical and biochemical oxygen demands and contains many colored substances. Dyes are a serious problem when dealing with textile waste because they are chemically and photolytically stable.

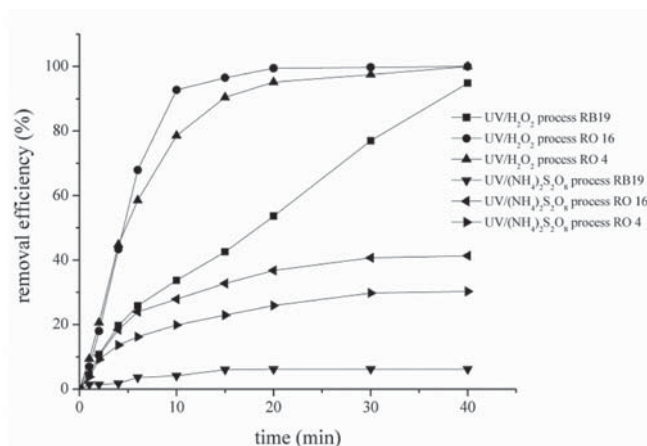
Advanced oxidation processes (AOPs) must be developed because textile run-off varies widely in composition and contains toxic compounds and dyes are very difficult to remove and degrade using conventional processes. AOPs have proven to be very effective for textile effluents [1,2]

In the present work, UV/H<sub>2</sub>O<sub>2</sub> and UV/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> processes were applied to decolorize solutions containing C.I. Reactive Blue 19 (RB 19), C.I. Reactive Orange 16 (RO 16) and C.I. Reactive Orange 4 (RO 4). The performance of these processes in terms of decolorization efficiency were compared.

Photochemical experiments were carried out in a batch photoreactor hand-made in our laboratory [3]. A stock solutions of dyes were made by dissolving 1.00 g dye in 1000 cm<sup>-3</sup> of deionized water. Working solutions were prepared freshly, before irradiation, by diluting the stock to desired concentration with deionized water. The pH of solutions was adjusted by addition of NaOH or HCl (0.1/0.01 mol dm<sup>-3</sup>) with pH-meter (SensIon5, HACH, USA). During irradiation, the solution was magnetically stirred in a constant rate and temperature was maintained at 25 ± 0.1°C by thermostating (F12-ED, Julabo, Germany). At required time intervals, 4 cm<sup>-3</sup> of samples were withdrawn and absorbance at 592 nm was measured using UV/vis spectrophotometer Cintra 1010 (GBC, Australia) to determine decolorization degree of solution.

Comparison of efficiencies of UV/H<sub>2</sub>O<sub>2</sub> and UV/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> processes on decolorization of RB19, RO16 and RO4 was presented in Fig. 1. For comparison of these processes we studied decolorization at optimum conditions for all processes. The results obtained in this study illustrate that UV/H<sub>2</sub>O<sub>2</sub> process was more effective than UV/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> process for all three dyes.

Electron acceptors such as hydrogen peroxide and ammonium persulfate were added into the solution in order to enhance the decolorization rate [4,5]. The rates for the decolorization of dyes under UV light, in presence of various electron acceptors are shown in Fig. 1.



**Figure 1.** Comparison of removal efficiency of RB 19, RO 16 and RO 4 by UV/ $\text{H}_2\text{O}_2$  and UV/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  process.  $[\text{dye}]_0 = 50 \text{ mg dm}^{-3}$ ,  $[\text{H}_2\text{O}_2]_0 = 25 \text{ mM}$ ,  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]_0 = 25 \text{ mM}$ , initial pH was 7, UV radiation intensity was  $730 \mu\text{W cm}^{-2}$ , temperature was  $25.0 \pm 0.1^\circ\text{C}$ .

From the economical point of view, the UV/ $\text{H}_2\text{O}_2$  process emerges as the most attractive oxidation system for reactive dye effluents in terms of complete decolorization followed by the UV/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  process.

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## Quantitative structure-activity relationships study to predict antifungal effect of some benzimidazole derivatives using ADME propertis

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Benzimidazole is a group of molecules which have shown potential for application in a variety of pharmacological targets. Biologically active benzimidazoles have been known for a long time and they can act as fungicides, as well as bactericides [1]. In the recent years they have attracted particular interest due to their anticancer and potential *in vitro* anti-HIV activity [2]. Quantitative structure-activity relationships (QSAR) analysis are useful tools in the rational search for bioactive molecules. This method included data collection, molecular descriptor selection, correlation model development and model evaluation. Good predictive models for antifungal activity of benzimidazole derivatives depend crucially on selection the right mathematical approach and the right molecular descriptor. In this context, the aim of the present study was to investigate the antifungal activity of some benzimidazole derivatives against *Saccharomyces cerevisiae* and to investigate relationships between determined minimum inhibitory concentration (MIC) and some calculated absorption, distribution, metabolism and excretion parameters, together called ADME parameters. Calculations of ADME parameters of studied compounds were performed using online PreADMET program. The complete regression analysis was carried out by NCSS statistical softwares.

Multiple linear regression (MLR) is the most used linear correlation method which can modeled the relationships between two or more explanatory variables and a response variable by fitting a linear equation to the observed data. Applying this method we have developed mathematical model that describe relationship between negative logarithms of molar MICs ( $\log 1/c_{MIC}$ ) and ADME parameters, *CaCo-2 cell and Plasma-protein binding (PPB)*.

$$\log 1/c_{MIC} = -2,4447 + 0.0131 \cdot CaCo-2 - 0.0670 \cdot PPB \quad (\text{Equation 1})$$

High correlation coefficient is not enough to select the equation as a model and hence statistical approaches were used to confirm the robustness and practical applicability of the equation. The statistical validity of the resulting model is determined by  $r$ ,  $s$ ,  $F$ ,  $PRESS$ ,  $r^2_{CV}$  and  $r^2_{adj}$ . The F-value is founded to be statistically significant at 99% level since the calculated F-value is higher as compared to the tabulated values. For the testing the quality of the predictive power equation the



LOO procedure was used. High value of PRESS (higher then one) and high value of  $r^2_{cv}$  and  $r^2_{adj}$  (higher then 0.5) is considered as a proof of the high predictive ability of the models.

**Table 2.** Statistical and cross-validation parameters

<b>r</b>	<b>s</b>	<b>F</b>	<b>PRESS</b>	<b><math>r^2_{cv}</math></b>	<b><math>r^2_{adj}</math></b>
0.8529	0.2286	25.3552	1.2561	0.6553	0.6988

To estimate the true predictive power of a model we calculated the biological activities of compounds using developed model and compared with the experimental values. The data show that the observed and the estimated values are very close to each other. The result of investigation indicate that the antifungal activity exhibited by the tested compounds is governed by the *CaCo-2 cell* and *Plasma-protein binding (PPB)* ADME parameters.

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## Uporedno određivanje toksičnih metala u biljnoj vrsti *Thymus serpyllum* sa različitih staništa u okolini Niša

### Comparative determination of toxic metals in plant species *Thymus serpyllum* at different locations in the vicinity of Niš

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U radu je ispitivan sadržaj toksičnih metala Pb, Cd, Cu, Cr u biljnoj vrsti *Thymus serpyllum* sa različitih staništa u okolini Niša metodom atomske-apsorpcione spektrometrije. Rezultati su pokazali povećan nivo Pb i Cd u biljnom materijalu sakupljanom u blizini lokalne deponije i pored auto-puta.

U tradicionalnoj medicini vrsta *Thymus serpyllum* – majčina dušica upotrebljava se kao čaj, aromatični začin i u aroma terapiji. Staništa ove biljne vrste su na sunčanim i suvim mestima po livadama, pašnjacima, na krajevima šuma, pored puteva i proplanaka [1]. Mikroelementi učestvuju u metabolizmu biljaka, strogo specifično i u određenim fazama rasta i razvika. Međutim, u većim koncentracijama bez obzira na fiziološku ulogu deluju toksično i utiču na iskorišćenost drugih bioelemenata. Neki metali pri malim koncentracijama ne deluju na biljke, ali su iznad nekog nivoa toksični (Pb, Cd, Cr), njihov sadržaj u biljci može biti indikator kontaminiranosti područja na kome raste, pri čemu akumulacija toksičnih metala u pojedinim delovima biljke zavisi od biljne vrste, pokretljivosti metala, sastava zemljišta, pH, količine padavina i prisustva drugih jonskih i molekulskih vrsta u zemljištu [2].

Analiziran je sadržaj Pb, Cd, Cu i Cr u nadzemnom delu biljke *Thymus serpyllum* sa lokaliteta u okolini Niša, sakupljan u fazi punog cveta. Isti je sušen na vazduhu zaštićen od svetlosti, a potom spaljivan bez plamena, žaren na 400 °C, 6 sati. Mineralni ostatak je rastvaran u HNO<sub>3</sub>, potom tretiran HCl kiselinom i konačno rastvaran u dejonizovanoj vodi. Sadržaj metala određivan je atomskom apsorpcionom spektrometrijom (AAS).

Sadržaj toksičnih metala u nadzemnom delu biljne vrste *Thymus serpyllum* sa različitih lokaliteta u mg toksičnog metala po kg biljnog materijala prikazan je u sledećoj tabeli.

**Tabela 1.** Sadržaj toksičnih metala u biljnoj vrsti *Thymus serpyllum* [mg/kg]

uzorak	Pb	Cd	Cu	Cr
I	0.84	0.06	0.84	< 1.00
II	2.42	0.25	1.06	< 1.00
III	6.62	0.42	3.20	< 1.00
IV	15.80	1.06	3.80	< 1.00

I – planinska livada na obroncima Leskovika (Aleksinac, 40 km od Niša); II – Gornji Dušnik – Suva planina (35 km od Niša) krečnjačko zemljište bogato gvoždem; III – 10 m od male lokalne deponije (Oblačinsko jezero, 20 km od Niša), IV – 20-30 m od auto-puta Niš-Aleksinac (20 km od Niša).

Sadržaj Pb u većini biljnih vrsta je normalno 0.5-3.0 mg/kg, mada je za neke biljne vrste toksični nivo ovog metala i preko 100 mg/kg [2]. Prema našim rezultatima, posebno je visok nivo Pb u cvetu biljke koja je rasla pored auto-puta (15.80 mg/kg) i u blizini lokalne deponije na kojoj se otpad spaljuje (6.60 mg/kg). U malim koncentracijama ne utiče vidljivo na razvoj biljaka, a pri višim koncentracijama izaziva brojne fiziološke, anatomske, morfološke promene. Pravilnik o kvalitetu čajeva R. Srbije predviđa nivo Pb ispod 2 mg/kg i do 5 mg/kg u biljnim mešavinama, tako da je sasvim zadovoljavajući kvalitet biljaka koje su rasle daleko od antropogenih izvora kontaminacije ovim metalom (uzorci I i II). Kadmijum dospeva u biljke preko korena, a iz vazduha preko nadzemnih organa. Verovatno je povećani nivo Cd u biljnom materijalu sakupljanom u blizini deponije na kojoj se otpad i spaljuje (0.42 mg/kg) i pored autoputa (1.06 mg/kg) rezultat akumulacije preko nadzemnih delova biljke. Ovaj metal usvaja većina biljaka čemu doprinosi njegova sposobnost da se dobro kompleksira sa  $\text{Cl}^-$  i  $\text{OH}^-$  jonima, što povećava njegovu pokretljivost u životnoj sredini i mogućnost izmenljive adsorpcije sa katjonima sličnih osobina ( $\text{Ca}^{2+}$  i  $\text{Zn}^{2+}$ ). Sadržaj Cu u nadzemnom delu biljke sa cvetom je u granicama za jednogodišnje zeljaste biljke i povrće (< 9 mg/kg). Bakra u zemljištu može biti i duplo više, ali je slabo pokretljiv katjon pošto se lako vezuje za minerale gline, absorbuje i kompleksira pa je slabo dostupan biljkama i ima ga manje nego u zemljištu. Visoki nivoi Cu u zemljištu izazivaju poremećaje u usvajanju drugih metala, posebno Fe i Mo. U ispitivanim uzorcima nivo Cr bio je ispod 1 mg/kg [3].

Rezultati ispitivanja sadržaja toksičnih metala Pb, Cd, Cu, i Cr, u nadzemnom delu biljke *Thymus serpyllum* sakupljene u punom cvatu na lokalitetima u okolini Niša pokazali su znatno povećani nivo istih u blizini izvora kontaminacije (deponija, auto-put). Rezultati su interesantni, s jedne strane jer ukazuju na neophodnu opreznost pri nabavljanju biljnog materijala od lokalnog stanovništva, a s druge strane ukazuju na potencijalnu primenu biljne vrste u fitoremedijaciji.

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## **Degradacija nikotina pomoću plazma reaktora baziranog na dielektričnom barijernom pražnjenju: direktan, indirektan i katalitički postupak**

### **Degradation of nicotine by using a plasma reactor based on dielectric barrier discharges: direct, indirect and catalytic process**

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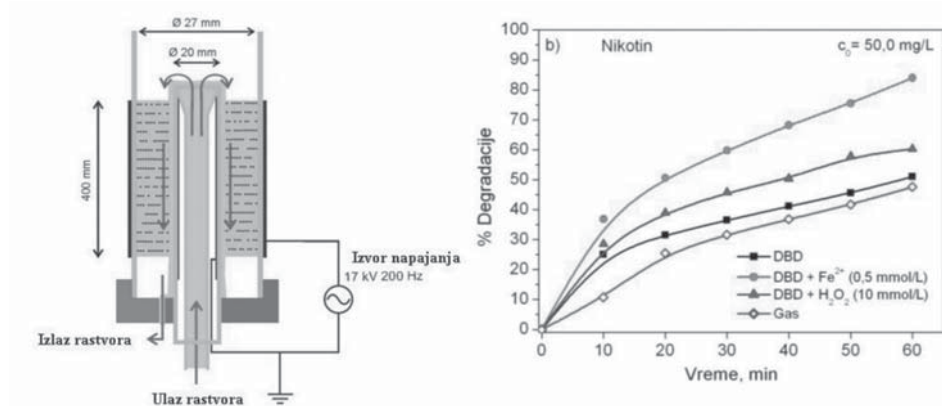
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Nikotin je alkaloid koji se nalazi u nekim biljkama, ali je njegov glavni izvor duvan, koji se koristi za proizvodnju cigareta. Uprkos poznatim rizicima upotrebe davana, pušenje je i dalje globalni problem jer negativni efekti nikotina na ljudsko zdravlje obuhvataju bolesti srca, rak i respiratorne poremećaje, a čak može da izazove i genotoksične promene. Pored zavisnosti koju stvara, nikotin je veoma toksično jedinjenje jer 40-60 mg može biti smrtonosna doza za odrasle ljude, što predstavlja mnogo višu toksičnost u odnosu na mnoge druge alkaloidne. Nikotin je takođe sastavni deo nekih farmaceutskih proizvoda i shodno tome, pored proizvodnje cigareta, lekovi bazirani na nikotinu su još jedan izvor ove supstance koja može da stigne u industrijske i komunalne otpadne vode. Ako sadržaj nikotina prelazi 500 mg/kg suve materije, ovaj otpad se klasifikuje kao toksičan i opasan (European Union Regulations). Zbog visoke rastvorljivosti nikotina u vodi, postoji ozbiljan rizik pri čuvanju, jer može doći do ispiranja nikotina iz otpada i njegove migracije u vodonosne slojeve, što je posebno opasno i za životnu sredinu i za zdravlje ljudi. Otpad koji ostaje posle proizvodnje cigareta mora se tretirati pre nego što se odloži. Na svetskom tržištu je prisutan konstantan porast proizvodnje davana i duvanskih proizvoda, što za posledicu ima porast nivoa različitog duvanskog otpada (sadrži visoku koncentraciju nikotina) sa 9000 tona u 2000. god. do 23.000 tona u 2007. godini. Metode za uklanjanje nikotina iz vodenih rastvora uključuju unapređene procese oksidacije (AOP), biološke procese kao što su aerobne i anaerobne biodegradacije, kao i adsorpciju na čvrstoj fazi [1,2].

U okviru ovog rada ispitana je efikasnost degradacije vodenih rastvora nikotina, pomoću plazma reaktora koji radi na principu dielektričnog barijernog pražnjenja (DBD, *Dielectric Barrier Discharge*) (Slika 1a) [3]. Početne koncentracije nikotina u rastvorima su bile 50,0 i 300,0 mg/L, a ukupna tretirana zapremina rastvora je bila 500 mL. Vreme tretmana je bilo 60 min, a kinetika degradacije je praćena na svakih 10 min. Tretman rastvora je izveden direktnim (bez i sa homogenim katalizatorima) i indirektnim postupkom. Direktan način podrazumeva recirkulaciju rastvora

kroz DBD reaktor, bez dodatnog uvođenja gasa u rastvor. Indirektan tretman podrazumeva barbotiranje gasa iz DBD reaktora kroz porozan difuzer u rastvor koji se nalazi u zatvorenom cilindričnom sudu. Protok rastvora kroz DBD reaktor je bio 100 mL/min, a protok radnog gasa (vazduha) je bio 5 L/min, dok je snaga pražnjenja iznosila 60 W. U direktnom postupku je ispitan i uticaj dodatka homogenih katalizatora:  $\text{Fe}^{2+}$ ,  $c_0 = 0,5 \text{ mmol/L}$  i  $\text{H}_2\text{O}_2$ ,  $c_0 = 10 \text{ mmol/L}$  na efikasnost degradacije. Efikasnost degradacije je merena 24 h od tretmana rastvora plazmom (Slika 1b). Efikasnost degradacije (%) nikotina je praćena HPLC analitikom tehnikom na aparatu Dionex UltiMate 3000 (Thermo Fisher Scientific, Bremen, Germany) opremljenim sa DAD detektorom (kolona: Hipsil Gold aQ, 150x3 mm, 3 $\mu\text{m}$ ; eluent: 10 mM fosfatni pufer, pH=3 i metanol, 60% i 40% izokratski, protok 0,4 mL/min; talasna dužina: 260 nm).



**Slika 1.** a) Šema DBD reaktora, b) Efikasnost degradacije (%) nikotina početne koncentracije od 50,0 mg/L pomoću direktnog, katalizovanog i indirektnog postupka korišćenjem DBD reaktora

Takođe, za uzorke pri početnoj koncentraciji od 300 mg/L nikotina koji su 60 min tretirani direktnim i indirektnim postupkom određeno je smanjenje hemijske potrošnje kiseonika (HPK). Degradacioni proizvodi nikotina, nakon 60 min tretmana pomoću svih ispitivanih degradacionih postupaka, su određeni UHPLC–Orbitrap–MS tehnikom (Thermo Fisher Scientific, Bremen, Germany).

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## **Degradacija nejonskih i anjonskih surfaktanata primenom reaktora na bazi dielektričnog barijernog pražnjenja (DBD)**

### **Degradation of nonionic and anionic surfactants using of the reactor based on dielectric barrier discharge (DBD)**

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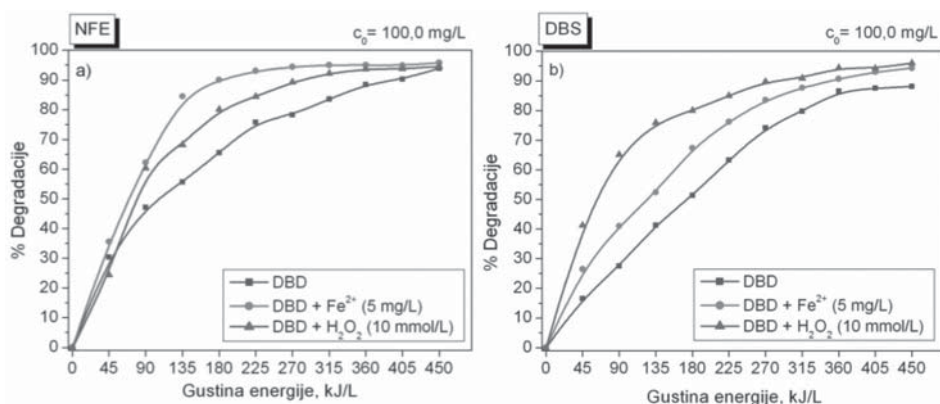
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Mnogi neželjeni fenomeni u životnoj sredini povezani su sa prisustvom surfaktanata u vodi i otpadnim vodama. Surfaktanti izazivaju eutrofikaciju površinskih voda i negativno utiču na floru i faunu. Neki detergentsi inhibiraju rast algi već pri koncentracijama od 1 mg/dm<sup>3</sup>, dok je toksična doza za ribe od 2 do 8 mg/dm<sup>3</sup>. Metode za uklanjanje surfaktanata uključuju unapređene procese oksidacije (AOP), biološke procese kao što su aerobne i anaerobne biodegradacije, kao i adsorpciju na čvrstoj fazi [1]. Ograničenja tradicionalnih procesa za prečišćavanje otpadnih voda, kao što su niska efikasnost i proizvodnja sekundarnog otpada, mogu se prevazići korišćenjem unapređenih oksidacionih procesa (AOP, *Advanced Oxidation Process*). Električna pražnjenja, a posebno neravnotežne (netermalne) plazme čine posebne klase AOP-a i predmet su ovog rada.

