EMEC21

21st European Meeting on Environmental Chemistry
November 30 – December 3, 2021, Novi Sad, Serbia

Association of Chemistry and the Environment

Serbian Chemical Society

Matica Srpska

www.emec21.rs

Scientific Committee
Jan Schwarzbauer, president

Organisational Committee
Branimir Jovančićević, president

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Vladimir Beškoski, president

BOOK OF ABSTRACTS

21st European Meeting
on Environmental Chemistry

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ASSOCIATION OF CHEMISTRY AND THE ENVIRONMENT

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Publisher

Serbian Chemical Society

Karnegijeva 4/III, Belgrade, Republic of Serbia

For the publisher

Dušan Sladić

President of the Serbian Chemical Society

Editors

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Cover page photo

Branko Lučić

Design and prepress

Beoživković, Belgrade

Printed by

RIS Studio, Belgrade

Circulation

150

ISBN

978-86-7132-078-8

Year

2021

Dear guests and colleagues,

This, already traditional, international meeting of researchers from all over the world in the field of environmental chemistry has been attracted together by 200 participants.

We will work both, live in a unique conference venue of Matica Srpska that is one of the most important academic institutions in Serbia, and, on-line, in new, challenging conditions created by the Covid-19 pandemic.

Researchers from Austria, Bosnia and Herzegovina, Croatia, Czech Republic, France, Germany, Greece, Italy, Japan, Montenegro, Poland, Portugal, Russia, Serbia, Slovenia, South Korea, Spain, and United Kingdom will have a chance to present and share new research results. Broad range of topics and interdisciplinary presentations will be discussed at the conference with main objectives to report the most advanced research progresses and to pave the way for future research and challenges.

I wish you fruitful work and safe stay in Serbia. Welcome to the City of Novi Sad, the European Capital of Culture 2022!

Branimir Jovančićević
President of the EMEC21 Organizing Committee

Association of Chemistry and the Environment - ACE

The Association of Chemistry and the Environment (ACE) is a non-profit-making scientific association founded in October 2000 by a group of European scientists. We aim to promote global contact between scientists in academia and research institutes, the commercial sector and social representatives within governmental and regulatory bodies to address environmental problems and to promote education in this area.

We strongly welcome scientists from diverse fields such as atmosphere science, biology, geology, industrial chemistry, medicine, sociology, soil science, toxicology and water science to play an active role within the organisation.

Serbian Chemical Society

The Serbian Chemical Society (SHD) is a voluntary, non-governmental and non-profit association established to pursue goals in the fields of chemistry, chemical technology, and related disciplines. The Society is one of the oldest chemical societies in the world, the ninth ever established. It was founded on the initiative of professor Marko Leko (who was also the first president of the Society) in 1897. Despite many difficulties, interruptions in work during both world wars, the Society has successfully achieved its goals and currently has about 800 members, dozen divisions and affiliates. The Society actively contributes to development of education in chemistry and chemistry related disciplines and for 89 years cultivates scientific publishing activity by publishing the Journal of the Serbian Chemical Society-JSCS (one volume of 12 month issues per year). It is an openly accessed journal (IF 1.24 in June 2021).

Environmental Chemistry Division was founded in 1982 by professor Petar Pfendt who was a first president of a Division. A professor Dragan Veselinović, professor Branimir Jovančićević and professor Bojan Radak, succeeded him. The current president of the Environmental Chemistry Division is a professor Vladimir P. Beškoski. Alongside the EMEC2021, the Division has been the organizer of the Symposium CHEMISTRY AND ENVIRONMENTAL PROTECTION since 1985. During all these years, facing various challenges, the Symposium has changed its names but managed to preserve quality, and enhance its significance to the scientific community and society as a whole. Researchers, scientists, and experts dealing with various aspects of environmental chemistry have recognized the opportunities that the Symposium provides as a unique platform for sharing ideas, the latest scientific achievements and technological innovations. This resulted in an increasing number of participants over the years. Furthermore, members of the Division are dedicated to promotion of science and they are responsible editors of the Environmental Chemistry Section of the JSCS issues. To this day, the Division has organized several roundtable discussions including internationally recognized scientists across the globe, many lectures and workshops. With great enthusiasm, honour and pleasure we are expecting the year 2025 when EuChemS DCE will, together with us, organise the 19th International Conference on Chemistry and the Environment (ICCE) in Belgrade.

Matica Srpska

Matica Srpska is the oldest Serbian literary, cultural and scientific society. Matica Srpska was founded in 1826 in Pest, during the liberation of Serbia from centuries of Ottoman occupation and the strengthening of awareness of the need to fully incorporate Serbian people in modern European trends at the same time maintaining their cultural identity. The activities of Matica were, from the very beginning, aimed at presenting Serbian culture to Europe and at enlightening the people. In order to achieve this, a rich publishing activity has been developed. The basis of this activity was the famous Letopis (Chronicle), first published in 1824. Later on, numerous other editions were published, among them one edition with a particular educational role, appropriately named Books for the People.

Matica Srpska has almost 2.000 associates today. Associates prepare articles for fifteen periodical publications of Matica and work on the preparation of publications of great significance for Serbian culture and science, such as the Serbian Encyclopedia, Serbian Biographic Dictionary, the Dictionary of Serbian Language, Orthography… The Library of Matica Srpska has over 3,500,000 books, and the Gallery of Matica Srpska houses a rich collection of Serbian eighteenth and nineteenth century paintings. The Publishing Center continues the tradition of the former Matica Srpska Publishing Company, whose editions were, for decades, recognizable throughout Southeastern Europe by the emblem MS, which signified high-quality and carefully selected literature from various fields. Every year Matica Srpska awards worthy accomplishments in various fields of culture and science.

Matica Srpska has been an example to many Slavic nations. Based on this model the following institutions were established: Czech Matica in 1831, Illyrian Matica in 1842 (in 1874 renamed to Matica Hrvatska); Matica Lužičkosrpska in 1847, Halych-Russian Matica in Lviv in 1848; Moravian Matica in 1849; Matica Dalmatinska in Zadar in 1861; Slovak Matica in 1863; Slovenian Matica in 1864; Matica Opava in 1877; Matica in the Teschen Princedom in 1898. (from which Silesian Matica was created in 1968); Polish Matica in Lvov (1882); Educational Matica in the Teschen Princedom in 1885; Educational Matica in Warsaw in 1905; Bulgarian Matica in Constantinople in 1909 and the new Bulgarian Matica in 1989. In the meantime, Matica Srpska has developed cooperation with many institutions and individuals worldwide.

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PROGRAMME

Tuesday, November 30th, 2021

18:00-20:00	Welcome cocktail	Restaurant "Veliki", Nikole Pašića 24, Novi Sad

Wednesday, December 1st, 2021

Time	Presenter	Title	Page
08:00-	**Registration**		
09:00-09:30	**OPENING CEREMONY** (Matica Srpska, Main Hall)		
Moderators	Branimir Jovančićević/Jasmina Nikodinović-Runić		
09:30-10:00	Plenary lecture Anne-Marie Delort	The Cloud Microbiota - Microorganisms-H_2O_2 Interactions	22
10:00-10:20	Section lecture Jasmina Nikodinović-Runić	Progressing Plastics Circularity: Mechano-Biocatalytic Approaches for Waste Plastic (Re)valorization (BioICEP Project Overview)	28
10:20-10:35	Huiyi Zhang	Removing Copper and Lead Ions from Water by a Dopamine Modified Marine Plastic Adsorbent	38
10:35-10:50	Malcolm Watson	Effect of Ozonation on the Speciation of Arsenic in Groundwater During Drinking Water Preparation	39
10:50-11:20	**Coffee break**		
11:20-11:35	Gilles Mailhot	New Sustainable Process for Wastewater Treatment Using Recycled and Recoverable Magnetite with Natural Iron Complexing Agent: an Example of Photochemical AOP	40
11:35-11:50	Nuno Ratola	Presence and Challenges of Volatile Methylsiloxanes in WWTPs	41
11:50-12:05	Marija Stevanović	The Embryotoxic Potential and Photocatalytic Degradation of Thiophanate-Methyl	42
12:05-12:20	Slađana Savić	The Effect of Power on the Degradation of Propranolol by Nonthermal Plasma Reactor	43
12:20-12:50	**Sponsor presentation – Analysis d.o.o.** Luka Mihajlović Trends in Analytical Approaches for Environmental Chemistry - a Review		
12:50-14:20	**Lunch break**		
Moderators	Polonca Trebše/Vesna Antić		
14:20-14:35	Minja Bogunović	Revisiting Humic Acid Adsorption onto Activated Carbon	44
14:35-14:50	Szabolcs Pap	Circular Economy-Based Phosphorus Recovery Technology Development to Create a Soil Conditioner: an Integrated Approach	45
14:50-15:05	Ana Fernandes	Uptake of Synthetic Musks and Volatile Methylsiloxanes by Pea Crops Grown in Sewage Sludge-Amended Soils	46
15:05-15:20	Vera Homem	Environmental and Agricultural Impacts of Using Sewage Sludge as a Fertilizer – Emerging Contaminants as a Case Study	47
15:20-15:40	Section lecture Vesna Antić	Migration of Toxic and Essential Trace Elements from Tinplate Cans to Meat Products - Possible Impact on Human Health	29

15:40-15:55	Suzana Gotovac Atlagić	Introduction of Innovative Green Material Chemistry Demonstrations in Early Education: Case Study Bosnia and Herzegovina	48
16:00-18:30	**City tour and visit of the City Hall** (Meeting point: in front of Matica Srpska)		

Thursday, December 2nd, 2021

Time	Presenter	Title	Page
08:00-	**Registration**		
Moderators	Jan Schwarzbauer/Maja Turk Sekulić		
08:30-09:00	Plenary lecture Tatjana Ćirković-Veličković	Emerging Food Contaminants	23
09:00-09:20	Section lecture Pierro Bellanova	Impact Of Tsunamis On Pollutants' Distribution	30
09:20-09:35	Patricia Tarín-Carrasco	Study of the Impacts of Large Wildfires on PM10 and Human Mortality in Portugal	49
09:35-09:50	Jan Schwarzbauer	Emission and Dispersion of Organic Pollutants by the 2021 Extreme Flood in Germany	50
09:50-10:05	Emira Hukić	Do Freezing and Heating Cycles Influence Differently on Soil Elements Leaching?	51
10:05-10:35	**Coffee break**		
10:35-10:50	Milica Stefanović	The Response of Badland Materials from Spain with Different Mineralogical Content on Seasonal Changes	52
10:50-11:05	Luisa Bellanova	Chemostratigraphic Distribution of Harmful Organic Contaminants in Flood Affected (Sub-)tropical Urban River Sediments (Chennai, India)	53
11:05-11:20	Filipe Rocha	Studying the Behaviour and Fate of Volatile Methylsiloxanes and Synthetic Musk Compounds in Soil	54
11:20-11:35	Dragana Vidojević	Inadequate Municipal Solid Waste Management and Soil Pollution in Serbia	55
11:35-11:50	Ioanna Pantelaki	Occurrence and Fate of Organophosphate Esters in a Municipal Wastewater Treatment PlantI	56
11:50-12:05	Maria Krishna de Guzman	Comparative Profiling of Microplastics in Differently sized Manila Clams from South Korea by Nile Red Staining and µFTIR	57
12:05-12:35	**Sponsor presentation – ANNAFER d.o.o. (LECO)** Pavel Jiros MS Technology Diversity to Provide Enhanced GC Separation, Detection and Identification Solutions		
12:35-14:00	**Lunch break**		
Moderators	Malgorzata Iwona Szynkowska-Jóźwik/Vladimir Beškoski		
14:00-14:30	Plenary lecture Albert Lebedev	Mechanisms of Formation of Disinfection By-Products in Water Treatment	24
14:30-14:50	Section lecture Lydia Niemi	Pharmaceuticals in the Aquatic Environment: A Rural Perspective and Cross-Sector Partnership Addressing the Issue in Scotland	31

14:50-15:05	Taja Verovšek	Wastewater Analysis Assessment: Prevalence of Drugs of Abuse in Educational Institutions	58
15:05-15:20	Christina Alina Schwanen	Structural Diversity of Organic Contaminants in a Meso-Scaled River System	59
15:20-15:35	Fábio Bernardo	Monitoring Volatile Methylsiloxanes Levels in Wastewater Collected from a Portuguese Wastewater Treatment Plant	60
15:35-15:50	Aleksandra Tubić	Presence of Arsenic and Microplastics in the Groundwater in the Vicinity of a LandfillTubić1	61
15:50-16:20	**Coffee break**		
16:20-16:35	Urška Šunta	Adsorption of Three Pesticides onto Different Polymer Types of Microplastic Particles in Alluvial Soil	62
16:35-16:50	Mojca Bavcon Kralj	Determination of Microplastics in Environmental Samples by Simply Applicable Method	63
16:50-17:05	Franja Prosenc	Method for Extraction, Quantification, and Identification of Microplastics from Soil and Compost	64
17:05-17:25	Section lecture Sonja Kaišarević	Neuroactive Compounds in the Aquatic Environment: Biomarkers of Effect and Their Integration into Adverse Outcome Pathways (AOPs)	32
17:25-17:40	Karla Jagić	Exposure to Polybrominated Diphenyl Ethers Associated with Car Dust	65
19:00-23:00	**Conference dinner at Restaurant "Wine House Kovačević"** (Kralja Petra 221, Irig) Transfer at 18:00h (the corner of Temerinska Street and Marija Trandafil Square, | 5 min. walk from Matica Srpska)		

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Time	Presenter	Title	Page
08:00-08:30	**Registration**		
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08:30-09:00	Plenary lecture Walter Gössler	A Closer Look at the Elemental Composition of Macrofungi, with a Focus on Arsenic	25
09:00-09:20	Section lecture Hideyuki Inui	Plants, An Attractive Partner for Phytoremediation and Phytomonitoring of Environmental Pollutants	33
09:20-09:35	Anna Irto	3-Hydroxy-4-pyridinone as Potential Chelating Agent for the Remediation of Ecotoxic Metals From Environmental Matrices	66
09:35-09:55	Section lecture Tatjana Anđelković	Phthalate Migration from Food and Medical Plastic Materials	34
09:55-10:10	Pascal Renard	Free Amino Acids Quantification in Cloud Water at the Puy de Dôme Station (France)	67
10:10-10:25	Roberto Di Pietro	Cd(II) Sorption by Novel Polymer Inclusion Membranes Based on L-Glutamic N,N-Diacetic Acid or Citric Acid from Aqueous Solution	68
10:25-10:55	**Coffee break / ACE General Assebly**		
10:55-11:10	Dmitrii Mazur	Estimation of Environmental Pollution Using Precipitation Analysis	69

11:10-11:25	Mark Popov	Thermal Desorption Gas Chromatography – Mass Spectrometry Determination of Toxic Rocket Fuel Transformation Products in Soils	70
11:25-11:40	Anna Sosnova	The Use of Two-Dimensional Gas Chromatography-Mass Spectrometry for the Study of Atmospheric Pollution in Arkhangelsk. Application of Chemometric Methods for the Purposes of Environmental Analysis	71
11:40-11:55	Tomas Latkin	Application of Two-Dimensional Gas Chromatography - High-Resolution Mass Spectrometry for Studying the Combustion Products of Nicotine and Herbal Cigarettes	72
11:55-12:10	Etienne Bourgart	Characterization of Nicotine Salts in E-Liquids and E-Cigarette Aerosols	73
12:10-12:25	Olga Polyakova	Balsamic Components and Contaminants in the Egyptian Mummy	74
12:25-13:55	**Lunch break**		
Moderators	Jelena Radonić/Đurđa Kerkez		
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14:15-14:30	Zuzana Redžović	Assessment of Water Quality and Metal Exposure in the Krka River Watercourse (Croatia) Influenced by the Wastewater Outlets	75
14:30-14:45	Mirjana Vojinović Miloradov	Transmission of Bioagens Sorbed onto Suspended Particulate Matter in Ambient Air During Urbanization Process in the City of Novi Sad	76
14:45-15:00	Jonathan Vyskocil	Meta-Omics Analyses of Cloud Microbial Metabolism of C1 Compounds	77
15:00-15:15	Polonca Trebše	Transformations of Resveratrol, Antioxidant Component of Sunscreen, under Disinfection Conditions	78
15:15-15:45	**Coffee break**		
15:45-16:00	Davide Vione	Advances in Photochemistry Modeling: The Equivalent Monochromatic Wavelengths Approach	79
16:00-16:15	Tijana Milićević	The Health Risk and Benefit Assessments for the Pelagic Fish Species' Consumers	80
16:15-16:30	Konstantin Ilijević	Bioelements and Non-Essential Elements in Honeybees and Their Hemolymph, Larvae, Pupae, Honey, Wax, Propolis and Bee Bread	81
16:30-16:45	Pablo Irizar	Sweet Conservation: Development of Sugar Based Epoxy-Silica Hybrids as Multifunctional Materials for Built Heritage Protection	82
16:45-17:00	Marko Ilić	Authentication of Extra Virgin Olive Oil Based on Fatty Acid Composition and Multivariate Statistics	83
17:00-	**CLOSING CEREMONY**		

PLENARY LECTURERS

Prof. Dr. Anne-Marie Delort

Institut de Chimie de Clermont-Ferrand, Université Cleront Auvergne, Aubierre, France

In addition to a general background in chemistry and molecular biology, Anne-Marie Delort's expertise covers Microbiology and NMR spectroscopy, and more recently Metabolomics (NMR and MS). She specifically studies microbial metabolism in relation with the environment. She has been a pioneer in studying the microbial population in clouds. Her studies concern the role of microorganisms in atmospheric chemistry and physics. This includes the transformation of organic matter, interaction with oxidants, formation of Ice Nuclei and Cloud Condensation Nuclei. More recently she has published a work on priority pollutants present in cloud waters. She also works on the biodegradation of plastics. She published 150 papers in international journals and 18 book chapters. She was invited speaker at 75 national and international conferences. She founded and was head of the Institute of Chemistry of Clermont-Ferrand (110 permanent staff, 250 in total). She is in charge of representing the CNRS at ALLENVI (Alliance Nationale de Recherche en Environnement) that gathers all the French institutions of research working in the environmental field.

Dr. Tanja Ćirković Veličković

Full Professor of Biochemistry at the Faculty of Chemistry, University of Belgrade, Serbia

Holds this position since 2013. She is also the coordinator of the university's Centre of Research Excellence for Molecular Food Sciences and an advisor in the area of international cooperation. After her graduation in Biochemistry from the University of Belgrade, she further specialized in immunology during her postdoctoral studies at the Department of Medicine at Stockholm's Karolinska Institute. In 2016 she was appointed full Professor of Food Chemistry at Ghent University and its global campus in South Korea. She is the President of the Serbian Proteomics Association and serves as a member of various scientific organizations, such as the Food Chemistry Division of the European Chemical Society (EuChemS), European Proteomics Association and the Executive Board of the Serbian Chemical Society (SCS). Since 2018 she is a corresponding Member of the Serbian Academy of Sciences and Arts. Her current research interests revolve around proteomics, including the identification and cloning of new respiratory and food allergens for the improvement of pollen and food allergy diagnoses and treatment or the influence of food processing on the protein structure of foods. For further details please visit: http://www.chem.bg.ac.rs/biohemija/grupe/Tanja_Cirkovic-en.html.

Prof. Dr. Albert Lebedev,

Department of Organic Chemistry, Moscow State University, Moscow, Russia

Professor of the Chemistry Department of the Moscow State M.V. Lomonosov University (Moscow, Russia), head of the laboratory of Organic Analysis. Albert Lebedev received his PhD in 1982 and DSc in 1992 in organic chemistry from the Moscow State M.V. Lomonosov University. He has published more than 250 scientific papers and reviews and made more than 200 scientific presentations all over the world. With experience in directing undergraduate and graduate research, he has taught in the field of organic chemistry and physicochemical methods in organic and environmental analysis of the same University. He is an author and an editor of several books on mass spectrometry including "Methods and Achievements of Modern Analytical Chemistry" (Lan, 2020), two editions of "Mass Spectrometry in Organic Chemistry" (Binom, 2003; Technosfera, 2015), "Basics of Mass Spectrometry of Peptides and Proteins" (Technosfera, 2012), and "Comprehensive Environmental Mass Spectrometry" (ILMPublications, UK, 2012). He actively employs mass spectrometry (environmental applications, proteomics, gas-phase reactions) in his research and teaching activities. Albert Lebedev is a founder and the first President of the Russian Society for Mass Spectrometry. He is a current representative of the RSMS in IMSF. In 2019 he became a recipient of the gold medal of RSMS "For outstanding achievements in mass spectrometry". He is a recipient of the State awards of Russian Federation in Science in 1983 and 2007.

Dr. Walter Goessler

Institut für Chemie Universität Graz, Austria

Dr. Walter Goessler is associate professor of Analytical Chemistry at the Institute of Chemistry at the University of Graz, Austria since 2003. His research focuses on the development and improvement of analytical methods with emphasis on inorganic analysis. The developed methods answer questions related to human health and our environment. Speciation analysis of nonmetals with elementselective detection (ICPMS/MS) and the biotransformation of arsenic compounds play a central role in his research. Ongoing projects are focusing on trace element accumulation and biotransformation in mushrooms and ultrafine particles in our air. For further information please see https://chemie.uni-graz.at/en/analytical-chemistry/research/ache/

PLENARY LECTURES

The Cloud Microbiota - Microorganisms-H_2O_2 Interactions

A.-M. Delort [1,]. (1) CNRS, Institut de Chimie de Clermont-Ferrand. Université Clermont Auvergne, France; [*]a-marie.delort@univ-bpclermont.fr.*

Our team works on microorganisms present in clouds collected at the puy de Dôme observatory which is a GAW (Global Atmosphere Watch) station[1]. We have shown that these microorganisms are metabolically active in clouds and we try to demonstrate that they can modify the chemical composition of clouds and be an alternative route to radical chemistry.

In this talk we present in more details our work related to the interactions of microorganisms with H_2O_2 which is the main sources of radicals in cloud waters.

Using microcosms mimicking the cloud environment we have determined biodegradation rates of H_2O_2 and compared them with photo-transformation rates[2,3]. In parallel a transcriptomics approach was used to look at the *in-cloud* activity of the cloud microbiota[4]. Finally the impact of H_2O_2 on cloud metabolism was assessed using a metabolomics approach[5]

We have shown that microorganisms can biotransform H_2O_2 thanks to their catalases, both *in lab* and *in-cloud* experiments. In parallel, this strong oxidant modulates the microbial energetic metabolism and many metabolic pathways. Considering that H_2O_2 concentration is highly variable (day *vs* night, seasons, pollution..), these interactions are very complex.

As H_2O_2 is a key component of atmospheric chemistry, work is in progress to integrate this microbial activity towards this oxidant in a multiphase atmospheric chemistry model within the frame work of two French ANR projects (METACLOUD and MOBIDIC).

References

[1] P. AMATO *et al.* Active microorganisms thrive among extremely diverse communities in cloud water. *PLoS ONE*. 2017,*12(8):e0182869.https://doi.org/10.1371/journal.pone.0182869*.me.

[2] M. VAÏTILINGOM *et al.* Potential impact of microbial activity on the oxidant capacity and organic carbon budget in clouds. *PNAS USA*, 2013, **110**, 559-564.

[3] N. WIRGOT *et al.* H_2O_2 modulates the metabolic activity of the cloud microbiome. *Atmos. Chem. Phys.* 2017, **17**, 14841-14851.

[4] P. AMATO *et al.* Metatranscriptomic exploration of microbial functioning in clouds. *Scientific Reports*, 2019, **9**, 4383.

[5] N. WIRGOT *et al*. Metabolic modulations of *Pseudomonas graminis* in response to H_2O_2 in cloud water. *Scientific Reports,* 2019, **9**, 12799.

T. Ćirković Veličković[1,2,3,4]. (1) University of Belgrade – Faculty of Chemistry, Belgrade, Serbia, (2) Serbian Academy of Sciences and Arts, Belgrade, Serbia, (3) Ghent University Global Campus, South Korea, (4) Ghent University, Faculty of Bioscience Engineering, Ghent, Belgium ; * tcirkov@chem.bg.ac.rs.*

The global production volume of plastics continues to rise. The continued growth in plastics production has not only led to an increasing volume of plastic waste released into the environment but has also contributed to food waste. Plastic polymers released into environment can be slowly degraded by microorganisms, heat, oxidation, light, or hydrolysis. The degradation of plastic will eventually result in formation of microparticles commonly known as microplastics, currently defined as plastic materials with various morphologies in the range of 0.1–5,000 µm. Primary microplastics are already microscopic in size from the point of manufacture. Common examples are microbeads that act as exfoliating agents in cleansers, facial scrubs and other cosmetic products, and virgin pellets that are used as raw materials in the production of plastic goods. Moreover, plastic particles have been ubiquitously detected in the environments of marine water, freshwater, agroecosystems, atmosphere, food, drinking water and biota. Estimates suggest 5.25 trillion plastic particles currently circulate in ocean surface waters. The presence of plastic particles in various environments also pose a threat to food security, food safety, and human health. Unfortunately, solid data on the prevalence of microplastic particles in the environment are still limited due to the analytical and technical challenges of extraction, characterization, and quantification from complex environmental matrices. Microplastics found in the diet can be derived from food additives (salt, sugar), drinking water, microplastics incorporated into the food chain (in particular shellfish) or released from plastic packaging during food processing. Interestingly, the highest reported concentration of microplastics comes not from the food chain, but rather from the processing of foods in plastics. Reusable plastic bottles have also been identified as a source of microplastics which could be generated through cleaning and refiling. In fact, infant exposure to microplastics is higher than was previously recognized due to the prevalence of polypropylene-based products used in formula preparation and highlight an urgent need to assess whether exposure to microplastics at these levels poses a risk to infant health. Apart from their physical presence as environmental pollutants, concerns have been raised regarding binding of the other components to microplastics, in which case, an interplay of contaminants can results in the outcomes that are not easy to predict. For instance, there is a substantial lack of knowledge on binding of allergenic proteins to microplastics and influence on the development of allergy and processes relevant for allergen degradation and presentation to the immune system (i.e. digestibility and bioavailability). EU funded project IMPTOX is investigating impact of micro (and nano)plastics on the allergic diseases. We aim to understand the effect of micro- and nanoplastics combined with potentially harmful environmental contaminants adhering to their surfaces and finding their way into the human body.

Acknowledgements

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 965173 (IMPTOX).

Mechanisms of Formation of Disinfection By-Products in Water Treatment

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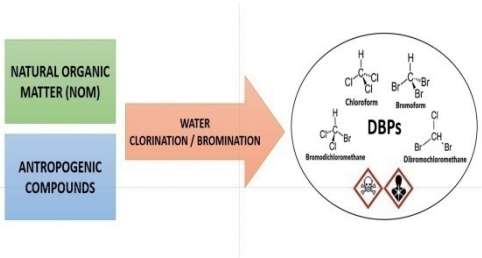

Although being successfully applied all over the world water disinfection brings to formation of hazardous disinfection by-products (DBP) from natural and anthropogenic compounds always present in water. Over 700 DBP are known so far, being formed from natural humic matter. Every anthropogenic compound shows its unique scheme of transformation with formation of dozens and even hundreds DBP. Reactions of electrophilic substitution, electrophilic addition, nucleophilic substitution, oxidation, and even radical substitution result in a consecutive array of DBP, finishing with haloforms. Identification of novel DBPs and study of the mechanisms of their formation represents a challenging scientific task aiming improvement of human health and prevention of ecosystems pollution.

Aqueous chlorination of humic matter and numerous emerging contaminants (UV-filters, pharmaceuticals, cosmetic products) were studied with GC-HRMS and LC-HRMS. The reactions were carried out in laboratory in conditions close to that used at the water treatment stations. Besides, drinking water from several Russian cities and from swimming pools was analyzed to find DBP. The studies involved various disinfecting agents, variation of ratios, pH values, reaction time and temperature addition of inorganic salts. GC-MS experiments were performed using high resolution time-of-flight mass-spectrometers Pegasus GCxGC-HRT (LECO Corporation) and Orbitrap Exactive (Thermo Scientific). LC-MS analyses were carried out with high-resolution TripleTOF 5600+ quadrupole time-of-flight (Q-TOF) (AB Sciex) and Orbitrap Tribrid (Thermo Scientific) mass spectrometers. Besides several low resolution GC-MS and LC-MS systems were used.

A number of novel DBPs including heterocyclic compounds and halogenated aliphatic amides were identified in the drinking water in terms of the study. Nevertheless, the most serious efforts were applied to the study of mechanisms of aquatic chlorination. Double bond appears to be more reactive in aqueous chlorination even than activated aromatic ring. Thus, primary reactions of active chlorine with resveratrol and avobenzone involve double bond, rather than aromatic ring. The presence of two double bonds in limonene allowed studying consecutive reactions of nucleophilic addition and elimination leading to a wide range of products with various number of chlorine atoms and hydroxyl groups. Although chlorination is usually conducted in the dark, radical reactions may still take place. Aqueous chlorination and bromination of benzalkonium chloride resulted in formation of numerous products with halogens in the aliphatic chain. On the contrary, aromatic ring remained unsubstituted. Aqueous chlorination of pharmaceutic doxazosin and arbidol demonstrated rather complex transformation including substitution, elimination, and oxidation processes. Bromides and iodides present in natural water form organohalogen species notably more toxic than the corresponding chlorinated ones. Long-term monitoring of volatile and semi volatile DBP in drinking water demonstrated fast penetration of bromine into the organic compounds at the initial stages of aqueous chlorination. Final DBPs (haloforms and haloacetic acids) contain much more chlorine than bromine due to higher content of chlorine in the reaction mixture and substitution of bromine for chlorine. The latter reaction (as well as substitution of iodine for chlorine) was studied on a wide raw of haloaromatic standards.

Acknowledgement

The research was supported by the RSF grant No 21-13-0037.

A Closer Look at the Elemental Composition of Macrofungi, with a Focus on Arsenic

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Fungi have an important position in ecosystems. Their roles involve rock and mineral transformations, bioweathering, fungal-clay interactions, and metal-fungal interactions formation. Therefore, fungi can also mobilize elements, effectively transform halogens, metals, metalloids, and organometallic compounds by reduction, methylation, and dealkylation. These processes are essential for the environment since transformations of metal(loid)s modify their mobility and toxicity.

Fungal fruit-bodies ("mushrooms") serve as important nutrient source for parasites, wild animals, and humans. They may accumulate remarkable concentrations of (trace) elements – a phenomenon that is still little known outside of the research community. For example, the King Bolete (*Boletus edulis*) is able to accumulate the essential trace element selenium (median 15 mg/kg, max. 74 mg/kg dry mass). At the same time this fungus also accumulates significant amounts mercury (median 2.3 mg/kg, max. 24 mg/kg dry mass) a heavy metal known for its toxic properties. The Fly Agaric (*Amanita muscaria*) is a selective vanadium accumulator. Concentrations of up to 440 mg V/kg dry mass have been determined in our laboratory (compared to on average < 1 mg V/kg dry mass in other species) [1]. The Violet Crown Cup (*Sarcosphaera coronaria*), a mushroom considered edible in previous days, is a known arsenic accumulator. In a recent study, we found up to 9000 mg As/kg dry mass in fruit-body samples of this mushroom species [2]. Such concentrations are hardly ever reported for any natural living organism. The edible ink stain bolete (*Cyanoboletus pulverulentus*) is also capable to accumulate up to 1300 mg As/kg [3].

As not all arsenic compounds have the same toxic properties, we have additionally determined the arsenic speciation in many different mushroom samples [4]. Our studies provide new exiting results with the respect to the arsenic speciation in mushrooms. For example, we discovered two new arsenicals for the first time in a living organism, one of them as the main arsenic compound in a parasitic mushroom.

The presentation covers analytical aspects as well as the results for the total element determinations and the arsenic speciation.

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SECTION LECTURES

Progressing Plastics Circularity: Mechano-Biocatalytic Approaches for Waste Plastic (Re)valorization (BioICEP Project Overview)

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Due to their benefits as a functional material, their extreme durability, longevity, low weight and low price, synthetic plastics, including polyvinyl chloride (PVC), PE, PS, PP, PUR, and PET, have become ubiquitous not only in work and social environments, but also in natural systems as contaminants. Plastic pollution has become a global threat, affecting all ecosystems, even remote ones like the pole regions, uninhabited atolls or deep ocean basins [1].

Effective plastic recycling poses a significant challenge for sustainability, as a plastic polymer currently degrades each time it is recycled [2]. Biotechnological solutions as part of a circular economy can form only part of more radical changes required in human behaviours like throw-away mentality symbolised by single-use consumer plastics or unnecessary packaging. Multilevel mitigation strategies to reduce the waste of natural resources started with policymakers banning and placing levies on single-use plastic consumer products to stimulate sustainable alternatives and changed consumer behaviour. Upcycling plastic waste from fossil sources in an open-loop process to biodegradable plastic and chemicals to valorise post-consumer plastic should be part of a rethinking towards a circular economy [3].

Facing the unabated growth of global plastic production and considering the shortcomings of traditional mechanical and chemical recycling technologies, biological depolymerisation and conversion technologies have been increasingly discussed, complementing end-of-life plastic treatment options. With a view to the economic circularity, selective removal of polymer-building blocks using enzymatic treatments under mild conditions and the ability to the selective recovery of monomers from mixed plastic substrates would be a real improvement.

EU Horizon 2020 research project BioICEP "**Bio Innovation of a Circular Economy for Plastics**" is transforming plastic waste into new polymers (www.bioicep.eu). It is a pan European-Chinese collaboration formed to reduce the burden of plastic waste in the environment. A number of innovative booster technologies are at the core of BioICEP solution accentuating, expediting, and augmenting mixed plastics degradation to levels far in excess of those current achievable. Our approach is a triple-action depolymerisation system where plastic waste will be broken down in three consecutive processes: 1) mechano-biochemical disintegration processes, including a new proprietary sonic-green-chemical technology to reduce the polymer molecular weight of the base polymer to make it amenable to biodegradation; 2) biocatalytic digestion, with enzymes enhanced through a range of innovative techniques including accelerated screening through novel fluorescent sensor and directed evolution; and 3) microbial consortia developed from best in class single microbial strains, which combined leads to highly efficient degradation of mixed plastic waste streams. The outputs from this degradation process will be used as building blocks for new polymers or other bioproducts to enable a new plastic waste-based circular economy [4].

Acknowledgements

This work was supported by the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No. 870292 (BioICEP) and by the National Natural Science Foundation of China (Nos. 31961133016, 31961133015, and 31961133014).

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Migration of Toxic and Essential Trace Elements from Tinplate Cans to Meat Products - Possible Impact on Human Health

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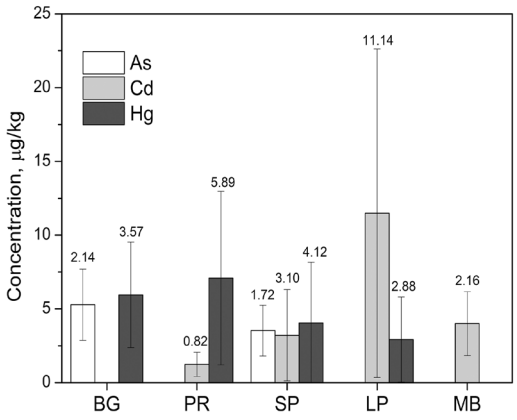

Figure 1. Comparative levels of As, Cd, and Hg in different meat products

Canned food can be contaminated with toxic elements from raw materials, additives, and spices during production or by migration from packaging material. The migration of metal ions from packaging into the preserved product depends on the can material, nature of the organic coating, its adhesion, porosity, and corrosion resistance. Several trace metals are prone to migration, among which tin, iron, lead, cadmium, chromium, nickel, zinc, and copper are considered the most common, as they are present in metal containers.

Concerns about food contamination with toxic elements, which has become a global problem, justifiably grow. The World Health Organization (WHO) encourages countries to conduct studies to assess exposure to chemical contaminants, including toxic elements, through diet. In this sense, representative data on food consumption can be combined with data on the concentration of contaminants [1]. Numerous serious health problems can occur due to excessive intake of heavy elements. It has been well established that more than 90–95% of the total daily exposure to toxic heavy elements comes from the diet [2]. In real circumstances, consumers are often and significantly exposed to toxic elements, primarily through canned food.

In armies worldwide, canned meat is one of the strategic foods thanks to its long-term sustainability and high nutritional value [3]. Canned meat products occupy an important place in the diet of members of the Serbian Armed Forces. They are high-quality products, largely specific compared to products of the same type intended for civilian use in Serbia, with a shelf life of at least four years. The specificity is reflected in the quality of packaging material, application of tin and varnish, quality of ingredients, and production process, which keep pace with international food safety standards.

The content of toxic and essential trace elements (As, Cd, Hg, Pb, Fe, Zn, Cu, Cr, Mn, Se, and Sn) was analyzed in five canned meat products (beef goulash [BG], pork ragout [PR], spam [SP], liver pate [LP], and meatballs in tomato sauce [MB]), which consumers of the Serbian Armed Forces regularly use. The influence of the storage period, the degree of the can damage, and the temperature of storage (20 °C and 40 °C) on the metal content in food was examined. The length of the storage influenced the increase of the concentration of certain toxic elements (especially Sn) in the examined meat products. Furthermore, induced damage to cans led to a statistically significant increase in Sn concentration in BG and MB (p <0.05) and Fe concentration at both storage temperatures, but without statistical significance. The obtained concentrations were compared with the maximum levels of toxic elements in food currently in force. The influence of raw materials, spices, and additives on the final metal content in canned samples was also examined. Finally, the potential health risk of consumers associated with the intake of toxic and trace elements through the examined canned products was assessed.

Acknowledgements

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Impact Of Tsunamis On Pollutants' Distribution

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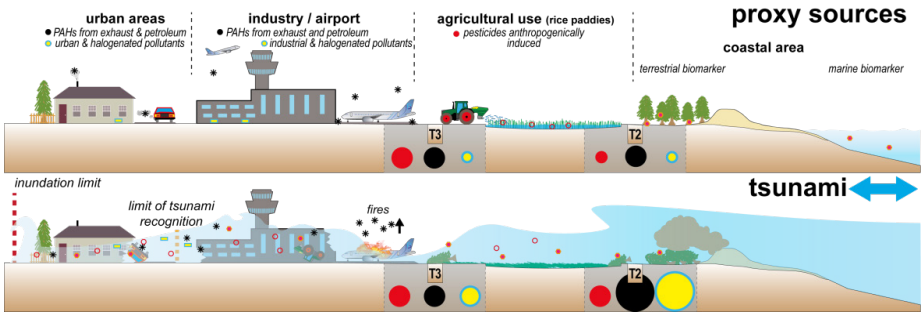

Conceptual model for distribution of anthropogenic chemical compounds in a pre-tsunami setting and during a tsunami. With concentration differences of three anthropogenic marker groups (pesticides; PAHs; halogenated compound). Inundation limit marks the max. distance water reached; limit of tsunami recognition marks the max. distance deposits can be detected. (Modified after [1])

Short-term, high-energy events, such as tsunami, possess an enormous destructive power. Major tsunamis of the last two decades, namingly the 2004 Indian Ocean and 2011 Tohoku-oki tsunami, left entire coastal stretches up to several hundreds of meters inland destroyed.

With tsunamis being relatively rare and only gaining attention in the last 50 years, research's early focus was the shear identification of past historic and prehistoric tsunamis, gaining an understanding of the basic processes and to study sedimentary features of the residual deposits.

Today, however, the focus is shifting, as the recent events have shown, that by all knowledge gained, the hazard potential by the destructive force, but also of secondary effects (*e.g.,* inundation, pollution, disease, etc.) had still been drastically underestimated. Recent studies [1],[2],[3] have shown that this type of natural hazard-related destruction is accompanied by the release of anthropogenic organic, inorganic, and nuclear pollutants or the erosive rearrangement of sediment-associated old burdens.

The understanding of a compound's chemo-physical associated distribution combined with different processes (*e.g.,* erosion, suspension, deposition) during alternating stages (*e.g.,* inundation, quasi-stillstand, backwash) and sometimes even multiple waves of a tsunami create a highly complex research topic.

In order to gain further understanding into the impact of tsunamis on pollutant's distribution we conducted an in-depth study along a survey area in Japan that was heavily affected by the 2011 Tohoku-oki tsunami. In a multi-step approach, we (I) identified the sedimentary remnants of the 2011 tsunami [1],[3]; (II) characterized the pollution and specific contaminant within these layers [3],[4]; (III) identified and documented pollution sources, that have been destroyed or caused a pollutant release of any kind during the tsunami [1],[3],[4]; and (IV) determined the lateral distribution of pollutants inland and along the inundated coastal stretch [3],[5]. By this, organic geochemical analyses, and the detection and distribution-characterization of pollutants have already advanced our understanding of processes during high-energy events and the related (long-term) public health-hazards emanating from these types of natural hazards.

Acknowledgements

This study was granted by the German Research Foundation (DFG, RE1361/32-1, SCHW750/22-1).

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Pharmaceuticals in the Aquatic Environment: A Rural Perspective and Cross-Sector Partnership Addressing the Issue in Scotland

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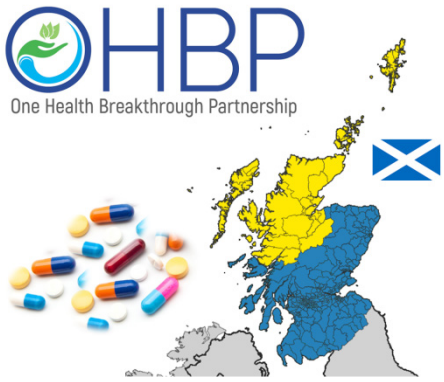

The presence of pharmaceutical residues in the aquatic environment is recognised internationally as an important public health and environmental issue. Pharmaceutical prescribing is now the most common medical intervention in modern healthcare, and usage is increasing in response to growing and aging populations, new technological advances, and pharmaceutical availability. Due to this extensive use and incomplete removal within wastewater treatment plants (WWTPs), pharmaceuticals have been widely detected in effluent-receiving surface water and aquatic environments around the world [1]. The environmental fate and risks are not fully characterised, but many compounds are of ecotoxicological and regulatory concern due to the effects in non-target organisms at trace, environmentally relevant concentrations.

In Scotland, knowledge gaps exist on pharmaceutical presence in rural regions, such as the Scottish Highlands, where historic monitoring has been limited [2, 3]. Rural areas may face challenges related to wastewater management and environmental pollution as WWTP infrastructure ages, wastewater volumes increase, and pharmaceutical usage continues to rise. To address this, four public agencies representing the environment, water, and healthcare sectors in Scotland have formed the One Health Breakthrough Partnership (OHBP). The OHBP brings together key regional and national stakeholders committed to reducing the environmental impact of healthcare practices through innovation, cross-sector engagement, and knowledge exchange. The partnership has adopted the One Health concept, which recognises that the health of humans, the environment, and animals are closely interconnected and interdependent – with water and water quality a central and significant factor to the wellbeing of all. Together the OHBP is driving research and innovation, influencing policy, and developing sustainable up-stream interventions to reduce pharmaceutical pollution in Scotland.

Acknowledgements

The One Health Breakthrough Partnership acknowledges project funding from the Scottish Government Water Industry Division, and the Centre of Expertise for Waters (CREW). Research contributors include: Karin Helwig, Adelou Aderemi, Lucyna Gozdzielewska, Jamie Harrower, Colin Hunter, Lesley Price, and Joanne Roberts (Glasgow Caledonian University); David Donnelly, Rachel Helliwell, Eulyn Pagaling, and Zulin Zhang (James Hutton Institute); Dan Merckel and John Redshaw (Scottish Environment Protection Agency).

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Neuroactive Compounds in the Aquatic Environment: Biomarkers of Effect and Their Integration into Adverse Outcome Pathways (AOPs)

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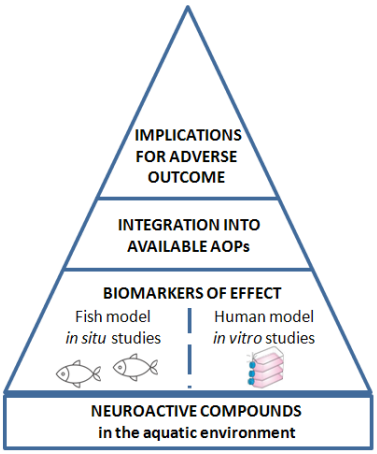

Neuroactive compounds (NCs) represent a large group of chemicals with the ability to affect the activity of the nervous system of target organisms via different primary modes of action (MoA). They include neuroactive pharmaceuticals, illicit drugs, stimulants and neuroactive pesticides. The global use of NCs is increasing worldwide which results in their constant release in the aquatic environment, making these compounds an emerging hazard with possible risk to aquatic ecosystems [1]. Lack of well characterized and widely accepted biomarkers of effect of NCs, clearly related to adverse effects in the exposed organisms, represent a challenge in the development of a biomarker-based strategy for impact assessment of NCs in the aquatic environment [2].

In our study, we are applying the holistic approach in search for sensitive biomarkers of effect of NCs, integrating three research avenues: (a) mechanistic *in vitro* study on human neuroblastoma cells treated with environmentally relevant NCs with various primary MoA, (b) *in situ* study on fish caged at the pollution hot spot in Danube and (c) integration of the responsive biomarkers in the adverse outcome pathway (AOP) framework database for prediction of adverse effects of NCs.

At the moment, our results point out the promising candidates for sensitive biomarkers of effect of NCs: synaptotagmin 10 (SYT10) - protein involved in exocytosis of neurotransmitters, myelin basic protein (MBP) – responsible for myelination of axons and neuroprotection, as well as several elements of serotonin, dopamine and GABA neurotransmitter pathways. While SYT10 and MBP are still not included as molecular targets in the AOP frameworks, observed changes in the expression of elements of the neurotransmitter pathways might imply to depression, agitation and epilepsy as possible adverse outcomes in affected organisms.

Using the presented research approach, we will continue in contributing to the development of biomarker-response patterns for NCs. Also, we stress the necessity of synchronisation of database on promising and most responsive biomarkers with events described in the existing AOPs for successful establishment of a strategy for impact assessment of NCs. Moreover, overall findings will contribute to the knowledge on neurotoxicity patterns which could be used in characterisation of environmental contaminants and mixtures of compounds with unknown primary MoA.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, PROMIS, Grant No. 6061817, BIANCO. The abstract content is the responsibility of the Faculty of Sciences University of Novi Sad, and it does not reflect the opinion of the Science Fund of the Republic of Serbia.

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Plants, An Attractive Partner for Phytoremediation and Phytomonitoring of Environmental Pollutants

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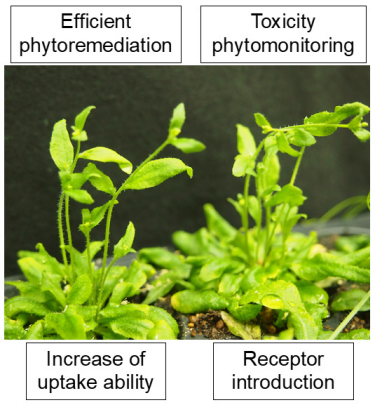

Plants play distinguished roles for our life. Crops and vegetables are necessary for daily foods, and flowers and forests provide peace and refreshment to have a prosperous life. Various types of plant-derived compounds are utilized as pharmaceuticals and personal care products. Furthermore, plants have a high affinity toward a sustainable life in terms of absorption of CO_2. Environmental chemistry also receives a lot of benefits from plants.

Phytoremediation recently becomes one of popular bioremediation technologies because of its sustainability. It is powered by photosynthesis and performed on site, leading to cost-effectiveness [1].Phytoremediation is a promising technology, but there are several limitations. Activity of plants is influenced by inappropriate climate and toxicity of pollutants. In addition, uptake of pollutants into plantsoften becomes problems since most of them are hydrophobic. Hydrophobic pollutants are rarely taken up into upper parts of plants although they are accumulated in roots [2]. Cucurbitaceae family, including cucumber, pumpkin, zucchini, and melon, was found to accumulate hydrophobic pollutants, such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs) in theirupper parts[3,4]. We have identified a factor responsible for efficient uptake of hydrophobic pollutants in Cucurbitaceae family [5]. That is a major latex-like protein (MLP), which can bind to hydrophobic pollutants and transport them from roots to upper parts of plants. Transgenic plants expressing *MLP* genes showed enhancement of accumulation of PCBs in upper parts of plants [6]. These results suggest that gene expression of MLPs takes away one limitation derived from application of plants.

Phytomonitoring is a new technique to monitor pollutants using plants. In general, environmental monitoring is achieved using instrumental analyses, using LC/MS and GC/MS. These techniques have advantages on determination of precise concentrations of pollutants in the samples.However, in order to analyze low concentrations of pollutants extraction, concentration, and purification are necessary prior to analysis. Plants have a tremendous ability to concentrate wide-spread pollutants through their root systems even if soil matrices are complexed. We employed chemical receptors responsible for receiving and transmitting endogenous and exogenous stimuli in animals for phytomonitoring. Aryl hydrocarbon receptor (AhR) and estrogen receptor (ER) are introduced into plants to monitor dioxins and endocrine-disrupting chemicals, respectively. These transgenic plants showed dose-dependent reporter activities in medium and soil contaminated with pollutants [6-9]. This phytomonitoring systems also provide toxicity information whereas instrumental analyses cannot.

Plants are attractive partners in the field of environmental chemistry to the future.

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Phthalate Migration from Food and Medical Plastic Materials

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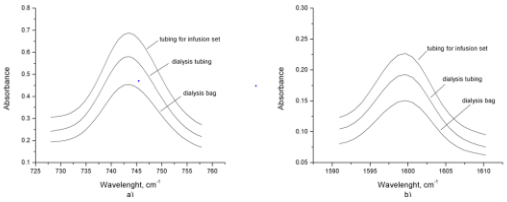

The FTIR spectrum of PVC samples: a) region 730-760 cm^{-1} b) region 1590-1610 cm^{-1}

Phthalates are usually used as plasticizers for plastic materials. Bearing in mind that phthalates can easily migrate to the environment, it is important to know their amlount in plastic material and food, as well as the conditions under which they can migrate from plastic articles into surrounding environment. The following phthalates were tested: dimethyl phthalate, di-n-butyl phthalate, benzylbutyl phthalate, di(2-ethylhexyl) phthalate and di-n-octyl phthalate.One of the reasons that those phthalates were selected as the target compounds is based on the detection frequency of phthalates in bottled water. Those 5 phthalates are the most frequently detected in bottled water specially in countries like Croatia, Serbia, Czech Republic, Thailand, Saudi Arabia, China, Pakistan etc.[1]. Since the majority of packaging materials in this investigation is from this application domain, we have followed the same phthalate selection as referenced above.

Their migration into milk, milk-based products, white brandies and synthetic wine and artificial saliva from plastic articles made of the following polymers: polyvinyl chloride (PVC), polyethylene terephthalate, high density polyethylene, low density polyethylene, polypropylene, polystyrene and polycarbonate was monitored.

A liquid-liquid extraction method was developed for three different types of food matrix: high fat food, low fat food and non-fat food. The quantification of phthalates in food samples using GC-MS technique was developed and optimized for determining phthalate concentration[2].

The development and optimization of the method for determining the concentration of phthalates in samples of PVC plastic articles using the GC-MS technique and the development of a new method of quantification phthalates in PVC plastic articles using the FTIR technique were performed[3]. This is the method for total phthalate content determination in the solid samples. Thus, for leaching potential, when determination should be done in the liquid recipient solution, GC-MS technique is appropriate technique.

Finally, the degree of migration of phthalates from plastic materials in contact with food and pharmaceutical products and PVC toys into the recipient model was examined.

The analysis of factors influencing the migration of phthalates from plastic articles to the appropriate recipient was performed.

Acknowledgements

This work received support from the Ministry of Education,Science and Technological Development of the Republic of Serbia undercontract no. 451-03-9/2021-14/200124.

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Potential of Cost-Effective Materials in Advanced Wastewater Treatment Processes

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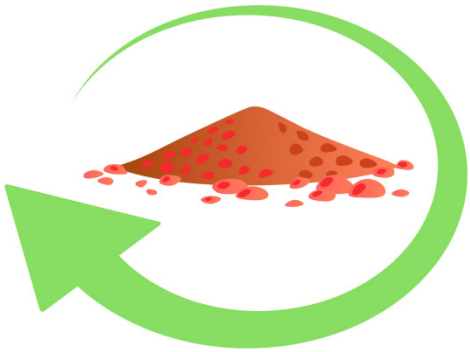

Water scarcity has become one of the most important issues around the globe due to rapid human population growth and the unsuitable exploitation of water resources. Pressure is directed toward countries to implement more sustainable and innovative practices and to improve international cooperation on water management. One particular contributor to the global water crisis is wastewater. Sustainable and innovative wastewater treatment hence present a global demand. The goal is to develop cost-effective, safe, les chemical intensive and sustainable water treatment. One of the approaches is to use green and cost effective materials. Many types of materials is investigated for this purpose, but severel types of material are wildely recognised so far: Carbon-based adsorbents; Nanomaterials and Microbial fuel cells.

Adsorption using carbon-based adsorbents and nanoadsorbents (CNAs) i.e., graphene (G), carbon nanotubes (CNTs), and activated carbon (AC) is considered as one of the most efficient, flexible, and easy to perform techniques for removal of heavy metals and organics from wastewater. However, some sorbents have certain limitations in terms of eco-friendliness, cost-effectiveness, selectivity, and regeneration ability. To overcome the above-mentioned limitations and achieve sustainable wastewater treatment and increase capacity for pollutant removal, surface modification of adsorbents with different functionalizing agents has been conducted to enhance their sorption capacity, selectivity for contaminants, creating good impact on the environment and high recyclability, and this will lead to cost-effective and energy saving process [1]. Nanotechnology has been cited, in different literatures, as one ofthe most advanced processes for wastewater treatment. It may be classified based on the nano-materials nature into three main categories: nano-adsorbents, nano-catalysts and nano-membranes. Nano-adsorbent can be produced using the atoms of those elements, which are chemically active and have high adsorption capacity on the surface of the nano-material. The used materials for development include activated car-bon, silica, clay materials, metal oxides and modified compounds in the form of composites. Nano-catalysts such as metal oxides and semiconductors have gained a considerable attention in wastewater treatment. Different types of nano-catalysts are employed for degradation of pollutants in wastewater, for instance, electrocatalysts. Nano-membrane technology represents the pressure driven treatment of wastewater and has been proved great for improving water quality. Nano-membranes can be developed from nano-materials such as nano metal particles, non-metal particles and nano-carbon tubes among others [2]. Recently, bioelectrochemical systems (BESs), such as microbial fuel cells (MFCs) and microbial desalination cells (MDCs), are proposed to be emerging and green technologies for wastewater treatment with simultaneous electricity generation from the catalyst exoelectrogens [3].

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, PROMIS call, Project no. # 6066881, WasteWaterForce

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ORAL PRESENTATIONS

Removing Copper and Lead Ions from Water by a Dopamine Modified Marine Plastic Adsorbent

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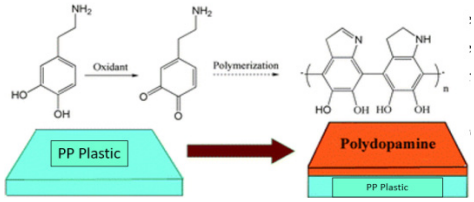

It is estimated that global plastic production reached 367 million tons in 2020 [1]. Plastic pollution has become an eye-catching environmental issue in recent years. When present in the marine environment waste plastic can adsorb a wide range of pollutants, including heavy metals and hydrophobic organic compounds [2]. This suggests a potential use of marine plastic waste as an adsorbent for the removal of contaminants industrial effluents [3].

Here, the adsorption of lead and copper (which are among the two most commonly found pollutants in different wastewater streams) using raw and modified marine plastic (PP- Polypropylene) under controlled laboratory conditions was investigated. PP ropes were collected from beaches across Northern Scotland, washed with DI water and then treated with a 4 mg/L dopamine solution for 24 h at pH 8.5. The modified plastics were then washed again using DI water and dried. 'Point of zero charge', scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy techniques were used to characterise the samples.

Both batch and column studies were conducted at lab-scale. In batch experiments, the impacts of temperature (20-40 °C), initial concentration (0.5-50 mg/L), pH (3-10), contact time (5-2880 min), and adsorbent dose (50-150 mg) were investigated. The adsorption capacity in real wastewater samples was also tested by using wastewater collected from a wastewater treatment plant. In addition, the column study confirmed how removal rate can be affected by flow rate (1-5 mL/min), bed height (7-13 cm), column diameter (1-4 cm), and initial concentration (0.5-2 mg/L). This research also studied the improvement in adsorption capacity/bed service time with combining modified plastic with commercial activated carbon columns in series.

Under optimal conditions, the adsorption capacity for functionalised samples can reach 316.67 µg/g for Cu and 525.00 µg/g for Pb, which was significantly better than unmodified plastics. The adsorption process was found to be endothermic, and fitted best with the Langmuir isotherm model and psuedo-second order model. In real wastewater samples, the adsorption capacity was slightly decreased due to the presence of other ions. In addition, column study results indicated combining modified plastic with activated carbon could extend the life of the activated carbon by almost 50%. The adsorption mechanism is likely to mainly involve electrostatic interactions, between positively charged metal ions and the negatively charged adsorbent surface (mainly $-O^-$ group) at optimum pH (pH~6). Desorption experiments using 0.2 M HCl also demonstrate that it is possible to reuse the plastic adsorbents.

This project provides a potential solution for marine plastic management and a new source for low-cost adsorbents. These new plastic-based adsorbents can be used as additives with existing commercial adsorbents to extend their service life, and reduce the operating cost for the current wastewater treatment systems.

Acknowledgements:

This work was made possible by the Developing Scotland's Workforce project funded through the European Social Fund and by the Scottish Alliance for Geosciences, Environment and Society (SAGES).

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Effect of Ozonation on the Speciation of Arsenic in Groundwater During Drinking Water Preparation

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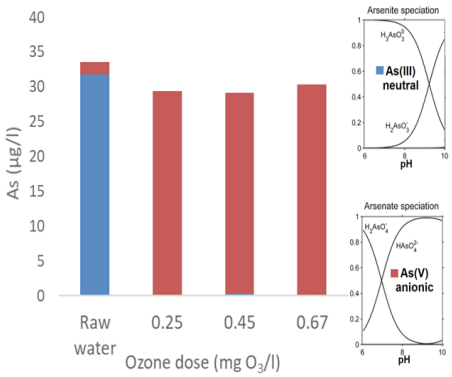

Graphical Abstract: Ozone is highly effective at oxidising As(III) to As(V) in drinking water **Introduction:** The natural contamination of drinking water sources with arsenic is a serious public health issue in many areas of the world, including Vojvodina. Deep aquifers are generally anoxic, and as a result, the arsenic, which originates from the minerals present in the aquifer, is usually dissolved in the water as arsenite (As(III)) [1]. As shown in the right-hand insert of the graphical abstract, within the typical pH range of groundwater sources (pH 6.5 to 8.5) As(III) is predominantly neutral. In contrast, arsenate (As(V)) is deprotonated in the same pH range, and is therefore anionic. The majority of technologies which are applied for the removal of arsenic from drinking water are thus considerably more effective at removing As(V), as its anionic nature allows for greater electrostatic interactions between floccs and/or adsorbent surfaces [2]. The determination and control of As species is therefore of great significance to drinking water treatment.This work therefore investigates the use of ozonation to oxide As present in a Vojvodina groundwater used for drinking water supply. The ozone dose required for this preoxidation step depends on the amounts of As and other contaminants present in the water. In this case, in addition to the As, ozonation is also required to oxidise ammonia and natural organic matter.

Materials and Methods: After ozonation with three different ozone doses (0.25, 0.45 and 0.67 mg O_3/l), a simple solid phase extraction (SPE) technique is applied to separate the two inorganic arsenic species prior to As determination by ICP/MS (Agilent 7700x). This method is based on the work of Yu et al [3]. Samples are first stabilised with the addition of 2.4 mmol EDTA and 85 mmol acetic acid. 10 ml of sample are passed through a pre-conditioned column of Supelclean™ LC-SAX anionic exchange resin. The As(III) present in the sample passes directly through the resin and is collected for analysis. Due to its anionic structure, As(V) is retained by the column and may be eluted with nitric acid.

Results and Discussion: The raw water contains around 33 µg/l of arsenic in total, approximately 95% of which is As(III). As can be seen in the graphical abstract, even the lowest dose of 0.25 mg O_3/l was sufficient to fully oxidise all the As(III) in the groundwater to As(V), although according to other parameters monitored, even the highest dose of ozone applied was insufficient to fully oxidise the NOM present (e,g. UV_{254} absorbance fell from 0.0588 to 0.0477).

Conclusion: In this work the effect of ozonation on the species of arsenic present in groundwater was investigated. The results show that even at a low dose, ozone effectively oxides all arsenic present in the water, suggesting it is highly suitable for application during drinking water preparation, as a first step in an arsenic removal treatment process, prior to species-sensitive As removal techniques such as coagulation/flocculation or adsorption.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, Program DIASPORA, GRANT No. 6485164, HYDRA.

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New Sustainable Process for Wastewater Treatment Using Recycled and Recoverable Magnetite with Natural Iron Complexing Agent: an Example of Photochemical AOP

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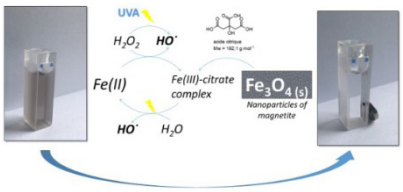
AOP (Magnetite/H_2O_2/Citrate/hν)



Organic pollutants degradation

Iron oxides are known as a noticeable catalyst used in (photo)Fenton processes in order to overcome the drawbacks of the traditional Fenton reaction. In the traditional Fenton process, the operational pH should be less than 4, to avoid iron precipitation and ensure a high production of HO·radical, a strong and non-selective oxidant, able to oxidize the recalcitrant organic pollutants in aqueous environments.

Magnetite is one of the most attractive iron oxides used in wastewater treatment due to its unique physicochemical properties. Magnetite is a spinel-mixed valence oxide, where Fe(III) ions occupy equally both octahedral and tetrahedral sites, and Fe(II) are placed in octahedral sites only [1]. The presence of Fe(II) can improve the production of HO· radical through the Fenton reaction [2]. In addition, magnetite can be easily separated from the heterogeneous system due to its magnetic properties. Recent works showed that magnetite under UVA irradiation can effectively promote Fenton reaction under different experimental conditions [3]. Moreover, the leaching of Fe from magnetite was very limited and much below the wastewater discharge limits.

Although the use of iron oxides in Fenton or photo-Fenton processes is believed to be desirable due to their ability to work in a wide pH, several modifications were carried out to increase their efficiency. Among them, addition of organic chelating agents, such as ethylenediaminetetraacetic acid, oxalate, tartrate, citrate, succinate and more recently Ethylenediamine-N,N′-disuccinic acid (EDDS) have been used to enhance the degradation efficiency of heterogeneous (photo)Fenton systems using iron oxides, especially at neutral pH [4].

The main goal of this work, involved in a largest project, is to develop a wastewater treatment process based on advanced oxidation processes (AOP) in order to eliminate contaminants of emerging concern. The process, which must be robust, cheap and sustainable, aims at the recovery of wastewater through its reuse, in agriculture for example. The process implemented is based on the Fenton process in which we use magnetite from the recycling of ferrous waste and citric acid as a complexing agent. A work of characterization of the iron-citrate complex was first conducted in order to follow the fate of the citric acid as it was done for EDDS [5]. In a second step, the magnetite/citric acid/H_2O_2 system was studied in order to optimize a process that would allow the efficient degradation of a target pollutant: carbamazepine.

During this work 3 main principles were put forward, i) recycled magnetite is an efficient material to trigger the Fenton process, ii) citric acid is a good natural iron complexing agent with no impact on the environment and iii) sunlight allows the photo activation of the process.

Acknowledgements

The authors wish to acknowledge the financial support of the “Région Auvergne-Rhône-Alpes” for their financial support through the “Pack Ambition Recherche”.

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Presence and Challenges of Volatile Methylsiloxanes in WWTPs

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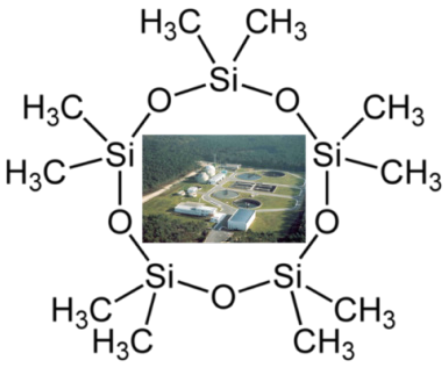

Volatile methylsiloxanes (VMSs) are emerging contaminants of increasing concern which have significant impact in WWTPs [1]. Comprised by a backbone of sequential Si-O bonds, they are frequently used in the manufacturing of personal care and other consumer products. Consequently, domestic and industrial effluents introduce these chemicals into WWTPs, where they partition between the water line, and predominantly the sludge line, and the air. In the atmosphere, the presence of VMSs may affect the workers of the WWTPs in a first stage, but the impact can reach the surrounding populations. Sludge, on the other hand, is being considered a value-added residue, by its conversion to biogas and as composting products for soil amendment. This helps the economic and energetic sustainability of WWTPs and the enforcement of circular economy principles [2]. Project LANSILOT (*LAunching New SILOxane Treatments: assessing effluent, sludge and air quality and improving biogas production in WWTPs*) was idealized and is being carried out to assess the presence and develop a solution to lower the VMS content in WWTPs, and includes their quantification in wastewater, sludge, air, and biogas along the different treatment steps of an urban WWTP and the initial effort towards a VMS removal technology from sludge based on aeration and subsequent degradation by advanced oxidation processes (AOPs). The variations in VMS concentration hourly, daily, weekly and seasonally demand a thorough monitoring to preserve the cogeneration (or other energy producing) facilities.

To the analysis seven VMSs (L3, L4, L5, D3, D4, D5, D6) in wastewater, liquid and solid sludge and passive air samples collected in an urban WWTP from Portugal, 30 mL, 20 mL, 2.5 g and 10 g of XAD were used, respectively, in liquid-liquid (water and liquid sludge) and solid-liquid (solid sludge and passive air) extractions with low volume of organic solvents followed by GC/MS quantification. The VMS removal experiments attempted were done using an aeration system on simulated sludge with added VMSs at different concentrations, combined with a bubble column reactor (BCR) with AOPs to decontaminate the resulting gas stream.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - national funds through the FCT/MCTES (PIDDAC); (ii) Projects LANSILOT (PTDC/CTA-AMB/32084/2017; POCI-01–0145-FEDER-032084) and AGRONAUT (PTDC/ASP-PLA/29425/2017; POCI-01-0145-FEDER-029425), both funded by FEDER through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) N. Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call - [CEECINST/00049/2018]; (iv) V. Homem thanks National funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus – Individual Call – CEECIND/00676/2017; (v) G. Pantuzza thanks FCT PhD programme for Grant 2020.07815.BD, supported by, under the Portugal 2020 Partnership Agreement and European Social Fund (ESF).

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The Embryotoxic Potential and Photocatalytic Degradation of Thiophanate-Methyl

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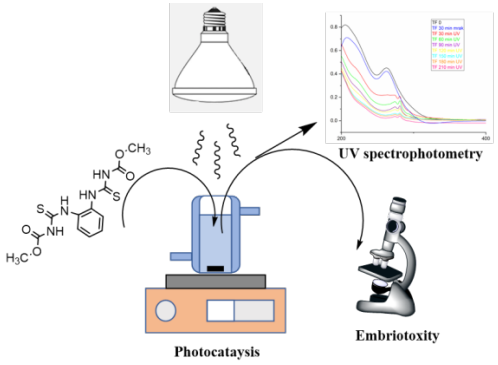

Pesticides are substances designed to protect plants from various types of diseases and pests [1]under UV irradiation is studied using synthesized Zinc oxide (ZnO. Synthetic organic pesticides, in addition to the high efficiency, have led to frequent adverse environmental impact, as a consequence of their high accumulation and toxicity. Due to the increased pollution of water with mixture pesticides, it is necessary to use different processes for their removal and degradation. Therefore, oxidative processes have been developed, commonly named as Advanced Oxidation Processes (AOPs). Among them, special attention was attributed to photocatalysis, as a process that enables the degradation of difficult-to-decompose organic molecules under the action of UV radiation in the presence of catalysts [2].

In this study the photocatalytic degradation of thiophanate-methyl (TM) in the presence of the TiO_2 Degussa P-25 catalyst was investigated. Different experimental conditions were varied, such as the concentration of the pesticide solution, the mass of the catalyst and the influence of the anions (chloride, sulphate, nitrate, etc.). The pesticide concentration in the reaction system was monitored based on the decrease in system absorbance using a Shimadzu 1800 UV spectrophotometer. For optimized conditions of complete photodegradation, the environmental acceptability of the defined degradation process was examined. The toxic effect of the TM solution before and after degradation was examined using the embryotoxicity test with *Danio rerio*, in order to prove the reduction of toxicity and the success of the degradation process [3]which raises the issue of potential influence of different formulation types on herbicide toxicity. The present study evaluated the toxicity and teratogenic effects of the active ingredient clomazone and its two formulations (Rampa® EC and GAT Cenit 36 CS, both containing 360 g a.i./l of clomazone.