U okviru ovog rada ispitana je efikasnost degradacije, vodenih rastvora dva anjonska i dva nejonska surfaktanta, pomoću plazma reaktora koji radi na principu dielektričnog barijernog pražnjenja (DBD, *Dielectric Barrier Discharge with water falling film*) sa tankim vodenim filmom rastvora koji se tretira [2]. Vodeni film tretiranog rastvora se konstantno obnavlja, tako da reaktor radi po principu protočnog reaktora, a samo pražnjenje se odvija na granici tečnost-gas. Pražnjenje je izvedeno u atmosferi vazduha na atmosferskom pritisku. U ovako dizajniranom pražnjenju, reaktivne vrste se prenose iz plazme u tečnu fazu u kojoj se reakcije sa zagađivačima i odvijaju. Ovo pražnjenje je u stanju da proizvede O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, •OH kao i druge aktivne vrste. Pored toga, ovo pražnjenje generiše UV zračenje, kao i jone (OH<sup>-</sup>, O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, O<sub>2</sub><sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>) i elektrone.

Efikasnost degradacije (%) nejonskih (Triton X-100 i nonilfenil-etoksilat -NFE) i anjonskih (natrijum-dodecil-sulfat -SDS i natrijum-dodecil-benzensulfonat -DBS) surfaktanata je praćena UV-VIS spektrofotometrijskom analizom [3] (GBC Cintra 10, GBC Scientific Equipment Pty Ltd., Australija) pri primenjenim gustinama energije od 45- 450 kJ/L. Početne koncentracije surfaktanata u rastvorima su bile 100,0 mg/L. Ispitan je i uticaj dodatka homogenih katalizatora (Fe<sup>2+</sup>, c<sub>0</sub> = 5 mg/L i H<sub>2</sub>O<sub>2</sub>, c<sub>0</sub> = 10 mmol/L) kao i vremena stajanja od 5 minuta i 24 h od tretmana

plazmom na efikasnost degradacije ispitivanih surfaktanata. Uvedena gustina energije je povećavana višestrukim prolascima rastvora kroz reaktor (10 puta) što odgovara ukupnoj unetoj gustini energije od 450 kJ/L. Na primeru Tritona X-100, pri početnoj koncentraciji od 300 mg/L, ispitano je smanjenje hemijske potrošnje kiseonika (HPK) za unete gustine energije od 225 i 450 kJ/L. Polazna toksičnost i toksičnost rastvora Tritona X-100 i NFE ( $c_0 = 100,0$  mg/L) posle tretmana plazmom (za 225 i 450 kJ/L), ispitana je pomoću *Artemia salina* test organizama [4].



**Slika 1.** Efikasnost degradacije nejonskog i anjonskog surfaktanata u zavisnosti od primnjene gustine energije mereno posle 24 h od tretmana plazmom u DBD reaktoru: a) NFE, b) DBS; ( $c_0 = 100,0$  mg/L,  $Fe^{2+}$ ,  $c_0 = 5$  mg/L i  $H_2O_2$ ,  $c_0 = 10$  mM)

Sa grafika (Slika 1) se može videti da je viša efikasnost degradacije u svim sistemima postignuta kod nejonskog (NFE) surfaktanta u odnosu na anjonski (DBS). Dodatak homogenih katalizatora je doprineo povećanju % degradacije surfaktanata.  $Fe^{2+}$  je efikasniji katalizator od  $H_2O_2$  kod degradacije nejonskih surfaktanata, dok je njihov uticaj kod anjonskih surfaktanata obrnut. Degradacija se povećala tokom stajanja od 24 h u odnosu na degradaciju koja je postignuta posle 5 minuta od tretmana plazmom. Tokom degradacije postignuto je smanjenja HPK vrednosti i toksičnosti plazmom tretiranih rastvora surfaktanata.

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## **Kontinualna analiza lako isparljivih organskih jedinjenja u ambijentalnom vazduhu urbane sredine primenom gasne hromatografije i masene spektrometrije**

### **Continuous Analysis of Volatile Organic Compounds in Ambient Air in Urban Areas by Gas Chromatography Coupled with Mass Spectrometry**

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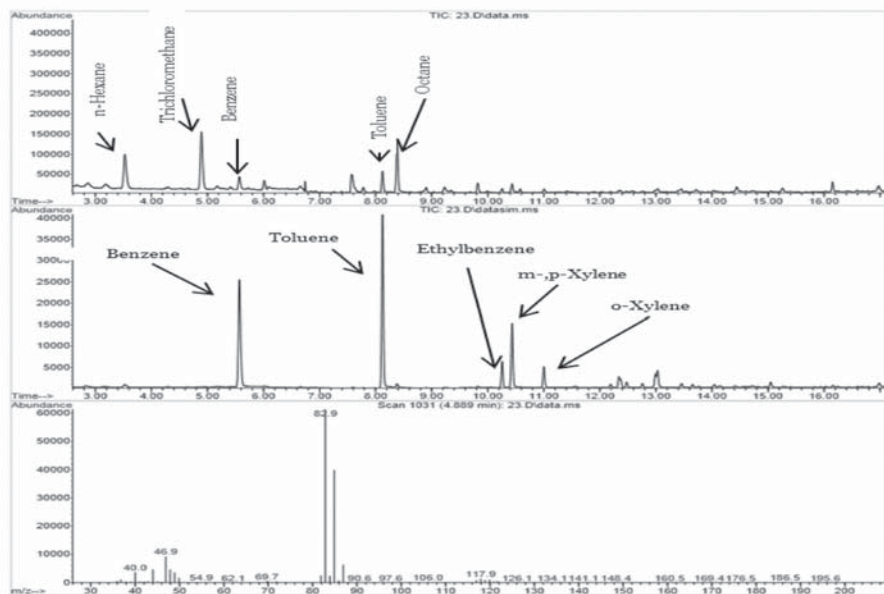
Urbane sredine predstavljaju područja u kojima je prisutno značajno zagađenje ambijentalnog vazduha. Lako isparljiva organska jedinjenja su jedna od najznačajnijih klasa zagađivača ambijentalnog vazduha [1]. Lako isparljiva organska jedinjenja u ambijentalnom vazduhu mogu biti prirodnog i antropogenog porekla [2]. U urbanim sredinama dominantni su antropogeni izvori među kojima se izdvajaju saobraćaj, manipulacija naftnim derivatima i industrijski izvori [3-6]. Pored direktnog negativnog uticaja koji imaju na ljudsko zdravlje, lako isparljiva organska jedinjenja su veoma reaktivna u ambijentalnom vazduhu što za posledicu ima nastanak sekundarnih zagađivača kao što su prizemni ozon, organske kiseline i sekundarni organski aerosoli [7-11]. Sve to ukazuje na potrebu da se precizno odrede masene koncentracije što većeg broja lako isparljivih organskih jedinjenja.

Uzorkovanje je vršeno u ulici Bulevar despota Stefana u Beogradu koja se nalazi u centralnoj gradskoj zoni i karakteriše je intenzivan saobraćaj. Ambijentalni vazduh je uzorkovan i koncentrovan korišćenjem sistema za kontinualno uzorkovanje koji se sastoji od pumpe, kontrolera masenog protoka i termalnog desorbera. Za razdvajanje i kvantifikaciju lako isparljivih organskih jedinjenja korišćena je tehnika gasne hromatografije sa masenim spektrometrom kao detektorom (GC-MSD) koji je direktno povezan sa sistemom za uzorkovanje. Jedna od značajnih karakteristika GC-MSD sistema korišćenog u ovom radu je odsustvo klasične pećnice. Grejni element i temperaturski senzor su obavijeni oko hromatografske kolone čime se omogućuje njeno brzo grejanje i hlađenje što za posledicu ima skraćivanje trajanja hromatografskog ciklusa. Primenjena tehnologija nosi oznaku LTM (*Low Thermal Mass*). Još jedna značajna prednost analitičkog sistema jeste i mogućnost jednovremenog rada u *sim* (Selective Ion Monitoring) i *scan* (full scan mode) režimu.

Na ovaj način u ambijentalnom vazduhu određeno je prisustvo mono aromatičnih ugljovodonika (benzen, toluen, etilbenzen i izomeri ksilena), alkana (n-heksan), halogenovanih ugljovodonika (hloroform), kao i varijacije njihovih koncentracija uzrokovane dnevnim i nedeljnim ciklusima. Na slici 1 prikazan je hromatogram ambijentalnog vazduha iz kog se vide prednosti mogućnosti



jednovenenog rada u *sim* i *scan* režimu. Prikazan je još i maseni spektar hloroforma kojim se potvrđuje prisustvo ovog jedinjenja u ispitivanom uzorku.



**Slika 1.** *scan* i *sim* hromatogram ambijentalnog vazduha i maseni spektar hloroforma

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## Process parameters affecting TiO<sub>2</sub> photo-catalytic activity

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One of the major global problems in modern days is confronting water pollution. Organic dyes are widely used in industries, and present widespread water pollutant. Titanium dioxide is the most commonly used photo-catalyst in combating the environmental pollution due to its excellent activity, stability, non-toxicity and cost-efficiency. The aim of this study was to investigate the effect of operating parameter – pH value of the solution on the photo-catalytic activity of TiO<sub>2</sub> in decolourisation process.

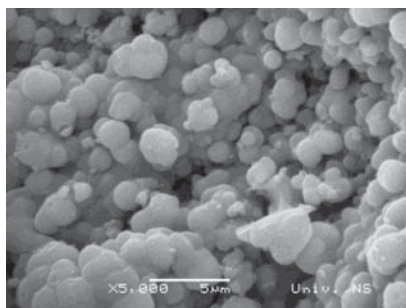
Titania-based catalyst was synthesized by a modified hydrothermal procedure from titanium *iso*-propoxide. The physico-chemical properties of the catalyst were characterized using BET method (Table 1.), XRD (not shown) and SEM (Fig. 1.) techniques, and photo-catalytic activity was tested in a reaction of methylene blue (MB) degradation, and monitored by using UV/VIS spectra.

**Table 1.** Textural properties of the TiO<sub>2</sub> catalyst

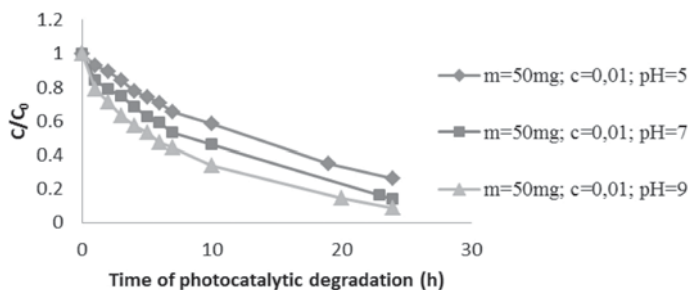
Specific surface area, S <sub>BET</sub> (m <sup>2</sup> /g)	Mean pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)
34.3	8.3	0.08

The results of catalyst textural properties indicate a relatively large surface area 34.3 m<sup>2</sup>g<sup>-1</sup> where the catalytic reaction could occur [1], thus photo-catalytic activity with the absence of internal diffusion restrictions for transport and/or contact of dye with catalytic active sites may be expected. XRD pattern has shown that catalyst contains almost 100% catalytically active anatase crystal phase (≈90% anatase, and ≈10% rutile crystal phase). Crystallite size of anatase phase, calculated by Scherrer's equation [2] was 23.3 nm in diameter; therefore relatively high catalytic efficiency can be projected. SEM micrograph shows that catalytic material is mainly homogenous with spherical particles, which exhibit negligible tendency to form agglomerates [3]. The secondary particles can also be detected, and estimated size of particles is over 100 nm.

It can be noted that the photo-degradation process is more effective when using a higher pH value (Fig. 2). This can be correlated with the fact that in aqueous system titania is amphoteric, and when pH is higher than the isoelectric point of catalyst, its surface is predominantly negatively charged, active 'OH species are formed, thus encouraging the adsorption of cationic species such as the examined dye. On the other hand, under acidic conditions, the dye photo-catalytic degradation was slower; the adsorption of cationic dye is more difficult due to a protonation of the functional groups [1,4].



**Figure 1.** SEM image of the  $\text{TiO}_2$  catalyst



**Figure 2.** MB photo-catalytic degradation at different pH

The obtained results show beneficial nano-structure of the catalyst, acceptable textural properties of the catalytic material (specific surface area and mean pore diameter), and suitable surface/bulk catalyst morphology on nano-scale. Structural characteristics of the catalyst have shown, almost exclusively, a presence of photo-catalytically highly active anatase crystal phase with the appropriate crystallite size. The rate of photo-degradation process increases with increasing pH value. The catalyst physic-chemical features had an impact on the final catalytic performance in the test reaction of MB decomposition.

### Acknowledgements

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## **Utvrđivanje hidroloških veza u slivu Crnojevića rijeke, putem nekih mikroelemenata kao indikatora**

### **Determination of hydrologic connection to the basin Crnojevića river through the microelements as an indicator**

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Literaturni podaci ukazuju na relativno malu veličinu (195km<sup>2</sup>), ali i kompleksnost sliva Crnojevića rijeke. Prve pouzdane podatke o postojanju hidrološke veze između kraških podzemnih voda Cetinskog polja i Crnojevića rijeke dao je Milojević, 1935. godine, ubacivanjem trasera u tzv. glavni ponor, jer se preko njege u kraško podzemlje puštaju otpadne i atmosferske vode Cetinja. Utvrđena veza u većem stepenu osvijetljena je i korišćenjem masenog pronosa zagađivača [1,2]. Izuzetak čine otpadne – galvanske vode stare fabrike “Obod” koje su 5 decenija puštane u poseban ponor, neposredno u krugu same fabrike. Problem je dakle, Crnojevića rijeka, kao recipijent i transporter industrijskih zagađivača, budući da je druga važna pritoka koja pothranjuje vodom Skadarsko jezero – resurs konzumne ribe i potencijalno izvoriste pijaće vode. Osvježenju kvaliteta jezerske vode doprinose sublakustrična vrela ili “oka”, poznata pod nazivom “Ceklinski ribolovi”. Brojni autori ukazuju na zavidan kvalitet vode “oka” ovog područja, ali i da je u površinskoj vodi i sedimentu Jezera, poslije ušća Crnojevića rijeke u Jezero, došlo do promjena naročito u pogledu sadržaja nekih polutanata [2,3].

“Oko“Grab”, je predmet istraživanja u pravcu dokazivanja moguće hidrološke veze sa ponorom stare fabrike “Obod” u Cetinju, putem nekih, za galvanske vode, specifičnih mikroelemenata (Cd, Cu, Zn, Ni, P), kao trasera. Pretpostavljeno je da se dio infiltriranih industrijskih i dr. otpadnih voda mogu pojaviti i na oko “Grab” budući da je dokazana hidrološka veza voda glavnog ponora i voda obodske pećine tj. izvorišta Crnojevića rijeke, koje je na visočijoj koti od “oka” Grab, za oko 30m. U periodu 2008/2009 godine po prvi put, zahvatani su uzorci i po dubini vodenog stuba “oka” Grab sa tri tačke: T1-površina, T2-dubina oko 15 metara i T3-dubina oko 30 metara, oko koje su sa nekoliko mjesta zahvaćena 24 uzorka površinskog sedimenta.

Rezultati istraživanja pokazuju da je temperatura vode optimalna u čitavoj vodenoj masi, dostiže 29 °C i ne pada ispod 7,5 °C, što pored ostalog uslovljava i usporen i proširen tok vodotoka na području zaliva Graba. Tokom proljeća i ljeta na ovoj lokaciji izrazita je bujna vegetacija koja pospješuje i porast organskih supstanci u vodi (TOC = 2,91 i TON = 3,14 mg/dm<sup>3</sup>); za svoju mineralizaciju oduzima vodi kiseonik, čija koncentracija značajno opada po dubini vodenog stuba, tako da je sadržaj rastvorenog kiseonika u vodi iznad površinskih sedimenata

na granici biološkog minimuma. Puferski kapacitet vode takođe opada po dubini (8,01-7,78-6,90). Elektrolitička provodljivost na površini vode imala je gotovo ujednačene vrijednosti od 270-300  $\mu\text{S}/\text{cm}$ , dok su se vrijednosti povećavale po dubini, u jednom navratu i do 436  $\mu\text{S}/\text{cm}$  u vodi na dnu, poslije obilnijih padavina. Istovremeno srednja vrijednost elektroprovodljivosti vode Crnojevića rijeke, na potezu vodotoka od izvora do "oka" Grab iznosila je 260  $\mu\text{S}/\text{cm}$ , gotovo kao i u površinskoj vodi vodotoka. U ovom podneblju hidrološka situacija povremeno se trenutno promijeni, tako da pri hidrološkoj situaciji srednje-velikih voda pojavljuje se zamućenje vode i povećavaju se vrijednosti do samog dna, što prate i vrijednosti ukupnog rastvorenog fosfora. Prirodni nivo hranjivih soli u vodi je odraz siromašne pedološke podloge u karstu, tako da je za nađene vrijednosti fosfata u vodi odgovoran antropogeni faktor. Porast fosfora, kadmijuma, bakra, nikla i cinka kako u vodi, tako i u površinskom sedimentu "oka" Grab može se pozdano pripisati učinku industrijskih aktivnosti na Cetinju. Ti uticaji u pogledu sadržaja Cd, Cu, Ni, Zn u vodi su značajno izraženiji nego što je to na izvoru Crnojevića rijeke [3]. Nađeno stanje svojstava vode i sedimenta na "oku" Grab pokazuje učinak antropogenog faktora. Predpostavka je da je to posledica kumulacije predmetnih mikroelemenata i dr. toksikanata u vremenu od preko 5 decenija aktivnosti fabrike "Obod", mineralizacije organskih materijala, kao i infiltracije atmosferskih voda koje spiraju nesanirana industrijska smetlišta. I bez obzira na to što fabrika već 2 decenije ne proizvodi, te da izostaje istraženost hidrološke moći "oka" Grab, a time i maseni protok istraživanih polutanata, traserska uloga njihovih sadržaja s pravom omogućava zaključak da postoji hidrološka veza na relaciji: galvanska voda ponora stare fabrike "Obod" - "oka" Grab.

Neophodno je sprovesti opsežniji monitoring, kao osnovni element integralnog upravljanja slivom Skadarskog jezera što nije ni do danas zaživjelo, uprkos ciljevima Okvirne direktive o vodi.

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## **Sadržaj teških metala u jestivom tkivu rečnih riba – indikator bezbedne hrane**

### **The content of heavy metals in the edible tissue of river fish - an indicator of safe food**

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U našim kopnenim vodama veći ili manji ekonomski značaj ima 29 vrsta riba. Privredni ribolov se vrši u nizijjskim rekama, Dunavu, Savi i Tisi. U navedenim rekama lovi se 12 vrsta riba, od kojih su 6 najznačajnije za ribolov: som, smuđ, šaran, mrena, deverika i kečiga. Akumulacija štetnih materija u jestivom tkivu rečnih riba je značajna ne samo sa stanovišta poznavanja zagađenosti životne sredine, nego i sa stanovišta higijenske ispravnosti jestivog tkiva (mesa) rečnih riba [1].

Stoga je cilj našeg istraživanja bio: 1) ispitivanje sadržaja teških metala i metaloida (olovo-Pb, kadmijum-Cd, živa-Hg, bakar-Cu, cink-Zn, gvožđe-Fe i arsen-As) u jestivom tkivu (mesu) 5 vrsta rečnih riba; 2) Utvrđivanje statističke značajne razlike između prosečnih sadržaja teških metala i metaloida u jestivom tkivu istih vrsta riba.