Comparing the obtained results of the influence of ions on the processes of photocatalysis, it was noticed that all ions have catalytic effects on the kinetics of the degradation process of TM. The presence of sulphates and carbonates had the greatest catalytic effect, while hydrogen phosphates and bicarbonates showed the lowest catalytic capacity.

The optimal experimental conditions were obtained using 0,2 g/L of TiO_2 and 5 mg/L of TM solution. In addition, the embryotoxicity test followed the analytical examination. Comparison of results obtained in embryotoxicity assay testing of the initial solution, partly and completely degraded samples confirmed suitability of applied degradation method. Increase in toxicity, compared to the initial solution, was registered in partly degraded sample. This observation can be attributed to increase in concentration of carbendazim (TM metabolite) more toxic than parent substance. Finally, completely degraded sample caused no mortality or adverse effects in *D. rerio* embryos after 120 h exposure. Toxicity of samples, in decreasing order is half degraded > initial >completely degraded sample.

Based on the obtained results it can be concluded that used photocatalytic degradation process can be successfully applied in pesticide contaminated water management.

Acknowledgements

This investigation was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants Nos. 451-03-9/2021-14/200214 and 451-03-9/2021-14/200135).

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The Effect of Power on the Degradation of Propranolol by Nonthermal Plasma Reactor

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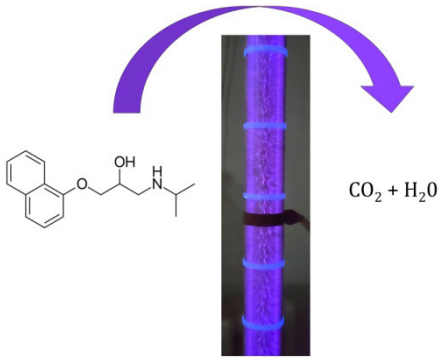

Propranolol (PRO) is a beta-blocker that is readily detected in surface water and hospital wastewater [1]. This pharmaceutical poses a danger for aquatic animals because it is commonly prescribed for heart diseases and anxiety issues [2]. Advanced oxidation processes are commonly tested for the decomposition of pharmaceuticals because they produce various reactive species at room conditions [3].

A liquid-falling film dielectric barrier discharge (DBD) reactor was used for the treatment of a PRO solution, with no catalysts added. A coaxial construction, accompanied by a peristaltic pump, enables the recirculation of the treated liquid. Ambient air was selected as a feed-gas for nonthermal plasma generation under three levels of power dissipated in plasma. Direct contact of liquid film with plasma in this coaxial reactor enables the efficient transfer of reactive oxygen and nitrogen species generated in plasma to the liquid phase.

The degradation rate of PRO, pH value, and conductivity were monitored after every cycle of treatment of PRO solution (100 mg/dm^3), and in the presence of scavengers (t-butanol and p-benzoquinone). The PRO concentration was monitored by HPLC-DAD, at 213 nm.

As expected, the highest applied power (60 W) contributed to the highest degradation rate (100%). At the same time, in these extreme conditions, pH values dropped from 6 to 2.5 and conductivity increased from 20 µS/cm to almost 1450 µS/cm in the tenth cycle of plasma treatment. Moreover, a high power yielded an excessive decontamination level, but also in the grand production of nitric acid.

On the other hand, lower values of power lead to less successful endpoints, over 85% and less than 60% of degraded PRO when 35 W and 15 W were applied, respectively. Accordingly, under these conditions, the total production of ions was less intensive. The maximum conductivity value was less than 500 µS/cm for PRO treated with plasma generated by 35 W of power, and under 130 µS/cm for 15 W.

To elude the exact role of reactive species, a pair of scavengers were added to a PRO solution. Both t-butanol and p-benzoquinone cut down the degradation efficiency to roughly 50%, which is 35% less than without scavengers. This result indicates an important role of hydroxyl radicals and superoxide anion radicals in air-generated nonthermal plasma.

Advanced oxidation using this type of nonthermal plasma reactor enables the production of active species *in situ* while working in ambient conditions [4]. The effectiveness of plasma treatment was confirmed with the degradation of propranolol, as a model compound for common waterborne pharmaceuticals.

Acknowledgements

This study was funded by the Ministry of Education, Science, and Technological Development of the Republic of Serbia; Contract numbers: 451-03-9/2021-14/200168 and 451-03-6812020-14.

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Revisiting Humic Acid Adsorption onto Activated Carbon

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Humic substances are ubiquitous in both ambiental and waste waters, which affect water treatments. They also sorb onto mineral surfaces of quartz sand [1, 2]. However, mechanisms still have to be investigated. Interest has been raised to understand how suspended particles influence efficiencies of water treatment technologies [3, 4]. This work aims to determine the influence of particulate matter of different origin, size, and concentration onto humic acid (HA) adsorption by powdered activated carbon (PAC), frequently tested in wastewater treatment. Quartz sand, usually used as filter material in waterworks, and kaolinite were used as surrogates for suspended solids. They were prepared by dry milling (PM100 Planetary Ball Mill, Retsch, Germany; stainless steel balls and jar, ball ϕ20 mm, speed 150 rpm, 30 minutes) and dry fractionation into two fractions each (125-63 μm and <63 μm), using a Sieve Shaker AS 200 (Retsch, Germany) with ISO 3310-1 test sieves. HA was measured as dissolved organic carbon (DOC) by Vario TOC select – Elementar. Initial concentration of DOC is selected to simulate its content in effluent of wastewater treatment plants (e.g. 1.5-38 mg/L) [5]. Kinetic experiments were conducted in synthetic clean water spiked with HA (5 mg/L) with 20 mg/L PAC dosed as: a) suspension (c = 1 g/L; time: 2-24 h) and b) dry (time: 48-96 h). The achieved HA load in equilibrium was 75 mg/g PAC and 81 mg/g PAC at 48 h, respectively. Results of isotherm test (PAC dose 12-70 mg/L and HA initial concentration 7.52 mg/L) were Freundlich parameters Kf= 33.78 (mg/g)/(mg/l)^n and n= 0.715 (R^2 = 0.64). Estimated interparticle mass transfer coefficients for wet PAC dosing was $1.8 \cdot 10^{-5}$ 1/s (software KIN, Worch [6]). Adsorption analysis (PAC dose 12-500 mg/L; $C_{(HA)}$= 6 mg/L; mixing time 72 h) showed that HA consists of 4 fractions, n=0.2; very weakly absorbable (<4%; Kf=5 (mg/g)/(mg/l)^n), low absorbable (42%; Kf=30 (mg/g)/(mg/l)^n), medium absorbable (36.5%; Kf = 50 (mg/g)/(mg/l)^n), and highly absorbable (17%; Kf = 80 (mg/g)/(mg/l)^n) with error 3.85%. Table 1 shows results of HA removal efficiency by PAC with and without suspended solids. At 15 mg/L, regardless of origin, suspended solids did not significantly remove HA in comparison to analytical bias and precision for DOC measurements (7% and 13%, respectively). At the concentration of 70 mg/L only quartz sand (particle size 125-63 μm) removed 17%. When it comes to influence of particulate matter on HA adsorption on PAC, the results in Table 1 show that it could not be observed.

Table 1. The removal efficacy of HA by PAC (20 mg PAC/L, HA Co =4.64±0.51 mgC/L)

Surrogate to suspended solids	Quartz sand		Kaolinite	
Fraction of material 125 - 63 μm <63 μm			125 - 63 μm	<63 μm
Samples	Removal efficacy, %			
HA + 15 mg/L of material	9[a]	5[a]	2[a]	no removal
HA + 70 mg/L of material	17[a]	no removal	15[a]	13[a]
HA + 20 mg/L PAC	34±16[b]	34±16[b]	34±16[b]	34±16[b]
HA + 15 mg/L of material + 20 mg/L PAC	34±30[b]	33±17[b]	28±3[b]	23±10[b]
HA + 70 mg of material + 20 mg/L PAC	25±10[b]	20±10[b]	35±10[b]	33±6[b]

[a] Single value[b] Average value ±Interval of confidence for triplicate measurements

Further research is needed to assess organic micropollutants removal efficiency by PAC in presence of both HA and particulate matter.

Acknowledgements

The authors acknowledge financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. OI172028 and Grant No. 451-03-9/2021-14/200125).

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Circular Economy-Based Phosphorus Recovery Technology Development to Create a Soil Conditioner: an Integrated Approach

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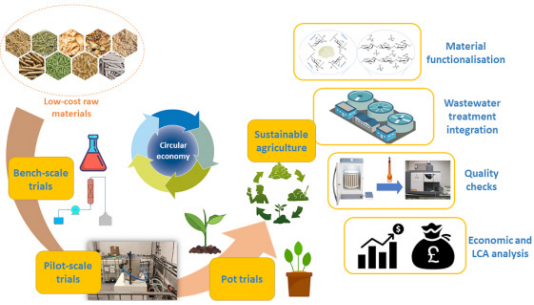

Within the transition from a fossil fuel reserve-based world to a bio-based economy, we face the vital need to close nutrient cycles and move toward more balanced resource management. Phosphorus (P) recovery from wastewater will become increasingly vital in the future as terrestrial rock phosphate deposits are limited [1].

The Environmental Research Institute (ERI) has been developing the FILTRAFLO™-P reactor (with Veolia Water Technologies) to recover P from wastewater/septic tank effluent through a filtration/adsorption process (Phos4You Project - INTERREG VB North-West Europe). This small unit employs enhanced gravitational filtration through adsorption media (here, a novel KOH deacetylated crab carapace-based chitosan-calcite adsorbent (CCM)) with continuous self-backwashing [2]. The trials were designed to assess how the FILTRAFLO™-P unit would operate under 'real' conditions (low and high P levels), and to ascertain the effectiveness of the adsorbent to recover P from final effluent. A six-week trial of this technology was carried out at the Scottish Water Horizons Development Centre at Bo'ness in January-February 2020.

High P recovery potential was achieved even at low P concentrations, bringing the residual effluent P level below 1 mg/L (EU limit for sensitive water bodies). Surface microprecipitation and inner-sphere complexation were postulated as key P adsorption mechanisms due to reduced concentrations of Fe, Ca, Cu, Mn and Ca. Also, the high inorganic carbon (carbonate) concentration in treated effluent indicated ligand-exchange through these metals (mainly Ca) [3]. The slightly increased turbidity noted in treated water (e.g., likely due to magnesium and potassium carbonates) may require integration/combination of the FILTRAFLO™-P unit with slow sand filtration. The results showed that the FILTRAFLO™-P unit with CCM could serve as a water polishing unit (with low P concentration effluents) and/or as a P harvesting unit (where P concentrations were high). Further, the quality assessment of the P-enriched CCM was based on elemental composition (macro nutrients and heavy metals), microbiological evaluation and quantification of organic micropollutants. The quality analysis indicated ~3% P_2O_5, trace levels (well below legislative limits) of heavy metals (i.e., Cu, Co) and organic pollutants (e.g., PCBs) and no detectable levels of target bacterial pathogens. A pot trial was conducted (at Ghent University) to examine P availability of CCP on river sand during 4-month growth of perennial ryegrass. The results showed that the ryegrass plants treated with the CCM adsorbent achieved higher plant dry matter and P concentration compared to the unfertilised control.

Overall, this study has shown a fully integrated approach, i.e., to assess the feasibility of lab to pilot-scale implementation; plant P-availability; the chemical/microbiological 'quality' of the saturated adsorbent.

Acknowledgements

This work was undertaken as part of the 'Phos4You' Project (NWE 292) with financial support from the INTERREG V B Northwest Europe Programme. Authors are also thankful to Cedric Mebarki and Veolia for their help in pilot plant design, supply and construction.

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Uptake of Synthetic Musks and Volatile Methylsiloxanes by Pea Crops Grown in Sewage Sludge-Amended Soils

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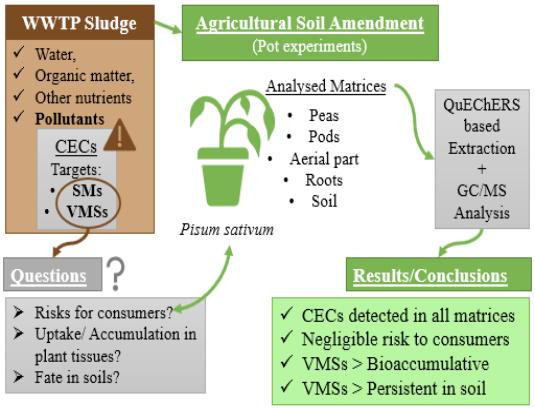

Sewage sludges are residues produced in large quantities in wastewater treatment plants (WWTPs). Due to their chemical composition rich in water, organic matter and nutrients required for plant growth [1, 2], they are particularly appealing as organic fertilizers, providing nutrients for plants and soil benefits [1]. However, the presence of pollutants in sewage sludges [2], may raise issues regarding their use on food crop production. Pollutants such as synthetic musk compounds and volatile methyl siloxanes [3,4], considered as contaminants of emerging concern (CECs), have not been extensively studied regarding their effect in the soil, interactions with plant growth or possible risks to human health. To overcome some of the knowledge gaps regarding SMs and VMSs in amended-soils and in the soil-plant system, an indoor pot experiment with peas *(Pisum sativum L.)* was conducted to assess the uptake of 17 target compounds from sludge amended soil. Four different application rates were tested and three sludge spiking levels of five key targets (HHCB, AHTN, D4, D5 and D6). At full maturity, the plants were harvested and separated into compartments (roots, combination of stems, leaves and tendrils referred to as 'aerial part', pods and peas), which were then analyzed using an extraction methodology based on QuEChERS extraction (Quick, Easy, Cheap, Rugged and Safe) followed by target quantification via GC-MS.

Six compounds (D3, D4, D5, D6, HHCB and AHTN) were detected in the plant compartments and yielded different behaviours, according to their chemical class. SMs were uptaken by the plant roots, having been detected in concentrations up to 350 ng/g dw, but did not translocate to above ground parts of the plants in all tested conditions, while VMSs were found in roots in concentrations up to 110 ng/g dw, and were translocated in nearly all conditions. A mass balance and bioconcentration factor (BCF) values revealed that VMSs are more bioaccumulative than SMs. It was also observed that accumulation of the pollutants in the amended soils was significantly limited by the presence of plants, when compared to the plant-free control soils. Lastly, a worst-case scenario analysis of human estimated exposure dose vs. tolerable weekly intake of the grown peas revealed no discernible risk to human health via ingestion. The application of sludge to agricultural soils may therefore be of great interest in the treatment of soils destined to the cultivation of legume crops.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); (ii) Project PTDC/ASP-PLA/29425/2017 - POCI-01-0145-FEDER-029425 - funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) National funds through FCT - Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus - Individual Call - CEECIND/00676/2017 (Vera Homem); (iv) Filipe Rocha thanks FCT for the PhD Research Scholarship (Ref. 2020.09041.BD).

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Environmental and Agricultural Impacts of Using Sewage Sludge as a Fertilizer – Emerging Contaminants as a Case Study

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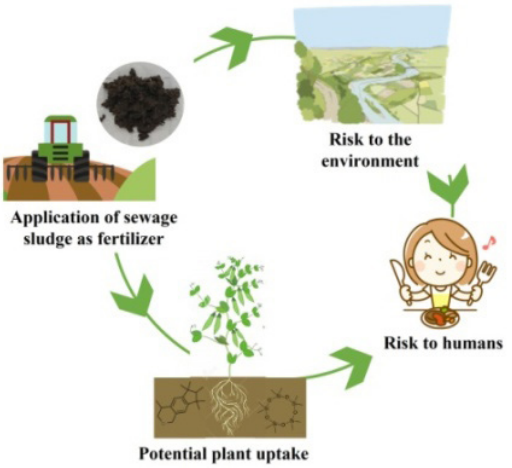

The amount of sewage sludge requiring disposal is increasing due to the progressive growth in the number of sewage system connections. This residue contains a high organic matter content and nutrients that are extremely valuables for soils [1], which makes it prone to be used as fertilizer. On the other hand, the potential presence of significant amounts of contaminants has raised concern among the scientific community. Considering this, the European Union (EU) has been promoting the use of sewage sludge in agriculture, encouraging the implementation of a circular economy model [2], trying at the same time to regulate its use to prevent harmful effects on the environment and humans. Although some member states have internally established concentration limits for some persistent organic pollutants in sewage sludges intended for agricultural use, the EU legislation only sets limits for 7 heavy metals (Cd, Cu, Ni, Pb, Zn, Hg, Cr) [2]. However, the potential impact derived from the presence of emerging pollutants in these residues have been clearly neglected. Thus, this work, carried out under the AGRONAUT project, intended to study, in a first phase, the concentrations of 2 classes of emerging pollutants – synthetic musks (SMs) and volatile methylsiloxanes (VMSs) - in sewage sludge from different Portuguese urban wastewater treatment plants (WWTPs) and in a second phase, if its application as agricultural fertilizers could promote the migration of the contaminants to soils and their uptake/translocation to a model crop (peas; *Pisum sativum*), assessing the environmental/human risks.

Results revealed the occurrence of both classes of pollutants in the collected sewage sludges. The predominant SMs were galaxolide (HHCB) and tonalide (AHTN), while for VMSs all cyclic congeners were present at relevant concentrations, mostly D4 and D5, followed by D6. The levels found (up to 65 mg/kg dw) are sufficient to cause risks to the soils, considering sewage sludge application rates above 0.5 kg dw/m^2/year. The study of the plant-soil system after application of sludge as fertilizer was carried out in a greenhouse. SMs were uptaken by plant roots up to 350 ng/g dw, but did not translocate to upper sections of the plant, while VMSs were detected in roots (up to 100 ng/g dw) and in other parts of the plants, including peas. The levels detected in peas were not enough to cause risks to humans due to ingestion, but potential risks were found in soils.

Acknowledgements

This work was financially supported by: i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE – funded by national funds through the FCT/MCTES (PIDDAC); ii) Project PTDC/ASP-PLA/29425/2017 – POCI-01-0145-FEDER-029425, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; iii) National funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus – Individual Call – CEECIND/00676/2017 (Vera Homem); iv) Nuno Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus – Institutional Call – CEECINST/00049/2018; v) Filipe Rocha thanks FCT for the PhD Research Scholarship (Ref. 2020.09041.BD).

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Introduction of Innovative Green Material Chemistry Demonstrations in Early Education: Case Study Bosnia and Herzegovina

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Figure 1 Secondary school students from Bosnia and Herzegovina performing the swelling study on domestic bentonite.

Expanding the variety of skills young pupils obtain in the late primary education and during the secondary education is in the focus of different EU programmes. By this, digital skills, communication, understanding of the environmental problematics or team work and team approach in problem solving are the most emphasized. At the same time, European countries are experiencing a decline in number of students choosing engineering and natural sciences for their professional pathway. It is not therefore surprising that a number of large-scale projects promoting exactly these professions are being funded [1].

Present study is showing how motivating these programmes can be even in EU accession countries, as shown through the case study in Bosnia and Herzegovina. In particular, the "RM@Schools" programme is being introduced in this country for only 2 years effectively and have shown that indeed such programmes can increase the young pupils' interest for the subjects such as geology, material sciences, green chemistry and mostly material chemistry in general. These innovative approaches are presenting the young population suitable "toolkits", hands-on experiments using real raw materials (ores or secondary raw materials, raw or recycled natural or synthetic polymers etc). The assessments are showing that interest of the children for science and engineering is increasing after attending, while the programmes are strengthening also the younger and new teachers' generation by providing them with tools for demonstrations of the attention-catching experiments on raw materials.

Present study has found that there is a need for constant renovation of textbooks in chemistry in Bosnia and Herzegovina to keep the pace with intensive investments and development of the raw material industrial sector in recent years. In particular, "toolkits" are currently being developed by the alumosilicates (Figure 1) which exist there in dozen millions of tons deposits. All of these potentials can be used to enrich the quality of science education and increase pupils understanding of green chemistry principles in materials processing [2,3]. Importance of such approach is even higher when taking into account that the EU accession countries need to strengthen their human potential in coming years, who will be development holders. Their understanding of green principles in mining and material processing will be crucial for sustainable development with respecting the environmental principles.

Acknowledgements

Authors thank the EIT RawMaterials Association for the "RM@Schools 4.0" project support (project agreement 20096).

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Study of the Impacts of Large Wildfires on PM_{10} and Human Mortality in Portugal

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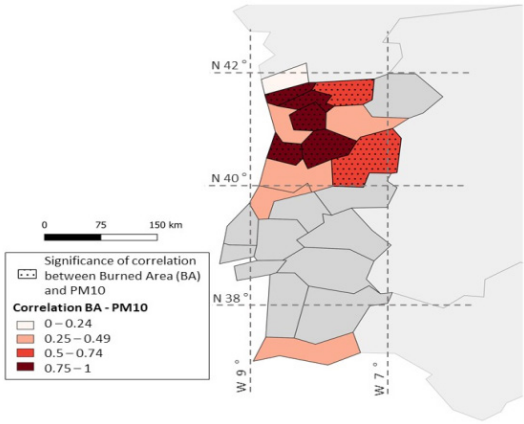

Uncontrolled wildfires are a major environmental problem that the current society must face. According to the European Forest Fire Information System (EFFIS), between 2000 and 2013 wildfires burned up to 740,000 ha of land annually in the south of Europe, Portugal being the country with the highest percentage of burned area per square kilometre [1]. One of the problems is the toxicity of the pollutants emitted from biomass burning on human health, being responsible for increases on cardiovascular and respiratory morbidity and mortality [2].

This study aims to describe the pattern of wildfires occurring during the fire season (June–July–August–September) from 2001 to 2016, considering those with a burned area above 1000 ha (referred to as "large fires"). During the studied period, almost 1 million ha of forest were burned in mainland Portugal from June to September alone. Although large fires only represent less than 1 % of the number of total fires, in terms of burned area their contribution is of 46 % (53 % from June to September).

Burned area and PM10 concentrations were correlated for each NUTS III region, with pollutant data obtained from the Portuguese Environment Agency (APA) air quality network. Also, associations between PM10 and all-cause (excluding injuries, poisoning and external causes) and cause-specific mortality (circulatory and respiratory) were studied for the affected populations using Poisson regression models, with mortality data obtained from Statistics Portugal.

A significant positive correlation between the studied variables were found in some cases. The north, centre and inland of Portugal are the most affected areas. This means that large fires have an impact on the health of the population due to Particulate Matter. The high temperatures and long episodes of drought expected in the future will increase the probabilities of extreme events and therefore the occurrence of wildfires.

Acknowledgements

This work was financially supported by the European Regional Development Fund–Fondo Europeo de Desarrollo Regional (ERDF-FEDER), Spanish Ministry of Economy and Competitiveness/Agencia Estatal de Investigación (grant no. CGL2017-87921-R (ACEX project)) and Project UIDB/00511/2020 of LEPABE (Portuguese national funds through FCT/MCTES PIDDAC). S. Augusto was supported by the Portuguese Foundation for Science and Technology (grant no. SFRH/BPD/109382/2015). N. Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call - [CEECINST/00049/2018].

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Emission and Dispersion of Organic Pollutants by the 2021 Extreme Flood in Germany

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In summer 2021 the western part of Germany faced an extreme flood event that affected in particular meso scale river systems in North Rhine/Westfalia and Rhineland /Palatinate. Within a few hours small rivers normally exhibiting low water flow changed to high water flow streams. Noteworthy, flooding occurred dominantly in river sections characterised by narrow valleys.

During the flood event many facilities with different amounts and quality of pollutants have been destroyed such as oil tanks, pesticide storages, sewage systems and resulting in a huge emission of a heterogeneous pollution in particular with organic compounds. These pollutants contaminated not only human settlements but have been dispersed along the river course. Major part of the pollution was associated not with the river water body but with the corresponding particulate matter, the suspended particulate matter and sediments.

Here, two major questions raised. Firstly, the risk potential of the sediments transported and deposited in the urban area, in houses and streets needed to be estimated. Secondly, the dispersion of the particle associated pollution needed to be characterized to identify potential long-term hot spots of accumulation.

In this study, sediment samples from urban areas as well as from wetlands have been sampled directly after the flood event. Four river systems (Erft, Ahr, Wurm and Inde rivers) have been considered.

The samples have been analysed by established methods for extraction and fractionation [1]. A GC/MS based non-target screening approach has been applied to identify environmentally relevant contaminants. This method is restricted to low to medium volatile, lipophilic substances.

The screening revealed a wider spectrum of contaminants covering petrogenic pollutants (e.g., PAHs, hopanes), technical agents such as rubber additives, detergents (e.g., LABs), sewage constituents like fragrances and UV absorber, as well as typical industrial substances (triphenylphosphine oxide). Most of the contaminants are well known anthropogenic river sediment constituents with long-term preservation [2,3].

As a first step, these compounds are classified according to their harmful effects as well as their potential to human uptake. Additionally, source specific compounds are quantified and discussed in terms of dispersion processes and long-term transport towards the most important sedimentation areas.

Results from this extreme flood event provides knowledge applicable also for future flood events expected in higher frequency and amplitude due to climate change.

Acknowledgements

This study has been financially supported by the German Research Foundation DFG.

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Do Freezing and Heating Cycles Influence Differently on Soil Elements Leaching?

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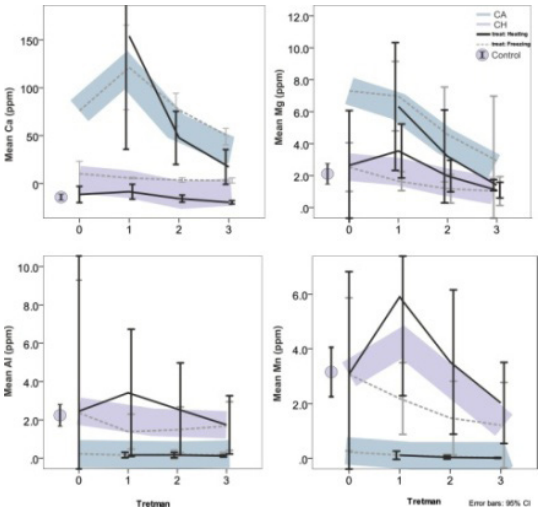

Research in forest ecosystems is focused on recent and past extreme events caused by drought, heat, storms and frost [1,2]. This research aims at exploring soil-specific processes of element leaching in relation to the impact of soil wetting cycles after freezing and heating. Loosely bound nutrients (ions/elements) react differently to thermodynamic conditions, which are interesting to analyze associated with climate change and soil water depletion. Soil drying is related to the increase in air temperature. Repeated drying and wetting increases mineralization of the organic matter, and thus increases the availability and losses of nutrients. The effect of freezing-wetting alters solution fluxes. Both processes are far from being predictable, and there is a lack of knowledge on this subject. The objective of this experiment was to investigate the effects of soil freezing-wetting and heating-wetting cycles on soil leaching processes. Our hypothesis is that freezing and heating of the soil, change the quality of the soil solute, i.e. mineral ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, $Mn^{2+,}$ NO_2^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) concentrations in leachate.

Two forest soil profiles, in European beech dominated stand on Mt Bjelašnica in Bosnia and Herzegovina (18˘15'44"E, 43˘42'25"N) were sampled. Soil type corresponded to Calcaric Cambisol (CA) and Chromic Cambisol (CH) according to IUSS Working Group WRB (2015). Soil was sampled by horizons (O, Ah, A/Brz, Brz1, Brz2). Porous plastic glasses were filled with 120g of air-dried soil, two representing different treatments (rewetting-freezing vs. rewetting-heating) and one representing the control. Treatments involved: a) four cycles of wetting the soil (2% intensity, 30', 120cm^3) and freezing (-10˘C) vs b) four cycles of wetting the soil (2% intensity, 30', 120cm^3) and heating for 3 hours at 40˘C. Control state involved wetting and drying at room temperature. After each wetting cycle, leachate was captured and left in freezer until determining concentrations of cations using Inductively coupled plasma optical emission spectrometer (Thermo scientific iCAP 6000 series) and anions using Dionex ICS 3000. We analyzed 16 samples per profile and per treatment, and 14 control samples, in total 78 samples.

The results obtained through this study point that different thermodynamic conditions influence different leaching intensity of soil ions. On the one hand, higher intensity of leaching of Al, Fe and Mn in CH soil was linked with heating-wetting treatments. On the other hand, more intense leaching of Ca, Mg and Na in CC soil was observed after freezing-wetting treatment. The experiment also showed lower leaching intensity of anions after heating-rewetting compare to freezing-wetting. Freezing-wetting cycles, like in our experiment, seems to have higher effect on the ion losses from temperate forest soils.

Acknowledgements

We acknowledge CLIMO COST Action CA15226 STSM support for project: Evaluation of the criteria of climate-smart forestry based on soil chemical properties in Bosnian beech forest sites.

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The Response of Badland Materials from Spain with Different Mineralogical Content on Seasonal Changes

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Fig.1.*Samples after finished experiments.*

Badlands are areas with limited vegetation, reduced or no human activity, and a great variety of geomorphic processes [1]. Badland materials have a different responsetothe same environmental conditions, because of differences in their mineralogical and physico-chemical characteristics. Many studies show that smectite-poorsediments are more resistant to different weathering treatments of freezing, thawing, wetting, and drying,than smectite-rich materials [2,3].In this paper, three unweathered samples of badlands from Spain were analyzed with the aim of monitoring, but also comparing physico-chemical changes caused by simulations of changes in climatic conditions. Selectedsediment samples havedifferent compositions. Besides quartz and calcite, the first sampleis composed of smectite and gypsum (3 UW), the second of smectite (4 UW), while the third sample is composed of neither smectite nor gypsum (5 UW). The experiment setup was designed in the way that each sample had three sub-samples, a sample for simulation of rain, snow, and a control sample (Figure 1). Sample_rain was treated with a rain intensity of ~850 ml/h for 10 minutes (~140 ml), while sample_snow was treated with crushed ice (~150 g). After precipitation simulations snow were put samples were placed in a climate chamber at - 3 °C together with a control sample. This was repeated for 15 cycles. Every cycle was documented with photographs. The leached solution was collected and its volume, pH, electrical conductivity (EC), and ion concentrations were measured. The second part of the experiment was based on exposing the samples after wetting to higher temperatures, 50 ° C. It was done in 8 cycles. FESEM and BET analyzes were performed for each sample before and after the experiments.The 3 UW samples had significantly different leachate pH and EC, while the leachate volume was similar for all samples during the experiment. Sulphate ions were leached in the highest concentrations during the whole experiment from the sample with both smectite and gypsum present. The sample with smectite has shown the highest disintegration of the structure, especially after the simulation of snow. The sample with smectite and gypsum has shown a lower degree of degradation than sample 3 UW due to the content of gypsum which increases the weathering resistance of the material. Sample 5 UW has shown the lowest degradation of the structure along with the weathering cycles. This study has proven that both mineralogical and physico-chemical properties of sediments are important for predicting their response to variable climate factors.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-9/2021-14/200287).

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Chemostratigraphic Distribution of Harmful Organic Contaminants in Flood Affected (Sub-)tropical Urban River Sediments (Chennai, India)

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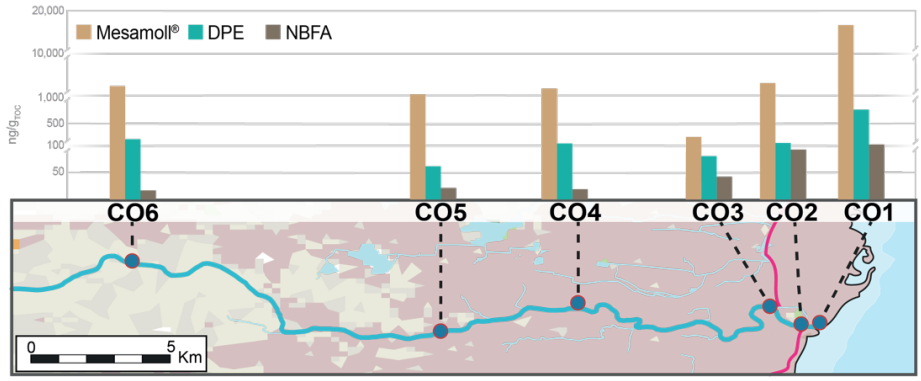

Contemporary surface pollution by Mesamoll®, 1,2-diphenoxyethane (DPE), N-benzylformamide (NBFA) (in ng/g$_{TOC}$) for the Coumriver in Chennai, India.

Extreme weather events, such as heavy rainfalls or floods, are projected to increase in frequency in the foreseen future, posing severe harm to fast growing coastal population centers[1]. A prominent example facing an increasing vulnerability to monsoon-induced floods are urban rivers in megacities, such as Chennai (India)[2]. Meandering through densely populated and urbanized areas, the rivers are permanently exposed to unknown environmental risks and anthropogenic alterations.The rapid growing population and industrialization in combination with these extreme floodscausethe release and distribution of xenobiotic compounds and other pollutants, harming local communities and the environment along a river's pathway[3],[4]. To determinethe unknown risks posed by these toxic river floods the preserved pollution signature from sedimentary records is studied.

This investigation evaluates the inorganic and organic pollutant assemblage along the Adyar and Cooum rivers (Chennai, India). Thereby heavy metals (Cr, Ni, Cu, Zn, Pb) show a continuous concentration decrease downstream towards the coast. Based on GC-MS analysis, four main groups of organic pollutants have been detected: (I) petrogenic compounds (hopanes, PAHs), (II) urban wastewater compounds (LABs, DEHA, methyl-triclosan, octocrylene), (III) technical compounds (Mesamoll®, DPE, NBFA), and (IV) pesticides (DDX). While most organic compound groups (II, III, IV) show source specific properties, the definite sources for other compounds(group I and heavy metals) remain vague based on amultitude of potential sources anddiffusiveness of anthropogenic emissions. The chosen approaches have shown that urban wastewater pollutants and technical organic compounds are suitable to assess the anthropogenic induced pollution and to reconstruct the flood history also in urban sedimentary floodplain archives. However, sedimentary archives in fast-growing, urbanized environments do not always allow a full environmental reconstruction, as anthropogenic alterations effect the archive's preservation potential.

Acknowledgements

This study was granted by a scholarship grant by the Indo-German Centre for Sustainability (IGCS).

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Studying the Behaviour and Fate of Volatile Methylsiloxanes and Synthetic Musk Compounds in Soil

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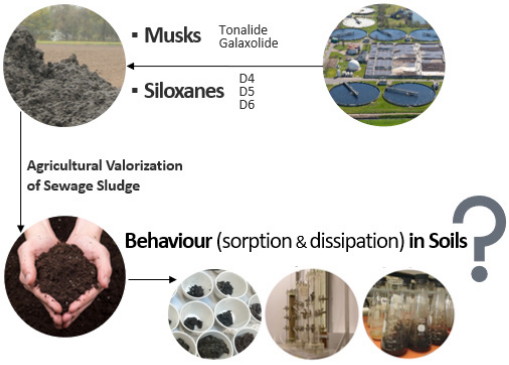

Volatile methylsiloxanes (VMSs) and synthetic musk compounds (SMCs) are two groups of emergent organic contaminants whose occurrence in municipal sewage sludge has been previously documented at significant levels [1,2]. Their widespread use in personal care products is appointed as its main route to wastewater treatment plants, where total degradation does not occur and, due to their hydrophobicity and tendency to bind to organic matter, these compounds end up accumulating in sewage sludge [3].

Valorisation of municipal sewage sludge has been promoted during the past years, contributing for a circular economy model, and avoiding its landfill deposition or expensive incineration. Due to sewage sludge high organic matter content and presence of nutrients prone to enhance soil agronomic properties, its recycling by composting for organic waste-based fertilizer production or reuse by direct application in agricultural soils are the preferable ways to use this waste. However, this practice also creates a possible contamination route to the soil compartment for micropollutants, such as siloxanes and synthetic musks [4]. As possible hazards and risks concerning these substances are not completely well-known, either for the environment, or for the safety of crops grown in sewage sludge-amended soil, it is important to study the behaviour and fate of these compounds in the soil compartment, a topic scarcely studied, especially for the VMSs congeners.

In this work, a preliminary study on the behaviour and fate of 3 cyclic VMSs (D4, D5 and D6) and 2 SMCs (tonalide and galaxolide) in soils is presented. A different set of sorption tests were performed using a batch equilibrium model (worst case-scenario) under the effect of different parameters (such as targets initial concentration, temperature, and soil organic matter content). Results revealed capacity of soils to adsorb the target compounds up to levels similar to those found in sewage sludges. Moreover, dissipation studies under temperature-controlled and aerobic/anaerobic conditions were also carried out in both spiked soils and mixtures of soil and stabilized sewage sludge. An experiment testing the effect of plant growth in spiked and non-spiked (amended) soil was also performed, showing lower amounts of all targets in pots with plant development.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); (ii) Project PTDC/ASP-PLA/29425/2017 - POCI-01-0145-FEDER-029425, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) National funds through FCT - Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus - Individual Call - CEECIND/00676/2017 (Vera Homem); (iv) Filipe Rocha thanks FCT for the PhD Research Scholarship (Ref. 2020.09041.BD).

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Inadequate Municipal Solid Waste Management and Soil Pollution in Serbia

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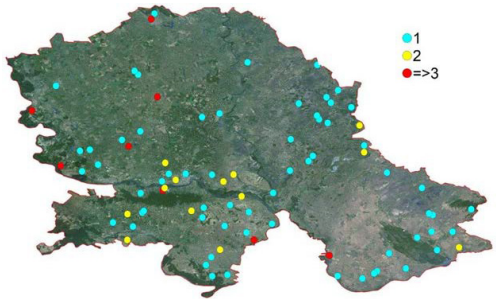

Localities where remediation values were exceeded for individual elements

An increase in urban population and the rising demand for food and other essentials, perpetuate a rise in the amount of waste being generated daily by each household. In Serbia, this waste is eventually thrown into open dump sites. It can cause severe impact on soil quality. Therefore, this study was aimed at assessing the effect of a solid waste disposal sites on surrounding soil in Serbia.

Based on the data from the Cadastre of Contaminated Sites maintained by the Environmental Protection Agency, in 2020, 213 potentially contaminated and contaminated sites have been identified and recorded on the territory of the Republic of Serbia. The main purpose of the Cadastre is to provide systematic data on sources of pollution such as the type, quantities, methods, and location of discharges of pollutants into the soil, in order to implement preventive or remediation measures. The largest share in the identified sites belongs to waste disposal sites - 71.83%, within which there are also unsanitary landfills, which are managed by local self-governments.

In the area of AP Vojvodina, the Provincial Secretariat for Urban Planning and Environmental Protection in 2020 investigated the soil quality of non-agricultural land in the area of 30 municipalities and cities, at 113 illegal landfills. A total of 1,130 soil samples were analyzed. Analysis of the content of heavy metals in soil samples shows that the remediation values were exceeded for cadmium, zinc, copper, nickel, mercury and arsenic, while the contents of lead, chromium and cobalt above the prescribed limit values were not identified in the soil samples. Analysis of the pesticide content and their metabolites in soil samples shows that the remediation values were exceeded for DDE / DDD / DDT and atrazine. Concentrations of total PCBs, PAHs and mineral oils exceeded the limit values, but did not exceed the remediation values. The analysis of the content of phthalate esters shows that in 319 out of a total of 1,130 samples the content of phthalate esters is higher than the remediation value. The finding suggested that waste disposal sites adversely affects soil in the study area.

Acknowledgements

The authors gratefully acknowledge the support from the Project of Matica srpska "Environmental issues, bioeconomy and analysis of possibilities for production of health and safety food in AP Vojvodina".

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Occurrence and Fate of Organophosphate Esters in a Municipal Wastewater Treatment Plant

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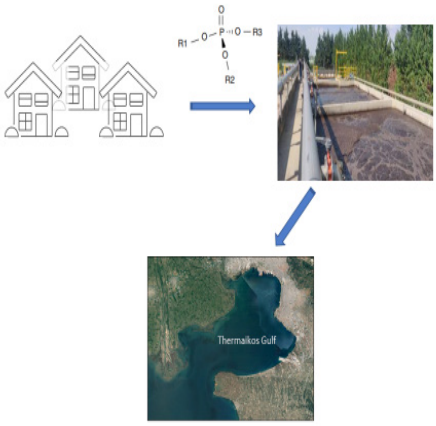

Organophosphate esters (OPEs) are organic esters of phosphoric acid containing either alkyl-chains or aryl groups and they may be halogenated or non-halogenated [1]. OPEs are used as additives in flammable materials(electrical, electronic devices, vehicles, polyurethane foam, fabrics) to prevent fire or delay its initiation. They are also used as plasticizers to protect or enhance the properties of plastics, fabrics and furniture [2]. Despite their benefits, there is a concern about OPEs, because many of them could persist in the environment and be hazardous to people and animals. People are exposed to OPEs in their everyday life through skin contact, ingestion of dust, inhalation, and dietary intake [1,3]. Several studies have reported the occurrence of OPEs in indoor air, house dust and surface water. However, less is known about the occurrence and fate of these chemicals in wastewater treatment plants (WWTPs) [4].

The aim of this study was to investigate the occurrence and fate of eleven OPEs (alkyl-, aryl- and chlorinated-OPEs) in a municipal wastewater treatment plant. For this purpose, wastewater and sludge samples were collected during the period 2020-2021.Analytical methods employing solid phase extraction or ultrasonic-assisted extraction followed by gas chromatography–mass spectrometry were developed and validated for determination of OPEs in dissolved fraction, total suspended solids and sludge.

The occurrence of OPEs, their removal efficiency in WWTP, partition between soluble and particulate fractions and finally possible environmental risk are discussed. Almost all target compounds were determined in influents and effluents of WWTP, with a detection frequency above 80%. TBOEP, TCPP and TPPO were the dominant compounds. Adequate removal rates were observed throughout the whole treatment process.

Acknowledgements

"This research is co-financed by Greece and the European Union(European Social Fund- ESF) through the Operational Programme "Human Resources Development, Education and Lifelong Learning" in thecontext of the project "Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5000432), implemented by theState Scholarships Foundation (IKY)".

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Comparative Profiling of Microplastics in Differently sized Manila Clams from South Korea by Nile Red Staining and µFTIR

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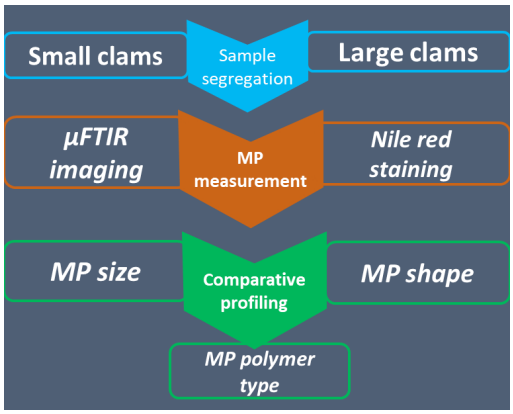

The high bioavailability of microplastics (MP) to marine biota has led to the contamination of seafood products. The safety of shellfish as food has become questionable due to the potential health risks associated with MP. As such, microplastics ingestion by commonly consumed shellfish is being investigated. In this study, market samples of clams (*Ruditapes philippinarum,* n=101) from South Korea were segregated into two different sizes (small and large) and analysed for microplastics contamination. Using alkaline digestion, MP were extracted and subsequently quantified using two of the most commonly used techniques in the field- Nile red staining (NRS) and µFTIR imaging [1], [2]. With NRS, the small (n= 51) and large (n= 50) clams were analysed individually. On the other hand, 8 composite subsamples (30 small and 31 large clams) were subjected to µFTIR imaging.

The average MP concentration based on NRS was 4.3 ± 5.2 MP/ g ww (wet weight of soft tissue) considering both small and large clams. In the subsamples, 3.2 ± 1.6 MP/ g ww and 3.8 ± 1.7 MP/g ww were detected based on µFTIR and NRS, respectively. NRS showed 18-75% higher MP quantity compared to µFTIR. This was considered to be a consequence of the co-staining of remnants of undigested biological which was confirmed by additional staining using DAPI. Due to this overestimation, only µFTIR data was utilized for the comparative analysis of the differently sized clams.

The MP abundance in both groups was comparable, with the small and large clams having 2.7 ± 1.7 MP/g ww and 3.6 ± 1.6 MP/g ww, respectively. Similarly, there was no significant difference observed in the concentration of MP fibers and MP non-fibers. In the small clams, only PS (polystyrene) and PET (polyethylene terephthalate) were identified from the fibers. In contrast, PP (polypropylene), PS (polystyrene), PE, and PET were found from the fibers that came from the large clams. The same 4 synthetic polymers were detected from the non-fibers obtained from both groups. Overall, PS was the most prominent type, accounting for 35-49% of total detected MP. In terms of MP size, 20-50µm was the most abundant followed by 50-100µm. Relative to the weight of the samples, the quantity of MP, classified according to size and polymer type, was similar in both groups.

In summary, the size of the clams had no effect on the MP content as suggested by the analogous concentrations of MP with respect to shape, size, and polymer identity. In addition, despite the simplicity, low-cost, and growing popularity of NRS, this method should be used with caution due to its propensity to overestimate MP quantity.

Acknowledgements

This study was supported by Ghent University Global Campus, Special Research Fund (BOF) of Ghent University (no. 01N01718), and Horizon2020 Food-EnTwin (no. 810752).

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Wastewater Analysis Assessment: Prevalence of Drugs of Abuse in Educational Institutions

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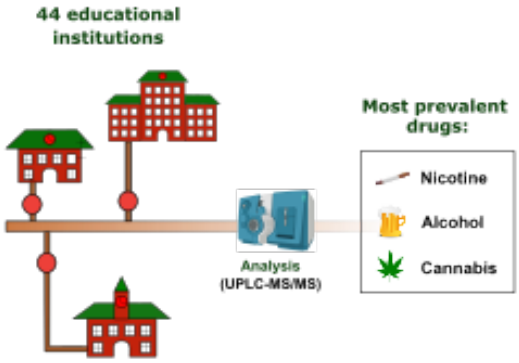

Licit and illicit drug use negatively impacts a young person's health, future socio-economical position and success [1]. For proper implementation of prevention programs targeting young people, accurate and timely information about the extent of substance use is required [2]. In this study, wastewater analysis was used to explore the prevalence of drugs in Slovenian educational institutions. Results were compared based on the level of educational institution, their geographic location and urbanization. Also, a comparison with available epidemiological data was made.

Seven-hour composite raw wastewater samples were collected at the end of the 2018/2019 academic year from 19 primary schools (6–15y), ten secondary schools (15–19y), nine higher educational institutions (19+y) and six mixed secondary and higher educational institutions (15+y). Participating institutions were located in urban (n=37) and non-urban (n=7) areas of 7 Slovenian municipalities.

Wastewater samples were analyzed for in total 16 drug residues of licit drugs (nicotine and alcohol), medications of abuse (morphine, codeine and methadone) and illicit drugs (cannabis, cocaine, amphetamine, methamphetamine, ecstasy and heroin) using reverse-phase liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). To determine residues of medications of abuse and illicit drugs, prior analysis wastewater samples were filtered and extracted using solid-phase extraction. For the determination of licit drug residues, samples were directly injected.

In general, nicotine, alcohol and cannabis residues were most frequently detected. Among medications of abuse, morphine and codeine were detected, while among stimulants, cocaine prevailed. There were differences in drug prevalence regarding the level of educational institutions, their geographic location and urbanization. However, level of education is the main factor in observed differences in drug prevalence. Good agreement with studies implementing wastewater analysis was observed, while there was a small agreement with survey data.

Acknowledgements

Financial support: Slovene Research Agency (ARRS Program group P1-0143 and Projects L1-9191, N1-0047 and N1-0143). Supporting data: National Institute of Public Health. Enabling wastewater sampling at the educational institutions and providing additional information: Headmasters of educational institutions. Sampling support: JP VODOVOD KANALIZACIJA SNAGA, d.o.o.; JP Central Wastewater Treatment Plant Domžale-Kamnik, d.o.o.; Komunala Novo mesto, d.o.o.; Komunalno podjetje Velenje, d.o.o.. Data processing support: Tome Eftimov, JSI.

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Structural Diversity of Organic Contaminants in a Meso-Scaled River System

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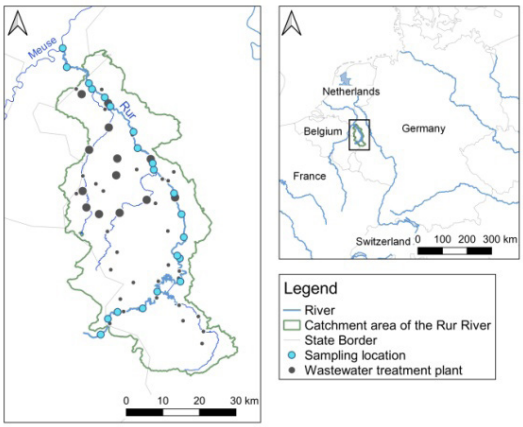

Particularly in the 20th century, anthropogenic activities such as changing of watercourses, increasing pollution and thus, rapid degradation impacted the river systems worldwide [e.g. 1-3]. Due to this intensive anthropogenic usage, a complex mixture of inorganic and organic contaminants entered and still enters freshwater systems, released by various emission sources [1,2]. However, because of the high dynamic nature of rivers, the individual occurrence, fate, and behaviour especially of organic contaminants are highly complex and not fully understood.

Here, a GC/MS non-target screening was applied to identify and determine the chemical diversity in the aqueous phase of the meso-scaled Rur River and to categorize indicative and relevant contaminants according to their load profiles for a distinct emission characteristic.

Besides very well-known or widely distributed contaminants (e.g. phthalate plasticizers), also so far unknown or only sporadically identified substances have been detected (e.g. AIBN/TMSN, BHT-quinone or methylphenylsulfone). In detail, the non-target screenings revealed the presence of more than 70 lipophilic to semi-polar substances. Many identified substances are of anthropogenic origin and used as e.g. pharmaceuticals, personal care products or in industrial processes. Based on the emission profiles, initial assessments were made about the stability and environmental behaviour of the contaminants.

Additionally, temporal variations in organic contamination were investigated over three sampling campaigns (2004, 2015 and 2020). Within this timespan, the overall composition of the contamination in the Rur has changed slightly, but nevertheless the high chemical diversity and structural variety remained.

Overall, the wastewater treatment plant (WWTP) in Düren (treated annual wastewater volume of 21 million m³ in 2016) shows a high input and influence on the chemical diversity in the river system in all campaigns. The diversity and loads of organic contaminants are clearly higher downstream than in the river upstream. However, this can be attributed to its diverse influents as the WWTP collects both municipal and industrial wastewaters. The paper industry plays a major role here, so that corresponding contaminants as TMDD or diphenoxyethane were also detected, partly with very high loads. Interestingly, the effluents of the even larger WWTP in Aachen (discharging into the Wurm tributary) no longer have a major impact on the contamination of the Rur River in 2020 compared to earlier analyses. This is probably due to an improved removal performance from a new ozonation system.

A detailed consideration such as that undertaken in this study is necessary as the occurrence of substances in a river system depends on many different factors. For a holistic assessment, not only the sampling locations and associated development of emission profiles must be considered, but also temporal variations and mitigation measures. Such a multi-parameter scenario provides an important basis for the mitigation and reduction of organic pollutants in our environment.

Acknowledgements

This study is supported institutionally by the Chair of Physical Geography and Geoecology and the Institute of Hydraulic Engineering and Water Resources Management (RWTH). Special thanks to the RWTH Scholarships for Doctoral Students.

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Monitoring Volatile Methylsiloxanes Levels in Wastewater Collected from a Portuguese Wastewater Treatment Plant

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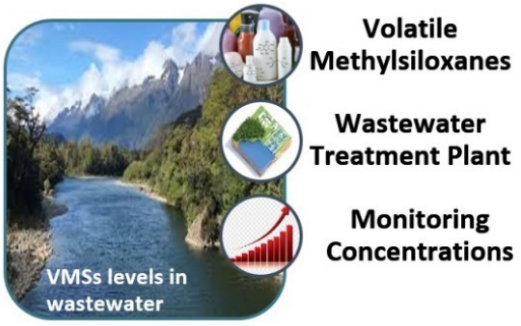

Volatile Methylsiloxanes (VMSs) are a group of compounds characterized by presenting a linear or cyclic Si-O backbone saturated with methyl groups [1]. These compounds are usually applied in cosmetics and personal care products [2]. It is estimated that about 90% of VMSs present in PCPs are volatilized during use, with the remaining 10% being discharged down-the-drain to wastewater treatment plants (WWTPs) [3]. After use, residues of these compounds will arrive to WWTPs, that are not prepared to degrade them. Treated effluents are usually discharged to a surface water body, making them the main exposure pathway to potential risks to ecological receptors [4].

A total of 7 VMSs (D3, D4, D5, D6, L3, L4 and L5) were studied in wastewater samples, collected in 2020 and 2021 from a Portuguese WWTP. The samples were extracted by a small-scale liquid-liquid extraction method followed by gas chromatography-mass spectrometry analysis (LLE-GC-MS). The sampling points included influent, preliminary treatment, primary treatment and secondary treatment (effluent).

It was possible to observe the VMSs concentration profile along the WWTP treatment stages. A decrease in the VMSs concentrations, from the influent to the effluent, was observed, possibly due to volatilization in the aeration tanks and sorption to sewage sludge. In the influent, D5 and D6 were the dominant compounds, with similar concentrations with those found in literature. The highest measured concentrations were around 6 μg L^{-1}. The effluent samples presented VMSs levels up to 0.15 μg L^{-1}. This work highlights the importance of monitoring VMSs concentrations throughout the year and study the effect of climate in the results. These results can help in future assessments of VMSs risk in the environment, since these compounds may cause ecological and toxicological effects.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); (ii) Project PTDC/ASP-PLA/29425/2017 - POCI-01-0145-FEDER-029425, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) Project POCI-01-0145-FEDER-032084 - LANSILOT - LAunching New SILOxane Treatments: assessing effluent, sludge and air quality and improving biogas production in WWTPs, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iv) National funds through FCT - Fundação para a Ciência e a Tecnologia, I.P., under the Scientific Employment Stimulus - Individual Call - CEECIND/00676/2017 (Vera Homem); (iv) PhD Grant PD/BD/137758/2018 – Fábio Bernardo, supported by FCT PhD programme, under the Portugal 2020 Partnership Agreement and ESF; (v) Nuno Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call - CEECINST/00049/2018.

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Presence of Arsenic and Microplastics in the Groundwater in the Vicinity of a Landfill

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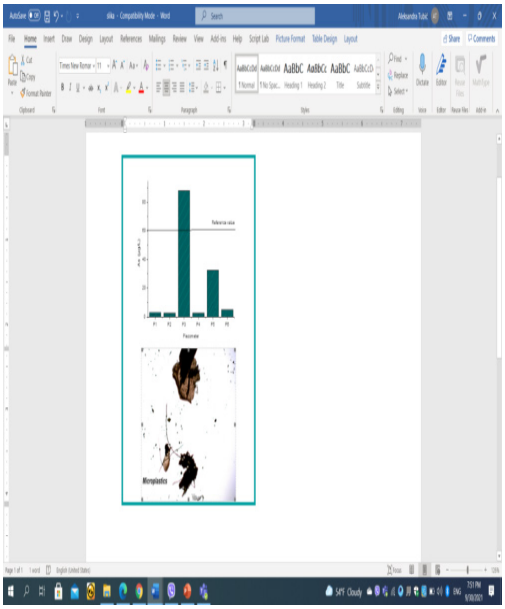

Introduction. When found in landfills, chemicals and other pollutants that make up municipal waste (parts of household appliances, electronic waste, plastic packaging, construction waste, car tires, waste containing asbestos, etc.) can leach into the groundwater. Numerous pollutants thus originate at landfills as the leachates are able to reach surface and groundwaters, posing a great danger to the environment and human health. Increased concentrations of arsenic in groundwater in the vicinity of the landfill may indicate leaching from waste, such as treated materials from wood, construction, industrial waste, etc. Arsenic is one of the parameters regulated and monitored in leachate and groundwater in the vicinity of landfills [1], and the remediation value is set at 60 µg/l. Plastic is one of the largest and most topical environmental issues, due to its diverse polymer structure, widespread use and resistance to degradation processes. Due to these properties and inadequate plastic waste management, there is a real possibility of plastic particles (microplastics) reaching the area surrounding a landfill. From all the above, there is a clear need to monitor pollutants in leachate and groundwater, where in addition to the parameters usually analysed according to the legislation, importance must be given to microplastics, not only because of their physical presence but also because of their ability to adsorb, concentrate and transport various pollutants. The aim of this work is to present monitoring results of arsenic and microplastics in groundwater in the vicinity of typical city landfill in Serbia.

Materials and methods. Monitoring was conducted in 6 piezometers (P1-P6) that serve to monitor groundwater quality at the landfill. Arsenic was measured with atomic absorption spectrophotometer, according to method USEPA 7010 [2]. Microplastics were isolated from the water using 30% hydrogen peroxide and filtration trough a sieve with a pore size of 63.0 µm and characterized by light microscope (Image Analyzing System Motic 2000) and Fourier transform infrared spectrometry (Thermo-Nicolet Nexus 670).

Results and discussion. Obtained results show that arsenic is detected in all the investigated piezometers in concentrations ranging up to 88.1 µg/l. The lowest concentrations were detected in piezometers P2 and P5, while P3 is the most burdened, with a trend of increasing arsenic concentrations, comparing with data obtained earlier on the same location [3]. It can be observed that microplastics are also present in the samples of groundwater from the landfill, in various forms, such as granules, ellipses and threads, with polyethylene, as dominant type of polymer identified.

Conclusion. Based on the obtained results it can be concluded that, arsenic concentrations can be very high in the groundwater around the landfill, which is combined with microplastic pollution, indicating increasing problems with landfill leachate contaminating groundwater in the vicinity of the landfill.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, Program DIASPORA, GRANT No. 6485164, HYDRA.

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Adsorption of Three Pesticides onto Different Polymer Types of Microplastic Particles in Alluvial Soil

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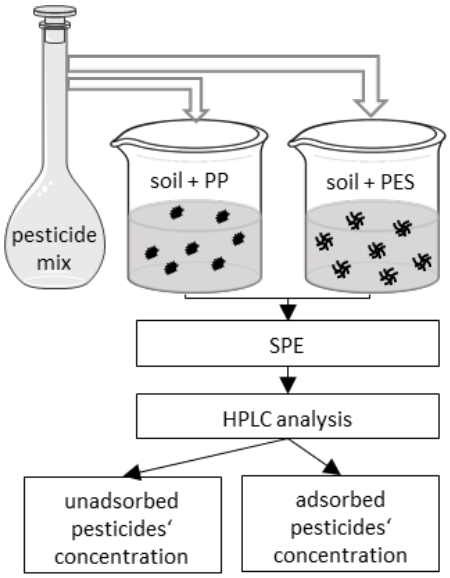

Microplastics (MPs), defined as particles smaller than 1 mm in diameter,are widely researched contaminant in water, soil, and air environments [1,2]. Due to their size, they can affect the growth of crops on agricultural land and life of other organisms, as well as they can act as a vector for organic chemical compounds (i.e. pesticides) [2]. On the agricultural soil, MPs can enter through fragmentation of larger plastics (for example from mulching and plastic debris on the field), irrigation with treated wastewater, and also with application of organic fertilizers, such as bio-waste compost or treated sewage sludge [2,3].

The accumulation of MPs on agricultural land over time may affect the mobility of pesticides in the soil. To address this question, we investigatedadsorption of three model pesticides (acetamiprid (ACE), chlorantraniliprole (CAP) and flubendiamide (FLU), all registered and allowed to be used in EU till 2024) onto MPs of twopolymer types (polypropylene (PP) and polyester (PES)), present in alluvial soil.We studied the adsorption of pesticides at 1 % and 5 % (w/w) of PP and PES content in alluvial soil, as well as with three concentrations of pesticides (1, 5 and 10 mg L^{-1}). The concentration of 1 % (w/w)MPs in soil is high, but already present in the soil [5], whereas 5% of MPs (w/w) in soils was chosen as a worse case scenario.

Pesticides' concentrations were determined in aqueous phase of all tested soil/MP mixtures using solid-phase extraction and HPLC. Adsorption of pesticides onto MPs were confirmed in soil/MPs mixtures at 5 % MPs content only.

Results of our study confirmed previous observations regarding the adsorption of pesticides and their polarity [6], namely that adsorption of ACE, CAP and FLU was dependent on their octanol/water partition coefficient (FLU > CAP > ACE) with the highest adsorption observed in the case of FLU. All tested pesticides were observed to adsorb onto PP and PES MPs, therefore their capability to act as a vector for these pesticides in soil was confirmed. Interesting observation regarding the soil intrinsic capacity to retain ACE, CAP and FLU in soil/MPs mixture in relation to soil only mixtures was made. Acquired data suggest that the presence of MPs in soil decreased the soil's intrinsic capacity to retain ACE, CAP and FLU, therefore indicating a possibility of a greater mobility of tested pesticides through the soil system at the presence of MPs.

Acknowledgements

This work was funded by the Slovenian Research Agency (ARRS), the research core funding No. P3-0388, project J2-8162, and the postgraduate research funding programme – Young researchers' programme (ARRS-SP-0510/21).

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Determination of Microplastics in Environmental Samples by Simply Applicable Method

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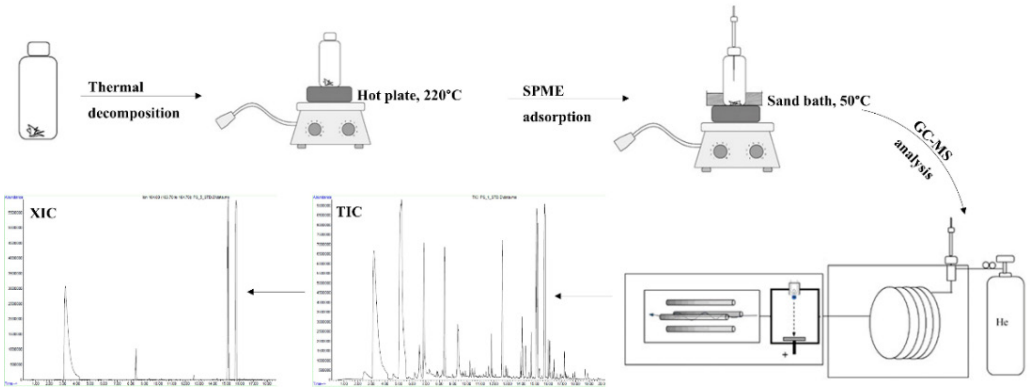

Microplastics (MPs) have gained significant attention in the last two decades and have beenwidely researched in the marine environment. There are, however, less studies on their presence,routes of entry, and impacts on the biota in the soil environment. One of the main issues in the studyof MPs is a lack of standardized methods for their identification in environmental samples. Currentlythe most commonly used techniques are thermal desorption gas chromatography–mass spectrometry (GC–MS) methods and pyrolysis followed by GC–MS.

In this study, headspace-solid phasemicroextraction followed by GC–MS analysis was developed for identification of MPs (polyethylene terephthalate, polystyrene, polyvinylchloride, polyethylene, and polypropylene) in analytical laboratorieswith basic equipment worldwide(SPME fiber, two hotplates, and a sand bath). The proposed method is based on the identification of compounds,which are formed during the well-controlled melting process of specific coarse (1–5) mm) and finefraction (1 mm–100 μm) MPs.

The method was successfully tested with referencecompounds and reference polymers. However, still some uncertainties in the identification of PEMPs in environmental samples with high load of hydrocarbons can occur due to PE'schemical structure and thermal degradation products. Robustness of the method andused equipment enable broader use, however it is subjected to manual procedure andMPs quantification depends on the skills of personnel.

Besides, some polymers(PS, PET, and PVC) have very high melting temperatures (>180 ◦C) or are of differentshapes, thicknesses, and sizes. These facts could potentially influence the polymers with lowermelting temperatures and can cause their incineration and dehydration.If this is the case, amultistep melting procedure with several melting events should be developed

Finally, the method was upgraded for the identification of individual polymerand polymers in mixtures and in different matrices (soil, algae biomass, fishes). The applicability of HS-SPME-GC–MS method showed promising results, it could be thus, proposed as a simple and widely applicable method for the determination of commonly present polymer MPs in environmental samples.

Acknowledgements

This work was funded by the Slovenian Research Agency (ARRS), the research core funding No. P3-0388, project J2-8162, and the postgraduate research funding programme – Young researchers' programme (ARRS-SP-0510/21).

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Method for Extraction, Quantification, and Identification of Microplastics from Soil and Compost

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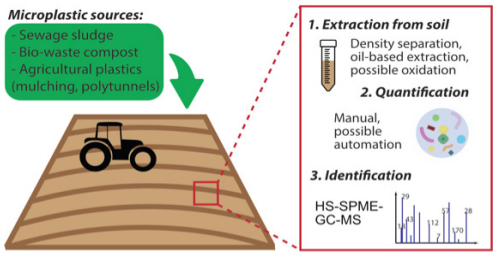

Plastics as a ubiquitous material are exposed to weathering in the environment, where they break down into smaller particles (<5 mm) called microplastics. The use of agricultural plastics(foils, mulching, polytunnels) and organic fertilisers (bio-waste compost and waste activated sludge) are the main source of microplastics in agricultural soil. Other sources include mismanaged waste, accidental or intentional littering, and car tire wear [1,2]. Well-developed methods for extraction, quantification, and identification are crucial for assessment of the microplastic contamination in the terrestrial environment and their routes of entry.

The aim of this study was to develop, optimise, and select the best methods for extraction, quantification, and identification of different microplastic polymers from soil and matrices of varying content of organic matter. We focused on the five most common plastic polymers that occur in the environment, polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET).

Two microplastic extraction methods were adapted from the literature, tested, and optimised in soil and compost, namelyoil-basedextraction with olive oil, and density separation with saturated $ZnCl_2$ solution [3,4]. Oil-based extraction was tested in three different vessels, PTFE tubes, glass tubes, and adapted plastic syringes. The methods were compared in terms of recoveries, ease of handling, and time consumption. Quantification was done by hand, however, a method for automatic quantification is under development. Identification was done by recently developed headspace-solid phase micro-extraction GC-MS (HS-SPME-GC-MS) [5].

The average recoveries of the two extraction methods were comparable. In alluvial soil, oil-based extraction yielded97 ± 2 %, while density separation 98 ± 3 %.In compost, oil-based extraction yielded 80 ± 11 %, while density separation yielded 98 ± 4 %. To extract microplastics from the compost samples, an oxidation step before and after extraction was added. Density separationwas proven to be more reliable for organic-rich matrices, easier to handle, and more time efficient.

In the identification process with HS-SPME-GC-MS, all five spiked polymers were confirmed. PET, however, had to be separated from the other polymers during the melting processin order toenhance the signal of identification compound.A new characteristic compound for the identification of PET has been identified amongst the degradation products.

Further optimisation of quantification and identification is needed in terms of time efficiency and ease of handling to make these methods widely applicable to regular agricultural soil monitoring.

Acknowledgements

The authors acknowledge the project (Agri-iMPact: Microplastic prevalence and impact in agricultural fields, Z2-2643) and the research core funding No. P3-0388 were financially supported by the Slovenian Research Agency.

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Exposure to Polybrominated Diphenyl Ethers Associated with Car Dust

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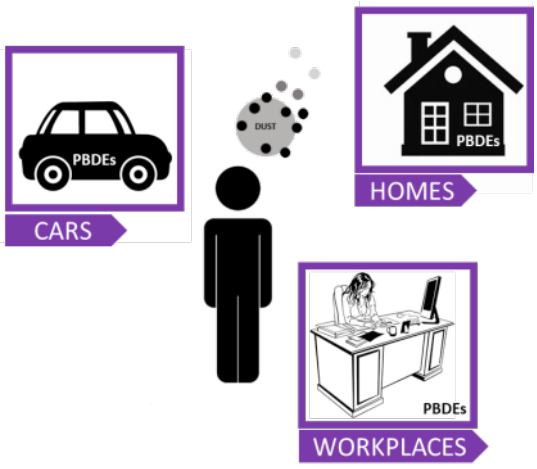

Polybrominated diphenyl ethers (PBDEs) are a class of commonly used brominated flame retardants added to polymers used in building material, household products, and vehicle interiors (seats, plastic parts and electronic). Alongside one's diet, ingestion of dust has been recognized as one of the main exposure pathways for humans, especially nowadays when people spend most of their time in different indoor microenvironments (homes, schools, workplaces, cars). Because of PBDEs' resistance to degradation and increasing evidence of their toxic potential, concerns have been raised about their adverse effects on human health.

The levels of 7 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, and -183) were measured in dust collected from 25 passenger cars aged between few months and 31 years using microwave-assisted extraction and GC-μECD for sample analysis [1]. The measured concentrations were used to estimate the exposure of adults via car dust ingestion calculating the estimated daily intake (EDI) for the worst case scenario, which takes into account maximum mass fractions of all of the detected congeners (∑PBDEs) and a high dust intake rate. A time-weighed model was used according to which people spend around 64 %, 22 %, and 4 % of their time in homes, workplaces, and cars, respectively [2]. In the case of occupational exposure (OE), for adults who spend more time in cars due to their occupation (e.g. taxi drivers), 26 % of time was presumed to be spent in cars. ∑PBDEs ranged between 0.60 and 5666.98 ng g^{-1} dust with a median value of 8.26 ng g^{-1} dust. Congener BDE-99 was detected in all of the samples, followed by BDE-183 and BDE-47 with a detection frequency of 96 % and 92 %, respectively. The mass fraction of these three congeners together contributed from 64 % to 100 % (median 79 %) to the sum of the mass fractions of all detected congeners in individual samples.