U ovom istraživanju prikupljen je 41 uzorak najčešće lovljenih riba: som (*Silurus glanis*), smuđ (*Stizostedion lucioperca*), šaran (*Cyprinus carpio*), mrena (*Barbus barbus*) i deverika (*Abramis brama*). Uzorkovanje je izvršeno 2007. godine, na toku Dunava uzvodno od Beograda, na lokaciji sela Belegiš.

Prikazani rezultati u ovom apstraktu odnose se na najtoksičnije metale, kao što su olovo i živa, dok će ostali rezultati biti prikazani u radu.

Najveći prosečan sadržaj olova utvrđen je u mesu šarana ( $0,056 \pm 0,011 \text{ mg/kg}$ ) a zatim u mesu soma ( $0,053 \pm 0,009 \text{ mg/kg}$ ) i mreene ( $0,044 \pm 0,012 \text{ mg/kg}$ ). Nije utvrđena statistički značajna razlika ( $p \geq 0,05$ ) između prosečnih sadržaja olova u mesu mreene, soma, odnosno šarana.

Sadržaj olova u pomenute tri vrste riba bio je statistički značajno veći ( $p \leq 0,001$ ) od sadržaja olova u mesu deverike ( $0,017 \pm 0,004 \text{ mg/kg}$ ) odnosno mesu smuđa ( $0,028 \pm 0,008 \text{ mg/kg}$ ).

Sadržaj žive u mesu smuđa bio je ispod granica detekcije (manji od  $0,1 \text{ mg/kg}$ ). Sadržaj žive u mesu šarana ( $0,382 \pm 0,123 \text{ mg/kg}$ ) bio je statistički značajno veći ( $p \leq 0,01$ ) od sadržaja žive u mesu mreene, odnosno deverike.

Nisu utvrđene statistički značajne razlike između sadržaja žive u mesu mreene i soma, ali je prosečan sadržaj žive u ove dve vrste ribe bio statistički značajno veći ( $p \leq 0,05$ ) od prosečnog sadržaja žive u mesu deverike.

Na osnovu dobijenih rezultata koji se odnose na sadržaj teških metala i metaloida, jestivo tkivo (meso) riba Dunava ne predstavlja toksikološki rizik u ishrani ljudi [2].

Utvrđeni sadržaj teških metala i metaloida pokazuje tendenciju odstupanja u odnosu na različite vrste riba, ali ne pokazuju prekoračenje utvrđenih normi shodno važećoj regulativi u Republici Srbiji [3].

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## Primena Zr dopovanog $\text{TiO}_2$ sorbenta za uklanjanje arsena iz vode

### Application of Zr doped $\text{TiO}_2$ sorbent for removal of arsenic from the water

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Prisustvo arsena u pijaćoj vodi, čak i u veoma niskim koncentracijama, može izazvati opasne posledice na zdravlje ljudi i životinja. U Srbiji na području Banata koncentracija arsena u pijaćim vodama prevazilazi maksimalnu dozvoljenu koncentraciju propisanu od strane Svetske zdravstvene organizacije [1, 2]. Toksičnost arsena zavisi od oksidacionog stanja i od hemijske forme. Oksidaciono stanje arsena ima važnu ulogu u sorpciji datog elementa a samim tim i na njegovu mobilnost u životnoj sredini [3]. Zato je vrlo bitno pozabaviti se metodama koje služe za uklanjanje arsena, kao i ispitivanjem uslova za uklanjanje arsena. Efikasnost sorpcije arsena iz vodenih rastvora određena je upotrebom  $\text{TiO}_2$  sorbenta dopovanog cirkonijumom, sintetisanog mikrotalasno-hidrotermalnom tehnikom. Mikrotalasnom digestijom rađeno je razaranje prethodno sintetisanog sorbenata radi utvrđivanja tačne koncentracije cirkonijuma. Sorbent je okarakterisan snimanjem XRPD i određeni su fizički parametri sorpcijom azota na 77 K [4, 5, 6]. Ispitivanjem zavisnosti sorpcionog koeficijenta od pH vrednosti, utvrđeno je da se As(III) najbolje sorbuje na pH 9, dok se As(V) najbolje sorbuje na pH 3. Ispitivanjem kinetike sorpcije utvrđeno je da, nakon 6h dolazi do uspostavljanja ravnoteže. Efikasnost sorpcije arsena opisana je Freundlich-ovim i Langmuir-ovim modelom izoterma [7]. Na osnovu koeficijenta korelacije ( $R^2$ ) zaključeno je da se sorpcija As(V) bolje opisuje Langmuir-ovim modelom, a As(III) Freundlich-ovim modelom. Vrednost Langmuir-ovog adsorpcionog kapaciteta ( $Q_0$ ) za As(V) je 32.34 mg/g, dok je vrednost Freundlich-ovog adsorpcionog kapaciteta za As(III) ( $K_f$ ) 7.93 mg/g. Prisustvo drugih jonskih vrsta ( $\text{SO}_4^{2-}$  i  $\text{H}_2\text{PO}_4^-$ ) u rastvoru negativno utiče na efikasnost sorpcije arsena.

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## **Masene koncentracije kalijuma, torijuma i uranijuma u zemljištu Beograda**

### **Mass concentrations of potassium, thorium and uranium in soil Belgrade**

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Prirodna radioaktivnost zemljišta zavisi od sadržaja radionuklida koji se u njemu nalaze, prvenstveno uranijuma, radijuma, torijuma i kalijuma. Ovi radionuklidi se značajno međusobno razlikuju kako po svojim fizičkim i geohemijskim osobinama, tako i u pogledu potencijalnih rizika za stanovništvo. Poznavanje sadržaja prirodnih radionuklida je neophodan uslov za procenu i kontrolu radijacionog rizika za stanovništvo i za izradu referentne baze na osnovu koje bi bile dokumentovane promene u radioaktivnosti životne sredine usled antropogenih aktivnosti. Istraživanja aktivnosti prirodnih radionuklida su takođe neophodna za primenu određenih mera u slučajevima kada se ustanovi povećanje radijacione doze u odnosu na preporučenu.

U radu su prikazane masene koncentracije kalijuma, torijuma i uranijuma u neobradivom zemljištu Beograda. Uzorci zemljišta su sakupljeni u toku 2006-2010. godine sa 70 lokacija. Osušeni uzorci zemljišta su mehanički usitnjeni, homogenizovani i upakovani u Marineli posude, koje su zatvarane hermetički i ostavljane da odstoje 40 dana da bi se postigla radioaktivna ravnoteža post-radonskih članova niza <sup>238</sup>U, pre gamaspektrometrijske analize. Analiza uzoraka izvršena je korišćenjem gamaspektrometra ORTEC-AMETEK sa 8192 kanala, rezolucije 1,85 i relativne efikasnosti 34% na 1,33 MeV za <sup>60</sup>Co. Za obradu spektara korišćen je softver Gamma Vision-32 [1].

U tabeli 1 prikazana je deskriptivna statistika srednjih vrednosti masenih koncentracija kalijuma, torijuma i uranijuma u neobradivom zemljištu Beograda.

**Tabela 1.** Deskriptivna statistika srednjih vrednosti masenih koncentracija K, Th i U u neobradivom zemljištu Beograda

Parametar	K (%)	Th (mg/kg)	U (mg/kg)
Opseg	1,6	12,9	3,5
Minimum	1,0	2,8	0,9
Maksimum	2,6	15,7	4,4
Srednja vrednost	1,6	9,5	2,6
Standardna devijacija	0,3	2,3	0,6
Medijana	1,6	9,6	2,7
Mod	1,5	9,6	2,8

Srednje masene koncentracije analiziranih elemenata u uzorcima zemljišta slične su prosečnim vrednostima na svetskom nivou, odnosno 1,3% za kalijum, 7,4 mg/kg za torijum i 2,8 mg/kg za uranijum [2].

Analizirani radionuklidi u uzorcima zemljišta Beograda nalaze se u širokom opsegu vrednosti, što je posledica velikog broja različitih geoloških struktura ispitivanih oblasti. Geološki sastav terena Beograda, geotektonski sklop, heterogenost konfiguracije terena (odnosno energija reljefa) utiču na dubinu pedološkog horizonta, poreklo, razmeštaj tipova zemljišta, a time i na odnos i sadržaj radionuklida u njima [3, 4].

Rezultati ovog istraživanja mogu poslužiti za preliminarnu procenu izlaganja populacije Beograda gama zračenju poreklom od prirodnih radionuklida u zemljištu. S obzirom na očekivani prostorni razvoj grada u veću aglomeraciju, podaci ove vrste su neophodni kao osnova za sveobuhvatnu procenu stanja životne sredine.

### Zahvalnica

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## Isopropyl alcohol in manual screen printing environment

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For more than 30 years, the printing industry has been continuously focusing on the question of how printing process can be performed using less isopropyl alcohol (IPA) due to the negative effects on workers health [1]. During the screen printing process, printers use cleanup solvents to remove the excess ink from the screens. These solvents contain toxic materials that pose a risk to workers and virtually all of them are classified as volatile organic compounds (VOCs) [2]. Therefore, the objective of this study was to evaluate the occupational exposure to IPA, quantitatively, by detailed field measurements in screen printing facilities (SPFs), as well as to determine the time variations of IPA concentrations between the investigated SPFs.

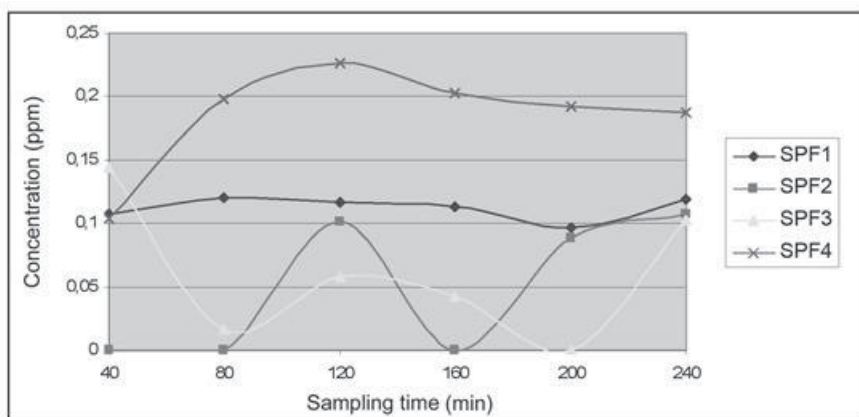
The air sampling was performed in four screen printing facilities (SPF 1-4) in Novi Sad during the manual printing process. Investigated facilities were small and similar in area (50 - 70 m<sup>2</sup>), number of employees (3 - 4) and the production volume (50 - 70 products per hour). The positions of sampling point were determined according to the technical characteristics of desk for manual screen printing process. Air was discontinuous sampled *in situ* for 6 times, once per 40 minutes, during 4 hours by mobile gas chromatograph Voyager (PerkinElmer Photovac Inc.).

Experimental results were confirmed the presence of isopropyl alcohol in screen printing environment (Table 1). The average concentration levels of IPA are much below the values of short-term exposure prescribed by the Occupational Safety and Health Standards (OSHA) [3] and the National Institute for Occupational Safety and Health (NIOSH) [4]. Such low IPA concentrations indicated that the investigated screen printing facilities uses non-alcohol solvents during the printing and cleaning process. Also, the installed ventilation fans and lower production volumes additionally decrease the exposure of employees' in manual screen environment.

**Table 1.** The average concentrations of IPA in screen printing environment

SPF	Average concentration (ppm)	MAC (ppm)	
		OSHA	NIOSH
1	0.112	500	2000
2	0.072		
3	0.061		
4	0.194		

The time variations of indoor IPA concentrations between the manual screen printing facilities are shown in Figure 1. The concentrations of IPA in SPF 1 were relatively constant during the sampling time; whereas in all others SPFs the increasing of IPA concentrations was observed at 120 min due to the intensive printing at the beginning of a print run. Obviously, the significant time variations of IPA concentrations were in SPF 2 and 3 due to the frequently interruptions of printing process.



**Figure 1.** Dependence of IPA concentrations on sampling time, SPF 1-4

Certainly, low IPA concentration levels indicated the tendency of the printers in the screen printing facilities to use the environmentally friendly solvents as the adequate replacement for IPA solvent.

### Acknowledgement

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## Effect of current density and $\text{H}_2\text{O}_2$ concentration on electrochemical decolorization of dye crystal violet at $\text{Ti}/\text{Bi}_2\text{O}_3$ anode

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Danijela Bojić, Aleksandar Bojić

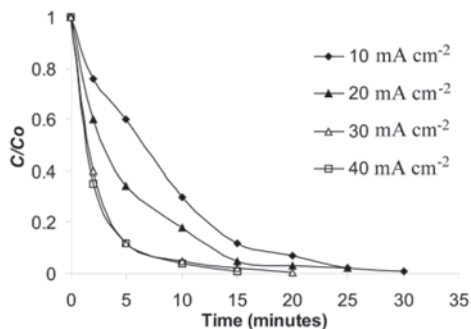
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Electrochemical oxidation is widely used for degradation of organic dyes. The oxidation of dyes is often done with hydroxyl radical,  $\bullet\text{OH}$ , electrogenerated at the anode. Anode material is a very important and the electrodes based on metal oxides are often used as the anodes [1-3]. Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) is an important material which has been recently applied as a photocatalyst in the processes for the removal of various organic compounds [4, 5]. The aim of this work was to investigate electrochemical decolorization of Crystal Violet on  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode, obtained by electrodeposition and calcination.

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{SO}_4$  and Crystal Violet (Sigma) were of AR grade. Electrochemical experiments were carried out using 510 DC potentiostat (Amel, Italy).  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode was prepared by electrodeposition from 0.1M  $\text{Bi}^{3+}$  in 1 M  $\text{HNO}_3$  on Ti substrate, at 0.60 V during 3 minutes, using Pt sheet as counter electrode and saturated calomel reference electrode, followed by calcination at 500°C for 90 minutes. Electrochemical decolorization was done using Crystal Violet solutions of 50  $\text{mgL}^{-1}$  dye, and 10 mM  $\text{Na}_2\text{SO}_4$  with  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode and Pt cathode. The dye concentrations were determined spectrophotometrically at 590 nm (UV-1650 PC, Shimadzu, Japan).

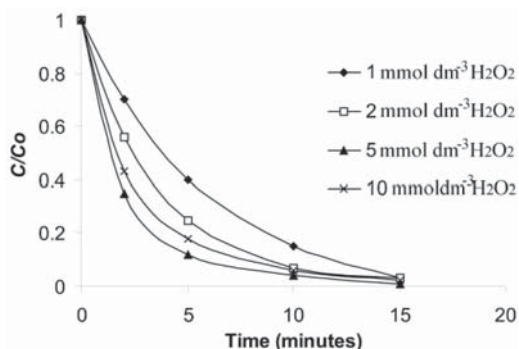
Current density,  $j$  and  $\text{H}_2\text{O}_2$  initial concentration are very important factors.  $\text{H}_2\text{O}_2$  decomposes at the anode at high voltages, providing  $\bullet\text{OH}$  radical, which then oxidizes the dye. Like in other advanced oxidation processes, its concentration depends on the  $\text{H}_2\text{O}_2$  initial concentration [1, 6].

The effect of current density on electrochemical decolorization of Crystal Violet at  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode is presented in Figure 1. The dye was decolorized in less than 30 minutes in the investigated range of  $j$  in the presence of 5  $\text{mmol dm}^{-3}$   $\text{H}_2\text{O}_2$ . All the decolorization reactions kinetics follows the pseudo-first order model. Reaction rate constants,  $k$ , for  $j$  values of 10, 20, 30 and 40  $\text{mA cm}^{-2}$  are: 0.1475, 0.1741, 0.2708 and 0.3371, with corresponding  $R^2$  values: 0.9854, 0.9865, 0.9766 and 0.9755, respectively. An increase of  $j$  causes the increase of  $k$ , but that increase is significant only up to 30  $\text{mA cm}^{-2}$ . Further increase of  $j$  causes only slight increase of  $k$ . Thus, it is assumed that optimal current density for this process is 30  $\text{mA cm}^{-2}$ .



**Figure 1.** The effect of current density on electrochemical decolorization of Crystal Violet at  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode ( $C_i(\text{H}_2\text{O}_2) = 5 \text{ mmol dm}^{-3}$ ).

An increase of  $\text{H}_2\text{O}_2$  initial concentration from 1 to 5  $\text{mmol dm}^{-3}$  causes the increase of  $k$ , but by further increase to 10  $\text{mmol dm}^{-3}$ , it starts to decrease because the generated  $\bullet\text{OH}$  radicals mostly react with the excess peroxide and produce hydroperoxyl radicals, which are less reactive than  $\bullet\text{OH}$  [6]. The  $k$  values for  $\text{H}_2\text{O}_2$  initial concentrations of 1, 2, 5 and 10  $\text{mmol dm}^{-3}$  are: 0.2171, 0.2466, 0.3371 and 0.2742, with  $R^2$  values: 0.9783, 0.9875, 0.9755 and 0.9739, respectively. Thus, the optimal  $\text{H}_2\text{O}_2$  initial concentration is 5  $\text{mmol dm}^{-3}$ .



**Figure 2.** The effect of  $\text{H}_2\text{O}_2$  initial concentration on electrochemical decolorization of Crystal Violet at  $\text{Ti}/\text{Bi}_2\text{O}_3$  anode ( $j=30 \text{ mA cm}^{-2}$ ).

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## Akutna toksičnost herbicida za organizme u vodi

## Acute toxicity of herbicides on aquatic organisms

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### Uvod

U radu su razmatrani parametri akutne toksičnosti za organizme u vodi (alge, dafnije i ribe) za aktivne supstance (a.s.) herbicida koje ulaze u sastav sredstava za zaštitu bilja (SZB) registrovanih za promet i primenu u Republici Srbiji 2012. godine [1]. Analizirani parametri su: srednja efektivna koncentracija inhibicije porasta (IC-50, 72 h) za alge; srednja efektivna koncentracija imobilizacije (EC-50, 48h) za dafnije i srednja smrtna koncentracija (LC-50, 96 h) za ribe [2]. Navedeni parametri toksičnosti za organizme u vodi predstavljaju osnovu za klasifikaciju i obeležavanje hemikalija i početnu procenu opasnosti i rizika.

### Materijal i metode rada

Korišćenjem dostupnih podataka na internetu [3] za navedene parametre akutne toksičnosti za organizme u vodi, izvršeno je rangiranje herbicida prema Pravilniku o klasifikaciji, pakovanju, obeležavanju i oglašavanju hemikalije i određenog proizvoda [2] na: veoma toksične, toksične i štetne. Kao osnovni izvor informacija o a.s. i broju SZB u Srbiji, korišćeni su podaci Uprave za zaštitu bilja iz novembra 2012. godine. Ovi podaci se rediguju i povremeno obnavljaju na sajtu Ministarstva poljoprivrede, šumarstva i vodoprivrede Republike Srbije [1].

### Rezultati istraživanja i diskusija

U Srbiji se u prometu krajem juna 2012. godine nalazilo 372 preparata SZB, dok je u novembru njihov broj porastao na 385. Ova SZB formulisana su na bazi ukupno 86 jedinjenja od kojih su 73 osnovne a.s. herbicida a 13 oblici (soli ili estri) prisutni u preparatima. U ukupnom broju preparata među kojima preovlađuju generici, na bazi jedne a.s. formulisano je oko 300 SZB, dok 85 SZB sadrži dve ili tri, a jedno SZB čak četiri a.s. Po broju registrovanih preparata ( $\geq 10$ ), najzastupljenija su SZB formulisana na bazi 14 a.s. prikazanih na Slici 1.