When the car dust samples were divided into three groups according to the year of manufacture of the car, the median of the detected ∑PBDEs was 316.53, 10.16, and 6.73 ng g^{-1} for cars manufactured between 1989-2000, 2000-2010, and 2010-2020, respectively. This is in agreement with the ban of penta and octa commercial PBDE mixtures use by the European Union in 2004.

The obtained EDI values originating from car dust (0.170 ng g^{-1} bw day^{-1}) exceeded those from homes (0.096 ng g^{-1} bw day^{-1}) [3] and workplaces (0.052 ng g^{-1} bw day^{-1}), with a contribution to the total EDI of 53 %. Consequently, the more time spent in a car, the higher the intake of contaminants, so the EDI in the case of OE adults was calculated to be 1.105 ng g^{-1} bw day^{-1} and its contribution to total EDI 92 %. Nevertheless, all of the calculated EDI values when compared to the corresponding threshold reference value suggested by the USEPA were orders of magnitude lower indicating no health risk from exposure to PBDEs contained in car dust.

What should be considered, though, is the fact that the EDI calculated for OE people driving cars manufactured after 2010 was 0.003 ng g^{-1} bw day^{-1}, which is considerably lower than those calculated for drivers exposed to dust in older vehicles (0.338 ng g^{-1} bw day^{-1} and 1.105 ng g^{-1} bw day^{-1} for cars manufactured between 2000-2010, and 1989-2000, respectively). These data confirm that the ban of the use of PBDEs has indeed led to a reduction in their concentrations in car dust.

Acknowledgements

This work has been supported in part by the Croatian Science Foundation under (project HrZZ-UIP-2017-05-6713).

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3-Hydroxy-4-Pyridinone as Potential Chelating Agent for the Remediation of Ecotoxic Metals from Environmental Matrices

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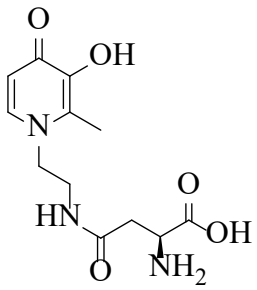

***Figure 1**. Structure of L2 3-hydroxy-4-pyridinone.*

In the last years the increase of pollution and its impact on diseases onset, led the scientific community to a great interest towards the study of the effect of contaminants, including metals, organic and inorganic compounds, on the environment and humans **[1]**. It is known that the biological and chemical activity of these substances should be attributed to some of the chemical forms in which they are present in the natural fluids. To better understand their mechanism of action, it is necessary to know either their analytical concentration, or their "*speciation*", i.e. a term indicating the distribution of the physical and chemical forms in which a component is present in a system **[2]**. Since these forms could have various effects towards environment and humans, the study of speciation becomes essential to gain information about their environmental impact, toxicity and bioavailability. Aluminium is a naturally occurring metal in various environmental matrices. In soils it is present in the form of aluminosilicates and oxides. Acidic rains can provoke soil acidification (pH $\leq$ 5.5), promoting the mobility of Al^{3+} which may hinder plants growth and cause a significant reduction of the concentration of nutrients like Ca^{2+} and Mg^{2+} in leaves, roots and shoots **[3]**.

On the other hand, iron is one of the most abundant metals found in the environment **[4]**. In plants it is mainly present in ferric (Fe^{3+}) form and plays fundamental roles in the photosynthesis, for nitrogen fixation and for plants growth. Iron can become an ecotoxic element for soils and plants when it is accumulated at significant concentration levels. In these matrices, Fenton reaction can produce reactive oxygen species (ROS), like -OH radicals, able to damage DNA, lipids and proteins **[5]**. The metal ecotoxicity symptoms might be soils bronzing and leaves stippling. The reason of change of colour in leaves could be, for example, the plants synthesis of enzymes aimed to control the effects of free radicals. In addition, Fe^{3+} can also compete with Zn^{2+} and Cu^{2+} in its uptake and transport within plant cells **[4]**.

On this light, the present contribution is focused on the results of a speciation study performed to evaluate if a compound (*L2*, **Figure 1**), belonging to the class of 3-hydroxy-4-pyridinones, could be an efficient chelating agent for the remediation of potentially ecotoxic metals such as Al^{3+} **[6]** and Fe^{3+} from soils and plants. In addition, another relevant issue appeared to be worth of investigating to ascertain if, from the thermodynamic point of view, along with the Al^{3+} and/or Fe^{3+}-sequestration by *L2*, there could be a possible significant competition with essential metals such as Ca^{2+}, Mg^{2+} **[3]**, Zn^{2+} **[7]** and Cu^{2+}, despite their different charge density, acid-base behaviour **[8]** and ionic radius.

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Free Amino Acids Quantification in Cloud Water at the Puy de Dôme Station (France)

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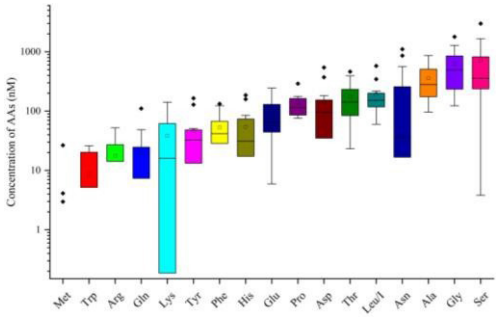

Free amino acids (FAAs) have recently been detected in cloud water [1,2], but commonly characterized in the atmosphere [3–7]. Eighteen FAAs were quantified in cloud water sampled at the puy de Dôme station (PUY - France) during 13 cloud events. This quantification has been performed using LC-MS and the standard addition method to overcome matrix effects. Total concentrations of FAAs vary from 1.2 µM to 7.7 µM, revealing high variability, from 0.5 to

4.4 % of the dissolved organic carbon measured in the cloud samples. Ser (Serine) was the most abundant AA (23.7 % in average), followed by Glycine (Gly) (20.5 %), and Alanine (Ala) (11.9

%). AAs quantification in cloud water is scarce but the results agree with the few studies that investigated AAs in this aqueous medium. The environmental variability is assessed through a statistical analysis. This work shows that AAs are correlated with the time spent by the air masses within the boundary layer, especially over the sea surface. The cloud microphysical properties fluctuation does not explain the AAs variability in our samples confirming previous studies at PUY. We finally assessed the sources and the atmospheric processes that potentially explain the prevailing presence of certain AAs in the cloud samples. The measured high concentrations of Ser could be explained by AA composition of aquatic organisms, such as diatoms species. The initial relative distribution of AAs in biological matrices (e.g., proteins extracted from bacterial cells) could explain the dominance of Ala and Gly. The analysis of the AAs hygroscopy indicates a higher contribution of AAs (80 % in average) that are hydrophilic or neutral, confirming hydrophobic AAs are less incorporate in cloud droplets due to their low solubility. Finally, considering their potential transformation in the cloud medium by biotic or abiotic (mainly oxidation) processes, the atmospheric lifetimes of AAs have been calculated. These AA atmospheric aging could explain the very low Met and Trp concentrations measured in our cloud samples which are very reactive, and the large one measured for Gly and Asn and in some extent for Ser and Ala which are very slowly transformed. This reveals the high complexity of the bio-physico-chemical processes occurring in the multiphase atmospheric environment.

Acknowledgements

This work was funded by the French National Research Agency. CO-PDD is an instrumented site of the OPGC, supported by the Université Clermont Auvergne, by the CNRS, and by the CNES. The authors are also very grateful for the financial support from the French ministry, ACTRIS Research Infrastructure, and FEDER. The authors also thank the I-Site CAP 20-25.

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Cd(II) Sorption by Novel Polymer Inclusion Membranes Based on L-Glutamic N,N-Diacetic Acid or Citric Acid from Aqueous Solution

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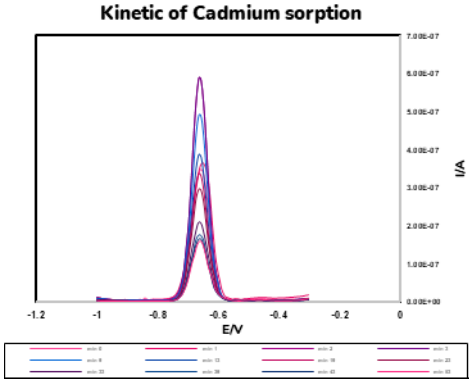

Despite the availability of many chelating agents able to efficiently bind metal cations in solution, only few are actually viable as a large-scale countermeasure to the persistent problem of metal-polluted wastes. For instance, among them, the non-biodegradable ethylenediaminetetraacetic acid (EDTA) ended up being overused, thus becoming a polluting agent itself, pointing out the necessity to search for new strategies for efficient cations removal and environmental remediation [1]. In this scenario, this contribution reports some preliminary results on a research focused on the development of novel ecofriendly efficient and "practically usable" materials. Although this goal is still far from being achieved, the fundamental idea of the material biocompatibility led to the synthesis of a series of novel and ecofriendly polymer inclusion membranes (PIMs), whose formulation is based on a biopolymer matrix, namely polylactic acid (PLA) including Aliquat336 (Ali, an ionic liquid) and L-glutamic N,N-diacetic acid (GLDA), the latter being a readily biodegradable chelating agent [2], or citric acid (Cit). Such material has already shown a remarkable chelating capability toward Cd^{2+} along with high tolerance to extreme conditions such as low pH and high electrolyte concentration. In this regard the chemometrics approach during the experimental design was of pivotal importance. This versatile method greatly simplified the assessment of the chemical behavior of these materials in heterogeneous solutions. In particular, the acid-base equilibria of L-glutamic N,N-diacetic acid and citric acid entrapped inside the polymeric membrane were investigated by potentiometric titrations in a pH range ranging from 2 to 11 and ionic strength between 0.1 and 3 mol dm^{-3}. Moreover, kinetics experiments for the sorption of the Cd^{2+} cation were performed by means of differential pulse anodic stripping voltammetry (DP-ASV) to assess the time required to reach equilibrium between the PIMs and a solution containing Cd(II), at different pH and chloride concentration values. This information was then taken into account while performing isotherm experiments by DP-ASV. Last, the surface structural characterization was performed by means of attenuated total reflectance infrared spectroscopy (ATR). The preliminary data obtained are encouraging and may suggest the use of these polymer inclusion membranes for remediation purposes.

Acknowledgements

This work has been financially supported by the University of Messina (Research&Mobility2017 Project cod. 009041). P. Irizar gratefully acknowledges his predoctoral grant from the MINECO (PRE2018-085888).

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Estimation of Environmental Pollution Using Precipitation Analysis

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Ambient air pollution has been outlined as one of the priority areas of the environment and health issues as it was stated already in the Declaration on Action for Environment and Health in Europe. Air pollution kills about 3 million people annually affecting each person and all regions of the world. Therefore, regular monitoring of air quality is considered of great importance for population health and wellbeing. Moreover, periodic non-target analysis, especially in highly populated areas, is required to reveal the changes in the local priority pollutants list and to discover new pollutants. Precipitations may reflect both the current state and the long term air pollution.

Samples of rain water and molten snow were extracted with dichloromethane using standard US EPA 8270 method. The prepared extracts were further analyzed using Pegasus® GC×GC HRT 4D instrument (LECO Corp., USA). Together with classic electron ionization (EI) some samples were analyzed using chemical ionization and electron capture negative ionization. Standard Mixtures from Restek (USA) were applied for identification and quantitation of priority pollutants, while other compounds were identified using NIST17 library as well as rules of fragmentation under EI.

This work presents the results of analysis of snow samples from urban areas of Moscow and Arkhangelsk, remotes areas of Russian Arctic, rain water samples from Moscow, and water from French clouds. High resolution mass spectrometry was the key analytical tool during identification of unknown compounds. Furthermore, addition of complementary ionization methods simplified identification. So, positive chemical ionization allowed identifying nonstandard phthalates widely present in environment. These methods also significantly increased sensitivity towards several classes of compounds (for example nitro-compounds or polyhalogenated derivatives). Some of them haven't been identified in environmental samples for a long time ago, i.e. persistent organic pollutants (POP) from the "Dirty dozen". Complexity of analyzed samples results in incomplete chromatographic separation, which may be overcome by the use of comprehensive two dimensional gas chromatography. Finally, the large data array was processed with various chemometric approaches to reveal any consistent patterns for distribution of pollutants helping to find the possible sources of air pollution.

GC×GC-HRMS with various ionization techniques was demonstrated to be crucial for non-target analysis of complex environmental mixtures. The proposed methods for analysis of precipitations were shown to be an efficient approach in elucidation of ambient air pollution.

Acknowledgements

This research was supported by Russian Science Foundation (grant no. 21-74-00024).

Thermal Desorption Gas Chromatography – Mass Spectrometry Determination of Toxic Rocket Fuel Transformation Products in Soils

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The use of gas chromatography - mass spectrometry methods to determine the transformation products of highly toxic rocket fuel based on 1,1-dimethylhydrazine (UDMH) in contaminated soils (near carrier rocket launch pads and at spent stages landing sites) requires solving the problems of matrix change and concentration analytes. For this purpose, methods of liquid extraction are used, as well as solid-phase microextraction from an equilibrium vapor phase, which are characterized by high labor intensity, high consumption of the extractant (liquid extraction) and significant matrix effects (SPME).

This study proposes an alternative approach to screening and simultaneous determination of a wide range of nitrogen-containing products of UDMH oxidation, based on direct thermal desorption of analytes from soil with cryofocusing and further gas chromatography-mass spectrometry analysis.

The effect of thermal desorption conditions (temperature, duration, sample weight and humidity) on the extraction efficiency and stability of analytes for the four types of soils (sandy, light, medium, and heavy loam) was studied. On this basis, the optimal parameters for the extraction of analytes were proposed: thermal desorption of a 5 mg sample at a temperature of 300 °C for sandy soil and 350 °C for loamy soils for 30 and 60 min, respectively. The achieved analyte recoveries were in the range of 20–90% in the case of sandy soils. It is shown that when cryofocusing is applied, the limiting moisture content of the soil sample should not exceed 10% to maintain effective chromatographic separation. The use of sorption traps for analytes instead of cryofocusing makes it possible to analyze soils with a moisture content of up to 20%.

The use of an isotopically labelled internal standard (pyridine-d_5) allowed increasing the reproducibility and accuracy of the analysis and developing a method for the simultaneous determination of 29 nitrogen-containing compounds of various classes in sandy and loamy soils with detection limits for most analytes in the range of 0.2-40 μg/kg and accuracy 70-130%. The developed method was tested in the analysis of real samples - sandy soil samples taken from the site of accidental crash of the Proton-M carrier rocket near the Baikonur cosmodrome in 2013. Most of the target analytes were found at the levels of 0.06-70 mg/kg. High accuracy of the developed sample preparation technique was confirmed by comparing the analysis results with that obtained by independent method of pressurized liquid extraction with acetonitrile.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (19-33-60011), a grant from the President of the Russian Federation (MK-1866.2020.3), and the Ministry of Education and Science of the Russian Federation (project state assignment No. 0793-2020-0007).

The Use of Two-Dimensional Gas Chromatography-Mass Spectrometry for the Study of Atmospheric Pollution in Arkhangelsk. Application of Chemometric Methods for the Purposes of Environmental Analysis

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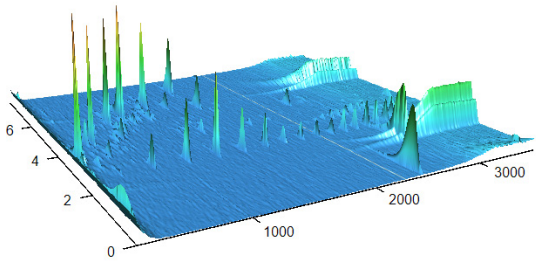

Environmental exposure assessment is an important step in establishing a list of local priority pollutants and finding the sources of the threats. Arkhangelsk is the largest city of North-European part of Russia, where a number of industrial facilities are located.

Arkhangelsk experiences subarctic climate with heavy snowfalls during 7 months. Therefore, snow analysis represents an efficient approach for the estimation of long-term air pollution during winter period due to accumulation and preservation of environmental contaminants by snow. Using polypropylene pipe for sampling allows to collect snow through the whole layer accumulated during winter period. Since most of the known priority pollutants are semi-volatile organic compounds, GC-MS represents the best tool for environmental monitoring. Typically, environmental samples contain a large number of components with close retention times on a non-polar column, which leads to their coelution. It makes the interpretation of the obtained data complicated. Considering this fact, the method of two-dimensional gas chromatography (GC×GC) is more informative for the purposes of environmental analysis. GC×GC method increases identification reliability by providing better separation and also by providing additional information on retention times along the second column. Considering a large number of isobaric compounds with the same integer m/z values, high-resolution mass-spectrometry becomes indispensable when dealing with non targeted analysis of environmental samples.

Ten snow samples were collected in January 2021 in Arkhangelsk. Sample preparation was carried out according to the US EPA 8270 Method. The dichloromethane extracts were analyzed using Pegasus GC-HRT+ 4D high-resolution mass spectrometer combined with Agilent 7890A gas chromatograph equipped with two chromatographic columns and a thermal modulator. Both targeted and non targeted approaches were applied. For the reliable identification available standards, NIST20 mass spectral library and manual structural elucidation were used. Concentrations of the targeted pollutants were determined using internal standards. As a result, it was possible to establish the concentrations of more than 150 substances. In addition to the classic priority pollutants listed by the US EPA (polycyclic aromatic hydrocarbons, phenols, phthalates, etc.), non-target analysis allowed identifying a wide range of other organic compounds, including alkyl pyridines, organophosphates, furans, organic acids, and many others.

Chemometric data processing methods were used to identify the differences in the nature of pollutants between the snow sampling sites. In addition, work was carried out with the novel ChromaTOF Tile program, which automatically determines the differences in two-dimensional spectra between samples. The effectiveness of using the ChromaTOF Tile program for the purposes of environmental analysis has been assessed. The use of chemometric methods of data processing made it possible to identify the most significant pollutants at each sampling point and to draw up a pollution map of the Arkhangelsk city.

Application of Two-Dimensional Gas Chromatography - High-Resolution Mass Spectrometry for Studying the Combustion Products of Nicotine and Herbal Cigarettes

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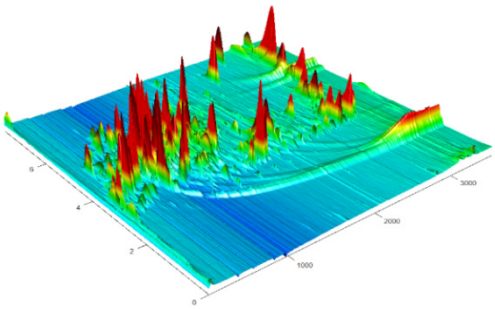

3D Total ion chromatogram of the combustion products of herbal cigarettes

Every year new formulations and modifications are introduced into the cigarette industry. At the beginning of this decade, in European countries, herbal cigarettes were introduced as a healthier substitution of the classic nicotine ones. They contain various mixtures of herbs that affect human receptors in a similar way to nicotine. However, there are practically no data on the combustion products of the herbal cigarettes. Due to the extremely complex composition of the combustion products of cigarettes, the identification of hazardous xenobiotics and the comparison of the combustion products of herbal and nicotine cigarettes represent a difficult task that can be solved by two-dimensional gas chromatography - high-resolution mass-spectrometry. In the present study, the combustion products of cigarettes obtained in the course of model experiments in a specially designed apparatus (apparatus simulating human lungs during smoking) were analyzed using GC × GC-HRMS (Pegasus HRT 4D, Leco, USA) mass spectrometer.

Chromatographic separation of the components was carried out using two columns of different polarity (the primary column Rxi-5ms, 30m, 0.25um from Restek; the secondary column Rxi-17ms, 1m, 0.25um from Restek). The detection and quantification of substances was carried out using a time-of-flight mass spectrometer with a recording rate of 200 full mass spectra per second.

The obtained chromatograms revealed more than 3000 peaks of organic compounds of various classes. Although herbal cigarettes lack nicotine-type compounds, the range of identified products by non target analysis was significantly wider. A large number of nitrogen-containing organic compounds have been identified in both herbal and nicotine cigarettes, namely pyridines, pyridazines, amides and their derivatives, etc. Phenols (phenol, aminophenols, methylphenols, etc.), polycyclic aromatic hydrocarbons and their derivatives (naphthalenol, methylnaphthalene, etc.) were found in large quantities.

According to the results of quantitative analysis, it was calculated that the amount of phenol was 50% higher in herbal versus nicotine cigarettes. Similar trend was observed for many dangerous ecotoxicants found when burning herbal cigarettes.

These compounds are not less dangerous, and potentially could be more harmful for human beings than nicotine and its derivatives. Nitrogen-containing organic compounds also have a detrimental effect on humans (pyridine, triazole, pyrrol and their derivatives, etc.). Some of the compounds found in both herbal and nicotine cigarettes are also rather dangerous carcinogens. A number of organohalogen compounds have been identified as well.

Acknowledgements

The work was carried out using the equipment of the Center for Collective Use of the NO "Arktika" NArFU with financial support from the Ministry of Education and Science of the Russian Federation (project state order No. 0793-2020-0007).

Characterization of Nicotine Salts in E-Liquids and E-Cigarette Aerosols

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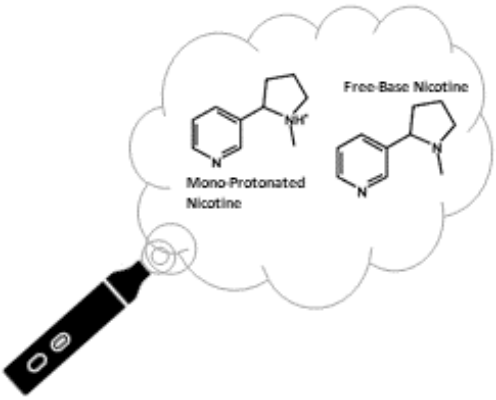

In less than 20 years, e-cigarettes have become worldwide and center controversies around their impact on environmental health. Recently, nicotine salt, a new type of e-liquid, gained a large share in US market and represent a growing tendency in France [1,2]. Nicotine salts consist in the addition of an organic acid to the e-liquid to proton nicotine, as nicotine exists as free-base nicotine (α_{fb}), and protonated nicotine [3]. Nicotine salts raise new concerns on e-cigarette addiction potential and toxicity [4]. Characterizing α_{fb} in e-liquids and aerosols is of primary importance. Although few approaches are described in literature [5], there is a need for standardized methods. This research aimed to compare the performance of those analytical methods.

Focus was set on nicotine benzoate and nicotine salicylate, with home-made e-liquid and two commercial references for each nicotine salt (JUUL, Flavour Power). Aerosol were generated with JUUL device using a standard linear vaping machine and collected either on quartz filters or dual impingers containing 20 mL of purified water. Experiments were performed according to CORESTA reference method 81. For both e-liquids and aerosol, α_{fb} was first assessed by pH measurements. Then, α_{fb} was quantified using gas chromatography coupled with mass detector (GC-MS) after liquid-liquid extraction (LLE). Lastly, e-liquids and aerosols were analysed by liquid chromatography coupled with ultraviolet detector (LC-UV) to quantify nicotine and acid ratios.

Overall, α_{fb} were low ($\alpha_{fb} < 0.02$) for e-liquids and aerosols. Even though, α_{fb} of e-liquids and aerosols were identical for JUUL products, 2-6 fold variations in α_{fb} were observed between e-liquids and aerosols for the other products. Those differences were measured regardless of the aerosol collection method. Indeed, the two method of aerosol collection gave similar results, despite higher entrapment efficiency of nicotine and acids for quartz filter (~90%) over impingers (~70%). Good correlations were observed between pH measurements and LLE, while ratios variations did not reflect variations in α_{fb}.

This work will help in the establishment of standardized method for α_{fb} determination in e-liquids as well as aerosols.

Acknowledgements

This work was funded by the French National Institute on Cancer (INCA) and the French Research Institute on Public Health (IReSP).

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Balsamic Components and Contaminants in the Egyptian Mummy

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To preserve mummies in Ancient Egypt various natural compounds and mixtures were used depending on the historical period. Bee wax, natural bitum, coal tar, conifer resins, plant and animal oils, aromatic plant constituents were the most popular ones. One of the important issues in the studies of mummies involves confirmation of the use of bee wax, conifer resins, and bitum in the textile bandages. Actually, the composition of organic compounds in a particular mummy may provide valuable information on the period of mummification. GC-MS is the best technique to carry on analysis of the materials related to mummies when it deals with the mentioned above classes of organic compounds.

In 1913, the Pushkin State Museum of Fine Arts (Moscow, Russia) acquired a clay coffin with a mummy at the de Rustafjaell sale in London (I, 1a 6122). According to de Rustafjaell, the coffin with the dried-up body was found at Gebelein and belongs to the Predynastic period. Radiocarbon dating of textile samples from the mummy has demonstrated that the mummy is genuine and dated back to the late Predynastic period (3347-3257 BC (1 σ, 68,2% probability) and 3356-3098 BC (2 σ, 95,4% probability).

Three samples of textile bandage (~0.5g each) were placed into glass vials with 3 ml of dichloromethane and subjected to the extraction in the ultrasonic bath. The procedure was repeated 3 times for each sample. The extracts of the same bandage were combined, dried over sodium sulfate and concentrated to 0.5 ml. The GCxGC-HRMS analyses were performed with Pegasus GC-HRT+ 4D high resolution time-of-flight mass spectrometer (LECO Corporation, USA) with resolving power above 25 000 and mass accuracy below 1ppm. Mass spectra were obtained in electron ionization, positive and negative chemical ionization modes. NIST 17 library and manual spectra interpretation were used for the identification, while perdeuterated PAH were used for the quantification.

Application of a powerful GCxGC-HRMS technique with complementary ionization tools allowed significantly widening the scope of organic compounds used for mummification. Oils and fats, beeswax, conifer resin, aromatic plant extracts, organohalogen compounds, various hydrocarbons used for embalming were reliably identified in the mummy. Although the presence of various types hydrocarbons, first of all steranes and triterpanes, allows proposing that bitumen from Gebel Zeit was used as a component of embalming mixtures already 5000 years ago, higher levels of less stable hydrocarbons introduce some doubts. Probably absorption of hydrocarbons took place during 5000 years of staying in the sands of Gebel Zeit or during transportation of the mummy to the UK and then to Russia. The identified terpenes allowed concluding that coniferous tar, i.e. processed by heating Pinaceae coniferous resins, was also applied for the embalming of the mummy. Iodinated and brominated compounds never reported earlier in the mummy samples, but detected herein due to much higher sensitivity of the electron capture negative ionization, may be considered as biomarkers of marine origin of some embalming components, probably sea plant oils. A representative group of hexadecanoic acid esters confirms the application of beeswax in the embalming mixtures, while dihydro-4-hydroxy-2(3H)-furanone, hexylcinnamate and neophytadiene demonstrate the use of aromatic plant substances. Besides natural ingredients GCxGC-HRMS allowed identifying a number of modern contaminants and pollutants, including phthalates, organophosphates and even DDT. The complexity of the embalming mixtures supports the hypothesis of the high social status of the child made on the basis of the preliminary study of the mummy.

Assessment of Water Quality and Metal Exposure in the Krka River Watercourse (Croatia) Influenced by the Wastewater Outlets

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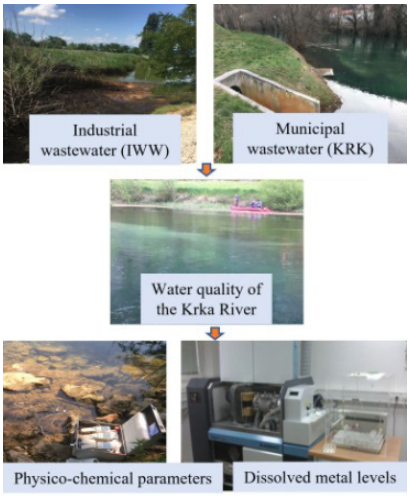

Due to its travertine waterfalls, many cascades and lakes, very rich and diverse flora and fauna, the Krka River represents exceptional natural value in the Republic of Croatia and worldwide. In accordance, middle and lower course of the river were proclaimed Krka National Park (KNP). Only 2 km upstream of the park border municipal and industrial wastewaters, which are released without proper purification, may threaten living world and tufa barriers of this karst phenomenon [1]. The aim of the present study was to evaluate water quality and metal exposure by means of physico-chemical water parameters (turbidity, conductivity, total dissolved salts, chemical oxygen demand, ammonia, nitrates, nitrites, total nitrogen and total phosphorus) and dissolved metal levels (Al, As, Cd, Co, Fe, Hg, Li, Mn, Mo, Ni and Zn).

Sampling was performed at eight locations: Krka River source (KRS) as reference site; tributary Krčić (TKR); industrial wastewater (IWW); municipal sewage of the Town of Knin (KRK); tributary Orašnica (TOR), impacted by industrial wastewater; tributary Kosovčica (TKO), nearby Knauf factory; tributary Butišnica (TBU), influenced by agricultural runoff and Brljan Lake (KBL), located in the KNP. Sampling campaigns were conducted in April and July 2021, as two seasons of higher and lower water level, respectively. Physico-chemical parameters were measured *in situ* and by Standard Methods for the Examination of Water & Wastewater, while metals were measured by high resolution inductively coupled plasma-mass spectrometry (HR ICP-MS). Water quality was estimated following the Directive on water quality status [2].

Chemical water status was the lowest in industrial effluents (IWW) in both sampling campaigns, which were therefore confirmed as a serious threat to the river water. Physico-chemical water parameters (especially chemical oxygen demand, ammonia, total nitrogen and phosphorus) also pointed to deteriorated water quality at anthropogenically impacted locations (TKO, KRK, TOR, TBU) but also at KBL, which is situated within KNP. Dissolved metal levels, especially of Mn, Fe, Co and Ni, showed the highest increase at IWW, TOR, KRK and TKO compared to KRS in both seasons. Those metals are known by their use in industry and confirmed potential impact of IWW to the Krka River and its tributaries. Only Hg levels were low at all sites, even below limit of detection. Concentrations of most metals were higher in July than April at all sampling sites, probably due to lower water level in the summer period.

Presented results indicated the influence of direct pollution sources and emphasized its potential threat to the preservation of the natural beauties of the Krka River. Therefore, proper purification of the wastewaters and implementation of water quality monitoring strategies of the Krka River are required.

Acknowledgements

The financial support of the Croatian Science Foundation for the project: "Integrated evaluation of aquatic organism responses to metal exposure: gene expression, bioavailability, toxicity and biomarker responses (BIOTOXMET)" (IP-2020-02-8502) is highly acknowledged.

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Transmission of Bioagens Sorbed onto Suspended Particulate Matter in Ambient Air During Urbanization Process in the City of Novi Sad

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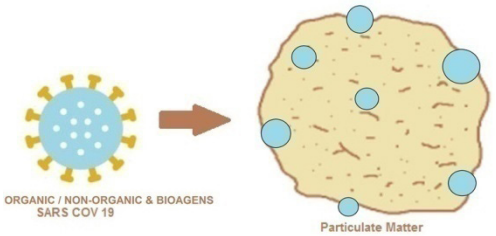

In the urbanization processes large amounts of suspended particulates as polluting substances are released in ambient air [1,2]. Suspended particulate matter -PM with radius smaller then 10um (PM10, PM2.5 and PM1) as well as nano particulates are characterized with vast active sorption spongy surface on which organic and non-organic hazard free molecules, bacteria, viruses (specially SARS COV-2) and other infectious bioagenses are attached. Currently in the city of Novi Sad there are 3.285 active [3] construction sites that generate high percentage of total PM in the urban ambient air and whole atmosphere.

Numerous researches has highlighted that suspended particulates can be inhalated deep into the lung and alveoli causing serious health consequences such as severe acute and chronic respiratory syndrome and disease with the lethal outcome.

The virus SARS COV-2 (Severe Acute Respiratory Sindrome Corona Virus) is very easily transmitted in contaminated air by air mass moving as consequence of virus concentration gradient. Virus is bio organic nano spherical particulate, chemical species, highly organized supra molecular icosahedral structure of capsid with genetic linear one chained RNK and protective two layer protein lipid shell. COV 19 virus is molecular substance with highly expressed parasite character with exponential infectivity and kinetic replication in symbiote – live cell. According to new experimental researches COV-2 survives and locates itself on suspended particulates, and particularly on aerosols of water foggy droplets attached with non-covalent inter molecular Jean-Marie Lehn bonds.

Concentration levels of suspended particulates on representative location of Novi Sad are monitored by laser optical sensors. Monitoring of PM concentration levels generated in urbanization processes has shown high concentration level of PM particulates in ambient air, which in combination with number of active construction sites in City of Novi Sad present reservoir for dissemination of infective bioagens, especially for COV 19.

Based on the research it can concluded that contamination potential of ambient air is in direct connection with urbanization activities and efficiency of PM mitigation measures on the source.

Acknowledgements

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".

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Meta-Omics Analyses of Cloud Microbial Metabolism of C1 Compounds

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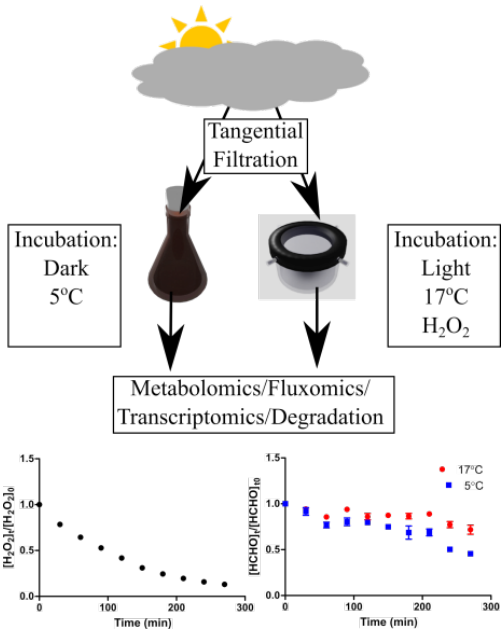

Current models of atmospheric chemistry do not include the contributions of detailed C1-microbial metabolism (methanol, formaldehyde, formate and CO_2), although studies have identified active microorganisms in clouds [1-5]. It is thus important to detail microorganisms' role in Carbon metabolism using modern techniques.Studies have identified increases of C1 compounds in clouds due to abiotic factors and the presence of microorganisms capable of utilizing these C1 compounds [3-5]. These works investigating C1 metabolism in clouds has culminated in the need to study the metabolic pathways of microorganisms in the atmosphere and their regulation by atmospheric conditions. New methods can allow improved analyses of the metabolic pathways of the communities present in clouds. The overarching objective of this work is to incorporate biotic utilization of C1 compounds into atmospheric chemistry models.

In order to generate a model integrating biotic parameters, this study will seek to examine the C1-compound metabolism of cloud communities using microcosm experiments mimicking typicalatmospheric scenarios: winter night (5°C, dark) *vs* summer day (17°C, light, H_2O_2). The modulation of metabolic pathways under these scenarios will be assessed using meta-transcriptomics and meta-metabolomics approaches. Previous studies had shown a strong modulation of cloud microbial metabolism by H_2O_2[6-7]. Metabolic fluxes will be measured by meta-fluxomics using ^{13}C-labelling. The initial steps for this project include the collection of microorganisms from cloud samples at the puy de Dômeobservatory in France and their incubation in cloud water-simulating media in the lab.