Od ukupno analiziranih 78 jedinjenja sa herbicidnim delovanjem za koje postoje dostupni podaci za **alge**, oko 52% (45 a.s.) pripada veoma toksičnim, 15% (13) toksičnim i 17% (15) štetnim. Samo se za dve a.s. (dihlobenil i mekoprop) može smatrati da nisu štetne za **alge**. Toksičnost herbicida za **dafnije** i **ribe** je znatno manja. Naime, od ukupno analiziranih 80 jedinjenja, veoma toksičnih za dafnije je 17% (15), toksičnih 19% (16) i štetnih 38% (33 a.s.). Za **ribe** od



ukupno analiziranog 81 jedinjenja, veoma toksičnim hemikalijama pripada 18% (16), toksičnim 17% (15) i štetnim 33% (28). U slučaju dafnija i riba se za 19%-22% analiziranih herbicida može smatrati da nemaju štetnog efekta.

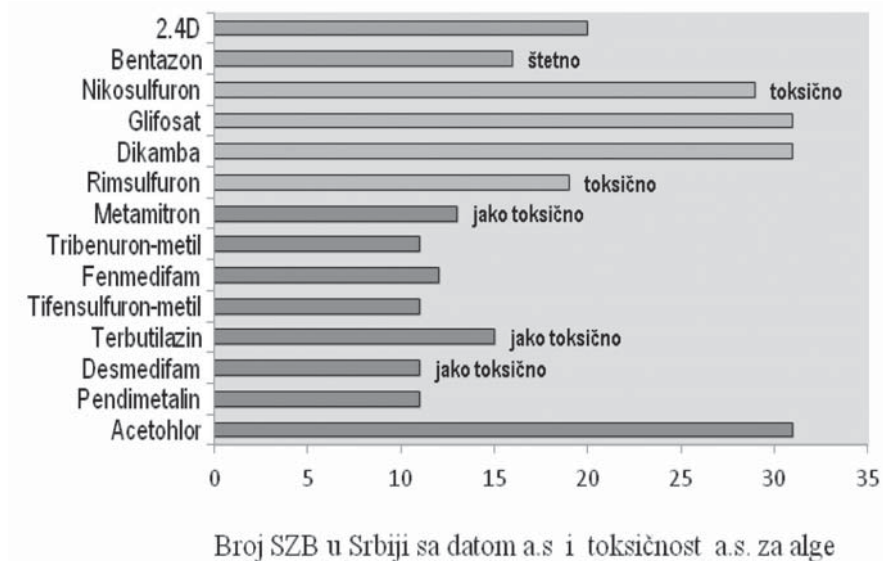
## Zaključak

Na osnovu prikupljenih podataka o akutnoj toksičnosti herbicida za organizme u vodi, može se zaključiti da za gotovo sva jedinjenja koja se koriste kao a.s. SZB u Srbiji raspoložemo sa dovoljno podataka za procenu efekata na organizme u vodi. Od ovih herbicida oko 70% spadaju u opasne po životnu sredinu i imaju znak opasnosti „N“.

Od 14 a.s. koje su najzastupljenije u Srbiji posmatrano sa stanovišta broja SZB i prikazanih na Slici 1, 12 su jako toksični i/ili toksični za alge, odnosno organizme u vodi.

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**Slika 1.** Najzastupljenije a.s. herbicida u Srbiji, broj SZB u kojima se nalaze i njihova toksičnost za alge

## **Fruktan iz *Brachybacterium sp.* CH-KOV3 - izolovanje, prečišćavanje i delimična karakterizacija**

### **Fructan from *Brachybacterium sp.* CH-KOV3 – isolation, purification and partial characterization**

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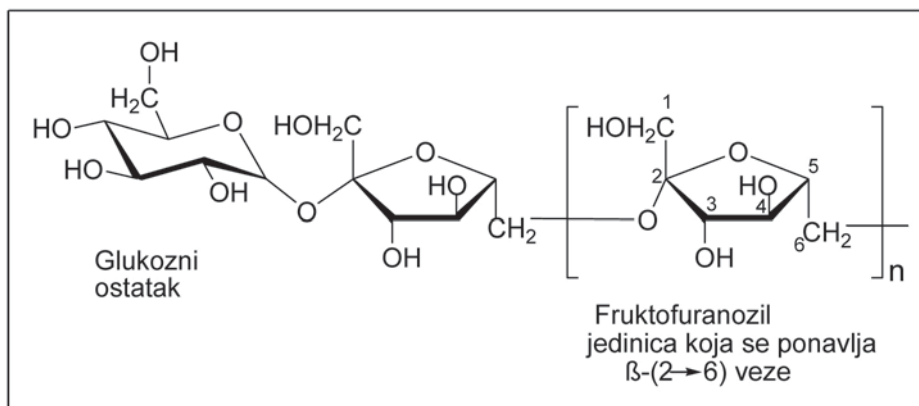
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Mikrobne polisaharide karakteriše velika strukturna raznolikost što omogućava veliki broj potencijalnih primena. Ekonomski značaj ovih polisaharida se ogleda u činjenici da su neki od ovih polimera danas široko zastupljeni biotehnoški proizvodi sa primenom u različitim oblastima: industriji hrane, kozmetici, poljoprivredi, farmaciji i medicini [1]. Poslednjih godina usled specifičnih reoloških i hemijskih osobina i činjenice da je netoksičan, velika pažnja je posvećena bakterijskom egzopolisaharidu fruktanu (levanu). Navedena svojstva omogućavaju potencijalnu široku primenu u različitim oblastima. Levan može biti upotrebljen kao stabilizator, emulgator, nosilac ukusa i mirisa, prebiotik, antioksidans i antitumorski agens, enkapsulator...

Cilj ovog rada je bio proučavanje strukturnih karakteristika egzopolisaharida čiji je producent *Brachybacterium sp.* CH-KOV3. Mikroorganizam je izolovan iz sedimenta kanala otpadnih voda južne industrijske zone Pančeva sa lokaliteta mesta ulivanja obrađenih voda HIP Petrohemije [2]. Analizom 16SrRNA gena upotrebom prajmera 27F (5'-AGAGTTTGATCMTGGCTCAG-3') i 1492R (5'-CGGCTACCTTGTTACGACTT-3') i sekvenciranjem identifikovan je kao *Brachybacterium paraconglomeratum*. Mikrobiološki dobijen polisaharid je okarakterisan hemijskim metodama, tankoslojnom hromatografijom, elementarnom analizom, FTIR i NMR spektroskopijom.

Na osnovu dobijenih rezultata, predložena je glavna strukturna karakteristika ovog polimera. Zaključeno je da je polisaharid koga proizvodi *Brachybacterium paraconglomeratum* CH-KOV3 homopolimerni polisaharid fruktan, sa osnovnim nizom koji se sastoji od D-fruktofuranoznih jedinica, povezanih međusobno  $\beta$ -(2,6)-glikozidnim vezama. Bočne grupe su fruktozni ostaci povezani za glavni lanac verovatno preko  $\beta$ -(2,1)-glikozidnih veza (Slika 1). Rezultati ukazuju da ispitivani polisaharid pripada polisaharidima levanskog tipa.



**Slika 1.** Hemijska struktura glavnog lanca fruktana (levana)

Dobijanje fruktana *Brachybacterium paraconglomeratum* CH-KOV3 je optimizovano gajenjem na različitim temperaturama (28, 37 i 45°C), pri različitim uslovima aeracije (0, 100 i 200 rpm) i koncentracije saharoze (40, 100, 140 g/L). Eksperiment je dizajniran i praćen upotrebom softvera Design-Expert 8.0.0.

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## **Osetljivost na teške metale i rast na aromatičnim jedinjenjima bakterijskih sojeva izolovanih iz zemljišta kontaminiranog naftnim derivatima**

### **Sensitivity to heavy metals and growth on aromatic compounds of bacterial strains isolated from soil contaminated with petroleum products**

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Aromatični ugljovodonici dospevaju u životnu sredinu na različite načine, kao što su izlivanje nafte, sagorevanje fosilnih goriva, upotreba pesticida, curenje benzina. Pošto su toksični i potencijalno karcinogeni, razvijaju se različite tehnologije za njihovo uklanjanje, a jedna od najvažnijih je bioremedijacija [1].

Brojna istraživanja pokazala su da teški metali utiču na mikrobne zajednice i njihovu aktivnost, jer izmenjuju esencijalne jone metala, ili modifikuju konformaciju proteina. Dejstvo metala zavisi od njegove koncentracije i dostupnosti u medijumu i vrste mikroorganizma. Teški metali su često prisutni u zemljištu kontaminiranom naftnim derivatima. Osetljivost na teške metale smanjuje biodegradacioni potencijal bakterija koje se koriste u procesu bioremedijacije [2].

U ovom radu ispitivana je osetljivost na teške metale i rast na aromatičnim jedinjenjima sojeva bakterija izolovanih iz kontaminiranog zemljišta uzorkovanog na različitim lokalitetima u Srbiji (Pančevo, Novi Sad, Niš). Za identifikaciju sojeva korišćena je analiza 16s rDNA sekvence. Korišćeni su sojevi *Bacillus* sp. NS032 (Genbank JF826527), *Pseudomonas aeruginosa* 67 (JN995661), *Pseudomonas aeruginosa* D3 (JN995664), *Rhodococcus* sp. RNP05 (JQ065876), *Oerskovia* sp. CHP-ZH25 (JX430000), *Gordonia* sp. CHP-315 (JX429999), *Cupriavidus* sp. CHP-YG38 (JX965398), *Micrococcus* sp. CHP-A35 (JX965396), *Sphingobacterium* sp. CHP-Y37 (JX965397), *Rhodococcus* sp. CHP-NR31 (JX965395).

Uticaj teških metala određen je metodom difuzije na Miler-Hintonovom agaru. Mogućnost rasta na različitim izvorima ugljenika (fenol, fenantren, natrijum-benzoat, 3,4-hidroksibenzojeva kiselina) ispitivana je na mineralnom medijumu za korišćenje ugljovodonika.

Na osnovu dobijenih rezultata može se zaključiti da *Bacillus* kao izvor ugljenika može da koristi fenol, fenantren i natrijum-benzoat, *Rhodococcus* i *Sphingobacterium* mogu da rastu na svim podlogama, a *Micrococcus* na fenantrenu i

natrijum-benzoatu. *Pseudomonas* označen kao 67 raste na 3,4-hidroksibenzojevoj kiselini, a drugi označen kao D3 na natrijum-benzoatu. *Oerskovia* sp. raste na fenantrenu, a *Cupriavidus* i *Gordonia* sp. ne rastu ni na jednom ispitivanom izvoru ugljenika.

Najmanju osjetljivost na kadmijum ( $\text{Cd}^{2+}$ ) pokazali su sojevi iz roda *Cupriavidus* i *Rhodococcus*, na nikl ( $\text{Ni}^{2+}$ ) *Rhodococcus* sp. i *Micrococcus* sp, na bakar ( $\text{Cu}^{2+}$ ) *Cupriavidus* sp. i *Micrococcus* sp, i na cink ( $\text{Zn}^{2+}$ ) *Gordonia* sp. i *Micrococcus* sp.

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## **Ispitivanje humifikacionih transformacija tokom bioremedijacije ugljovodonika na pilot postrojenju**

### **Humic Substances Transformation During Bioremediation of Petroleum Hydrocarbons on Pilot Experiment**

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#### **Uvod**

U ovom radu, proučavana je mogućnost primene autohtonog zimogenog konzorcijuma mikroorganizama za bioremedijaciju naftnog zagađenja, kao i mogućnost nastanka huminskih supstanci tokom procesa bioremedijacije. Naime, neki istraživači (1) smatraju da tokom biorazgradnje policikličnih aromatičnih ugljovodonika (PAH) nastaju supstance slične huminskim, što je veoma značajno, s obzirom da huminske supstance predstavljaju jedan od ključnih elemenata kvaliteta zemljišta.

U cilju ispitivanja navedene hipoteze, dizajnirano je pilot postrojenje za bioremedijaciju, i praćenje promena u ugljovodoničnom sastavu, kao i promena u sastavu huminskih supstanci.

#### **Materijal i metode**

Pilot eksperiment bioremedijacije je realizovan u otvorenim sudovima od 1 m<sup>3</sup> u količini od 0,6 m<sup>3</sup> u trajanju od 90 dana. Jedan sud predstavlja kontrolu i u njemu su umešani piljevina, pesak i otpadni mazut. Piljevina se dodaje u cilju povećanja retencionog vodnog kapaciteta, aeracije, ali i kao alternativni izvor ugljenika. U drugi sud su pored piljevine, peska i otpadnog mazuta dodati biostimulatori, izvori azota i fosfora (amonijum-nitrat i kalijum-difosfat) i biomasa.

Huminske supstance su ekstrahovane iz 40g uzorka sa 200 ml NaOH/Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (2). Nakon odvajanja taloga, huminske kiseline precipitiraju iz supernatanta za-kišeljavanjem sa 6M hlorovodoničnom kiselinom do pH 1. U supernatantu se nalazi fulvo frakcija, koja se na DAX smoli razdvaja na frakciju fulvo kiselina i na frakciju nehuminskih supstanci (3).

Ukupni ugljovodonici nafte (TPH) su određivani prema ISO 16703 (4).

## Rezultati

Početna vrednost TPH u pilot postrojenju je iznosila 22 g/kg. Na kraju eksperimenta, ukupni ugljovodonici su smanjeni na 7 g/kg u sudu sa biomasom, dok je u kontrolnom sudu ta vrednost iznosila 19 g/kg. Sadržaj huminskih kiselina, u početnom uzorku ih je bilo 0,23%, na kraju eksperimenta u inokulisanom sudu sadržaj huminskih kiselina je porastao na 0,70%, dok je u kontrolnom sudu primećeno neznatno povećanje sa 0,23% na 0,27%.

Humifikacija je praćena kvantifikacijom i monitoringom nastanka huminskih supstanci. Parametri koji mere razvoj huminskih supstanci su: stepen ekstrakcije ( $TE = C_{HS}/C$ ), odnos huminskih prema fulvo kiselinama ( $C_{HA}/C_{FA}$ ), indeks polimerizacije ( $IP = C_{FF}/C_{HS}$ ) (5).

$C_{HA}$ ,  $C_{HS}$ ,  $C_{FF}$ ,  $C_{FA}$  i  $C$  predstavljaju rastvoreni organski ugljenik redom u huminskim kiselinama, u huminskim supstancama, u fulvo frakciji, u fulvo kiselinama i ukupni organski ugljenik u čvrstom uzorku.

U Tabeli 1. su prikazani parametri koji opisuju i kvantifikuju procese humifikacije, na početku eksperimenta i na kraju eksperimenta.

**Tabela 1.** Sadržaj ugljenika u čvrstoj frakciji, rastvorni ugljenik u huminskim frakcijama i parametri humifikacije

	C mg/g	C <sub>HS</sub> mg/g	C <sub>HA</sub> mg/g	C <sub>FA</sub> mg/g	C <sub>FF</sub> mg/g	C <sub>HA</sub> /C <sub>FA</sub>	IP	TE
Početni uzorak	49,5	6,05	3,40	2,04	3,17	1,67	0,52	0,12
Kontrola	48,8	6,28	3,61	1,91	3,1	1,89	0,49	0,13
Sud sa biomasom	42,2	7,9	4,82	1,16	2,5	4,15	0,31	0,19

IP: C<sub>FF</sub>/C<sub>HS</sub>; TE: C<sub>HS</sub>/C; FF: fulvo frakcija (fulvo kiseline+nehuminske supstance)

Dobijeni rezultati pokazuju da je procenat huminskih kiselina tokom procesa bioremedijacije porastao više od tri puta, što je potvrđeno i povećanjem sadržaja C u huminskim kiselinama u odnosu na početni uzorak, dok je C koji pripada fulvo kiselinama opao za 44%. Može se pretpostaviti da je biodegradacija ili transformacija u huminske kiseline uzrok navedenog smanjenja.

## Zaključak

*Dobijeni rezultati ukazuju na nastanak huminskih supstanci tokom eksperimenta, potvrđujući hipotezu o simultanom procesu bioremedijacije i humifikacije, što je veoma važno sa aspekta ozdravljenja zemljišta.*

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## **Ispitivanje bioremedijacionog potencijala zimogenih i alohtonih mikroorganizama na sedimentu uzorkovanom iz kanala otpadnih voda industrijske zone Pančeva**

### **Bioremediation potential of the zymogenous and allochthonous microorganisms on the sediment sampled from the the wastewater canal of Pančevo industrial area**

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#### **Uvod**

Bioremedijacija je metoda koja omogućava prečišćavanje svih sfera životne sredine kontaminirane najrazličitijim zagađujućim supstancama [1]. Cilj ovog rada bio je istraživanje bioremedijacionog potencijala mikroorganizama koji razlažu ugljovodonike, radi njihove potencijalne primene u dekontaminaciji sedimenta kanala otpadnih voda (KOV) industrijske zone Pančeva [2].

#### **Materijal i metode**

Bioremedijacioni potencijal zimogenih (izolovanih iz sedimenta KOV) i alohtonih mikroorganizama (izolovanih sa drugih lokacija kontaminiranih ugljovodonicima) je proučavan na uzorku sedimenta uzorkovanom na mestu ulivanja otpadnih voda HIP Petrohemije. Eksperimentalni fermentacioni model sistemi (28°C, 200 rpm, 30 dana) su sadržali uzorak sedimenta suspendovan u tečnoj mineralnoj podlozi (10% m/V).

Smanjenje sadržaja zagađujućih ugljovodonika praćeno je kroz promenu sadržaja ukupne ekstrabilne organske supstance (EOS) kao i promenu grupnog sastava tj. maltena (alifatičnih, aromatičnih, masnih kiselina i NSO jedinjenja) i asfaltena. Broj ukupnih aerobnih mezofilnih hemoorganoheterotrofnih bakterija (UBA) i mikroorganizama razlagača ugljovodonika (RUV) je analiziran 1, 15. i 30. dana fermentacije. HP0 je model sistem analiziran u nultom vremenu. U cilju kontrole uticaja abiotičkih faktora na smanjenje koncentracije ugljovodonika, analiziran je i prethodno sterilisan model sistem (HP1). Ispitivan je bioremedijacioni potencijal inokuluma alohtonih razlagača ugljovodonika *Rhodococcus sp.* RNP05, *Pseudomonas sp.* NS009 (HP2), inokuluma zimogenih sojeva *Pseudomonas sp.* CH-KOV5, *Rhodococcus sp.* CH-KOV17, *Bacillus sp.* CH-KOV21, (HP3) i inokuluma ukupnih zimogenih mikroorganizama (HP4).

Alohtoni (*Rhodococcus sp.* RNP05, *Pseudomonas sp.* NS009) i zimogeni sojevi (*Pseudomonas sp.* CH-KOV5, *Rhodococcus sp.* CH-KOV17, *Bacillus sp.*



CH-KOV21) su izolovani i okarakterisani sekvenciranjem 16SrRNK gena a selektovani su prema mogućnosti upotrebe alifatičnih, aromatičnih i policikličnih aromatičnih jedinjenja kao jedinog izvora C atoma.

### Rezultati i diskusija

Broj UBA nakon 30 dana fermentacije bio je u opsegu  $10^5$  -  $10^6$ , odnosno  $10^4$  -  $10^6$  RUV bakterija. U inokulisanim uzorcima HP2-HP4 udeo RUV u UBA je iznosio više od 90% što ukazuje da je ta frakcija mikroorganizama bila dominantna tokom fermentacije.

Sadržaj ukupne EOS u uzorku HP0 je bio 4,5 g/kg, a nakon 30 dana 4,2 g/kg u sterilnoj HP1 kontroli, 2,8 g/kg u HP2, 2,2 g/kg u HP3 i 3,3 g/kg u HP4. Rezultati ukazuju da je do smanjenja sadržaja organske supstance od više od 50% došlo u model sistemu inokulisanom biomasom zimogenih sojeva razlagača ugljovodonika HP3.

Osim smanjenja ukupne EOS pri fermentaciji je došlo i do kvantitativne i kvalitativne promene u grupnom sastavu. U poređenju sa uzorkom HP0 uočeno je smanjenje udela maltena uz srazmeran porast udela asfaltena u svim inokulisanim model sistemima. Najveća smanjenje maltenske frakcije sa početnih 55% na 46% zabeleženo je u uzorku HP4.