Challenges to the project include the difficulty of sampling the low biomass communities found in clouds and the ability to maintain these communities in lab with modified chemical conditions. In case the concentrations are too low to properly conduct the various experiments necessary, a community of isolates from clouds will be made in-lab and used in lieu of cloud samples.

This project will seek to optimize the sampling of cloud communities for downstream microcosm experiments and meta-transcriptomic, meta-metabolomic, and other analyses. The intention of all these analyses are to create a carbon cycling model for the atmosphere incorporating microbial metabolism with current knowledge of abiotic transformations.

Acknowledgements

The authors acknowledge the support through the funding of the METACLOUD ANR French program.

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Transformations of Resveratrol, Antioxidant Component of Sunscreen, under Disinfection Conditions

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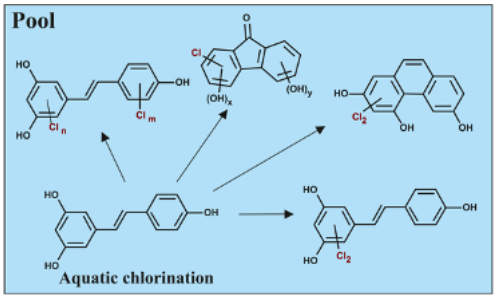

Overexposure to ultraviolet (UV) irradiation from the sun plays an important role in the development of skin cancers and skin aging. This awareness is reflected in the development of newer sunscreen formulations with protection extending to the long range of UVA wavelengths to ensure optimal photoprotection.

Sunscreens are one of the most widely adopted public strategies to protect from UV irradiation. Chemical UV-filters are compounds incorporated on sunscreen formulations to absorb specific wavelengths of ultraviolet radiation, UVA (320–400 nm), UVB (290–320 nm) or both. The high capacity of UV-filters to absorb UV should remain stable for the entire period of sun exposure in order to achieve the expected photoprotection for commercial sunscreen products [1].

Antioxidants (AOxs) are often used in the cosmetic industry to reduce skin ageing due to UV radiation and in sunscreen formulations to complement the photoprotection offered by the UV-filters, preventing or reducing potentially photogenerated reactive species. Different topical antioxidants are used to replenish the natural reservoirs in the skin. Topical AOxs have the potential to diminish the ROS generated from the UVA radiation. Different AOxs, such as Vitamin C, E, A, selenium, silymarin, polyphenols, resveratrol and beta-carotene may be used in the sunscreens [2].

In this study we focused on stability of resveratrol as pure substance as well as a sunscreens' ingredient after aquatic chlorination as a common disinfection processes for swimming pool waters. Given that the use of sunscreen products is essential, with resveratrol being an antioxidant and a substance of benefit in such formulations, we investigated chlorination products resulting from the exposure of resveratrol to chlorinated water. For the identification of corresponding DBPs (disinfection by-products) gas chromatography - high resolution mass spectrometry (GC-HRMS) with electron ionization for the determination of semi volatile compounds and ultra pressure liquid chromatography - high resolution mass spectrometry (UPLC-HRMS) with electrospray ionization and registration of both positive and negative ions have been used for the polar and non volatile ones correspondingly. Various mono-, di-, tri- and tetrachlorinated products have been identified and the chlorination pathway has been proposed.

The toxicity measurements revealed a lower luminescence inhibition of resveratrol chlorination products in comparison to inhibition due to chlorinated water alone, suggesting a part of chlorine was spent on reaction with resveratrol. The same effect was observed in the case of sunscreen containing resveratrol. Which chlorinated product contributes to the overall toxicity is speculative because of lack of standards.

Acknowledgements

The reported study was funded by RFBR, project number 19-33-90042. This work was performed using instrumentation of the Core Facility Center "Arktika" of the Northern (Arctic) Federal University under financial support of the Ministry of Science and Higher Education of the Russian Federation (state assignment project No. 0793-2020-0007). The authors also acknowledge the financial support from the Slovenian Research Agency, the research core funding No. P3-0388, No. J2-8162 and bilateral scientific collaboration between Slovenia and Russia 2019-21.

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Advances in Photochemistry Modeling: the Equivalent Monochromatic Wavelengths Approach

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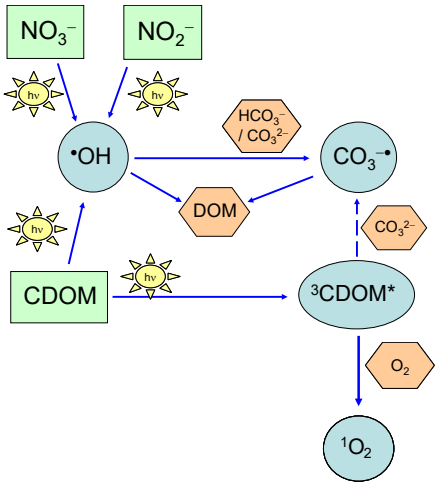

Photochemical reactions play a key role in the transformation of contaminants, and particularly biorecalcitrant pollutants in sunlit surface waters [1]. The relevant processes, rates and overall importance can be predicted by photochemical modeling, based on sunlight irradiance and spectrum, water chemistry and depth, as well as pollutant photoreactivity (absorption spectrum, direct photolysis quantum yield and second-order reaction rate constants with photochemically produced reactive intermediates, PPRIs). Several pieces of evidence suggest that modeling is able to predict quite well the photochemical fate of several contaminants in surface waters [2].

A major issue that is connected with modeling is the polychromatic nature of sunlight, of the absorption spectra of contaminants and of the natural chromophores and photosensitizers (nitrate, nitrite and chromophoric dissolved organic matter, CDOM). The latter are the sources of PPRIs such as •OH, $CO_3^{\bullet-}$, $^1O_2$ and CDOM triplet states, ^{3}CDOM* [3]. Therefore, the monochromatic Lambert-Beer equation describing radiation absorption is to be applied for each relevant wavelength, and the results summed up together. Unavoidably, numerical integration is a fundamental prerequisite of photochemical models that considerably complicates calculations compared to the relatively simple monochromatic equations. Therefore, photochemical modeling usually requires dedicated software [4] to be carried out that, although freely available, might not always be easy to customize.

This contribution shows how it is possible to overcome this difficulty by using monochromatic Lambert-Beer equations for photochemistry modeling instead of polychromatic, integral ones. The key to successful approximation is the definition of the equivalent monochromatic wavelength (EMW or λ_{eq}) [5]: it is the single wavelength which, when used in the Lambert-Beer equation that is monochromatic by nature, approximates the behavior of the polychromatic system.

Comparison between polychromatic and monochromatic, EMW-based equations was carried out and showed that nitrate photochemistry (•OH and $CO_3^{\bullet-}$ source) can be described with EMW = 315 nm, nitrite photochemistry (producing the same PPRIs as nitrate) with EMW = 360 nm, and CDOM photochemistry (source of all PPRIs) with EMW = 560 nm. The EMW approach worked less well in the case of CDOM, because of the large overlap (a couple of hundreds nm) between CDOM absorption spectrum and the spectrum of sunlight. In this case a simple monochromatic equation struggles to summarize the behavior of polychromatic radiation, which has so many different wavelengths, in terms of water-column penetration and CDOM absorption. The solution was a modification of the Lambert-Beer equation by addition of an exponent that allowed the curvature to be changed, thereby emulating the behavior of the polychromatic system.

The EMW approach allows for excellent agreement to be obtained between integral equations and monochromatic ones, with an error that is orders of magnitude lower than the inherent uncertainty of photochemistry models. It is thus possible to highly simplify calculations with virtually no loss in accuracy, and this advance paves up the way for extending photochemical modeling to a global scale (some examples will be provided in this sense).

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The Health Risk and Benefit Assessments for the Pelagic Fish Species' Consumers

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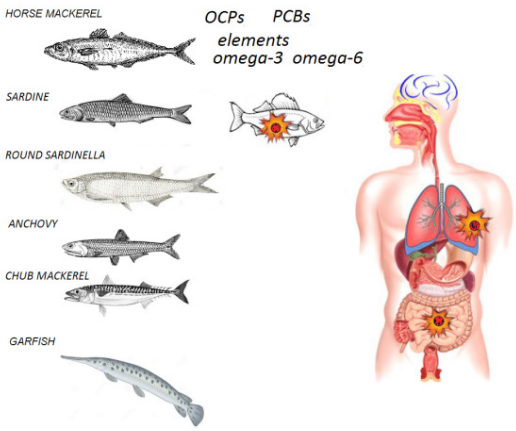

To balance the ingestion of healthy omega-3 and omega-6 fatty acids and adverse chemicals the assessments of benefits and risks of the fish consumption should be of the great importance. Elements, Persistent organic pollutants – POPs (organochlorine pesticides – OCPs and polychlorinated biphenyls – PCB), and omega-3 and omega-6 fatty acid contents were determined in six small pelagic fish species from the Adriatic Sea in Croatia to assess health risks for consumers. 16 element, 24 POPs and 14 fatty acid contents were determined in edible fishes to assess worst-case scenario, diseases development risks and benefit-risk for consumers. The results of this study were published in the scientific journal [1].

Element concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS), POPs by high-resolution gas chromatography (HRGC) and fatty acid content by gas–liquid partition chromatography (GLPC). The results of our study showed that diet based on chub mackerel and round sardinella have highest DI of essential omega-3 fatty acids and lower daily intake (DI) of POPs than other fishes. By consuming anchovy and round sardinella lower ingestion of toxic elements can be ingested. There was not observed non-carcinogenic (HI) nor carcinogenic (CR) risks based on POP concentrations, while based on element concentrations, there was low HI ($0.1 \geq HI \geq 1$) and the maximum HIs and outlier values (several horse mackerel and anchovy samples) showed the presence of HI (HI>1). The most significant contributor to total non-carcinogenic and carcinogenic risks was inorganic As. Acceptable CR for consumers was assessed, but maximum CR for consumers of horse mackerel and anchovy ($CR \geq 1 \times 10^{-6}$) showed adverse effects on human health. There were low HIs for developing cardiovascular, nervous, and reproductive diseases, and maximum HIs were higher than 1. Acceptable ($1 \times 10^{-4} \geq CR \geq 1 \times 10^{-6}$) risks were observed for developing cancer of nervous system and reproductive organs. Among investigated fish samples, those with higher ΣBR (benefit-risks) and BR for inorganic As than median value have a higher risk than benefits in the human diet (most of them were collected in 2015) [1].

Acknowledgements

The authors received funding provided by Croatian Science Foundation (Project OPENTOX, No. 8366), institutional financing 2018–2021 Project "Persistent Organic Pollutants – Environmental Impact Assessment and Stability of Human Genetic Material"; Institute of Physics Belgrade (document No. 0801–116/1) and Faculty of Chemistry (contract No. 451-03 68/2020-14/200168) grants and grant for postdoctoral investigation for Dr. Tijana Milićević (contract No. 451-03-1338/2020-14) and bilateral contract between Institute of Physics and Institute for Medical Research and Occupational Health (No. 337-00-205/2019-09/22) funded by Ministry of Education and Science of the Republic of Serbia.

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Bioelements and Non-Essential Elements in Honeybees and Their Hemolymph, Larvae, Pupae, Honey, Wax, Propolis and Bee Bread

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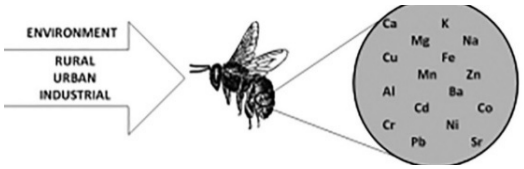

In our previous research we have explored concentrations of 16 elements in samples collected from 3 different environments: Golija (rural region), Belgrade (urban region) and Zajača (industrial region). These three locations were chosen due to their distinctly different degrees of urbanization and industrialization.

Macroelements (Ca, K, Mg, Na), microelements (Cu, Fe, Mn, Zn) and non-essential elements (Al, Ba, Cd, Co, Cr, Ni, Pb, Sr) were determined in the whole body of honeybees, but the major novelty of the research was that hemolymph of the bees was analysed as well.

Significant spatial but also seasonal variations in content of bioelements and non-essential elements were observed. These findings have raised several important questions which are addressed in our current study. In order to better understand how bees' environment does affects concentrations of elements mentioned above, dust and pollen collected from the same locations were analysed. They represent 2 major sources of bio elements and toxic elements for the bees: food and atmospheric deposition.

For the better understanding of dynamics of investigated elements the scope of our research was further extended to the analysis of bee bread, honey, crops, wax, propolis, larvae and pupae.

The samples were digested in accordance with the US EPA SW-846 Method 3052. Closed microwave digestion system (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy) was used for digestion with 5 to 8 ml of concentrated HNO_3 and 1 or 2 ml of concentrated H_2O_2 (depending on the mass and type of the sample).

Concentrations of: Al, Ba, Cd, Co, Cr, Cu, Ca, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were determined by ICP-OES (iCAP 6500Duo, Thermo Scientific). Very low concentrations of: Co, Cr, Cd and Pb, which occurred in some samples were confirmed by ICP-MS (iCAP-Q-ICP-MS, Termo Scientific).

Ratios between concentrations in the samples from industrial region and urban region were calculated and compared for different matrices. Concentrations of toxic metals such as Pb and Cd were significantly elevated in dust samples from the industrial site, and similar trend was observed for pollen, bee bread, wax, propolis, and the whole bees. Elevation of concentrations was not observed (or it was present in significantly lesser extent) for the samples of honey, larvae and pupae.

Acknowledgements

This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No: 451-03-68/2020-14/200168, 451-03-68/2020-14/200007, 451-03-68/2020-14/200125, and 451-03-68/2020-14/200178).

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Sweet Conservation: Development of Sugar Based Epoxy-Silica Hybrids as Multifunctional Materials for Built Heritage Protection

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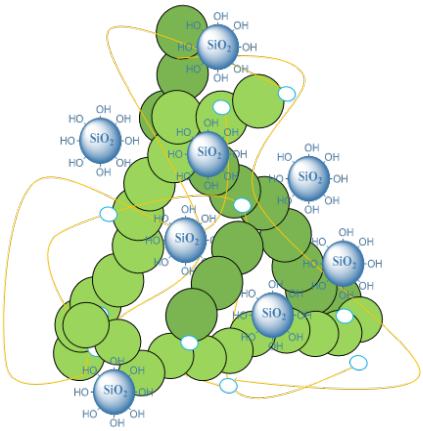
Nanoreinforced epoxy-silica hybrid material



This research is focused on the exploration of sustainable strategies for the design of an eco-friendly BPA-free epoxy-silica hybrid, reinforced with SiO_2 nanoparticles, with consolidating and hydrophobic properties, to be used in stone conservation.

For this purpose isosorbide, a sugar derivative epoxy precursor, was selected as starting compound coming from renewable natural sources and converted into isosorbide diglycidylether (ISO-DGE) [1]. Starting from this compound, thermoset epoxy materials were developed by the selection of suitable hardening agents and further by functionalization with two aminosilanes i.e.: bis[3-(trimethoxysilyl)propyl]amine (NPTEOS) or (3-aminopropyl) triethoxysilane (APTS), adding fixed amounts of silica-forming additives mixtures (i.e. tetraethoxysilane (TEOS), isobutyltrimethoxysilane (iBuTMS), octyltriethoxysilane (OcTES) and (3-glycidyloxypropyl)trimethoxysilane (GPTMS), to gain hybrid organic-inorganic networks. A combination of spectroscopic techniques such as Fourier Transform Infrared (FTIR), Attenuated Total Reflection Infrared (ATR-FTIR) and Raman was exploited to assess the ISO-DGE synthesis, clean-up and curing procedures with selected amines, as well as to characterize the hybrid networks, whereas the homogeneity of the insertion of inorganic domains into organic matrix and of the crosslinking degree was ascertained by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS). Moreover, the thermal-mechanical and hydrophobic properties of the materials were investigated by thermogravimetric analysis (TG-DTA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and contact angle measurements. Once the optimal epoxy-silica hybrid formulation was defined, nanoparticles were prepared and characterized by FTIR and X Ray Difraction (XRD) to evaluate their suitability to be incorporated into the hybrids. Finally, the epoxy-silica nanocomposite material was deeply studied to determine the nanofiller distribution and effect into the hybrid network. The results such obtained indicated excellent thermo-mechanical (T_{onset}, T_g and T_α of 327, 55.9 and 70.1 °C, respectively) and hydrophobic (105°) properties thus showing that the selected formulation fullfill the first requisites for a correct stone conservation product.

Acknowledgements

This work has been financially supported by the project PHETRUM (CTQ2017-82761-P) from the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) and by the European Regional Development Fund (FEDER). P. Irizar gratefully acknowledges his predoctoral grant from the MINECO (PRE2018-085888). P. Cardiano thanks the Italian Ministry of University and Research (MIUR), PON R&I project AGM for CuHe (ARS01_00697), for Contact Angle measurements. The authors are grateful to the technical support provided by the Raman-LASPEA laboratory, the Nuclear Magnetic Resonance laboratory and to the Macrobehaviour, Mesostructure, Nanotechnology: Unit of Materials and Surfaces of The Advanced Research Facilities of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF).

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Authentication of Extra Virgin Olive Oil Based on Fatty Acid Composition and Multivariate Statistics

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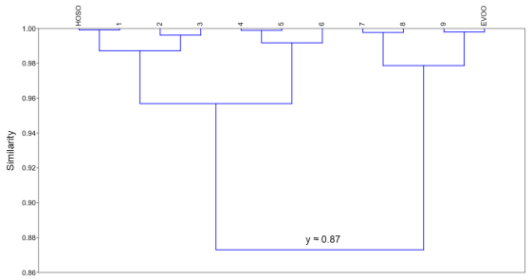

Vegetable oils are a very important part of everyday human diet. Extra-virgin olive oil (EVOO) is recognizable by its nutritional and sensory characteristics, oxidative stability and high quality in terms of health. High-oleic sunflower oil (HOSO) contains more oleic and less linoleic acid comparing to standard sunflower oil. Adding HOSO to EVOO is a common example of market frauds because it is difficult to prove [1-3].

Food authentication is the process by which a food product is verified as complying with its label description [1-3].

The aim of this work was to separate the simulated oil blend samples according to their content of EVOO and HOSO applying hierarchical cluster analysis to peak surface areas of prominent fatty acids.

Pure oil samples of EVOO and HOSO were collected from Processing Technology of Vegetable Oils and Fats Unit at the Department of Food Preservation Engineering, Faculty of Technology Novi Sad, University of Novi Sad, Republic of Serbia. Nine simulated oil blend samples (1-9) with different proportions of EVOO and HOSO (10:90%, 20:80%, 30:70%, 40:60%, 50:50%, 60:40%, 70:30%, 80:20%, 90:10%, respectively), as well as the pure samples of these two oils, were prepared for GC-MS analysis. Fatty acids present in the oil blends were derivatized into corresponding fatty acid methyl esters (FAMEs) using a reagent trimethylsulfonium-hydroxide (TMSH). Semi-quantification of prominent fatty acids: palmitic, linoleic, oleic and stearic, was performed using an AMDIS algorithm of the ChemStation software (Agilent Technologies). Sample preparation, derivatization and semi-quantification of prominent fatty acids was performed in accordance with reference [4].

Based on the obtained numeric values of the peak surface areas of prominent fatty acids, similarity dendrogram with the level of similarity $y \approx 0.87$ was created using PAST4 software. Dendrogram was obtained by hierarchical cluster analysis using a *Paired Group* algorithm and *Correlation* similarity measure. Samples 1, 2 and 3, with high content of HOSO, were grouped together with the pure sample of HOSO. Likewise, samples 7, 8 and 9, with high content of EVOO, were grouped together with the pure sample of EVOO. Samples 4, 5 and 6, with almost equal contents of EVOO and HOSO, were grouped separately in the middle. This method has shown the potential for authentication of vegetable oils.

Acknowledgements

The authors gratefully acknowledge the support from the Project of Matica srpska "Environmental issues, bioeconomy and analysis of possibilities for production of health and safety food in AP Vojvodina" and Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. **451-03-9/2021-14/200134**).

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POSTER PRESENTATIONS

Determination of Polyacrylamide Based Flocculants by Off-Line Thermochemolysis-GC-MS Analysis

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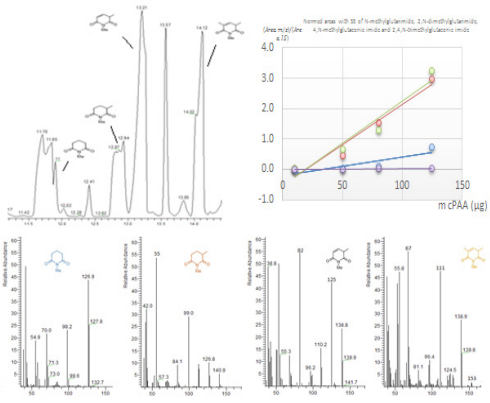

Polyacrylamide (PAA) refers to a group of high molecular weight water-soluble polymers [1, 2]. As a flocculation agent, it is widely used in wastewater treatment and sludge dewatering processes [3]. Therefore, it is a common constituent in sewage sludges, which are partly used in land applications due to their fertilizer and soil conditioning properties [4]. Polyacrylamide is not considered a toxic compound itself [2]. However, considering its wide usage and the obvious direct release into the environment as well as the concern about a possible indirect phytotoxic effect [5], there is a need for analysing PAA in the environment.

This study aimed to transfer a previously developed method by Kronimus & Schwarzbauer (2007) for online TMAH-thermochemolysis GC-MS analysis of cationic PAA (cPAA) into an offline concept. The developed off-line thermochemolysis concept in the presence of trimethylanillin hydroxide (TMAH) induces degradation of cPAA into specific glutarimide derivatives as pyrolysis products. These pyrolysis products appeared in typical pattern of homologues allowing not only an unambitious identification of the polymer but also a pyrolysis based quantification.

Experiments were carried out on pure cPAA, spiked samples, and sewage sludge samples from Germany and China. Furthermore, thermochemolysis experiments on sewage sludge samples revealed the same specific degradation products, as the experiments on pure cPAA and spiked samples.

This study opened the possibility to detect cPAA even at lower concentrations in complex matrices, hence an application to environmental samples has become feasible.

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Quantitative Determination of Polyvinylcaprolactam in Waste Water by Continuous Flow Off-Line Pyrolysis-GC/MS-Analysis

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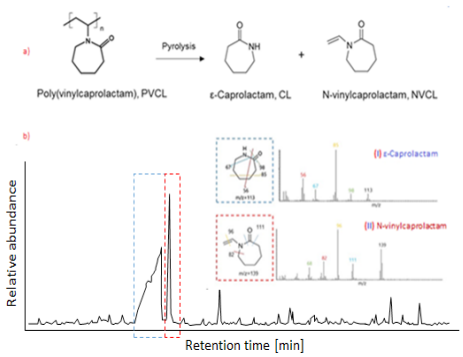

Since the first development of synthetic polymers in the early 20th century, their production and application areas have increased significantly [1]. Most of them are plastic insoluble in water. Significant amounts of water-soluble polymers are produced and used, either as solids, films, or water-based solutions. The most commonly used water-soluble polymers are polyethylene glycol, polyacrylamide, poly(N-vinylpyrrolidone), and poly(N-isopropylacrylamide). Some water-soluble polymers are less significant in the environment because of their biodegradability, such as polyethylene glycol (PEG) [2].

However, many water-soluble polymers, such as herein studied poly(vinylcaprolactam) (PVCL), showing a much lower degradation potential than PEG, are discharged into sewage treatment plants. High production rates and broad fields of application indicate their potential occurrence in wastewater and surface waters. Therefore, it is necessary to establish an analytical method for determining whether water-soluble polymers enter the environment with wastewater from water treatment plants in measurable concentrations [3].

Poly (vinylcaprolactam) is a non-ionic, water-soluble, non-sticky, non-toxic, thermosensitive, biocompatible, and poorly biodegradable polymer [4]. It has a hydrophilic lactam structure as a side group and a hydrophobic carbon chain as the backbone. Therefore, PVCL has good solubility in both polar and non-polar solvents [5].

PVCL is suitable for applications such as aerosol sprays, pump sprays, and lotions. Furthermore, PVCL is a biocompatible polymer due to its stability against hydrolysis and is suitable as an environmentally friendly flocculant. PVCL is used as a binder for toxic substances such as phenols in wastewater treatment plants [6].

Pyrolysis-gas chromatography/mass spectrometry (Pyr-GC/MS) is a common technique used in polymer science to analyse the chemical composition of polymers. The only study presenting ecological data on water-soluble polymers in an aqueous medium was performed by Antic et al. [7]. Pyrolysis of commercial PVCL, of spiked water samples as well as of wastewater samples was performed in a tube furnace at 550 °C under a continuous nitrogen flow. GC/MS was used for identification of specific degradation products, while GC-FID analysis was performed for quantitative determination. The concentration of PVCL was calculated on the basis of one of the main pyrolytic product, ε-caprolactam. Spiked water samples, wastewater samples were pre-extracted with hexane and diethyl ether prior to pyrolysis.

The application of the developed method on real environmental samples revealed that PVCL was present in effluents from wastewater treatment plants in concentrations around 4.01 mg/L.

Acknowledgements

This study was financially supported by DFG (Grant No. SCHW750-25)

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Air Pollutants Released by Heating Plants in the City of Užice

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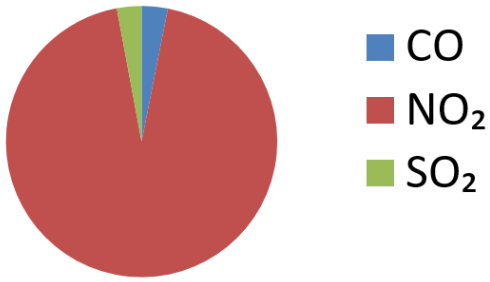

Figure 1. Ratio of mean concentrations of air pollutants

Air quality monitoring plays a crucial role in keeping the environment healthy. It is aimed at controlling and detecting air pollution levels in urban and industrial areas, and represents an essential precondition for taking concrete measures to reduce the quantity of harmful substances in the atmosphere and their impact on global warming.

The geographic position of the City of Užice is quite unfavourable. The city centre is densely populated, and there arenumerous home furnaces using less environmentally-friendly fuels (wood, coal, oil, heavy oil, etc.), but most of these pollutants lack gas emission control systems. In the winter months, due to the unfavourable weather conditions (low temperatures, lack of wind and precipitations), the concentration of air pollutants cumulativelyrises over a longer period [1]. Poor-quality fuels and old furnaces with incomplete fuel combustion further increase the adverse effects on air quality. In the Republic of Serbia, the greatest sources of nitrogen and sulfur oxides belong to the Energy Production and Distribution category [2].

The concentrations of air pollutants were measured at a heating plant (in a boiler room). The heating plant is located in a separate building downtown, and there are three natural gas boilers there, which are in use during the period from October to April. The boilers are set to the automatic mode, i.e. once the high limit set point is reached, the boiler automatically turns off. The temperature keeps falling until it reaches the low limit set point, when the boiler automatically turns on and the temperature rises again up to the high limit set point, thus ending a cycle. All the boilers use feed water.

In the midst of the heating season, in December 2018, in a single day, three measurements were performed at 30-minute intervals on the smoke tube of a boiler.

The emissions of carbon monoxide (CO), nitrogen oxides (NO2) and sulphur oxides (SO2) were monitored using the portable HORIBA PG 350 SRM gas analyser with the waste gas sampling and conditioning system. The waste gas temperature ranged between 142 and 147°C, whereas the waste gas volumetric flow rate ranged between 7825 and 7939 Nm3/h. The mean mass concentrations of CO, NO2 and SO2 were 3.1 mg/m3, 1121 mg/m3 and 3.4 mg/m3 respectively. The ratio of mean concentrations of the examined gasses is shown in Figure 1.

Even though there is a serious concern about the air quality in the City of Užice, the measured concentrations fall within legal limits: GV NO2 = 200 mg/m³, GV SO2 = 35 mg/m³ and GV CO = 100 mg/m³ [3].

The results indicate that the gasification of heating plants and home furnaces is necessary as they have a significant impact on the air quality in the City of Užice.

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Particle Pollution of Children's Playgrounds in the City of Novi Sad

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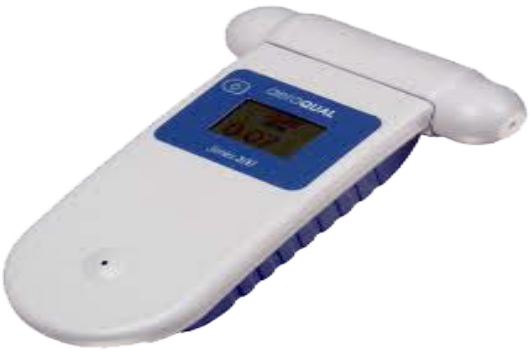

Figure 1. Aeroqual monitor

Recreation in the general anthropological sense is a special human activity, which contributes to the development and preservation of physical and mental health, maintaining vitality, quality of life, rest, and pleasure. All that can be relaxed, rested, and revitalized for children today is play in certain locations in the city - children's playgrounds.

Playgrounds and their position concerning major roads in real systems can serve to determine the optimal model in clarifying the origin of pollutant emissions and their interaction, indicating the need to determine the interdependence of the present pollutants and time of measuring. For this reason, three children's playgrounds in Novi Sad, in different parts of the city and, the area of different traffic frequencies were selected. Playgrounds are generally located in a green, parks, or an environment similar to parks. As awareness of air pollution and its effects, especially on children, grows, so does the pressure on city governments to establish an effective and coordinated response. To begin with, the first and most logical action is to measure individual pollutants in the air. City governments can select air quality information from state supervisory stations. However, supervisory stations are generally remote and do not present local sources of pollution and micro-climate effects, and often do not report current changes in air pollution or provide alerts if pollution levels suddenly rise. Therefore, relying on air quality information produced from state monitoring stations may lead to one of two options:

A) to underestimate the problem of children's playgrounds, or

B) goes beyond the problem of playgrounds.

Accordingly, the object of this research is to evaluate the quality of air in children's playgrounds and their immediate surroundings based on an indicative measurement of particulate air pollution.

At each playground, 10 particulate pollution measurements (particle sizes 2.5μm and 10μm) were made in 2018 using an Aeroqual monitor [1] with a laser particle counter, Figure 1. The measurement results indicated a slight variation in the concentration values: for $PM_{2.5}$ particles of 26-30 μg/m^3 and PM_{10} particles between 28 μg/m^3 and 30 μg/m^3. However, these values are still within the permitted range, so it can be said that the air was moderately clean [2]. According to the Regulation on Monitoring Conditions and Air Quality Requirements [3], the limit value for the mean daily concentrations of PM_{10} is 50 μg⁄m^3 and the annual 40 μg⁄m^3. This phenomenon is possible, given that the temperature and humidity of the air during the measurement were low, 17 - 18^{o}C, and 47 to 49%, respectively.

City administrations considering the future of children view particulate air pollution monitoring at the site of exposure - children's playgrounds as an opportunity to protect the young lives for which they are responsible.

Acknowledgements

The authors thank the financial support of the City Environmental Protection Administration, Novi Sad, Republic of Serbia, within the project number: VI-501-2 / 2018-18B-15.

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GC-MS Analysis of Essential Oils From Liverworts. Comparison of Extraction Methods of the Volatile Components

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Secondary metabolites are natural products resulting from metabolism that are not essential for normal growth, development or reproduction of the plant or organism. These plant constituents have diverse biological properties from an evolutionary point of view which go back to ancient times [1]. Plants produce volatile organic compounds (VOCs) in various tissues against the stresses to which they are exposed e.g. against herbivores, plant viruses, pathogens, temperature, humidity, shelf life, etc.. VOCs can be produced during the plant's physiological activities such as plant development, seed formation and germination, pollination and fruit ripening. These compounds are synthesized in all parts of plants, especially flowers, fruits, roots, xylems and cells, and while they can be effective in the tissues they produce, they can be transferred to other parts of the plant and exert their effects there [2]. Over the past few decades, the approach to studying biologically active natural products has changed so much that it can be said that a new science has been born [3].

Liverworts are small spore-forming plants with simple morphological organization. On the other hand, many liverwort species demonstrate wide geographical distribution and grow under diverse ecological conditions. Because of this, the identification of these plants is especially challenging. One of the outstanding features of the liverworts is their chemistry. They produce a wide array of secondary metabolites, mainly terpenoids and aromatic compounds. Many of these compounds are characterized by unique structures, and some have not been found in any other plants, fungi, or marine organisms [4,5].

In this paper, comparison of the volatile components composition in the samples obtained by hydrodistillation in Deryng apparatus and Head Space Solid-Phase Microextraction (HS-SPME) of liverworts was described. Different sample preparation techniques showed considerable differences in volatiles composition, especially with respect to sesqui- and diterpenoids. The composition of the essential oils of liverworts obtained by hydrodistillation were investigated by means of GC-MS analysis. Despite the fact, that the major components in all analyzed samples were the same the relative amounts of the individual components varied. The major differences concern especially sesqui- and diterpenoids composition in the essential oils received after hydrodistillation and volatiles extracted by HS-SPME.

Acknowledgements

The work was supported by grant no. POWR.03.02.00-00-I020/17 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development. This work was partly supported by a grant National Science Centre no. 2017/27/B/NZ8/01091.

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Hyphenated Techniques in the Study of Lead and Cadmium Species in Herbs

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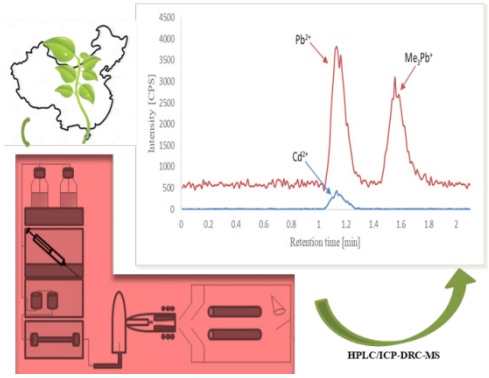

Speciation analysis of samples of Chinese herbs requires the use of selective and sensitive methods, because cadmium and lead and their compounds, even in low concentrations, cause toxic effects in living organisms. The implementation of the determination of lead and cadmium in the form of speciation complex matrix, which are plant tissues, a combination of two different techniques, one of which serves to separate species and the second identifies them qualitatively and provides information about the quantities of analytes in samples [1]. The current state of knowledge indicates that providing data on only the total content of a chemical element in a food sample is not sufficient. Toxicity and bioavailability depend not only on the dose and method of administration, but above all on the chemical form of the element, because not all lead species are equally toxic to the human body [2]. The major concept of the research was to develop and validate the sensitive analytical procedure that will allow the determination of possible/occurring speciation of lead and cadmium in samples of Chinese herbs. The object of research on the speciation of Pb and Cd was the roots, because earlier studies showed that these elements accumulate to the greatest extent in these parts of plants [2–5]. Thanks to the speciation analysis, it is possible to study the speciation of elements in the tested samples [6]. The samples analyzed include the following forms: Cd^{2+}, Pb^{2+} and $(CH_3)_3Pb^+$. Applying the advanced high performance liquid chromatography combined with inductively coupled plasma mass spectrometry equipped with dynamic reaction chamber – HPLC/ICP-DRC-MS for analysis of environmental samples such as the Chinese herbs, provided the results characterized by high sensitivity, low values of quantification and detection limits and high precision. These studies will be a source of information for the scientific discipline of analytical chemistry, environmental and food chemistry on the content of toxic forms of lead and cadmium in Chinese herbs, will enable routine testing of food with the same or similar matrix, and will contribute to the development of analytical techniques used when working with complex biological matrix.

Acknowledgements

The work was supported by grant no. POWR.03.02.00-00-I020/17 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development and the National Science Center in Poland, grant no. 2017/25/B/ST4/00374.

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Comparison of ICP-MS, ICP-OES, INAA, and WDXRF Techniques in Measuring Elements in Coniferous Needles Samples

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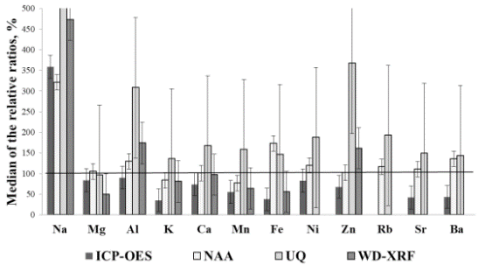

Fig. 1. Median of relative ratios.

The elemental composition of plant matrices has been conventionally determined by spectrometric techniques such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [1]. Wet mineralization (digestion) of samples requires time, equipment, and usage of aggressive and toxic chemicals which are the main drawbacks of those routinely used techniques [2].

The need for suitable analytical methods for direct and multi-elemental analysis of plant samples has been increased in recent years [3]. Instrumental Neutron Activation Analysis (INAA) is one of the techniques for direct analysis which has been previously applied in environmental studies, nevertheless it is not a commonly used technique for plant samples.

X-ray fluorescence (XRF) is another technique with the possibility of performing multi-element analysis directly on solid samples with numerous advantages.

Although non-destructive techniques (INAA and XRF) are widely accepted in various fields of screening tests regarding the analytical approach, their performance needs to be evaluated in plant sample analysis. The main aim of this research was to assess how reliable non-destructive techniques are in detecting elements in conifer needles regarding routinely used spectrometric techniques.

A total of 49 plant samples of four conifer species (*Pinus nigra*, *Abies alba*, *Taxus baccata*, and *Larix decidua*) were measured using two routinely used (ICP-MS and ICP-OES) and two non-destructive instrumental techniques (WD-XRF and INAA). A quality control program included NIST pine needles certified reference material (1575a) analysis using all examined techniques.

The techniques were compared by examination of relative ratio (element concentration measured using investigated analytical techniques divided by concentration determined by ICP-MS (figure 1)) and by correlation. Precision of all examined techniques was additionally investigated.

This study confirmed that non-destructive spectroscopic techniques can be successfully applied on plant samples since sample preparation for these techniques is fast and in good accordance with the principles of green chemistry. Investigated standardless XRF method can also produce well-correlated results, compared to other techniques based on calibration standards. Obtained results suggest that the high accuracy of the analysis can be ensured by additional analytical and quality control steps (the use of internal standards, standard addition, *etc.*).

Acknowledgements

This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-68/2020-14/200168).). A part of the research was supported by the project of bilateral cooperation between the Institute of Physics Belgrade and the Joint Institute for Nuclear Research, Dubna, Russia.

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Effect of Sample Preparation on Portable X-Ray Fluorescence Spectrometry Analysis of Contaminated Soils

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Toxic metals in soil are routinely determined by several analytical spectroscopic techniques (Atomic Absorption Spectrometry AAS, Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES,and Inductively Coupled Plasma Mass Spectrometry ICP-MS)[1]. Those techniques measure metals from aqueous samples. Procedures of sample dissolution or extraction typically involve a lengthy process which requires the use of harsh conditions. Sample preparation procedures make these routinely used techniques generally time-consuming and too expensive [2]. On the other side, the need for reliable, economical, and environmental friendly technique for soil composition measuring has been growing in the environmental field, so has the demand for time and cost-efficient analytical methods for soil analysis [3].

X-ray fluorescence spectrometry (XRF) is a multi-element analytical technique for direct, non-destructive analysis of various materials (including soils) with minimal sample preparation. The most attractive advantage of XRF is the wide dynamic range (from mg kg^{-1} to 100%). A portable X-ray fluorescence spectrometer (PXRF) is also capable of in-situ analysis in a short time (30–120 s) [4].

In situ PXRF analysis provides flexibility and allows rapid collection of data for a large number of samples, andproduces real-time data that can be used for rapid decision making. It is well-known that the physical characteristics of the sample play an important role in obtaining accurate results when it comes to XRF methods. Therefore it is important to determine how reliable in situ PXRF results are.

Analytical accuracy and precision could be generally improved if adequate sample preparation procedure is applied compared to in situ measurements.

The aim of this research was to determinate in what extent sample preparation procedure changes measured concentrations of elements and is that change the same for all investigated elements. Does soil sample homogenization or further pressing into the compact pellet systematically affect measured concentrations?

Soil samples from 32 industrial, potentially contaminated sites were collected from a depth of 10 cm, 30 cm, and 50 cm. Such soils provide wide concentration range of different elements. Samples were first directly analyzed in the field, without any sample preparation using the Thermo Scientific™ Niton™ XL3t GOLDD^{+} PXRF Analyzer. The second PXRF analysis was performed in the laboratory on the dry,ground, and homogenized soil powder sample. One aliquot of soil powder was digested for AAS analysis, while another aliquot was pressed into a 32 mm diameter pellet and analyzed using PXRF.

The quality control program involves comparison of the results with AAS reference technique. Additionally, certified reference materials of stream sediment (STSD-3) and soil (NCS DC 77301) are analyzed with different sample preparation procedures.

Acknowledgments

This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-68/2020-14/200168).

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Effect of pH Value on Di(2-Ethylhexyl) Phthalate Extraction Recovery from Synthetic Wine

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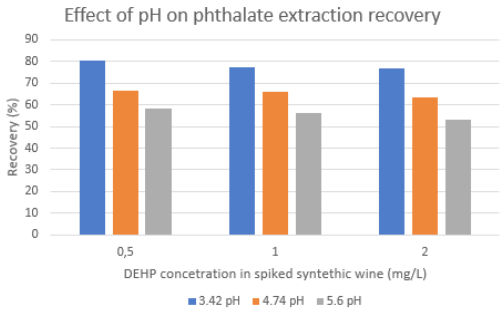

Phthalates are esters of phthalic acid with aliphatic and aromatic alcohols. Due to their chemical and physical properties, they can easily migrate into the environment, food and beverages. WHO recognized them as environmental contaminants which are commonly observed due to their widespread use as plasticizers [1]. Drinking water, beverages and alcoholic drinks can be contaminated by plastic equipment used during production or by migration from the packaging material [2]. Di(2-ethylhexyl) phthalate (DEHP) is considered as endocrine disruptor, being able to negatively modulate hormonal functions and pathways, interfering with estrogens and thyroid hormones [3]. The aim of this study was to investigate the influence of pH value on the DEHP extraction recovery from samples of synthetic wine.

Synthetic wine was prepared according to the instructions given in the literature [4]. Volume of 1 L of synthetic wine contained 15 v/v% solution of 96 v/v% ethanol and 6 g of tartaric acid (99.8%).

Samples of synthetic wine (10 mL) were spiked with phthalates by weighing 50, 100 and 200 µl of phthalate standard solution of concetration 100 µg mL^{-1}. Concentration of DEHP in the wine samples were 0.5 mg L^{-1}, 1.0 mg L^{-1} and 2.0 mg L^{-1}.

Extraction of DEHP from a 10 mL sample of synthetic wine was performed with 5 mL of *n*-hexane as the extraction agent. The pH value of the synthetic wine samples was varied before extraction and adjusted with 5 mol of L^{-1} NaOH to the following values: 3.42, 4.74, 5.60. Manual shaking and ultrasonic waves in the ultrasonic bath were used as the type of agitation, while the extraction time was 10 minutes.

All samples and calibration standards were analysed by gas chromatograph 6890 (Hewlett-Packard) equipped with a mass selective detector (MSD) 5973 (Agilent) and a DB-5 MS capillary column (30 m×250 mm×0.25 mm). The MSD was used in the single ion-monitoring mode (SIM). The identification and quantification of target compound was based on the relative retention time, the presence of target ions and their relative abundance. For quantification, peak area ratios of the analyte to the internal standard dibuthyl adipate (DBA) were calculated as a function of the concentration of substances. Linearity was investigated in the DEHP concentration range 0.1 – 10.0 µg mL^{-1}. The calibration curve for the range of 0.25 to 2.5 µg mL^{-1} was linear with a correlation coefficient (R^2) 0.999.

Obtained results indicate that the recovery value decreased from samples with pH value at 3.42 to 5.60. From the concentration point of view, obtained recovery values decreased with increasing of spiked concentration. The best recovery value was achieved with samples at the lowest spiked concentration (0.5 mg L^{-1}). The best recovery value (80.60%) was achieved from sample with the lowest spiked concentration (0.5 mg L^{-1}) and at the lowest pH value, 3.42. The lowest recovery value (53.14%) was achieved from sample with the highest spiked concentration (2 mg L^{-1}) and at the highest pH value (5.6).

Acknowledgements

This work received support from the Ministry of Education, Science and Technological Development of the Republic of Serbia under contract no. 451-03-9/2021-14/200124.

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Effect of Sugar Content on Di(2-Ethylhexyl) Phthalate Extraction Recovery from Synthetic Wine

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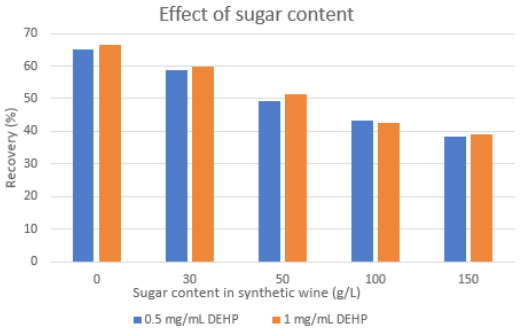

Phthalates (phthalic acid derivatives) are extremely widespread in our environment due to their commonly usage as plasticisers in many plastics and a wide range of products [1]. Phthalates are a class of endocrine disruptors and because of their migration ability, they can be found in foods and drinks [2]. Some of phthalates, such as di-[2-ethylhexyl]-phthalate (DEHP), are recognized as highly toxic compounds that can cause reproductive and developmental toxicity [3]. The aim of this study was to investigate the influence of sugar content on the DEHP extraction recovery from samples of synthetic wine.

Synthetic wine was prepared according to the instructions given in the literature [4]. Volume of 1 L of synthetic wine contained 15 v/v% solution of 96 v/v% ethanol and 6 g of tartaric acid (99.8%).

The influence of sugar content on the extraction of DEHP from wine was examined by changing the composition of wine by adding sugar. The sugar content in wine samples were 0, 30, 50, 100 and 150 g L^{-1}.

Samples of synthetic wine (10 mL) were spiked with phthalates by weighing 50 and 100 of phthalate standard solution with concentration at 100 µg mL^{-1}. Concentration of DEHP in the wine samples were 0.5 mg L^{-1} and 1.0 mg L^{-1}.

Extraction of DEHP from a 10 mL sample of synthetic wine was performed with 5 mL of *n*-hexane as the extraction agent. Manual shaking and ultrasonic waves in the ultrasonic bath were used as the type of agitation, while the extraction time was 10 minutes.

All samples and calibration standards were analysed by gas chromatograph 6890 (Hewlett-Packard) equipped with a mass selective detector (MSD) 5973 (Agilent) and a DB-5 MS capillary column (30 m×250 mm×0.25 mm). The MSD was used in the single ion-monitoring mode (SIM). The identification and quantification of target compound was based on the relative retention time, the presence of target ions and their relative abundance. For quantification, peak area ratios of the analyte to the internal standard dibuthyl adipate (DBA) were calculated as a function of the concentration of substances. Linearity was investigated in the DEHP concentration range 0.1 – 10.0 µg mL^{-1}. The calibration curve for the range of 0.25 to 2.5 µg mL^{-1} was linear with a correlation coefficient (R^2) 0.999.

Obtained results showed that sugar content in the synthetic wine samples effected achieved recovery value. In the range of sugar content from 0 to 150 g L^{-1}, there is decreasing trend in obtained recovery values. The best recovery (66.47%) value was achieved from samples without sugar content and 1 mg mL^{-1} spiked concentration, while the lowest recovery value was obtained for samples with the highest sugar content (150 mg L^{-1}). There is a slightly difference in recovery values for samples with different level of spiked concentration, and except for sample with sugar content at 100 g/L, all other samples showed better recovery for 0,5 mg mL^{-1} spiked level concentration.

Acknowledgements

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Speciation Analysis of Chromium in Mineral Fertilizers

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Chromium is a metallic element occurring in the environment mainly in the the form of compounds on the +III and +VI oxidation state [1]. Cr(III) is considered to be a trace element essential for proper metabolism of glucose, lipids and proteins in mammals, while Cr(VI) poses a threat to biological systems due to its mutagenic and genotoxic effects [2]. Cr(VI) compounds was classified by the International Agency for Research on Cancer as a Class I Carcinogen for humans [3]. Cr(III) and Cr(VI) differ in their physicochemical properties, and consequently chemical and biochemical reactivity. Cr(VI) compounds are generally very well soluble, mobile and bioavailable compared to poorly soluble Cr(III) compounds [4]. Therefore, for proper evaluation of the toxicological effects of chromium and its distribution and transport in the environment, it is necessary to determine not only the total content of this element in the sample, but also identification and determination its speciation forms. According to the Regulation (EU) 2019/1009 laying down rules on the making available on the market of EU fertilising products, the limit for Cr(VI) concentration in mineral fertilisers is 2 mg/kg.

Speciation analysis is a major analytical challenge in environmental studies due to the possibility of spontaneous processes of change chemical form of the analyte during transport, storage or sample preparation for analysis. This is especially important in the case of chromium occurring at different oxidation states, where the the contribution of its various forms depends on many factors, including pH and redox potential.

For extraction of Cr(VI) content from fertilizer samples, an alkaline extraction was applied. This consisted of 1.25 g of fertilizer being weighed into a 50 mL vessel and 25 mL extraction solution containing 0.5 $mol \cdot L^{-1}$ NaOH and 0.28 $mol \cdot L^{-1}$ Na_2CO_3 added. Then, 1 mL of 4 $mol \cdot L^{-1}$ $MgCl_2$ was added in order to prevent oxidation of Cr(III) during the extraction procedure, and 0.5 mL buffer solution of each 0.5 $mol \cdot L^{-1}$ K_2HPO_4 and KH_2PO_4. Cr(VI) analysis were performed using ion chromatography technique with UV-Vis detection based on post-column derivatization with 1.5-diphenylcarbazide at 540 nm and UV-Vis spectrophotometry. The accuracy and the precision of the proposed procedures were evaluated by analysing the certified reference materials: SRM 2700 (NIST) with certified Cr(VI) content (14.9±1.2 $mg \cdot kg^{-1}$) and CRM 041 with certified Cr(VI) content (148±2 $mg \cdot kg^{-1}$).

Total Cr content was determined by ICP-OES technique after microwave digestion in closed system, using a mixture of HNO_3 and HCl.

Acknowledgements

The project is co-financed by the National Centre for Research and Development of Poland within BIOSTRATEG Programme under Grant No. BIOSTRATEG3/347464/5/NCBR/2017.

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n-Alkanes as a Forensic Tool in Assessing the Origin of Leveling Material Typically Used in Archaeological Site Vinča – Belo Brdo (Serbia)

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Fig. 1. Archaeological site Vinča – Belo Brdo. Sampling locations. Pottery found at the sampling site.

One of the world-famous archeological sites on the territory of Serbia is Vinča – Belo Brdo, the type-site of the Vinča culture, which dominated the cultural sphere of the Central Balkan area around 7000 years ago. Archaeological layers that are several meters in height are the dominant landscape feature seen from the Danube River, and alot of archaeological remains have been excavated in this part of the site. The absolute dates of this Vinča sequence confirmed the occupational span of the site of ca. 800 years [1].

On the vertical profile of the site some clear units are visible, among them archaeological layerscontaining the destroyed buildingsand the overlaying leveling layers, which are typical for this locality. There is a decades-long dilemma about the origin of this levelling material, which is most probably brought by local inhabitants to cover the destroyed and/or burnt remains of houses, clearing the areas for a new settlement.

This study aims to help in resolving this dilemma using an organic geochemical approach which is based on *n*-alkane distribution. Five samples originating from the leveling layers and four samples, that in the archaeological context mark the house, were investigated. The analysis included isolation and characterizationof *n*-alkanes fromsoluble organic matter (OM) using the usual procedure [2]. The main objective of this work was to determine and compare the origin of the OM between different settlement layers where houses from the early Neolithic were located, and particularly the overlaying leveling layers.

In archaeological samples, OM was predominantly formed by microorganisms, with a certain contribution of terrestrial plants. The distribution of *n*-alkanes in those samples showed the prevalence of short-chain *n*-alkanes with a maximum at *n*-C_{18}, which could be explained by thermal degradation of biomass during fire [3]. On the other side, organic-geochemical parameters for the leveling layers indicateda significantly higher amount of OM and an odd-over-even predominance among long-chain *n*-alkanes showing avery similar composition as the oldest geological layers that are the basis of this locality [2]. These results contributed to resolving the dilemma about the origin of leveling material typical for the Belo Brdo site confirming the theory that the leveling material was excavated at a site in their vicinity and used for covering the burnt debris.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Grant No.451-03-9/ 2021-14/200026).

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Degradation of PLA in Sewage Sludge and Methods of its Determination

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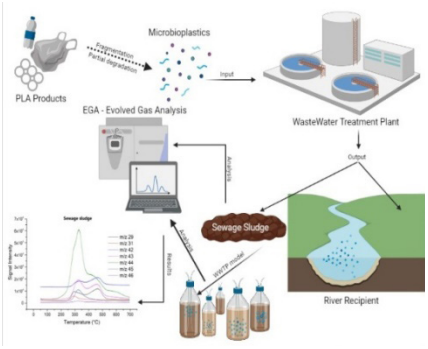

Because pollution by plastics was declared as one of the most critical environmental problem of our time, to mitigate the environmental impact, plastics are slowly being replaced by bioplastics in many applications. Bioplastics are considered to by polymeric materials that comes from renewable sources, are recyclable and/or biodegradable. However, the biodegradation of bioplastics is largely dependent on both the material itself and the environment in which the biodegradation takes place and therefore complete degradation often occurs only in industrial composts. In the environment only partial degradation and/or fragmentation of bioplasts into micro and nanoplastics occuresaster than is common with conventional plastics [1,2]

In the case of microplastics (MPs) contamination, wastewater treatment plants (WWTPs) represent the link between the natural and anthropogenic water cycle. WWTPs are considered to be MPs receptors from domestic and industrial wastewater. As the technological line of wastewater treatment was not adapted for treatment of MPs from wastewater, WWTPs were identified as a potential main source of MPs in aquatic environment. In the anthropogenic water cycle, MPs are found mainly in wastewater and inflows and outflowes of WWTPs [3

PLA is a biodegradable polymer that is increasingly found in wastewater in the form of MPs. As there is still no information about what happens to PLA when it goes through the whole process of wastewater treatment, the aim of our work is to determine whether PLA undergoes complete or only partial decomposition and develop reproducible methods of PLA analysis in complex matrices such is sewage sludge. To study PLA in sludge, we use WWTP in laboratory scale, with which we simulate the conditions of WWTP. The amount of PLA is then determined in the dried sludge by pyrolytic method, i.e. evolved gas analysis (EGA). The fact that the EGA can be used for determination of PLA has already been demonstrated by an previous experiment in which we proceeded similarly to that reported by David et al [4]. The dried sludge (matrix) was spiked with PLA to create concentrations in range of 0,1% - 5,0%. By analyzing these samples, the characteristic molecular weights *m/z* were determined for PLA, which can be used for both qualitative and quantitative analysis. This work will provide the necessary information on the biodegradation of PLA in sewage sludge, which is needed as PLA gradually replaces conventional plastics in many industries. It can be assumed that their widespread use over time will cause an increased concentration of PLA microplastics (microbioplastics) in the inflow to the WWTP.

Acknowledgements

The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2018124 and financial support of project FCH-S-21-7398.

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Research of Methods for Poly(3-Hydroxybutyrate) Biopolymer Quantification in Soil Matrix and Soil Leachate

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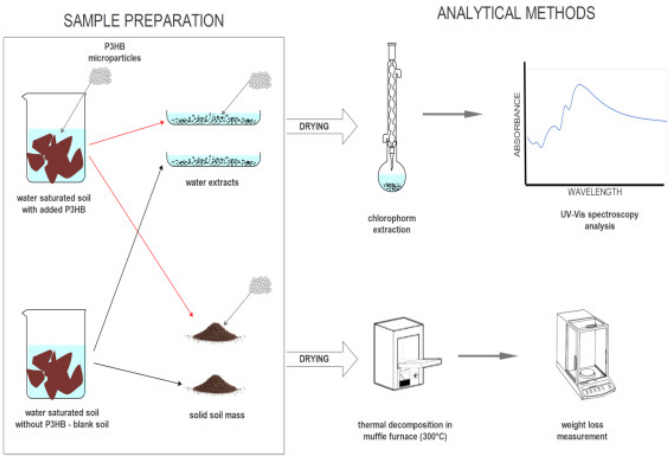

Gradual increase of microplastics (MPs) in soils has become an emerging environmental concern, which deserves public attention. In spite of many scientific publications contributing for better knowledge of microplastic fate in the soil system, there is still lack of data to properly understand the transport mechanism and interaction of MPs in the soil matrix [1]. In recent years, bioplastic poly(3hydroxybutyrate) (P3HB) has become a new potential threat for the soil ecosystem due to its imperfect biodegradation pattern, which may lead to abundance of P3HB microparticles in soil [2,3]. Up to now, there is no validated scientific method used for the proper quantification of P3HB content in the soil matrix, neither good knowledge about the interaction and the transport processes of P3HB microparticles in the soil matrix.

The aim of this study is to develop a method for quantification of P3HB content in soil and water extracts. We have been developing two simple analytical methods. First method is based on chlorophorm extraction followed by UVVis spectroscopy. Second method is based on thermal decomposition of P3HB in the soil (300 °C) by using muffle furnace. As it has been shown in the pilot experiments, these methods seem to have promising results for the quantification of P3HB content in soil.

The main output of this poster is to provide knowledge about the instrumentalization and validity of our given methods.

In the future prospects, these given analytical methods can play an important role in the instrumentalization of soil column experiments, which will give new data to determine transport mechanisms of P3HB MPs in the soil profile.

Acknowledgements

The financial support of project FCHS217398 of Ministry of Education, Youth and Sports is acknowledged.

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Comparative Study of Removal Efficiency for Ni and Cd from Industrial Wastewater and Aqueous Solution by Sunflower Husk Using ICP-OES and LIBS

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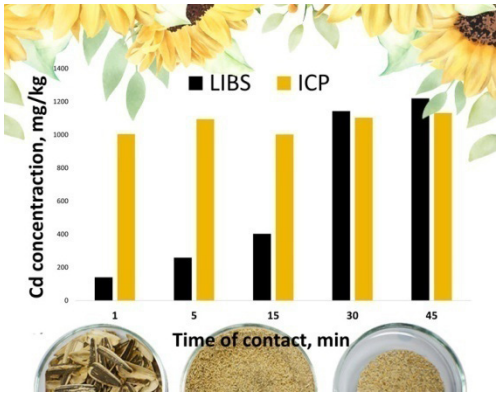

With the growth of the industrial world and the rise of anthropogenic activities, environmental challenges have also increased. Wastewater, especially from industrial sources can contain a wide variety of heavy metals [1]. The presence of heavy metals in water resources is a cause for concern due to their toxicity and tendency to bioaccumulation, which leads to significant problems for the environment as well as for animals and humans [2]. There are various conventional treatment technologies that are used for the removal of heavy metals from wastewater such as reverse osmosis, electrodialysis, ultrafiltration, industrial ion exchange process, and chemical precipitation. These techniques have some drawbacks such a being expensive due to high reagent and energy requirements, incomplete metal removal at low concentrations of heavy metals and generation of sludge [1]. Therefore, biosorption has been the subject of research by scientists for almost 70 years in order to find efficient, effective, and low-cost biomaterials for wastewater treatment [3]. In this study, a sunflower husk treated with 1% hydrochloric acid was used to evaluate removal efficiency for Ni from real wastewater samples, as well as to estimate the adsorption capacity as a function of contact time between the heavy metal ions such as Cd in the aqueous solution and the sunflower husk as a biosorbent. Two techniques were used for quantitative analysis, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) as a standard reference method and laser-induced plasma spectroscopy (LIBS) as an innovative non-standard analytical method. What makes the LIBS superior from the other standard optical techniques is that it allows fast multi-elemental analysis without prior sample preparation, leads to minimal sample damage, and is considered almost non-destructive, this method is also by the principles of green analytical chemistry, which means that it does not use toxic reagents and therefore no chemical waste [4]. The results of these two methods were compared, to examine the possibility of using laser-induced plasma spectroscopy as an alternative green analytical technology for quantitative analysis of sunflower husk as a biosorbent and evaluation of biosorption efficiency as a function of contact time.

Acknowledgments

Authors thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for the financial support to the research through institutional funding (Contract number 451-03-9/2021-14/200017).

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Green Analytical Method Selection for Analysis of Soil: LIBS vs XRF

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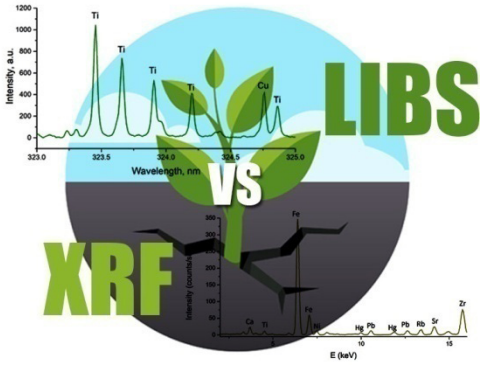

X-ray Fluorescence (XRF) is the most commonly used non-destructive method offering the user a portable handheld analyzer that delivers fast, accurate results. On the other hand, in the past two decades, with recent advances in laser technology,laser-induced breakdown spectroscopy (LIBS) becomes a more and more popular analytical method for the analysis of solid samples. The ability to provide a fast and multielement analytical response directly from a solid sample makes both LIBS and XRF very versatile tools for soil analysis [1]. Both methods have their advantages, however, in certain circumstances, one is better to use over the other. This paper focuses on the analytical capability of both methods for soil quality management. The main LIBS advantage against XRF is that it can be used for detection of all elements of the Periodic Table, including light elements (C, N, O, S) important for estimation of soil quality [2].

For this paper, 2 samples of soil were used. A real sample was collected in the INS Vinča and certified reference material Metals in Soil obtained from Sigma Aldrich were used for these experiments. A real soil sample was dried at 70°C, homogenized, and sieved using a 100 mesh sieve. Single element calibration standards of Cu, Hg, Ni, Pb, and Cd from J.T. Baker were used for standard addition samples preparation [3]. To homogenized sample portions of fixed mass (5 g) varying amounts of certified standard analyte solutions are added, and the mixture is diluted with 20 ml deionized water. Mixtures were homogenized and dried at 70°C overnight. The obtained powdered materials were used for the preparation of pressed pellets, including the CRM sample. All samples were analyzed by a unique TEA CO_2 based LIBS setup developed in INS Vinča and commercially available Niton XL3 handheld XRF analyzer, Thermo Fischer Scientific.

The precision and accuracy of the LIBS method were evaluated and compared to those obtained by XRF. The preliminary results showed that limits of detection for most of the investigated elements are comparable or better than those obtained with XRF.

Acknowledgments

Authors thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for the financial support to the research through institutional funding (Contract number 451-03-9/2021-14/200017).

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Acid-Base Characterization of Humic Substances in Environments of Variable Salinity: A Case Study of the Nerbioi-Ibaizabal Estuary

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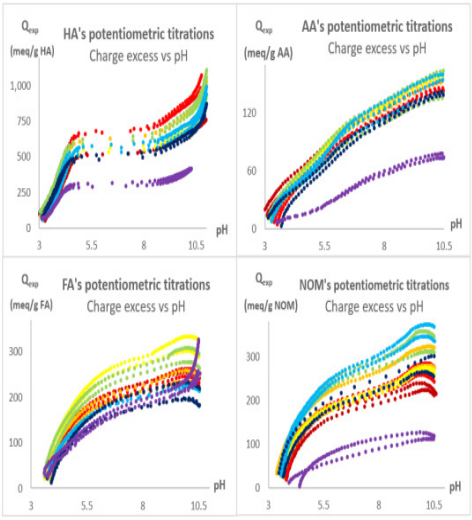

The ability of humic substances to form stable complexes with heavy metals could cause the mobilization, and even the removal, of these persistent pollutants, still present in the sediments of the Nerbioi-Ibaizabal estuary. Thus, the aim of the present work was to study autochthonous humic substances' acid-base behavior as a first step in the investigation of their metal complexing properties. With that aim, several methodologies for the determination of total acidity and for the characterization of the proton binding sites were investigated, employing as samples humic acids isolated from the estuary's sediments (HA), as well as several standards: humic acid purchased from Alfa Aesar (AA), and fulvic acid (FA) and natural organic matter (NOM) obtained from the International Humic Substances Society (IHSS). The classical characterization of the total acidity by potentiometric titrations [1] revealed values of 11.0 ± 0.2 mmol OH^-/g for AA and 15.8 ± 0.5 mmol OH^-/g for HA, in contrast to the 4.3 ± 0.7 mmol OH^-/g AA and 16.7 ± 2.4 mmol OH^-/g HA recorded through conductimetric titrations [2] with $Ba(OH)_2$, and 2.4 ± 0.3 mmol OH^-/g AA using NaOH as titrant. Regarding the characterization of the proton binding sites, acid-base potentiometric titration data were collected at different ionic strengths. Principal Component Analysis (PCA) of the recorded buffering capacity disclosed two different kinds of binding sites for HA, three for FA and NOM, and four for AA; the same number of sites were determined when data were fitted to the fully optimized continuous pKa spectral (FOCUS) model [3], which offered the possibility to include multiple sites. The IHSS's model [4], nevertheless, only considers two different kinds of ionizable groups, carboxylic and phenolic, which led to a higher uncertainty in the pKa values for the compounds with higher diversity. Ionic strengths in the range of 0.01-0.75 mol/L NaCl demonstrated to have a noticeable impact on the acidity constants for all the substances, whose behavior was successfully modelled using an extended Debye-Hückel type of equation [5]. The identification of the main chemical groups was also assayed using spectroscopic techniques, such as Ultraviolet-Visible (UV-Vis), Fourier-transformed-Infrared (FT-IR) and fluorescence. These revealed the presence of both carboxylic and phenolic groups, and no impact of the ionic strength in the structure, as expected; the pH, on the other hand, only seemed to have effect on the intensity of the peaks.

Acknowledgements

This study was supported by the University of the Basque Country (UPV/EHU) and Dr. Abul Hussam is acknowledged for his advice with the FOCUS model.

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The Anions Profile as an Important Property of Soil in European Beech Forests

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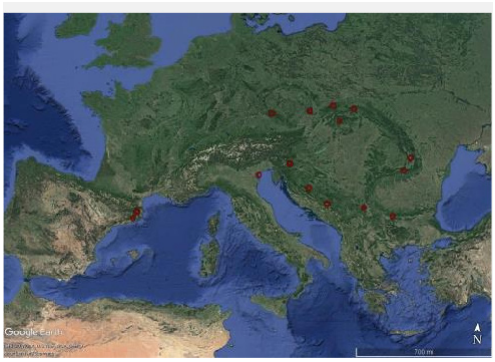

Figure 1. Soil sampling sites across Europe.

As the forests decrease in their size and quality, the forest ecosystems, as well as the ecosystems services and climate also change. Hence many of the animals and plants are relocated or brought into jeopardy of distinguishing. Directly and indirectly climate changes affect the growth and productivity of forests through changes in soil properties, temperature, draught, atmospehric falls and other factors. The effects of climate change on soils are expected mainly through alteration in soil moisture conditions and increase in soil temperature and CO_2 levels [1]. These changes influence complex forest ecosystems since concentration of soil organic carbon, nitrogen cycles, water and nutrient retention, filter functions and erosion control are also affected.

The hustle enviroment lead to forest extiction due to changes in the formation and conservation of soil structure, available water-holding capacity, soil nutrient cycling, and soil biodiversity transport of nutrients. The forest trees slowly extinct, decompose and change nitrogen cycles, content of organic carbon and other factors that influence the rest of forests ecosystems.

In this study, the most abundant anions of European beech forest soils were investigated due to their specific roles in forests ecosystems. The carbonate and sulfate play important role in soil structure, water holding capacity and soil density. On the other hand, phosphate and nitrate ions can be regarded as markers of undisturbed forest ecosystems. The chloride is relatively uninvolved in neither biological nor inorganic chemical reactions [2]. Leaching in forest soils is limited by physco chemical reactions and roots needs.

The framework of this study is to develop adequate database of forest ecosystems, and their response to climate change. This will involve analysis of physicochemical properties, anion and elemental composition. For that purpose, 80 soil samples from 15 soil profiles (0-10 cm, 10-20 cm, 20-40 cm and 40-80 cm) were collected from beech forests of Spain, Czech Republic, Slovakia, Germany, Poland, Romania, Serbia, Italy, Bosnia and Herzegovina and Slovenia (Figure 1). Dionex ICS 3000 was used for anion analysis. The obtained results pointed out relatioship of sulfate and carbonate according to the soil type, while others anions did not exhibit such behavior. Climate change leads to leaching of basic cations which leaves the soils more acidified and this can be even more severe in soils containing high concentrations of sulfates [3]. The database of the major anion profile can be used for building apropriate model for assessing and predicting the effects of the climate changes on forest ecosystems The outcomes of this study will be compiled with the research conducted on pollution induced and climate change effects regarding aquatic, atmospheric and terrestrial systems, which will be operationalized in a geo-spatial and temporal forecasting model. The obtained models may be used as screening techniques for predicting the environmental stress caused by climate change in forest mountain regions.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Grant No. 451-03-9/ 2021-14/200026 and 451-03-9/2021-14/ 200168) for financial support.