Udeo alifatičnih ugljovodonika u inokulisanim model sistemima je smanjen uz istovremeno povećanje udela NSO jedinjenja. Taj trend je naročito izražen kod uzoraka HP2 i HP3 gde je udeo alifatičnih ugljovodonika nakon 30 dana bio 37%, odnosno 38% u odnosu na početnih 50% kod HP0. Istovremeno, došlo je do promene u udelu aromatičnih jedinjenja i u povećanju udela masnih kiselina u uzorcima posle 30 dana eksperimenta. Udeo masnih kiselina je sa 6% kod uzorka HP0 porastao na 13% kod HP2 tj. na 12% kod HP3, što ukazuje na intenzivne oksidacione procese.

### Zaključak

Rezultati dobijeni u eksperimentu, pokazuju da su najveći bioremedijacioni potencijal pokazali uzorci HP2 inokulisan alohtonim sojevima *Rhodococcus sp.* RNP05 i *Pseudomonas sp.* NS009 i HP3 inokulisan, zimogenim bakterijskim sojevima *Pseudomonas sp.* CH-KOV5, *Rhodococcus sp.* CH-KOV17, *Bacillus sp.* CH-KOV21.

### Zahvalnica

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## **Risk assessment of PBDE intake via fish using @risk software**

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Polybrominated diphenyl ethers (PBDE) are substances used as flame retardants in variety of materials, where they show direct benefits. However, these substances are persistent in the environment, lipophilic and able to bioaccumulate in the food chain.

The aim of this study was to assess the risk due to PBDE intake via marine fish, freshwater fish and their products using semi-probabilistic methodology.

Using @RISK software, we conducted Monte Carlo simulation of PBDE exposure, considering all relevant databases. Data on PBDE concentration have been obtained from the Institute of Meat Hygiene and Technology, Belgrade. The available GEMS/Food Cluster Diets database (FAO/WHO, 2012) [1] was used for the purpose of intake assessment. Data on body weight at the individual level have been obtained from the database of Department of Endocrinology, Clinical Centre Vojvodina.

Monte Carlo simulation has shown distribution of total PBDE intake via marine fish, freshwater fish and their products. Values of 5th, 50th and 95th percentile of the total PBDE intake distribution are  $5.34 \times 10^{-5}$ ,  $3.04 \times 10^{-4}$  and  $1.40 \times 10^{-3}$  µg/kg bw/day, respectively. We also assessed the distribution of PBDE intake for each food group. PBDE intake originating from fish products was estimated to contribute mostly to the total PBDE intake, since 95th percentile of their distribution was  $1.32 \times 10^{-3}$  µg/kg bw/day.

Adverse effects for PBDE congeners would be unlikely to occur at doses of less than approximately 100 µg/kg bw/day (JECFA) [2]. Thus, obtained results have indicated that the risk of PBDE intake via marine fish, freshwater fish and their products is acceptable for studied population.

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## Noncovalent interactions of hazardous aromatic compounds

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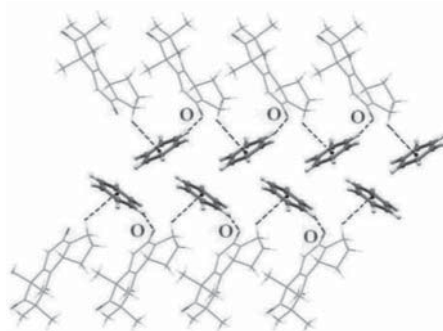
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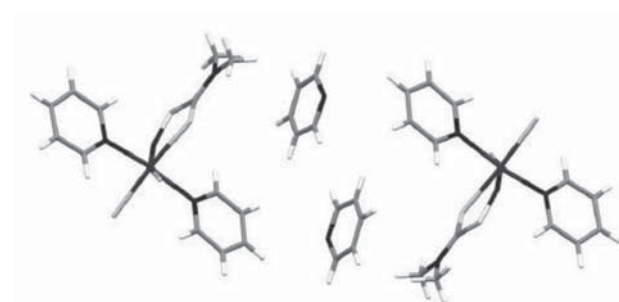
Aromatic compounds received wide attention in environmental science because of their presence as pollutants and potential health threats. A huge number of pollutants are derivatives of benzene and pyridine [1,2]. These aromatic molecules manifest their harmful effects through interactions with other aromatic rings that constitute proteins and nucleic acids. Therefore, understanding noncovalent interactions of benzene and pyridine is very important in analysis of their impact on the environment. Here we present our results on interactions of benzene and pyridine molecules with mutual parallel orientation at large horizontal displacements (offsets).

The search of Cambridge Structural Database (CSD) has shown that in the crystal structures preferred parallel benzene/benzene interactions are at large offsets (3.5-5.0 Å), and not at the offset of 1.5-2.0 Å, typical for stacking interactions. By performing DFT-D calculations at B2PLYP-D/def2-TZVP level of theory, we obtained interaction energies of about -2.0 kcal/mol for the large offsets (3.5-5.0 Å), which is 71% of the strongest interaction energy between two benzene molecules [3]. By visually analyzing the crystal structures, we found that large offset values enable benzene molecules to build additional interactions with surrounding molecules, which leads to increased stabilization of the whole systems. *Figure 1* shows building additional CH/O and aromatic CH/ $\pi$  interactions by two parallel benzene molecules at large horizontal displacements in crystal structure CENNUE.



**Figure 1.** Parallel benzene/benzene interactions with large offsets in crystal structure CENNUE (syncarpurea benzene solvate)

Parallel interactions at the large offsets were also observed in pyridine/pyridine and benzene/pyridine systems. CSD search showed that in the crystal structures preferred parallel pyridine/pyridine interactions are also at large offsets (4.0-6.0 Å). Calculated energies at B2PLYP-D2/def2-TZVP level of theory for pyridine/pyridine and benzene/pyridine dimers at large offsets (4.5 Å) are about -2.2 and -2.1 kcal/mol, respectively, which is 53% and 59%, respectively, of the strongest interaction energies [4]. Visual analysis of crystal structures showed that in these systems the additional stabilization by building simultaneous interactions is also possible due to large pyridine/pyridine offset values. Crystal structure KINLIC (Figure 2) depicts the building of additional interactions by two pyridine molecules at large offset values.



**Figure 2.** Parallel pyridine/pyridine interactions at large offset values in crystal structure KINLIC (dibromo-(dimethylamino(thiocarbonyl)thiamin,S)-dipyridyl-titanium(IV) pyridine solvate)

The described energy preservance at large offset values suggests that interactions between aromatic pollutants can be relatively strong even if they are not overlapping, which is of particular importance in terms of dilution, typical for the environment.

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## Određivanje $^{137}\text{Cs}$ u borovim iglicama sa teritorije Srbije

### Determination of $^{137}\text{Cs}$ in pine needles from Serbia

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U cilju očuvanja životne sredine neophodna je stalna sistematska kontrola svih radionuklida u njoj. Glavni izvori zagađenja vazduha su nuklearne probe i akcidenti na nuklearnim postrojenjima. Tom prilikom radionuklidi dospevaju u atmosferu u obliku aerosola, a zatim se zavisno od vazdušnih strujanja rasprostiru na široko područje. Čestice dugoživičkih radionuklida apsorbuju se na vodenom talogu, izlučuju se iz atmosfere u obliku padavina i uključuju u biološki ciklus.

**Bioindikatori** su organizmi koji svojim prisustvom ili odsustvom na nekom području ukazuju na kvalitet i stanje životne sredine. Osnovni kriterijum za izbor bioindikatora je da on treba da bude zastupljen u velikom broju, rasprostranjen po celoj monitoring površini i na širokom geografskom području, da omogućava da razlikuje zagađenje putem vazduha i zemljišta, da se lako i jeftino uzorkuje i identifikuje i da je već korišćeno u bioindikatorskim studijama [1]. Na osnovu dosadašnjih ispitivanja iglice bora zadovoljavaju ove uslove i one su pasivni bioindikatori zagađenja vazduha [2]. Kod folijarne kontaminacije četinarskih vrsta najviše koncentracije  $^{137}\text{Cs}$  su izmerene u iglicama i granama [3].

Cilj ovog rada je da ispita sadržaj radionuklida  $^{137}\text{Cs}$  u uzorcima borovih iglica koje su sakupljene na 5 lokacija u Srbiji (Subotica, Beograd – Kalemegdan i Kaluđerica, Zlatibor, Surdulica) u periodu od januara do marta 2013. godine.

Uzorci borovih iglica su osušeni na temperaturi od 80°C, homogenizovani i upakovani u Marineli posude. Analiza uzoraka izvršena je korišćenjem gamaspektrometra ORTEC-AMETEK sa 8192 kanala, rezolucije 1,85 i relativne efikasnosti 34% na 1,33 MeV za  $^{60}\text{Co}$ . Za obradu spektara korišćen je softver Gamma Vision-32 [4]. Aktivnost  $^{137}\text{Cs}$  određena je na osnovu linije na 661,66 keV, a aktivnost  $^{40}\text{K}$  određena je na osnovu linije na 1460,8 keV. Vreme merenja je iznosilo 100 000 s.

U tabeli 1. su prikazane specifične aktivnosti  $^{137}\text{Cs}$  i  $^{40}\text{K}$  u uzorcima borovih iglica sakupljenih na 5 lokacija u Srbiji u 2013. godini.

**Tabela 1.** Specifične aktivnosti  $^{137}\text{Cs}$  i  $^{40}\text{K}$  u uzorcima borovih iglica sakupljenih na 5 lokacija u Srbiji u 2013. godini

Broj	Lokacija	$^{137}\text{Cs}$ (Bq/kg)	$^{40}\text{K}$ (Bq/kg)
1.	Subotica	MDC	430±70
2.	Beograd-Kalemegdan	MDC	390±90
3.	Beograd-Kaluđerica	MDC	470±70
4.	Zlatibor	1,6±0,9	280±60
5.	Surdulica	2,3±1,2	520±80

\*MDC-ispod granice detekcije

U zavisnosti od vrste bora specifične aktivnosti  $^{40}\text{K}$  nalaze se u širokom opsegu vrednosti od 280 Bq/kg (Zlatibor) do 520 Bq/kg (Surdulica).

Uočena je varijabilnost specifičnih aktivnosti  $^{137}\text{Cs}$  u ispitivanim uzorcima borovih iglica. U tri uzorka aktivnosti su bile ispod granice detekcije, a u dva iznad: 1,6 Bq/kg (Zlatibor) i 2,3 Bq/kg (Surdulica). Ove razlike se mogu objasniti razlikama u lokalnim vremenskim uslovima i razlikama u konfiguraciji terena.

Ovo su preliminarni rezultati istraživanja borovih iglica kao bioindikatora zagađenja vazduha u cilju unapređenja monitoring kvaliteta vazduha u Srbiji.

### Zahvalnica

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## **Zastupljenost ekoloških sadržaja u nastavnim planovima i programima srednjih stručnih škola Republike Srbije**

### **Presence of ecological content in the curricula of vocational schools in the Republic of Serbia**

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Ekološko obrazovanje podrazumeva dva osnovna pristupa ostvarivanju u nastavnoj delatnosti. Prvi je ekološki pristup, i najviše se uklapa u nastavne sadržaje biologije, geografije, fizike, hemije, tehničkog obrazovanja i matematike. Drugi se odnosi na čoveka u društvu i uklapa se u nastavne sadržaje istorije, srpskog jezika, sociologije, likovne i muzičke kulture. Ekološko obrazovanje se shvata, sa jedne strane, kao nastavni princip koji obuhvata sve predmete, a sa druge strane, kao ekološko obrazovanje mora steći priznanje u određenim (pojedinačnim) nastavnim predmetima obradom specifičnih tema (npr. problem otpada, voda, šuma, atmosfere, itd.), sadržajno i metodički [1]. Svest o zaštiti životne sredine (kao cilj ekološkog obrazovanja) ne gradi se na pretpostavci čovekove vladavine, nego partnerstva sa prirodom. [2].

Interesantni su faktori koji su u vezi sa postignućima u eko-vaspitanju i obrazovanju u formiranju svesti o zaštiti životne sredine i kulture učenika, a to su: porodica, dečji vrtić, škola, fakultet, preduzeće, društvene organizacije i dr. Činioci ekološkog vaspitanja mogu biti: spoljašnji ili sredinski, unutrašnji ili činioci ličnosti. Činioce ličnosti je moguće svrstati u dve grupe: činioci koji se mogu podvesti pod pojam motivacije i činioci koji se mogu podvesti pod pojam kompetencije [3].

Cilj ovog rada je analiza zastupljenosti ekoloških sadržaja u planovima i programima srednjih stručnih škola Republike Srbije. Ekološki sadržaji u nastavnim planovima i programima u srednjem stručnom obrazovanju u Srbiji, prema važećim nastavnim planovima i programima, ograničeni su na nastavu opštih predmeta (pre svega hemije i biologije), kao i na predmet Ekologija u pojedinim profilima srednjeg stručnog obrazovanja. To znači da u mnogim srednjim stručnim školama učenici nemaju dodir sa ekološkim nastavnim sadržajima koji su neophodni svakom čoveku kako bi razvio svest o zaštiti životne sredine i svojim ponašanjem dao doprinos održivom razvoju planete. Primenom deskriptivne i komparativne analize dobijeni su rezultati koji pokazuju da ni u jednom obrazovnom profilu koji školuje učenike ekološki sadržaji nisu zastupljeni sa više od 3,5% kroz opšteobrazovne, opštestručne i užestručne predmete. Srednje stručne škole u srednjoškolskom sistemu obrazovanju Republike Srbije pokrivaju veliki broj



područja rada sa širokom lepezom obrazovnih profila. Područja rada srednjih stručnih škola koja se bave obrazovanjem učenika su: *Poljoprivreda; Geodezija i građevinarstvo; Saobraćaj; Šumarstvo i obrada drveta; Proizvodnja i prerađa hrane; Ekonomija, pravo i administracija; Zdravstvo i socijalna zaštita; Hemija, nemetali i grafičarstvo; Mašinstvo i obrada metala; Tekstilstvo i kožarstvo; Elektrotehnika; Trgovina, ugostiteljstvo i turizam; Kultura, umetnost i javno informisanje; Geologija, rudarstvo i metalurgija*. Iz prikazanih rezultata zapaža se da je udeo nastavnih sadržaja vezanih za ekologiju i zaštitu životne sredine neopravdano nizak. Potrebna za ekološkim obrazovanjem vezana je za sve obrazovne profile i sve ljude, jer se odnosi na sredinu u kojoj živimo i u kojoj radimo, a koja je svakim danom sve ugroženija i zagađenija. Ekološko obrazovanje posebno je važno za obrazovne profile koji su direktno usmereni na proizvodnju i prerađu hrane ili radnike u hemijskoj industriji. Budući radnici u industriji za proizvodnju i prerađu hrane moraju da znaju sve postupke za bezbedno rukovanje namirnicama, načine i puteve njihovog zagađenja, ekološke i zdravstvene opasnosti koje donose sastojci koji se dodaju hrani kao aditivi, kao i mere za bezbedno odlaganje otpadnih bioloških materijala. Nizak udeo ekoloških sadržaja kako u trogodišnjim, tako i u četvorogodišnjim obrazovnim profilima (koji se kreće od 0,26% do maksimalno 1%) nije dovoljan za sticanje ovih znanja koja su neophodna budućim radnicima u proizvodnji i prerađi hrane. Slična je situacija i u ostalim obrazovnim profilima - na primer, budućim radnicima hemijske industrije takođe imaju mali broj časova posvećenih ekološkim nastavnim sadržajima. Najveća zastupljenost ovih sadržaja u struci *Hemija, nemetali i grafičarstvo* je u obrazovnim profilima *gumar i plastičar* i to 1,15%, a najmanja u obrazovnim profilima štamparske struke, svega 0,13%. Budući da se radi o radnim mestima sa povećanim rizikom, neophodno je da radnici hemijske i grafičke struke budu detaljnije upoznati sa ekološkim i zdravstvenim rizicima njihove struke. Od svih prikazanih nastavnih programa, najveći udeo ekoloških nastavnih sadržaja imaju budućim radnicima rudarsko-geološke struke, u kojima je zastupljenost i do 3,43%, kao i pojedini obrazovni profili poljoprivredne struke (npr. veterinarski tehničar) i mašinske struke (*Mehaničar termoelektrotehničkih postrojenja*). Međutim, ni u jednom obrazovnom profilu koji školuje učenike u srednjim stručnim školama ekološki sadržaji nisu zastupljeni sa više od 3,5%.

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## **Ecological impact prediction of military activities: Prediction of decomposition products of munitions under different conditions**

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The objective of the study was to present some aspects of ecological influence of military activities. The presented calculation methods for explosive materials decomposition products can be useful for estimation of ecological influence of munitions demilitarisation activities.

Military activities cannot be underestimated in environmental research. It must be emphasised that munition are the most consumed goods in warfare itself, or in preparations for it. Many aspects of such activities can be concerned, from direct toxic or lethal effect to noise and stress pollution [1, 2]. Energetic materials and other dangerous materials, as main parts in any munitions, must be primarily investigated as key pollutants. Also, unexploded, discarded, abandoned or unattended munitions are also possible as pollutants. In such cases, not only the direct impact, but total effect on environment must be considered, where indirect effects could be more dangerous. Such examples range from social (devastation of wildlife because of depopulation, poverty or lack of order) to technological field (secondary poisoning, altered flora, disturbances of species etc).

Modern munition are mostly made of metals (steel, aluminum, copper, zinc, antimony etc.) and energetic materials (nitroaromatics, nitramines, nitric esters, halogenated compounds, white phosphorus, lead or mercury salts etc.). Energetic materials can be considered as direct pollutants, as mostly are toxic, but the products of their decomposition are to be of special concern. Very vivid example is the influence of munitions dumped in lake Lomtjärn, Sweden, during the period after Second World War. After many decades, extremely high levels of mercury were detected, because of the decomposition of energetic materials in underwater self-explosions [3]. Today, there are many significant efforts in the world to develop new energetic materials, primarily with much lower toxicity.

But, the determination or estimation of amount of the decomposition products is not always a straightforward process. In some cases, it is fairly easy to determine it (initial amount of lead or mercury is also a final). In the case of primary or secondary explosives, the known initial composition is transformed to pretty unknown mixture of decomposition products. The composition of products is influenced by many factors (decomposition mechanism, conditions, initiation method etc.). Mostly used energetic materials are organic chemical compounds, consisted of C, H, N and O atoms. The conditions of process is of a key importance, which is also presented in [4].

The proposed methods for calculations of detonation products are Avakjan's semi-empirical method and numerical model with minimal free-energy criterion. Both methods are implemented in computer program XW [5, 6]. Results of decomposition products calculations are presented in Tables 1 and 2.

**Table 1.** Results of calculated decomposition products for detonation of mostly used military energetic materials

Energetic material	Decomposition products, mol/kg						
	H <sub>2</sub> O	H <sub>2</sub>	CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	C <sub>(s)</sub>
TNT	8.344	2.663	1.653	14.767	0.000	6.604	14.399
RDX	11.842	1.664	3.755	7.659		13.506	2.092
HMX	11.849	1.665	3.757	7.664		13.514	2.093
Tetrite	7.072	1.634	4.359	12.070		8.707	7.949
PETN	11.783	0.869	10.171	5.644		6.326	0.000

**Table 2.** Results of calculated decomposition products for isobaric combustion of mostly used military energetic materials (70 bar)

Energetic material	Decomposition products, mol/kg						
	H <sub>2</sub> O	H <sub>2</sub>	CO <sub>2</sub>	CO	O <sub>2</sub>	N <sub>2</sub>	other
Double base gunpowder (NGB)	7.977	6.679	3.791	19.024	0.000	4.882	0.370
Single base gunpowder (NC)	8.807	5.299	4.863	17.520		4.3639	0.373
RDX	8.105	4.064	8.105	4.064		12.866	4.118
HMX	8.888	3.841	3.126	10.387		12.896	2.272

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## Health risk assessment of VOCs in Belgrade semi-urban area

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It is shown that some volatile organic compounds (VOCs) can have adverse health effects, from respiratory and allergic, to kidney, liver and central nervous system damage. Benzene and toluene are considered among the most toxic and carcinogen VOCs. The variety of harmful effects on human health points to the need for their monitoring and evaluation of their health impact. In this study, VOCs concentrations were measured on-line during the spring of 2010 using Proton Transfer Reaction Mass Spectrometer (PTR-MS). The measurements were performed in the semi-urban area, 10 km far from Belgrade centre, 6 m above ground. The PTR-MS operated at standard conditions ( $E/N = 120$  Td, average  $H_3O^+$  ion signal of  $3 \cdot 10^6$  cps, with less than 2%  $O_2^+$ ). It was programmed to monitor 15 masses at 100 ms per mass with average measurement cycle of around 4 s. In accordance with their characteristics, eight VOCs were chosen for assessment of individual health risk.

Statistical parameters of 1-h averaged VOCs concentrations are presented in Table 1. The most abundant were compounds with protonated masses  $m/z$  33 (methanol) with mean concentration of  $13.31 \mu g m^{-3}$  and  $m/z$  59 (acetone) with  $13.38 \mu g m^{-3}$ .

**Table 1.** Statistical parameters of 1-hour mean VOCs concentrations [ $\mu g m^{-3}$ ] measured in Belgrade semi-urban area, in the spring 2010

Species	Mean	Min	Max	10 <sup>th</sup> Perc.	95 <sup>th</sup> Perc.	Std. Dev.
$m/z$ 33 (methanol)	13.31	4.02	62.09	5.51	26.10	7.29
$m/z$ 42 (acetonitrile)	0.55	0.22	3.62	0.30	1.01	0.32
$m/z$ 45 (acetaldehyde)	6.68	1.66	30.47	3.02	13.28	3.73
$m/z$ 59 (acetone)	13.38	5.29	57.60	6.78	25.10	6.88
$m/z$ 79 (benzene)	3.09	0.54	17.71	1.12	7.78	2.36
$m/z$ 93 (toluene)	8.17	0.87	55.31	2.07	21.67	7.38
$m/z$ 95 (phenol)	1.19	0.23	11.30	0.50	2.50	0.92
$m/z$ 105 (styrene)	0.77	0.13	13.78	0.34	1.74	0.81

Health risk assessment associated with exposure to VOCs was performed using the US EPA health risk assessment model [1]. Toxicity data - chronic reference dose (RfD) and slope factor (SF) for individual species, considering exposure through inhalation, were obtained from US EPA Integrated Risk Information System [2] and Risk Assessment Information System [3] databases. Carcinogenic and non-carcinogenic effects were considered separately. The health risk associ-

ated with exposure to carcinogenic compounds was assessed by calculating the incremental lifetime cancer risk (ILCR) and non-carcinogenic by calculating the hazard quotient (HQ). They were estimated using the following equations and the parameters used in calculation are given in Table 2.

$$\text{ILCR} = C \cdot \text{IR} \cdot \text{EF} \cdot \text{ED} \cdot \text{SF} \cdot \text{BW}^{-1} \cdot \text{AT}^{-1} \cdot 10^{-3} \quad (1)$$

$$\text{HQ} = C \cdot \text{IR} \cdot \text{EF} \cdot \text{ED} \cdot \text{RfD} \cdot \text{BW}^{-1} \cdot \text{AT}^{-1} \cdot 10^{-3} \quad (2)$$

Table 2. Values of parameters used for calculation of ILCR and HQ

Parameter	Value
Concentration (C)	Chemical specific ( $\mu\text{g m}^{-3}$ )
Inhalation rate (IR)	$20 \text{ m}^3 \text{ day}^{-1}$
Exposure frequency (EF)	350 days year <sup>-1</sup>
Exposure duration (ED)	30 years
Body weight (BW)	70 kg
Period over which the exposure is averaged (AT)	70 x 365 days = 25 550 days for carcinogenic effects 30 x 365 days = 10 950 days for non-carcinogenic effects

Values of SF, RfD and calculated ILCR and HQ for analyzed VOCs are presented in Table 3. The ILCR values for acetaldehyde and benzene exceed the value of  $1 \cdot 10^{-6}$ , which corresponds to the exposure to unpolluted air (US EPA). HQ values indicate that the major contributor to non-carcinogenic health risk is acetaldehyde, but the hazard index (HI), obtained as sum of HQ values of individual VOCs is lower than 1, suggesting no adverse non-carcinogenic health effects as a result of inhalation exposure to them.

Table 3. Values of slope factor (SF), reference dose (RfD), and calculated incremental lifetime cancer risk (ILCR) and hazard quotient (HQ) for analyzed VOCs

Chemical	SF ( $\text{mg kg}^{-1} \text{ day}^{-1}$ ) <sup>-1</sup>	RfD ( $\text{mg kg}^{-1} \text{ day}^{-1}$ )	ILCR	HQ
Methanol	-	$1.14 \cdot 10^0$	-	$3.20 \cdot 10^{-3}$
Acetonitrile	-	$1.71 \cdot 10^{-2}$	-	$8.81 \cdot 10^{-2}$
Acetaldehyde	$7.70 \cdot 10^{-3}$	$2.57 \cdot 10^{-3}$	$6.04 \cdot 10^{-6}$	$7.12 \cdot 10^{-1}$
Acetone	-	$8.83 \cdot 10^0$	-	$4.15 \cdot 10^{-4}$
Benzene	$2.73 \cdot 10^{-2}$	$8.57 \cdot 10^{-3}$	$9.90 \cdot 10^{-6}$	$9.88 \cdot 10^{-2}$
Toluene	-	$1.43 \cdot 10^0$	-	$1.57 \cdot 10^{-3}$
Phenol	-	$5.71 \cdot 10^{-2}$	-	$5.71 \cdot 10^{-3}$
Stryrene	-	$2.86 \cdot 10^{-1}$	-	$7.38 \cdot 10^{-4}$

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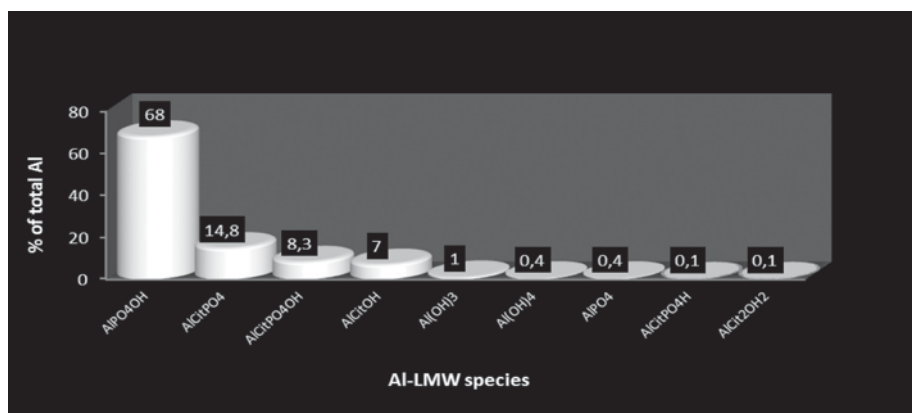
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## Speciation of Al(III) in Human Blood Plasma by Computer Simulation

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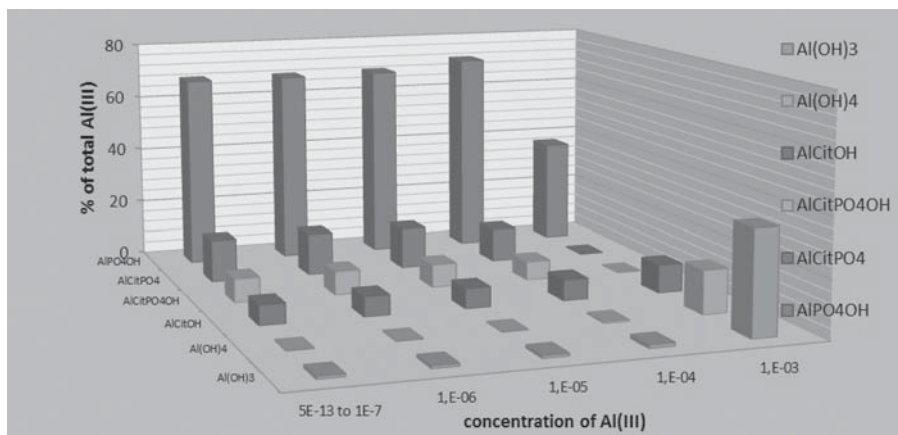
Aluminum is generally regarded as toxic or detrimental element <sup>[1]</sup>. Nevertheless, its compounds are widely used from medicines to car industry. Normally, despite oral intake ranged from 5 to 10 mg daily (food, food additives, drinks, atmospheric dust), aluminum is very little absorbed in serum and tissues<sup>1</sup>. Normal serum levels are 0.04-0.07  $\mu\text{mol}/\text{dm}^3$  <sup>[2,3]</sup>. However, high levels of aluminum may accumulate in tissues of patients who have renal insufficiency or kidney failure and are treated by dialysis fluid that contained aluminum or are given aluminum based gels to control high plasma phosphate level. These patients may develop blood, bone, brain diseases which at least partly may be linked to the excess of the aluminum. In blood, aluminum is transported by transferrin to lungs, liver, bones and other tissues including brain. In blood aluminum may exist as bound to proteins (transferrin, albumin), low-molecular weight ligand complexes (LMW) and as free ion. Its chemical form is important for its transport to tissues and cells, accumulation and excretion thus, knowledge of identity, stability and concentration of various aluminum species is necessary for understanding its toxic kinetics. Direct measurement of concentrations of various forms of aluminum in blood and other human tissues is difficult owing to small concentration of metal ions.



**Figure 1.** Distribution of Al(III) species in human blood plasma at physiological conditions (pH=7.4, I=0.15mol/dm<sup>3</sup>, T=37°C)

In this work, we construct a multi-phase model of human blood plasma including 9 metals, 40 ligands and over 6000 complexes. Almost all stability constants of binary and ternary complexes were cited from literature database (JESS, IUPAC,

NIST) at physiological conditions ( $T=310\text{ K}$ ,  $I=0,15\text{ mol/dm}^3\text{ NaCl}$ ). The speciation of aluminum(III) ion in human plasma has been studied by computer simulation using the program HySS2009<sup>[4]</sup> (program suite Hyperquad2008). Physiological distribution of  $\text{Al}^{3+}$  ion was compared with previously obtained results using the program ECCLES and it was found that agreement between main complexes percentage was better than 95%. The results obtained with HySS calculation are shown in **Figure 1**. Distribution with different total  $\text{Al(III)}$ -ion concentration ranging from  $5 \times 10^{-13}$  to  $1.0 \times 10^{-3}\text{ mol/dm}^3$  could be seen in **Figure 2**.



**Figure 2.** Distribution of Al-LMW species depended on different concentration of aluminum

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## **Determination of Formaldehyde And Acrolein in Ambient Air Using DNPH- Adsorbent Cartridge with HPLC-UV Detection**

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Aldehydes and ketones (carbonyls) are of increasing concern due to their potential adverse health effects and environmental prevalence. Carbonyls present in ambient air are produced directly from incomplete combustion of biomass and fossil fuels and indirectly through atmospheric photooxidation reactions involving ozone and hydrocarbons. Some carbonyls are released into indoor air from building materials, furniture, consumer products, tobacco smoke, etc. Short- term exposure to formaldehyde and acrolein is known to cause irritation to the eyes, skin, and mucous membranes of the upper respiratory tract [1]. This paper describes a method for the determination of formaldehyde and acrolein in ambient air utilizing a coated-solid adsorbent followed by high performance liquid chromatographic detection [2].

A known volume of ambient air (approximately 430 L) is drawn through a cartridge coated with acidified 2,4-DNPH at a sampling rate of 0,3 mL/min for an 24 hours period. After sampling, the sample cartridges and field blanks are individually capped and placed in shipping bags. Sample identifying tags and labels are then attached to the shipping bags. The samples are then placed in a polypropylene shipping container cooled to subambient temperature (~ 4°C), and returned to the laboratory for the analysis. The cartridges may either be placed in cold storage until analysis or immediately washed by gravity elution with 5 mL of acetonitrile from a plastic syringe reservoir into a 10 mL volumetric flask. The flasks are then filled up with formaldehyde free deionised water. For HPLC analysis, the 2,4-DNPH-formaldehyde and 2,4-DNPH-acrolein derivative are determined using reverse phase HPLC with an dual wavelength absorption detector (VWD) operated at 360 nm. To determine formaldehyde and acrolein, the HPLC system is operated in the gradient program mode, with water and acetonitrile mixture as mobile phase. Chromatographic separation was performed on C-18 column.

Validation parameters for method development were examined and statistically processed according to Compendium Method TO-11A [2]. Linearity of the calibration curve was examined in range from 160 to 5002 ng/ml (4,7-147,4 µg/m<sup>3</sup>) for formaldehyde and from 70 to 4140 ng/ml (4,3-229,0 µg/m<sup>3</sup>) for acrolein. Correlation coefficient ( $r^2$ ) and response factor (RSD%) for each analyte was



greater than 0,999 and less than 5,0 %, respectively. The coefficient of variation (CV%) of the response for replicate HPLC injections was 2,5 % for formaldehyde, and 3,8 % for acrolein (should be  $\pm 10$  % or less), day to day, for analyte calibration standards at 1000 ng/ml level for each analyte. The precision and uncertainty of the determination of formaldehyde and acrolein in ambient air was influenced by two parameters, the reproducibility of the analytical procedure and the variation over time of the analyte concentration in the air. Generally, the latter has a much higher effect than the former, although it is difficult to quantify the effect in view of the variability of source strengths and weather conditions. Reproducibility of the method was determined by sampling the air from one location in six sampling events simultaneously, in the same period of time within same sampling conditions. Reproducibility expressed as RSD%, was 3,96 %, and 8,08 % for formaldehyde and acrolein, respectively. The spiked samples are prepared in the laboratory by spiking a blank cartridge with a solution of derivatized carbonyls in acetonitrile. Triplicate spiked samples at three concentration levels (LD, LQ and MDK), were performed. Triplicate nonspiked samples were also processed. Recoveries ranged from 97,6 to 100,9 % with RSD varying from 2,12 to 3,84 % for formaldehyde and from 77,5 to 97,7 % with RSD varying from 1,21 to 4,50 % for acrolein. Each sampling event should include a collocated sample. The absolute percentage differences between collocated duplicate sample was 14,10 % for formaldehyde ( $n = 12$ ) and 19,70 % for acrolein ( $n = 12$ ).

The proposed method was applied in determination of formaldehyde and acrolein in ambient air of the city of Belgrade and its area. According to National regulations [3], the limit value of the emission for formaldehyde and acrolein in ambient air during 24 hour sampling, was set to 0,1 mg/m<sup>3</sup>. In period from October 2012 to March 2013 concentration of formaldehyde and acrolein was monitored in two locations near Belgrade (Crljani and Livnica). The average concentration of formaldehyde and acrolein was 0,018 and 0,011 mg/m<sup>3</sup> respectively, and never exceeded limiting value.

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## **Fazi metodologija određivanja kvaliteta podzemne vode/pijaće vode u gradu Zrenjaninu**

### **Fuzzy methodology for determining the groundwater/drinking water quality in the city of Zrenjanin**

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Praćenje kvaliteta podzemne vode, koja se upotrebljava kao pijaća voda, i kvalitativno donošenje odluka na osnovu dobijenih podataka predstavlja kompleksan i multidimenzionalan zadatak za donosiocje odluka. Glavni razlog za to su neodređenosti koje se javljaju pri svim koracima, počev od uzorkovanja pa sve do analiza. Fazi logika uspešno upravlja sa ovim neizvesnostima prilikom ocenjivanja kvaliteta pijaće vode.

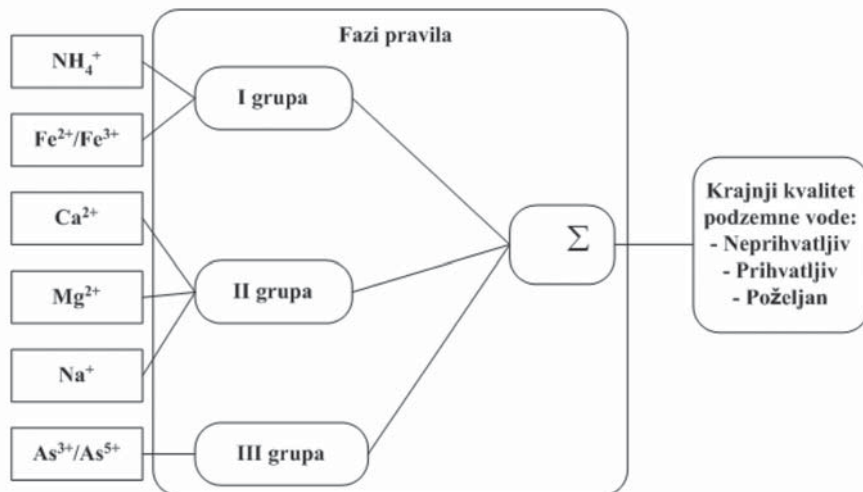
Podaci fizičko-hemijskih parametara podzemne vode korišćeni u radu preuzeti su iz laboratorije JKP „Vodovod i kanalizacija” Zrenjanin. Analizirana su uzeta dva karakteristična bunara. Prvi se nalazi na dubini od 98-118 m dok se drugi nalazi na dubini od 36-61 m. Odabrano je 6 karakterističnih parametara: amonijak, ukupno gvožđe, kalcijum, magnezijum, natrijum i arsen na koje će se primeniti fazi metodologija za procenu kvaliteta podzemne vode.

Fazi model kvaliteta podzemne vode je kreiran na taj način što je 6 odabranih parametara podeljeno u 3 različite kategorije. Prvu grupu čine katjoni ukupnog gvožđa i amonijaka, druga grupa je struktuirana od kalcijumovog, magnezijumovog i natrijumovog jona dok je treća grupa sačinjena od jonskog oblika arsena. Jedinjenja arsena se posmatraju pojedinačno jer arsen ima dokazano kancerogeno dejstvo na ljudski organizam.

Fazi metodologija je evaluirana prema sledećim koracima (slika 1): fazifikacija odabranih parametara podzemne vode, kreiranje fazi pravila, fazi odlučivanje upotrebom fazi operatora i defazifikacija u klasične krajnje vrednosti. Klasifikacija kvaliteta podzemne vode posmatranog lokaliteta je podeljena u tri grupe: Poželjan, Prihvatljiv i Neprihvatljiv. Unutar ovih grupa nalaze se procenti koji predstavljaju stepen pouzdanosti. Stepen pouzdanosti nam pokazuje sa kojom verovatnoćom je voda pouzdana za piće.

U fazi analizi je utvrđeno da uzorci iz bunara 1 daju neprihvatljiv kvalitet podzemne vode sa stepenom pouzdanosti od 22,5 % dok uzorci iz bunara 2 imaju prihvatljiv kvalitet podzemne vode sa vrednostima stepena pouzdanosti od 61,25 % i 22,5 %. Rezultati isključivo pokazuju da kvalitet pijaće vode u Zrenjaninu zavisi prvenstveno od geološke strukture zemljišta. Naime, koncentracija arsena je izuzetno povišena u višim slojevima zemljišta, dok je u nižim slojevima ispod graničnih vrednosti. Povišena koncentracija arsena u vodi za piće je prirodnog porekla,

ali takva koncentracija deklasifikuje ovu vodu i smatra se neprihvatljivom. Pokrajinska sanitarna inspekcija početkom 2004. zabranila je za piće i pripremanje hrane vodu iz zrenjaninskog vodovoda zbog višestruko povećane koncentracije kancerogenog arsena. Zabrana važi i danas.



**Slika 1.** Fazi metodologija određivanja kvaliteta podzemne vode

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## Solid-phase extraction followed by high-performance liquid chromatography with diode array detection for screening of dicamba herbicide in water

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Valéria Guzsány<sup>3</sup>, Snežana Jakšić<sup>2</sup>

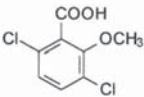
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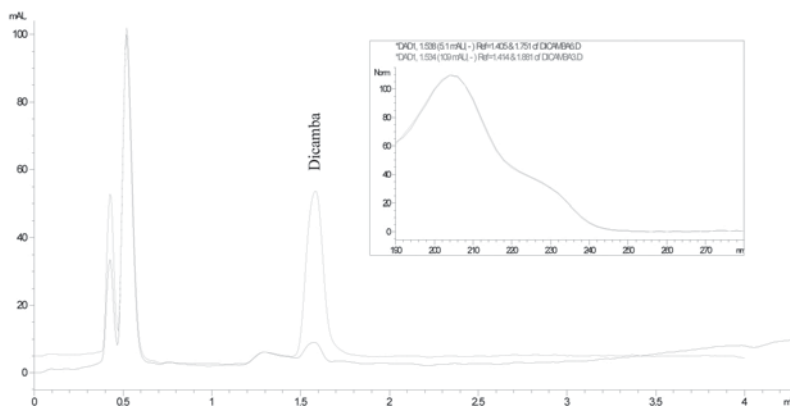
Chlorinated acids are selective agricultural herbicides which are widely employed in agriculture and gardening for control the growth of different unwanted vegetable species in crops. Because of high water solubility and toxicological risk of some acid herbicides and their metabolic products, monitoring of their concentration in surface and groundwater is very important task. The acidic herbicides are manufactured in formulation as free acids, as their alkaline salts or as esters. The unionized free acids vary in water solubility (Table 1), but the acidic herbicides most frequently exist in ionized form at environmental pH values. Acidic herbicides formulated as salts are water soluble, while those formulations prepared as esters are less water soluble. In the environment, acidic herbicides formulated as esters have short hydrolysis half-life time (24–48 h) and therefore they are generally present as ionized acids. For most analytes, especially for the acidic herbicides, solid phase extraction (SPE) is the choice of sample treatment, which is followed by appropriate chromatographic separation and sensitive determination of target components. For the acidic herbicides, combination of physico-chemical parameters influences their extraction from aqueous solution. Ionogenicity (pKa) and hydrophobicity (logK<sub>ow</sub>) are especially important in determining the approach of SPE for efficient sample clean-up for further chromatographic analysis of chlorophenoxy acid herbicide in water samples.

**Table 1.** Physico-chemical properties of dicamba acidic herbicide

Common name/ molecular formula/ CAS No.	Systematic name	Structure	pKa	Aqueous solubility (mg/l)	logK <sub>ow</sub>
Dicamba C <sub>8</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>3</sub> (1918-00-9)	3,6-dichloro-2-methoxy-benzoic acid		1.9 [1]	4500 [2]	2.21 [3]

The acidic herbicides are polar and non-volatile compounds, and do not lend themselves to direct analysis by gas chromatography. Using high performance liquid chromatography (HPLC) the acidic herbicides can be analyzed in the ionic

form, the molecular (unionized acid) form or as the ester. Generally, the mechanism of separation/clean-up on SP extraction sorbent, used to extract the acidic herbicides from aqueous solution, is based on Van der Waals interactions (reversed phase bonded silica sorbents) or by electrostatic interactions (anion exchange). The present work describes screening method for efficient sample clean-up procedure for the determination of dicamba acid herbicide in water, using SPE. Methodology is based on the use of polymer-based weak anion exchange SPE sorbents (Strata X-AW) for fast extraction of the dicamba from the water samples and on optimised instrumental analytical method based on reversed-phase HPLC with diode-array detector (DAD, 210 nm) for determination of target analyte from the extract. The chromatographic separation was carried out on Zorbax C<sub>18</sub> (50 mm × 4.6 mm, 1.8 μm) using an isocratic elution profile and mobile phase consisting of 13 mM phosphate buffer pH 3.4 and acetonitrile. Method validation was performed by analysing freshly spiked tap water samples with dicamba at levels between 0.5 and 5 μg/ml. Average recovery of the method ranged between 86.7-95.8%. Besides the regularly shaped and well-defined peaks belonging to the investigated dicamba pesticide, the SPE-HPLC-DAD chromatograms (Figure 1) contained of peaks which probably have origin from the solvent/mobile phase. There were no significant interfering peaks in the elution region of dicamba pesticide.



**Figure 1.** Comparison of chromatograms and the appropriate UV apex spectrums (as insets) of dicamba herbicide peaks of fortified tap water extract (lower) and standard dicamba solution (upper)

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## Characterization of potentially hazardous metals for the environment in ashes of the soft brown coal from the Kovin deposit (Serbia)

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Toxic metals which are found in coal deposits can be very hazardous for the environment because during coal combustion they are either released into the atmosphere or concentrated in the ashes. Characterization of these metals is very complicated task due to matrix complexity, wide range of concentration levels, interferences encountered during laboratory analysis etc.

The Kovin coal deposit is divided in two exploitation fields: western – field “A”, and eastern - field “B” (Figure 1). The coal-bearing Pontian sediments are part of the “Banat-Morava” depression and they are made up of loosely bounded sand and clay with three coal seams. Forty three samples of coal from all coal seams, from both fields, were collected from the four borehole cores and ashed at 815°C.

The concentrations of potentially hazardous trace elements in ashes were determined by total digestion of the ashes in closed microwave digestion unit followed by ICP-AES analysis performed according to the EPA 200.7 standard.



**Figure 1.** Fields »A« and »B« of the Kovin coal deposit. Four excavation points from which the samples were collected are marked by dots.

Concentrations of the twelve potentially hazardous trace elements, namely: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se and Th were compared with the Clarke values for the ashes of the brown coals in order to determine if their concentrations are elevated. Coal ash from all three seams has higher content of Cr and Ni (more than twice) compared to Clarke values for brown coal ashes (using the geometric mean value). The other analysed elements occur in concentrations similar to Clarke values.

## **Application of HPLC/MS and tandem mass spectrometry for the identification and quantification of organic pollutants in river water**

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Contamination of water ecosystem is becoming an increasingly serious problem. The highest level of contamination is usually observed at river waters, which receive the contamination from various sources like insufficiently cleaned industrial and urban waste water or direct discharge of untreated wastewater, residuals of agrochemical washed down from the fields, atmospheric contaminants captured by rainwater etc.

Many various studies have been published which document presence of various classes of organic as well as inorganic and organometallic pollutants in the river water, e.g. pharmaceuticals and personal care products [1], PAHs [2], polychlorinated biphenyls [3], polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-furans [4], pesticides [5], hormones [6] or mercury [7]. These contaminants show important adverse effects mainly on water biota like feminization of fish species, which raises problems in reproduction. Many of these compounds show lipophilic character, which (together with their resistance against degradation) results in their accumulation in bottom sediments, from where they can be released during floods. Via water used for irrigation these compounds can enter also terrestrial environment.

In the last period the negative influence of these contaminants (namely residuals of pharmaceuticals used as female contraceptives) on human health has been also discussed. In the case where surface water is used as a source for drinking water preparation these hormonal steroids are not completely removed during standard drinking water preparation procedure (which is usually coagulation with  $\text{Fe}_2(\text{SO}_4)_3$ , flotation, sand filtration and disinfection). It was declared that even these low levels of female contraceptives during long-term consumption may increase the risk of prostate cancer in men [8].

This study is focused on the determination of residues of pharmaceuticals in Danube and Sava rivers in Serbia. Sampling and analyses of targeted compounds were realized by the team of Serbian students from five Serbian universities during their stay at the Department of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology.



### Acknowledgement

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## Ekstrakcija nikosulfurona iz zemljišta

### Extraction of nicosulfuron from soil

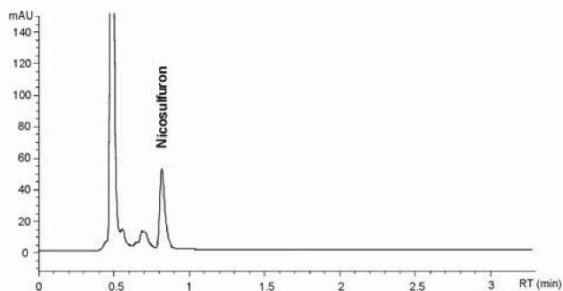
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Petar Sekulić<sup>1</sup>, Dragana Šunjka<sup>3</sup>, Snežana Jakšić<sup>1</sup>

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Zemljište predstavlja glavni recipijent u kome se adsorbuju i razgrađuju pesticidi, koji u njega dospevaju direktnim putem, kao posledica kontrolisane primene pri suzbijanju korova [1]. Nikosulfuron je selektivni sistematični herbicid, apsorbuje se listom i korenom, relativno brzo se prenosi do meristemskih tkiva. Ovaj herbicid inhibira sintezu acetolaktat sintetazu (ALS), ključni enzim koji učestvuje u biosintezi amino-kiselina sa razgranatim alifatičnim nizom (valin, leucin i izoleucin) u biljkama i zaustavlja deobu ćelija i rast biljke [2]. Nikosulfuron se primenjuje nakon nicanja kukuruza za suzbijanje jednogodišnjih i višegodišnjih uskolisnih i širokolisnih travnih korova. U poređenju sa tradicionalnim herbicidima koji se primenjuju u količini >1kg/ha, nikosulfuron je efikasan u malim količinama <100 g/ha [3]. Postojanost nikosulfurona u zemljištu zavisi od pH, temperature, vlažnosti zemljišta i sadržaja organske materije u zemljištu [4]. S porastom temperature ubrzava se razlaganje nikosulfurona, kako pod uticajem hemijskih faktora (hidroliza, oksidacija) tako i pod uticajem mikroorganizama [5]. Višegodišnja primena ovog herbicida može da dovede do povećanja koncentracije toksičnih proizvoda degradacije, koji mogu predstavljati zagađivače životne sredine i izazvati neželjene efekte u aktivnosti zemljišnih mikroorganizama [6]. Slaba isparljivost i duža postojanost ovog herbicida utiču na mogućnost povećanog rizika od kontaminacije rotirajućih useva i vodenih sistema. Ostaci nikosulfurona se često detektuju u zemljištu, površinskoj vodi i pojedinim usevima [7]. Cilj ovog rada je optimizacija metode ekstrakcije, prečišćavanja i određivanja nikosulfurona u zemljištu. Istraživanjem je obuhvaćeno, iznalaženje najpogodnijih rastvarača za ekstrakciju nikosulfurona iz zemljišta uz prečišćavanje dobijenog ekstrakta na čvrstoj fazi (SPE) reverzno faznom tečnom hromatografijom. Određivanje nikosulfurona izvršeno je tečnim hromatografom (HPLC) Agilent 1100 Series sa UV-DAD detektorom i Zorbax Eclipse XDB-C<sub>18</sub> (50mmx4,6mmx1,8μm) kolonom pri čemu su eksperimentalni uslovi (mobilna faza, protok mobilne faze, temperatura kolone, talasna dužina UV-DAD detektora) bili predhodno definisani [8]. Zemljište je ekstrahovano sledećim rastvaračima: acetonitrilom (ACN), smešom metanol/fosfatni pufer pH 7 (2:1, v/v) i smešom ACN/fosfatni pufer pH 7 (1:1, v/v). Uzorci su hromatografisani uz mobilnu fazu ACN i 0,1% CH<sub>3</sub>COOH. Temperatura kolone pri određivanju je iznosila 25 °C, talasna dužina UV-DAD detektora 230 nm. Pri ovim uslovima retenciono vreme nikosulfurona iznosilo je 0,831 minuta (slika 1).



**Slika 1.** Hromatogram nikosulfurona iz ekstrakta zemljišta prečišćenog preko SPE kolone

Na osnovu vrednosti prosečnog testa povrata ekstrakcije nikosulfurona može se zaključiti da je značajna vrednost od 88,41% dobijena za postupak ekstrakcije nikosulfurona iz zemljišta smešom metanol/fosfatni pufer pH 7 (2:1, v/v) i prečišćavanjem preko Chromabond-NH<sub>2</sub> i Oasis HLB SPE kolone. Ponovljivost merenja određena je hromatografskom analizom standardnog rastvora nikosulfurona masene koncentracije 1,0253 µg/ml u deset ponavljanja.

### Acknowledgments

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## Natkritična ekstrakcija etarskog ulja majkine dušice (*Thymus serpyllum* L.)

### Supercritical fluid extraction of essential oil from wild thyme (*Thymus serpyllum* L.)

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Majkina dušica (*Thymus serpyllum*) pripada rodu *thymus* koji u svetu obuhvata oko 300-400 vrsta, sa velikim brojem podvrsta, varijeteta, subvarijeteta i formi, a u flori Srbije zastupljeno je oko 30 vrsta ovog roda [1]. Majkina dušica sadrži etarsko ulje i zbog toga poseduje fungicidno, antiseptičko i antioksidativno dejstvo. Koristi se kao antiseptik, anthelmintik, karminativ, ekspektorans, sedativ i tonik, konzervans, aromatik, stomahik, antispazmotik, itd. Etarsko ulje iz lišća se koristi u parfemima, sapunima i pastama za zube. Osim primene u kozmetici, majkina dušica se koristi kao začim. Fenolni monoterpeni u etarskom ulju majkine dušice, timol i karvakrol najviše doprinose prijatnom mirisu njegovog etarskog ulja, a poznato je i da inhibiraju lipidnu peroksidaciju i ispoljavaju veoma snažno antimikrobno dejstvo na različite vrste mikroorganizama.

Etarska ulja, nazvana „isparljivim“ uljima [2] su aromatične uljne tečnosti koje se dobijaju iz različitog biljnog materijala (cveća, pupoljaka, semena, lišća, grančica, kore, herbe, drveta, voća, korenja i drugih biljnih delova). Termin „etarsko ulje“ potiče od strane švajcarskog reformiste medicine, Paracelsus von Hohenheim iz 16. veka. On je efektivnu komponentu leka nazvao *quinta essentia* [2]. Postoji veliki broj različitih metoda kojima je moguće izolovati etarska ulja i biljne ekstrakte. Najzastupljeniji postupci dobijanja etarskih ulja su: hidrodestilacija, ceđenje, fermentacija, anfleraž postupak, ekstrakcija sa organskim rastvaračima i ekstrakcija sa natkritičnim ugljenik(IV)-oksidom.

Postupak natkritične ekstrakcije je mnogo selektivniji u odnosu na konvencionalne načine ekstrakcije i predstavlja optimalno rešenje kada se zahtevaju proizvodi bez tragova rastvarača (npr. za prehrambene, kozmetičke i farmaceutske proizvode). Ekstrakcija natkritičnim ugljenik(IV)-oksidom na niskoj temperaturi i pod visokim pritiskom ne izaziva termičku degradaciju i zagadenje ekstrakta organskim rastvaračem. Ekstrakti dobijeni ovom metodom zadržavaju prirodniji organoleptički profil i aromu same biljke ali je ova tehnika znatno skuplja od konvencionalnih načina ekstrakcije [3]. Budući razvoj u ekstrakciji bioaktivnih jedinjenja biće sigurno vezan za postupak

natkritične ekstrakcije, koji zauzima posebno mesto s obzirom na porast restriktivnih mera u zakonskoj regulativi koja se odnosi na životnu sredinu, toksikologiju i zdravlje ljudi.

U ovom radu etarsko ulje majkine dušice izolovano je iz osušene herbe *T. serpyllum* postupkom natkritične ekstrakcije. Natkritična ekstrakcija ugljen(IV)-oksidom izvedena je na postrojenju Autoclave Engineers SCE Sreening System na pritisku od 10 MPa i temperaturi od 40 °C. Ostvaren prinos natkritičnog ekstrakta etarskog ulja iz majkine dušice iznosio je 0,58 mas %.

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## **Antioksidativna aktivnost hidrolata hajdučke trave (*Achillea millefolium* L.)**

### **Antioxidant activity of hydrosol from yarrow (*Achillea millefolium* L.)**

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Hajdučka trava (hajdučica, sporiš) je naš najpoznatiji i najčešće upotrebljavan narodni lek, kako iznutra tako i spolja. Koristi se kao tonik, stomahik, stimulans, antispazmodik, emenagoh, fibrifug itd. Destilacijom sa vodenom parom iz hajdučke trave se proizvodi skupoceno etarsko ulje koje se koristi u medicini, farmaciji i kozmetici. Ukoliko je ovo ulje tamnije plave boje, utoliko se više ceni i skuplje plaća, jer ima više azulena, od čega potiče lekovitost ulja i hajdučke trave [1].

Destilacija vodenom parom je jedan od najstarijih, ali i jedan od najčistijih načina dobijanja etarskih ulja. Koristi se u svim slučajevima kada sirovina sadrži relativno visok procenat etarskog ulja i kada su komponente etarskog ulja stabilne na temperaturi destilacije.

Hidrolati (mirisne vodice, hidrosoli) su nus proizvodi destilacije etarskog ulja. Hidrosoli obično sadrže komponente etarskog ulja rastvorne u vodi kao i druge u vodi rastvorne komponente iz biljnog materijala koji se tretira. Svaki litar hidrolata sadrži između 0,05 i 0,2 mililitra (manje od 1%, obično 0,01 – 0,04%) rastvorenog etarskog ulja [2]. Svaki je hidrolat jedinstven jer sadrži vodorastvorne supstance iz konkretnog biljnog materijala, a određuju ga i uslovi destilacije.

Uz adekvatnu tehnologiju hidrolati se mogu koristiti u kozmetičkoj, prehrambenoj i farmaceutskoj industriji ili u veterinarskoj i ljudskoj medicini. Danas to ostaje neiskorišćeno, i firme koje se bave proizvodnjom etarskih ulja hidrolate uglavnom bacaju. Uz adekvatnu tehnologiju ovi bi se nus proizvodi mogli doraditi i prodavati po visokim cenama.

Pošto hidrolati nisu u koncentrovanom obliku kao etarska ulja i manje su aromatični od etarskih ulja, oni se mogu koristiti u nerazblaženom obliku u prehrambenoj i kozmetičkoj industriji. Mogu se koristiti u obliku sprejeva, kao osveživači vazduha, za pripremanje krema, maski, sapuna, i tonika za kožu, u inhalacijama, kao baza vodicama za čišćenje lica, posle brijanja i za negu usne duplje, za pripremanje terapijskih kupki, sprejeva za osvežavanje stopala, kose, umesto vode prilikom peglanja odeće, za deodorisanje sportske opreme (prostirki za jogu, sportske obuće i odeće). Značajno je napomenuti i to da su etarska ulja zabranjena za upotrebu kod kućnih ljubimaca ali hidrolati se mogu koristiti za negu i higijenu kućnih ljubimaca. Hidrolati se u prehrambenoj industriji koriste kao poboljšivači

ukusa i arome, konzervansi i biljni čajevi. Prema Paolini i sar. [3] hidrolati se takođe upotrebljavaju u organskoj poljoprivredi protiv gljiva, plesni, i insekata i za đubrenje zemljišta.

Za potrebe ovog rada etarsko ulje i hidrolat hajdučke trave izolovani su iz sirove herbe *Achillea millefolium* L., *Asteraceae*, postupkom destilacije sa vodenom parom na industrijskom uređaju SP-450. Temperatura u toku hidrodestilacije u sudu SP-450 se kretala od 100°C-115°C, na atmosferskom pritisku, a ceo proces hidrodestilacije je trajao 2 sata. Izolovano etarsko ulje je tečnost tamno plave boje sa visokim procentom azulenskih jedinjenja. Dobijen je hidrolat snažnog aromatičnog mirisa pH vrednosti 3,8. Ispitivan je antioksidativni potencijal i sposobnost hidrolata hajdučke trave da neutrališe DPPH radikale.

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## **Efikasnost filtracije kroz rečno korito Save**

### **Riverbank filtration efficiency of Sava River**

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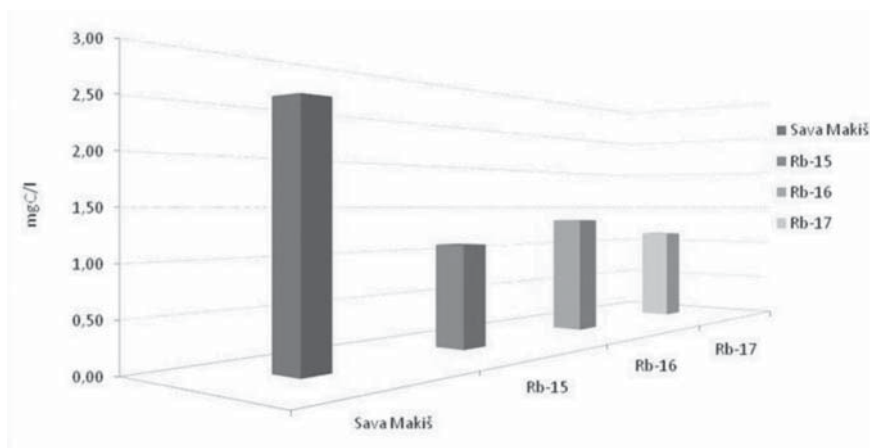
Čista voda za piće je jedan od najvećih globalnih ekoloških i zdravstvenih problema našeg vremena. Zahtevi za snabdevanje vodom za piće visokog kvaliteta su sve veći, zbog čega se razvijaju nove tehnologije za tretman vode degradiranog kvaliteta, kao što su membranska filtracija, napredna oksidacija i slično. Međutim, sve više se koristi stara metoda, filtracija kroz rečno korito, zbog relativno niskih troškova i održivosti kvaliteta podzemnih voda.

Filtracija kroz rečno korito je prirodan proces kojim se materije iz infiltrirane površinske vode efikasno uklanjaju ili im se koncentracija značajno smanjuje na putu od reke do bunara. Uklanjanje ili smanjenje koncentracije polutanata je rezultat kombinacije fizičko-hemijskih i bioloških procesa kao što su: biodegradacija, filtracija, sorpcija, hemijska precipitacija, redoks reakcije i razblaživanje podzemnom vodom. Pomenutim procesima se iz vode efikasno uklanjaju suspendovane materije, čestice, biodegradabilna jedinjenja, bakterije, virusi, paraziti, značajno se smanjuje koncentracija jedinjenja podložnih sorpciji, a sadržaj rastvorenih materija postaje uravnotežen.

U radu smo pratili totalni organski ugljenik (total organic carbon, TOC) kao kumulativni parametar kvaliteta vode. Procesom infiltracije se najveći deo TOC-a uklanja već na prvim centimetrima granične površine reka-vodonosni sloj. Smanjenje koncentracije i ponašanje organskih materija tokom infiltracije zavise od različitih faktora, kao što su retenciono vreme, redoks uslovi, osobine zemljišta i hidrogeološki uslovi [1]. Nakon infiltracije kroz rečno korito, u vodi dolazi do hemijskih promena usled transfera elektrona, promene vremenskih prilika, razmene jona i razmene gasova [2].

Razmatranu sredinu karakteršu anoksični uslovi i gvožđe-nitratna redukciona sredina. Za ovakve uslove karakteristično je sporo, ali kontinuirano uklanjanje organskih materija, za razliku od oksičnih uslova, u kojima se organski ugljenik brzo uklanja. I u jednim i u drugim uslovima se mogu postići slične rezidualne koncentracije organskog ugljenika, pod uslovom da je retenciono vreme u anoksičnim/anaerobnim uslovima dovoljno dugo [1]. Na primeru sadržaja TOC-a tokom 2010. i 2011. godine za merni profil Sava Makiš, za koji je izmerena srednja koncentracija TOC-a (36 merenja) iznosila 2,50 mgC/l i prosečne koncentracije TOC-a izmerene u podzemnoj vodi na bunarima beogradskog izvorišta Rb-15, Rb-16 i Rb-17 (slika 1), od 1,10 mgC/l, 1,34 mgC/l i 1,13 mgC/l respektivno, objašnjeno je smanjenje koncentracije TOC-a u podzemnoj vodi u odnosu na rečnu vodu od skoro 50%.





**Slika 1.** Prosečna koncentracija TOC-a u Savi i bunarima Rb-15, Rb-16 i Rb-17 tokom 2010. i 2011. godine

Inicijalna infiltracija u oksidnim uslovima, karakterističnim za gornji sloj akvifera, veoma je važna za efikasno uklanjanje organskog ugljenika. Koncentracije TOC-a u bunarima pokazuju određene varijacije tokom perioda ispitivanja. Te promene se ne mogu pripisati različitim koncentracijama TOC-a u površinskoj vodi. Eksperimentima je potvrđeno da su dominantni redukcionni uslovi faktor koji najviše utiče na uklanjanje organskog ugljenika. Takođe se pretpostavlja da je promena sadržaja DOC-a u dubljim slojevima akvifera zasnovana na promeni redoks uslova [1].

Može se zaključiti da je neophodno vršiti kontrolu i monitoring sistema za filtraciju kroz rečno korito da bi se izbegle drastične promene koje utiču na efikasno uklanjanje TOC-a u posmatranoj sredini.

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## **Efikasnost ekstrakcije PAH-ova i PCB-a iz zemljišta ASE metodom („Accelerated Solvent Extraction“)**

### **PAH and PCB extraction efficiency from soil by ASE method („Accelerated Solvent Extraction“)**

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Ekstrakcija policicličnih aromatičnih jedinjenja (PAH) i polihlorovanih bifenila (PCB) iz zemljišta je važan korak u identifikaciji i kvantifikaciji ovih toksičnih i kancerogenih jedinjenja [1]. Brzina procesa ekstrakcije i minimalna potrošnja rastvarača su takođe važan ekonomski i ekološki faktor. Otud je cilj ovog rada bio da dokaže da se ekstrakcijom istom smešom rastvarača (heksan:acetona, 1:1 zapreminski odnos) dobijaju zadovoljavajuće vrednosti „recovery“-ija, a da je istovremeno preciznost detekcione tehnike u granicama koje propisuju EPA metode [1,2]. U ovom radu prikazana je efikasnost automatske tečne ekstrakcije (Accelerated Solvent Extraction u daljem tekstu ASE) PAH-ova (tabela 2) i PCB-ija (tabela 1) iz zemljišta praćenjem procenta prinosa („recovery“) spajkovano standarda PAH i PCB kongenera iz matriksa zemljišta za koje je prethodno utvrđeno da je sadržaj PAH i PCB < 10 µg/kg. U aplikacijama proizvođača [3], [4] opisani su posebni uslovi ekstrakcije za PAH a posebni za PCB sa aspekta izbora rastvarača.

Korišćenjem metode gasno-masene hromatografije za praćenje procenta prinosa („recovery“) konstatovano je da se isti kreće u opsegu 78,03% (Acenaphthylene,) do 106,4% (Benzo(k)fluoranthene) za PAH-ove, odnosno 92,9% do 99,93% za PCB kongenere.

**Tabela 1.** „Recovery“ PCB iz zemljišta (Spajkovano sa 0,2 mg/kg PCB kongeneri),

PCB kongener	Prosečni „recovery“ za (n=3)	RSD %
PCB 28	92,93	7,45
PCB 52	94,93	7,29
PCB 101	94,93	5,47
PCB 118	96,60	4,78
PCB 153	97,59	4,73
PCB 138	99,93	3,46
PCB 180	94,60	6,71

**Tabela 2.** Recovery standarda 0,2mg/kg PAH ( PM831)

PAH	I serija Prosečni „recovery“ za (n=6)	II serija Prosečni „recovery“ za (n=6)	% prinosa („recovery“) [5] AN1025*	I serija RSD%	II serija RSD %
Naphthalene,	94,93	101,87	72,5	11,77	8,31
Acenaphthylene,	78,03	82,83	82,3	9,51	11,24
Acenaphthene,	89,13	96,23	81,2	9,89	6,47
Fluorene,	89,46	95,57	79,5	10,37	8,10
Phenanthrene,	89,78	94,41	95,3	9,07	5,80
Anthracene,	89,29	94,75	85,2	7,59	4,38
Fluoranthene,	89,28	97,71	90,8	8,89	4,50
Pyrene	85,31	95,22	86,2	8,52	7,31
Benz(a)anthracene,	82,66	84,65	84,7	9,85	8,31
Crysene,	87,13	91,09	114	10,25	8,59
Benzo(b)fluoranthene	90,96	98,18	89,2	10,80	8,26
Benzo(k)fluoranthene	87,64	106,10	84,7	8,62	15,81
Benzo(a)pyren,	90,78	98,68	77,7	8,73	8,35
Indeno(1,2,3-cd)pyrene	92,73	98,34	83,5	12,87	13,52
Dibenz(a,h)anthracene	89,43	100,16	77,7	13,26	12,03
Benzo(ghi)perylene	81,96	93,36	87,5	18,65	16,12

I serija: Metoda 1 : uključena opcija uštede rastvarača;

II serija: u Metoda 2 : opcija uštede rastvarača isključena

[5] AN1025\*: spajkovana koncentracija PAH-ova bila je 5ug/g na 5g zemlje.

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## Interactions of the major allergen of egg white and epigallo-catechin 3-gallate

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Egg is one of the most prominent sources of important nutrients in human diet. Ovalbumin (OVA), the most prevalent protein in hen egg white (~60-65% of total protein content) is a glycoprotein which consists of 385 amino acids and represents the major allergen from avian egg white that causes IgE-mediated food allergic reactions particularly in children; the prevalence of OVA allergy is estimated between 1.6% and 3.2% among children and 0.6% among adults [1].

The involvement of OVA in allergic reactions prompts more studies on this very important serpin and allergen. Also, its ability to interact with small physiologically active molecules, such as polyphenols and purine alkaloids, warrants thorough analysis. (-)-Epigallocatechin-3-gallate (EGCG) is the major active principle of green tea which exerts beneficial effects on human health, including hypersensitivity disorders.

The aim of our work was a detailed analysis of the nature and biological significance of interactions between the major green tea catechin, epigallo-catechin 3-gallate (EGCG), and major allergen of egg white, ovalbumin (OVA).

The effects of the OVA/EGCG complex formation on the structure of OVA were assayed by circular dichroism spectroscopy, tryptophan emission fluorescence, and *in silico* modeling, whereas the physiological significance of the binary complex was assessed by assays employing interaction with IgE, basophils and monocytes. Binding of EGCG to the surface of OVA induces a conformational change of the protein. The EGCG-binding site in OVA only partially overlaps with the known IgE-binding regions (residues 24-33 and 56-182) and it is quite remote from the immunodominant IgE-binding epitope (residues 364-372). *Ex vivo* studies showed that OVA in the presence of EGCG binds IgE and stimulate degranulation of effector cells (basophils), but its uptake proceeds at the slower rate in freshly isolated human monocytes.

Protein conformation, digestibility and aggregation are important for biological activities of dietary proteins that elicit hypersensitivity reactions in humans, such as IgE-binding capacity, uptake by antigen-presenting cells, activation of effector cells in allergy, and even sensitizing potential of food allergens.

We provide further evidence in support of the proposed mechanism in which EGCG interactions with the food antigens contribute to its diverse biological activities and may impair uptake of antigens by antigen-presenting cells.

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## **Proteomic and Immunological Characterization of *Ambrosia artemisiifolia* Allergens by 2-D Immunoblot and Tandem Mass Spectrometry**

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Short ragweed (*Ambrosia artemisiifolia*) pollen represents one of the major seasonal sources of allergenic pollen proteins in Europe, particularly in Pannonia valley of Balkan region. It affects up to 36 million people worldwide [1], causing more allergic reactions and related diseases in humans, than all other plants together [2]. Serbia is severely affected by this plant and threatened by its airborne pollen [3, 4].

Up to date, the Allergome.org allergen database contains 11 ragweed allergens: the Amb a 1 group (pectate lyase) with 5 isoallergen groups and its variants (isoforms), Amb a 3-10 groups including Amb a CPI (cystatin protease inhibitors). About 95% of ragweed-sensitized human patients display IgE antibodies to Amb a 1 major allergen [5]. Although the pectate lyase Amb a 1, the major allergen of ragweed, was identified as long ago as the 1960s, little is known about the allergenicity of the 5 Amb a 1 isoallergens and other allergens present in ragweed pollen. Still, ragweed extracts used for immunotherapy are standardized against whole Amb a group.

Complete proteome of defatted pollen extract was analyzed. Isoallergens of short ragweed pollen extract have now been characterized for their allergenic potential to determine whether a single Amb a 1 isoallergen or even a specific isoform (variant), several isoallergens or a combination with other allergens could be included in a future recombinant SIT vaccine.

Pollen extract of short ragweed was prepared as previously described [6] and subjected to 2-D electrophoresis. Pollen proteome spots were excised after coomassie blue brillinat (CBB) staining and in gel digested [7] for liquid chromatography coupled with Orbitrap tandem mass spectrometry (LC-MS/MS) according to Van Duijn [8]. Parallel to that, Western blot of the CBB gel was probed with the pooled sera of 6 patients allergic to short ragweed (grade 4 and 6).

All Amb a allergen groups were identified: pectate lyase group (Amb a 1/2), plastocyanins (Amb a 3), non-specific Amb a 5 group, polcalcin/polcalcin like protein groups (amb a 9/10), lipid transfer proteins (Amb a 6) profilins (Amb a 8), including cystatine protease inhibitors (Amb a CPI) and their isoforms and auto-proteolytic fragments, accounting for more than 15 distinctive allergen isoforms. The highest IgE reactivity of pooled patient sera by immunoblotting was observed for Amb a 1.0102 variant of Amb a 1.01 isoallergen that is the most abundant, followed by its natural variant E1XUL2, Amb a 1.0304 and Amb a 1.0402 isoforms,

that are still evidenced in Uniprot database as existing on the transcript level. Other Amb a 1 isoallergens as well as other detected ragweed allergens showed only moderate to weak IgE reactivity.

Amb a 1.01 is the most abundant Amb a 1 isoallergen, and presumably the most important ragweed isoallergen. However, a larger panel of ragweed-allergic subjects has to be analyzed with regard to IgE and T cell reactivities, to be able to choose a candidate for a recombinant vaccine for specific immunotherapy of ragweed allergy.

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**6. simpozijum Hemija i zaštita životne sredine**  
*6<sup>th</sup> Symposium Chemistry and Environmental Protection*

**OKRUGLI STO**

*ROUND TABLE*



Tempus





## **OKRUGLI STO**

### **Modernizacija poslediplomskih studija hemije i srodnih programa i potrebe uprave, industrije i javnosti**

Milan D. Antonijević<sup>1</sup>, Branimir Jovančičević<sup>2</sup>

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TEMPUS projekat pod nazivom „Modernizacija poslediplomskih studija hemije i srodnih programa” (Modernisation of Post-Graduate Studies in Chemistry and Chemistry Related Programmes – MCHEM) započet je još 2010. godine. Osnovni cilj TEMPUS MCHEM projekta je da doprinese stvaranju kvalitetnih, fleksibilnijih i boljih master obrazovnih programa i kurseva hemije koji ispunjavaju zahteve i potrebe šire društvene zajednice kao što su poslodavci, profesionalne ustanove i specifična radna mesta širom cele Srbije.

Rukovodeći se težnjom da se što bolje prilagode Bolonjskom procesu sve visokoškolske ustanove u Srbiji u kojima se hemija izučava kao osnovna disciplina: Univerzitet u Beogradu – Hemijski fakultet, Tehnološki fakultet i Fakultet za fizičku hemiju; Univerzitet u Novom Sadu – Prirodno-matematički fakultet – Departman za hemiju, biohemiju i zaštitu životne sredine; Univerzitet u Kragujevcu – Prirodno-matematički fakultet – Hemijski departman; Univerzitet u Nišu – Prirodno-matematički fakultet – Hemijski departman i Visoka poslovna tehnička škola strukovnih studija Užice su u saradnji sa Univerzitetom u Griniču (Engleska), Univerzitetom u Ahenu (Nemačka), Univerzitetom u Brnu (Češka Republika) i Univerzitetom u Novoj Gorici (Slovenija), pristupile izvođenju više zadataka koji čine ovaj projekat među kojima je jedan od osnovnih ciljeva bio da se uspostave REFERENTNI OBRAZOVNI STANDARDI ZA HEMIJU I SRODNE DISCIPLINE (Benchmark standards for Chemistry) koji bi bili usklađeni sa zahtevima Evropske agencije za obezbeđenje kvaliteta u visokom obrazovanju (Quality Assurance Agency for Higher Education) i sa Evropskom markom za kvalitet u oblasti hemije (The Chemistry Quality Eurolabels for Eurobachelor®, Euromaster® & Eurodoctorate).

Pored toga razvijeni su savremeni individualni programi za niz kurseva master studija kao što su: (1) Napredne analitičke tehnike u zaštiti životne sredine, (2) Uticaju na životnu sredinu, (3) Procesi u životnoj sredini, (5) Remedijacija, (6) Procena rizika po ljudsko zdravlje i životnu sredinu.

Paralelno s tim pripremljeni su kursevi za kontinualnu edukaciju: (1) Masena spektrometrija u detekciji zagađivača životne sredine; (2) Hemija životne sredine – atmosferski gasovi; (3) Planeta Zemlja: minerali, stene, rude od pojave do rudnog bogatstva; (4) Primena skenirajuće elektronske mikroskopije sa energo-disperzivnom spektrometrijom (SEM-EDS) u zaštiti životne sredine; (5) Metode prečišćavanja otpadnih voda; (6) Ilustrativni eksperimenti i predavanja

u nastavi opšte i fizičke hemije u srednjim školama; (7) Remedijacija; (8) Monitoring zagađivača i uzorkovanje; i (9) Projektovanje sopstvenog monitoringa industrijskih otpadnih voda.

U finalu projekta organizovani su studijski boravci za studente master studija hemije i srodnih disciplina iz Srbije koji su putovali na Univezitete centralne Evrope: Grinič, Brno, Nova Gorica i Ahen. Rezultati rada ovih studenata predstavljeni su na 6. simpozijumu - Hemija i zaštita životne sredine koji organizuje Srpsko hemijsko društvo uz učešće MCHM projekta i njegovih saradnika.

MCHM projekat je preuzeo poseban zadatak na ovom Simpozijumu da organizuje Okrugli sto na kome će se prvo informisati srpska stručna i naučna javnost iz oblasti hemije životne sredine o postignutim rezultatima na projektu, a u isto vreme i da se sagledaju sadašnji problemi, nedostaci ili prednosti trenutnog obrazovanja iz oblasti hemije i srodnih disciplina ali ne samo iz ugla akademske zajednice, već predstavnika osnovnog i srednjeg obrazovanja, industrije i državnih institucija (uprave i inspekcije).

### **Osnovne teme Okruglog stola su:**

- Uvođenje zaštite životne sredine u celokupni obrazovni sistem Srbije.
- Poređenje Srpskog visokoškolskog sistema sa evropskim sistemima.
- Uloga srednjoškolskog obrazovnog sistema na formiranje svesti i interesovanja mladih za interdisciplinarne nauke.
- Značaj interdisciplinarnih nauka u razvoju društva kao i kompleksnost razvoja interdisciplinarnih studijskih programa.
- Značaj uticaja krajnjih korisnika (studenata, privrede i državnih institucija) u kreiranju novih studijskih programa. Učešće korisnika doprinosi boljem sagledavanju potreba za određenim profilima obrazovanog kadra i obezbeđuje zapošljivost svršenih studenata.
- Razvoj kurikulumu u skladu sa Bolonjskim kreditnim sistemom. Direktna povezanost studentskog angažovanja sa brojem nastavnih sati, prakse i krajnjih kredita koje kurs nosi.
- Poznavanje teorija učenja i prevashodno karakteristike generacije studenata koja se upisuje
  - Sposobnosti novih generacija
  - Dijapazon pažnje
  - Glasno/Vizualno pamćenje
  - Korišćenje novih tehnologija.
- Načini prenosa znanja na određenim nivoima (Blumova taksonomija)
  - Jasna povezanost između ciljeva, ishoda i ispitivanja
  - Prirodna nadogradnja znanja
  - Interaktivno učenje
  - Korišćenje povratne informacije (Feedback/Feedforward) kao izuzetno uspešnog metoda učenja
  - Učenje kroz rešavanje slučaja (Problem Based Learning - PBL)
  - Praktična nastava (Learning by Doing - LbD).

- Razvoj novih metoda učenja
  - Korišćenje IT u učenju
  - Učenje na daljinu
  - Kontinuirano učenje.
- Značaj istraživačkog potencijala institucije u prenosu savremenih znanja studentima
  - Istraživanje u funkciji edukacije (Research informed teaching).
- Uticaj povezanosti Srpskih viskokoškolskih institucija sa evropskim i svetskim institucijama na razvoj i modernizaciju interdisciplinarnih studijskih programa.
  - Prenos znanja, informacija, zajednički kursevi i programi.
  - Prohodnost studenata ka evropskim institucijama i obratno.
- Modeli evaluacija naučnog procesa koji imaju za cilj dalju modernizaciju i poboljšanje kvaliteta studija koje vodi ka formiranju kvalitetnog školovanog kadra sposobnog da kritički razmišlja i inovativno pristupa rešenju problema.
- Kontinuirana edukacija nastavnog kadra.



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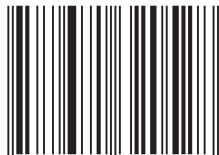


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