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Micro Liquid-Liquid Extraction-Gas Chromatography-Mass Spectrometry Method for the Analysis of Bisphenol A in River Water Samples

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Figure 1. The mouth of the river Švrakava in Vrbas (Banja Luka, Bosnia and Herzegovina)

The presence of certain chemicals in the environment, such bisphenol A (BPA) can adversely affects human health by damaging the endocrine system. BPA (4,4'-dihydroxy-2,2-diphenyl propane) can interact with specific receptors and therefore interfere with the hormonal action of human cells. BPA is a chemical synthesized worldwide with over 5.5 million tons per year and is defined as one of the endocrine-disrupting compounds (EDCs) [1].

BPA is known as a monomer for the synthesis of polycarbonate plastics, epoxy, and polyester resins, and it is also used in the production of thermal paper. Consequently, it can be found in materials used to produce CDs and DVDs, baby bottles, containers for beverages and foods, toys, and medical devices. Traces of BPA can leak from these materials leading to releases to the environment and causing pollution.

Some studies have shown that the BPA is mainly found in water, soil, and sediments [2]. The primary sources of BPA in the aquatic environment are domestic and industrial wastewater and runoff from agriculture [3]. It has been found that the presence of BPA in the aquatic ecosystem may have a potentially harmful influence on the reproductive system and metabolic processes of organisms such as fish and mussels. Furthermore, it has been reported that human exposure to BPA could cause several health issues, including various types of cancers, obesity, cardiovascular and neurodegenerative disorders [4].

The bisphenol A (BPA) concentration was determined in 12 surface water samples of the Vrbas River and its five tributaries. The samples were taken in the area that belongs to the city of Banja Luka (Bosnia and Herzegovina). BPA was isolated using micro liquid-liquid extraction followed by derivatization and gas chromatography-mass spectrometry analysis (GC-MS). Silylation was used as a derivatization method to increase volatility and allow GC-MS determination of BPA. The limits of detection (LOD) and quantification (LOQ), obtained by confirming the procedure, were determined at 4 and 10 ng L^{-1}, respectively. The concentrations of BPA were ranged between 33 and 354 ng L^{-1}, and all were above the LOQ value. The lowest amount of BPA was found in the sample collected in the river Vrbas near Švrakava estuary upstream from the city of Banja Luka. The highest concentration of BPA was recorded at the confluence of the Crkvena and Vrbas rivers, which is located in the city center. This study shows that population and human activity could affect the level of BPA in the environment, and therefore constant monitoring of the concentration of this compound is required.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract No: 451-03-9/2021-14/200116).

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Occurrence and Transformation of Antiviral Drug Umifenovir (Arbidol) in Municipal Wastewater

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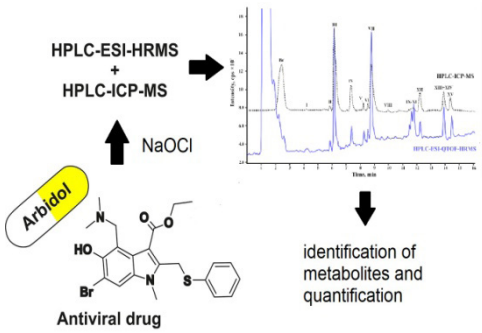

Introduction

Umifenovir (trade name Arbidol) is one of the most used medical antiviral drugs in Russia and several other countries during the COVID-19 pandemic.

The study proposes an original combination of HPLC-HRMS and HPLC-ICP-MS methods to study the ongoing transformation processes of umifenovir during disinfection and oxidation with atmospheric oxygen.

Materials and methods

The chemical composition of by-products formed during the oxidation of umifenovir in model experiments was established by HPLC-HRMS. An HPLC-ICP-MS method was used for quantitative standard-free analysis based on data on the elemental compositions of target analytes.

The developed approach was used to study samples of wastewater and sediments at a municipal wastewater treatment plant and river accepting the treated wastewater.

Result and discussion

An HPLC-HRMS method revealed 14 by-products of umifenovir transformations, which are formed during model chlorination and oxidation by atmospheric oxygen. Their elemental compositions were determined, and structures were proposed. The study showed that the dominant process in umifenovir chlorination is the oxidation of sulfur-containing moiety. The simultaneous use of both mass spectrometry detection methods demonstrated a significant advantage, based on the absence of the need to use standard samples for each of the detected by-products of umifenovir oxidation. As a result, the concentration of each by-product was determined under various parameters of model experiments (pH values, active chlorine concentration, chlorination or oxidation time). It was found that the reaction proceeds very quickly, thus it is impossible to estimate the reaction kinetics. The pH value affects the displacement of the equilibrium towards the formation of certain products, but their component composition does not change.

Arbidol and several by-products of its transformation have been found in real environmental objects. The content of arbidol in bottom sediments at treatment facilities was 1260 ± 80 μg kg^{-1}, and the concentrations in water at the stage of rough cleaning and chlorination were 780 ± 50 and 460 ± 30 ng L^{-1}, respectively.

Conclusion

The original combination of HPLC methods with detection in the HRMS and ICP-MS mode opens up great prospects for the search and identification of new bromine-containing disinfection by-products, as well as for assessing their content in complex matrices without the use of certified standard samples.

Analysis of real objects demonstrates the possibility of secondary pollution of ground and surface waters, due to the ability of umifenovir and its transformation products to accumulate in activated sludge at treatment facilities and bottom sediments of natural water bodies.

Acknowledgements

This research was performed using instrumentation at the Core Facility Center "Arktika" of the Northern (Arctic) University and was supported by the Russian Science Foundation (grant No. 21-13-00377).

Volatile and Semi-Volatile Organic Pollutants in Russian Arctic Atmosphere: Marine Field Study 2020

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Introduction

The study of the chemical composition of the Arctic air and its temporal trends is an important task. Its solution contributes to a deeper understanding of chemical pro-cesses in the atmosphere of the polar regions, their impact on climate change and the state of the ozone layer, as well as the assessment of risks for Arctic ecosystems and human health. Nevertheless, the currently available literature data on the chemical composition and levels of atmospheric pollutants at high latitudes are notably incomplete. The purpose of the work involved obtaining up-to-date data on the levels of a wide range of VOCs and SVOCs in the atmosphere of the Russian Arctic.

Air sampling and analysis

The advanced technique of thermal desorption gas chromatography - high-resolution mass spectrometry (TD-GC-HRMS) with an orbital ion trap (Orbitrap) mass analyzer providing exceptional sensitivity and selectivity of the analysis was used. Air sampling was carried out at 16 points along the mainland coast, covering the entire Russian sector of the Arctic from the White Sea to the East Siberian Sea. Approximately 2 L of air was pumped at a rate of 50 mL/min through a preconditioned stainless steel three-bed sorption tubes packed with Tenax TA, Carbograph 1TD, and Carboxen 1003 sorbents. One hundred and thirty-eight VOCs and SVOCs included in EPA methods 8260B and 8270 were chosen as target analytes.

Result and discussion

The combination of sorptive preconcentration of analytes with the use of Orbitrap high resolution instrument provided an exceptionally high sensitivity of the analysis. Typically, the obtained LODs lied in the range 1–100 pg on tube or 0.5–50 ng/m^3 in air. Out of 138 analytes, only 52 were not detected in any sample. The number of com-pounds that could be quantified in particular samples varied from 26 to 66.

Among VOCs, representatives of three groups of compounds were detected - halogenated aliphatic hydrocarbons (alkanes, alkenes), aromatic hydrocarbons, and their halogenated derivatives. The first two groups were predominant and their representatives (the major one is Freon 113) were found in comparable quantities (for most samples 1–36 μg/m^3). As expected, aromatic hydrocarbons were mainly represented by BTEX group: benzene (0.08 - 5.9 μg/m^3), toluene (0.07–3.1 μg/m^3), ethylbenzene (0–8.2 μg/m^3), as well as xylenes with typical concentrations of tenths μg/m^3. Surprisingly, not a single priority VOC with O, N, or S atoms was detected in any of the collected samples.

The SVOCs found in the studied air samples can be conditionally divided into 5 groups: CHO-compounds, N-containing compounds, halogenated compounds, PAHs, and phthalic acid esters (phthalates). Benzoic acid was the dominant SVOC. Among the nitrogen-containing compounds only pyridine was detected in noticeable concentrations (0.010–0.22 μg/m^3). The most common representatives of phthalates were bis-(2-ethylhexyl) phthalate, di-n-butyl phthalate, and diethylphthalate. Polycyclic aromatic hydrocarbons, with the exception of the six most hardly volatile compounds, were found in the majority of the collected air samples in concentrations comparable to phthalates (units of μg/m^3). Naphthalene and its methylated derivatives were detected in the highest concentration. The last SVOC group, which includes halogenated compounds, was represented mainly by 2-chlorophenol, as well as some other chlorophenols in trace concentrations.

Conclusion

The first reliable dataset so far dealing with the levels of volatile and semi volatile organic priority pollutants in the White, Barents, Kara, East Siberian, and Laptev Seas was obtained. Although the concentrations of the majority of analytes were several orders of magnitude below the established safe levels, xylenes, ethylbenzene and phenol require special attention in future demonstrating the levels comprising 15%, 40% and 60% of the safe values correspondingly.

Acknowledgements

This research was supported by the Ministry of Science and Higher Education of the Russian Federation (project No. 0793-2020-0007).

Transformation of Organic Substances in the Environment and Under the Influence of Chlorinating Agents

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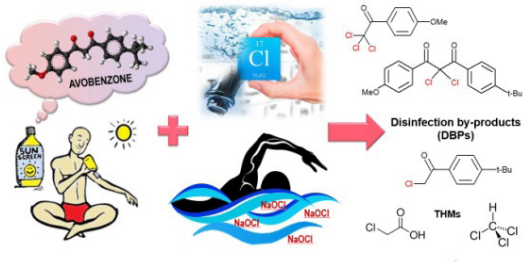

In recent years, sunscreen cosmetics have become increasingly popular. They are used to combat skin aging and prevent cancer. The components included in these products are considered safe, but under the influence of disinfectants at water treatment plants or in swimming pools, they are transformed into compounds whose toxicity is currently poorly understood and may be an order of magnitude higher. In addition to anthropogenic compounds, a similar script can occur with natural organic substances that undergo numerous changes and reactions in the environment due to a set of physico-chemical and biological factors, such as sunlight, contact with various oxidants and consortia of microorganisms. As a result, products are also formed that may be more toxic than the original compounds.In this regard, studies conducted in two main directions are considered relevant, one of which has an applied value associated with reducing the formation of organochlorine compounds (primarily trihalomethanes and haloacetic acids) in drinking water by optimizing the conditions of chlorination and water purification in general. And the second - fundamental - is aimed at studying the mechanisms of aqueous chlorination of organic substrates with various functional groups.

The chlorination products were analyzed using a Pegasus ® GC-HRT mass spectrometer (LECO Corporation, St. Joseph, Michigan, USA) connected to an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, California, USA), Trace 1310 gas chromatograph combined with a high-resolution Orbitrap Exact GC mass spectrometer (Thermo, USA), Agilent 1100 HPLC-DAD chromatograph, Trace 1310 chromatograph with TriPlus RSH autosampler (Thermo, USA) and LC-30 chromatograph (Shimadzu, Japan) with TripleTOF 5600+ mass spectrometer (AB Sciex, Canada) with a DuoSpray ion source. Avobenzone photodestruction experiments were carried out in a UVA/UVB/UVC photoreactor (20 W, CLEO). Analyses of samples from freshwater and seawater pools on avobenzone photodestruction were carried out by HPLC-UV-Vis and GC-MS. The toxicity of avobenzone and resveratrol, as well as by-products of their transformation, was evaluated on marine luminescent bacteria *Vibrio fischeri* NRRL-B-11177 (Dr. Lange GmbH, Dusseldorf, Germany).

Based on the results of chromatographic (GC and HPLC) and mass spectrometric studies, detailed schemes of transformation of avobenzone [1], resveratrol [2] and limonene were established under conditions of aqueous chlorination or bromination, as well as in the presence of additives of Br^-, I^-, Cu^{2+}, and Fe^{3+} salts [3]. The products of water chlorination in real samples of fresh and sea water from swimming pools were studied. The range of DBPs significantly depends on the composition of water and the predominance of one or another ion in it. The toxicity of brominated compounds is usually higher than that of their chlorinated analogues. The possibility of replacing halogen with halogen in aromatic substrates under conditions of aqueous chlorination is investigated.

Acknowledgements

The reported study was funded by RFBR, project number 19-33-90042.

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Diclofenac Removal by H_2SO_4 –Functionalized Activated Carbon Produced from Walnut Shells

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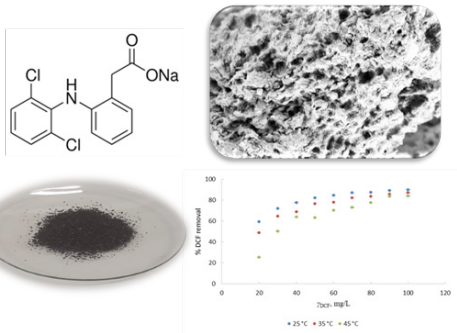

Pharmaceuticals are compounds used to treat and prevent diseases in both humans and animals and as growth promoters in veterinary medicine [1]. They are biologically active and persistent in the environment. Although they are detected in drinking and surface water, and in wastewater [2] in low concentrations, these substances are recognised as emerging contaminants (ECs). They can be harmful to the environment causing aquatic toxicity, genotoxicity, endocrine disruption etc. [3]. Therefore, it is necessary to detect and effectively remove pharmaceuticals from the environment.

Diclofenac (DCF) belongs to a group of non-steroidal anti-inflammatory drugs, among which exhibits the highest acute toxicity. It is commonly used to treat inflammation and pain in pathologies, such as rheumatoid arthritis. Because of its extensive consumption, it is frequently found in aquatic environments. DCF has been found in both drinking water (at concentrations below 10 ng/L) and wastewater [4].

Studies showed that conventional treatment processes are relatively inefficient in removing DCF from wastewater [5]. When removing pharmaceuticals, adsorption onto activated carbon as an adsorbent showed high efficiency due to its high surface area.

The aim of this study was to investigate the adsorption of diclofenac onto H_2SO_4-functionalized activated carbon produced from walnut shells in batch processes. Diclofenac batch adsorption was studied through equilibrium and thermodynamic perspectives with isotherm at three different temperatures. Adsorption kinetics was also assessed.

According to obtained data, the maximum adsorption capacity of 24 mg/g was achieved. The values of 1/n for Freundlich isotherm was less than unity, which indicates that the adsorption was nonlinear and favourable. In order to describe adsorption mechanisms, kinetic models were also calculated. Adsorption kinetics followed the pseudo-second-order model closely. Activated carbon from walnut shells proved to be an effective adsorbent for diclofenac removal.

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Application of Advanced Oxidation Process for Removal of Endocrine Disruptor, Bisphenol A from Landfill Leachate

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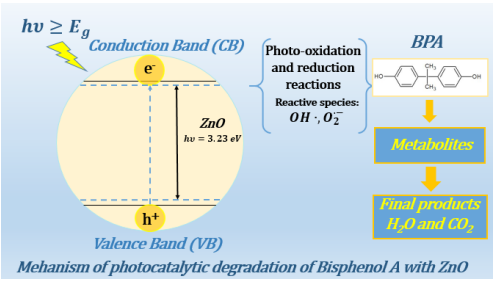

Mehanism of photocatalytic degradation of Bisphenol A with ZnO

Bisphenol A (BPA) presents widely produced synthetic compound with multiple propose such as production of polycarbonate plastics, epoxy resins and various care products. Although it has short half-life, BPA is characterized as pseudo-persistent micropollutant due continuous emission into environmental media. BPA with endocrine disruptor effects migrates into aquatic matrices through point sources such as sewage effluent, landfill leachate (via hydrolysis of BPA from plastics) or natural degradation of polycarbonate plastic [1].

Landfill leachate is complex wastewater media and mixture of organic and inorganic substances and various emerging micropollutants. This research is based on the possibility of application of BPA advanced oxidation degradation in leachate sample**.** Raw leachate sample was taken from non-sanitary landfill without previous treatment.

Advanced oxidation processes are based on *in-situ* generation of highly reactive species such as hydroxyl radicals (HO•) and superoxide radical anions ($O_2^{\bullet -}$) which have non-selective nature in destruction of recalcitrant organic pollutants [2]. The nanosemiconductor-assisted photocatalysis is one of most investigated water remediation technology. Zinc oxide (ZnO) was chosen as nano-photocatalyst owing to excellent properties such as chemical stability, high catalytic activity and wide band gap energy [3].

Prior to treatment, BPA was quantified in raw leachate sample. The measured level of BPA was 70 μg L^{-1}. The photocatalytic experiment was applied on laboratory scale level. The ZnO nanopowder in concentration of 1 g L^{-1} was added in acidified leachate sample. The suspension was magnetically stirred in order to achieve homogenous diffusion of nanoparticles in sample. Artificial illumination was conducted in time interval from 5 to 90 minutes in order to provide kinetic of decomposition of target pollutant.

Prior to analytical analysis, all treated samples were filtered through 0.45 μm filters to remove nanoparticles and pre concentrated on Oasis HLB cartridges for solid phase extraction (SPE).

The obtained results have shown slow degradation mechanism. A kinetic of BPA transformation showed a slow increase from 2.78% to 9.60% in first 30 minutes of treatment. After 90 minutes, only 31.14% of BPA was decomposed.

The insufficient transformation of BPA could be affected due to complex composition of landfill leachate. Inorganic ions (HPO_4^-, SO_4^{2-}, Cl^-, NO_3^- and others) present in high level in wastewater can compete with other present organic pollutants for adsorption on active sites of photocatalyst surface which is one of main stages in photocatalytic mechanism [4]. This phenomenon could lead to deactivation of active surface and inhibition of photocatalytic process.

In order to provide higher degradation efficiency, further research will be focused on application of photocatalytic treatment merged with other water remediation technique.

Acknowledgements

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".

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Fabrication and Regeneration Assessment of Date Seed Activated Carbon for Removal of Emerging Pesticides from Aquatic Systems

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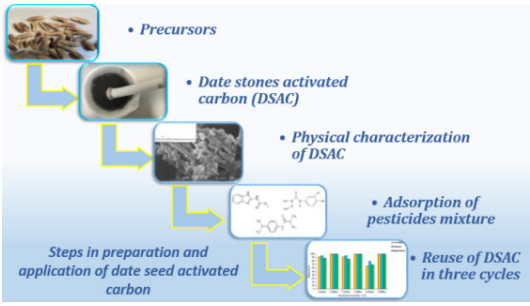

Pesticides could be emitted into environmental compartments via different sources such as agricultural runoff, industrial effluents, and chemical spills [1]. The continuous introduction of emerging pesticide residues into water ecosystems and their persistence has demand the exploration of newly and cost-effective water remediation technologies. Carbendazim, linuron and isoproturon were selected as target pesticides for evaluation of adsorption performance due their environmental and health negative effects initiated by their complex physicochemical properties, toxicity and occasionally their high stability. In this study, fabrication of low-cost activated carbon from date seeds (DSAC) was carried out through multi-step procedure which included: washing of raw precursors, drying, and carbonization at 300˚C for 30 minutes, grinding and impregnation with 30% phosphoric acid.

Morphology features of produced DSAC before and after pesticide adsorption were examined by scanning electron microscopy (SEM). The results have demonstrated a well-developed and uniform surface, forming an orderly porous structure and a predominately microporous character. DSAC showed a highly developed BET surface area (307.450 $m^2\ g^{-1}$). The Barrett-Joyner-Halenda (BJH) adsorption cumulative volume of pores was 0.018 $cm^3\ g^{-1}$ while the total pore volume was 0.1452 $cm^3\ g^{-1}$.

Recovery and reusability of prepared activated carbon is essential task from environmental and economic point of view. Regeneration procedure was achieved with adsorption/desorption process through three sequenced cycles (C1, C2 and C3). Desorption was performed in order to remove the linked molecules of pesticides on the adsorbent and to regenerate the adsorbent [2,3]. The thermal desorption at high temperature level (500˚C) was sufficient for separation of pesticides mixture.

Results have shown that efficiencies of adsorption were 92.73% for carbendazim, 95.70% for linuron and 87.85% for isoproturon, after the first recovered cycle. After third regeneration cycle adsorption decreased down to 66.39% for carbendazim, 79.42% for linuron and 69.59% for isoproturon, respectively. The desorption efficiency was 100% for all the investigated samples.

According to obtained results it can be concluded that in competitive adsorption system, linuron showed the greatest adsorption tendency to newly formed adsorbent. The efficiency order for analysed pesticides follows linuron > carbendazim > isoproturon.

The results indicate that DSAC could be successfully used three times after regeneration to extract and recover pesticides from aqueous waste. The regenerated DSAC showed very high capacity to desorb pesticides as well.

DSAC can be graded as a cost-effective and environmentally friendly separation medium for water purification based on these characteristics.

Acknowledgements

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain". Ali Hgeig would like to thank the Ministry of Higher Education in Libya for his PhD grant supporting this research.

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Recycling of Cellulose Acetate from Cigarette Butts by Chemical Methods and its Application

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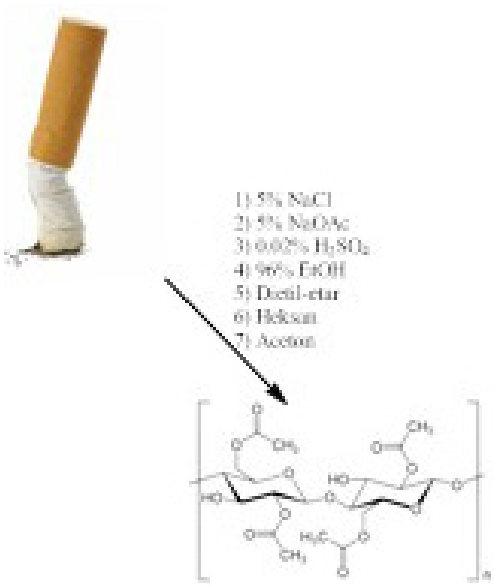

Cigarette butts are one of the most common types of frequent and used toxic waste all around the world. Smoking is one of the main problems of the modern world and a major risk factor for human health. A large number of studies link it to the appearance and development of diseases of the cardiovascular system, high blood pressure and carcinogenic diseases. It has been reported that about 130 chemicals are present in the cigarette butts but far more chemicals (around 100 000) have been identified in tobacco smoke (many of them are products of combustion or chemical transformations of tobacco ingredients present. The main ingredient of butts is cellulose acetate (95%). Other very toxic components of cigarette butts are heavy metals, PAHs, phenols and nicotine. Therefore, cigarette butts are hazardous waste and therefore a major environmental problem.

Cellulose acetate is not easy biodegradable polymer so that it can be present in the environment for more than a decade in that form. On the other hand, cellulose acetate is suitable for making plastics that would find its application, for example, for filling cartridges for 3D printers, for making toys, plastic products and similarly. The aim of our work is to recycle cellulose acetate from tobacco waste and obtain a plastic that would have further applications. In that way, we would remove hazardous waste from the environment, to which we would still (after chemical treatment) force the application.

In this regard, the collected crude filters were treated with aqueous solutions of sodium chloride, sodium acetate and sulfuric acid (respectively), at room temperature for half an hour. After separation of the aqueous phases, the crude filters were extracted with ethanol, diethyl ether and hexane, after which cellulose acetate was precipitated by the addition of a mixture of acetone and water. After separation of the organic phase and drying of the product, over 90% pure cellulose acetate was obtained. It is important to emphasize that all organic solvents used in this reaction can be recycled.

Acknowledgements

This research was funded through a grant for pilot projects in the field of ecology and environmental protection obtained by Climathon - A Global Climate Action Programme.

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Influence of Microbial Community on Power Generation Using MFC System

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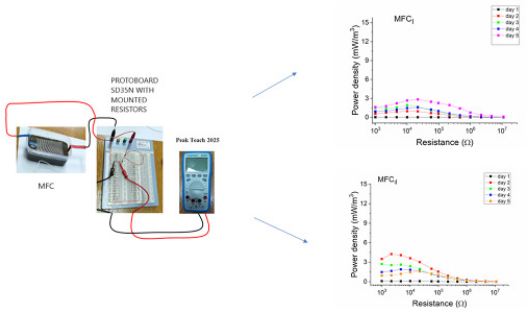

Introduction

Global worldwide population and urbanization in general have created an increasing need for new energy sources. These sources need to be renewable, but it is also very important to respect the principles of environmental protection. Microbial fuel cells (MFC) are a green technology that is attracting more and more attention in the last decade. MFC presents a system which produces electrical current through metabolic processes of microorganisms such is the decomposition of organic matter. In this process chemical energy is directly converted into electrical energy [1-3].

The performance of MFC depends on several factors: temperature, the composition of the sediment, the material from which the electrodes are made, but certainly, one of the prominent factors is the activity of a microbial community. In this paper, efficiency of two MFC systems will be compared to obtain the highest current and power generation. One of them contains only river sediment as a source of microorganisms, while the other was biostimulated by microorganisms isolated from the same river sediment [2-3].

Methods

The river sediment was placed between a set of inox electrodes in a plastic container, with a total volume of 201 cm^3 (MFC I). The second MFC (MFC II) was made in the same way, but a consortium of microorganisms, *Clostridium* sp., *Bacillus* sp. and *Tepidibacter* sp. isolated from the river sediment was added to the sediment. The set of resistors already established in our previous studies were used for the measurement of the amount of voltage, which was then used to obtained the values of current and power [4].

Results

After five days of measuring the generated voltage via MFC I and II, the results for current and power density were obtained. In MFC I, the highest current density was recorded on the fifth day and was 76 mA/m^3 while the power was 1.5 mW/m^3. With MFC II, the results were visibly higher, where the current was increased three times (up to 210 mA/m^3), and the power by as much as 4 times higher compared to the results of MFC I (6 mW/m^3).

Conclusion

Results show that MFC I has lower values than the sediment stimulated by a consortium of microorganisms in the MFC II. The community of microorganisms greatly contributes to improving the performance of the sediment itself, by generating more power density.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No. 451-03-9/2021-14/200026 and 451-03-9/2021-14/ 200168).

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Electrochemical Degradation of Phenols on PbO_2/Graphene Nanoribbons Electrodes – a Combined Experimental and DFT Approach

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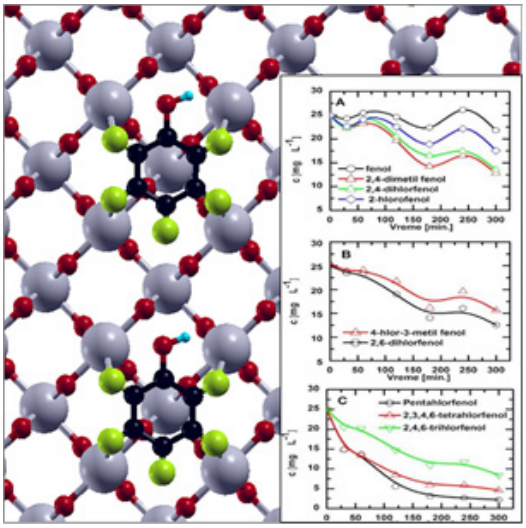

Electrochemical degradation of organic pollutants represents a promising technology for the depollution of waste water in the future. The concept comprises that the harmful pollutants are fully degraded into carbon dioxide and water using only electrical current, without any extra chemicals involved and with zero remnant waste [1]. The precise design of electrode materials, which should be highly efficient in generation of oxidizing OH radical and resistant to corrosion in applied electrochemical conditions, as well as careful control of experimental conditions, are of primary interest to achieve this goal [2,3]. Also, sophisticated and complex degradation pathways require knowledge on the fundamental principles beyond the oxidation process, in order to assure favourable outcome of the process and avoid formation of unwanted byproduct species.

In this contribution, a nanocomposite anode based on PbO_2 and graphene nanoribbons (PbO_2/GNR) was used for electrochemical oxidation of a mixture of phenol and chlorinated phenols. 0.1 M Na_2SO_4 (at pH = 3) was used as a supproting electrolyte. Tracking of phenols concentration revealed a degradation by up to 91 percents within 300 minutes at potential 2.3 V. The best degradation efficiency (91.4 %) was obtained for pentachlorphenol – a compound with the highest number of chlorine atoms, while the removal of phenol has achieved about 12%. Chromatographical tracking of degraded compounds has shown a rather complex oscillatory kinetics of phenol and trichlorphenols degradation, while pentachlorphenol concentration has been decreasing constantly within electrolysis.

The findings were complemented with periodic density functional theory (DFT) calculations of phenol and pentachlorphenol adsorption properties on the electrode surface models – PbO_2 crystal and graphene sheet. According to the obtained results, no adsorption of any of the investigated compounds on PbO_2 surface was observed. However, adsorption of phenol on graphene was thermodynamically favorable, while pentachlorphenol did not exhibit affinity for adsorption on graphene. Obtained theoretical and experimental results corroborate indirect mechanism of electrooxidation, where electrogenerated OH radicals on the electrode boundary initiate the oxidation of phenol and chlorophenols, resulting in subsequent generation of chlorine radicals and hypochlorite anions - which further continue to oxidize the species in the solution. Observed affinity of phenol to be adsorbed on graphene, which is the component of the anode, is among the possible causes of its low removal efficiency compared to the chlorinated phenols.

Acknowledgements

The research was funded by the Ministry of Education, Science, and Technological Development of the Republic of Serbia, Grant No. 451-03-9/2021-14/200017.

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SiO_2 and TiO_2-Hybrid Material for Removal of As(V) and Pb(II) Ions from Aqueous Solution

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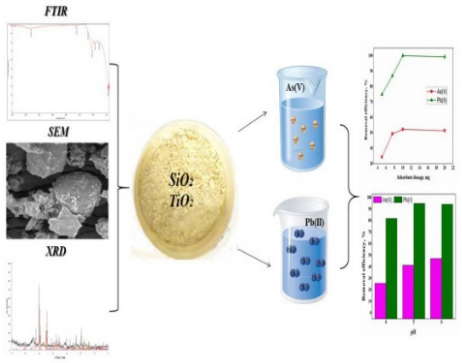

The aim of this research was to investigate As(V) and Pb(II) adsorption behaviour onto mineral heterostructures based on the mixture of Si and Ti-oxides (MHO). Heavy metals are discharged into water bodies from various industries which cause environmental pollution and public health problems due to their toxicity, persistence, high solubility, and mobility [1]. The conventional methods of heavy metal decontamination include chemical precipitation, ion exchange, membrane separation and reverse osmosis [2]. However, the adsorption process for heavy metals removal has been investigated as a cost-effective method, usually easy to manage, maintain and consolidate within the entire wastewater treatment plant.

The metal-oxide heterostructures with a high surface area and specific affinity for heavy metals adsorption from aqueous solutions have demonstrated a promising performance in practical engineering applications [3]. The most common hybrid adsorbents are consisted of metal-oxides combinations such as: iron oxides (maghemite: γ-Fe_2O_3, hematite: α-Fe_2O_3, magnetite: Fe_3O_4, goethite: α-FeOOH), manganese oxide (α-MnO_2), zinc oxide (ZnO), titanium oxide (TiO_2), aluminum oxide (γ-Al_2O_3), magnesium oxide (MgO) and cerium oxide (CeO_2) [4-6].

In this study, synthesized SiO_2 and TiO_2-hybrid material for removal of As(V) and Pb(II) ions from aqueous solution was investigated. The adsorption experiment was conducted in a batch system, using the initial concentrations of 100 µg L^{-1}, at appropriate pH_i for selected ions ($pH_{Pb(II)}$=5 and $pH_{As(V)}$=6). The experimental optimization was performed by varying the parameters such as the mass of the adsorbent and pH of initial ion solution. The maximum removal efficiency of Pb(II) and As(V) was 99,8 and 52.2 %, respectively (experimental conditions: m_{ads}=10 mg, V=10 mL, t=24 h and T=25 °C).

The characterization of MHO adsorbent was carried out using the following techniques: X-ray diffraction (XRD), gas adsorption/desorption isotherms (BET), scanning electron microscopy (SEM) and the Fourier-transform infrared spectroscopy (FTIR). XRD patterns of the MHO sample have shown that the main contribution originates from the diopside phase, $CaMgSi_2O_6$ (84.0 wt. %), while the other oxide-contributions comprised of a hexagonal structure of titanium oxides (anatase and rutile, in total 2.2 wt. %), and iron (titanium) oxides (hematite and titanomagnetite, in total 12.2 wt. %). The FTIR was used to analyze the functional groups present in MHO and recorded numerous vibrations and stretching of functional groups (dominantly Si-O-Si, Si-O-Al and Si-O-Ti bonds), which confirmed that the synthesized material consists of mineral oxides. The SEM analysis indicates a large number of uneven thin forms of nanoplatelets which is complementary confirmed by increased porosity and large surface size (S_{BET} = 271.7 m^2 g^{-1}).

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-9/2021-14/200135 and 451-03-9/2021-14/200287).

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Removing of Chromium(VI) and Arsenic(V) from Water Solution Using Modified Lignin Microspheres

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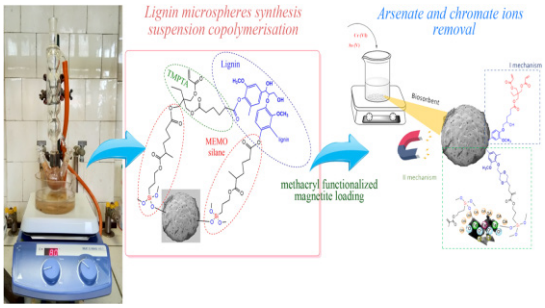

With the development of the industry and growth of the population, there is an increasing amount of waste, which, due to inadequate treatment, pollutes water. The group of the most dangerous pollutants present in water includes heavy metals, such as As, Cd, Pb, Ni, Hg, Cr, etc. [1]. Heavy metal ions are highly toxic and not biodegradable, but are prone to accumulation in the body in certain tissues and organs [2].

In recent years, natural materials, originating from waste or renewable sources, have been increasingly used as adsorbents in the removal of heavy metal ions from water, due to their low cost, high prevalence and beneficial impact on the environment [3]. Lignin, cellulose and hemicellulose are the main polymers of wood biomass [4]. Lignin is represented as a by-product in the paper and pulp industry [5]. Chemical modification of lignin was performed using acrylate derivatives (L-AC). Modified lignin microspheres (LMS) were synthesized by inverse suspension copolymerization using L-AC, trimethylolpropane triacrylate (TMPTA) and methacryl functionalized magnetite modified with MEMO silane or with methacryloyl chloride (MACM1 or MACM2). The procedure of inverse emulsion-suspension copolymerization developed by Popović et al. [6] was used. In a summary, disodium laureth sulfosuccinate (surfactant) was stirred in water solution for 30 min at 80 °C. Afterwards, TMPTA, L-MAC, MACM1 or MACM2 and the initiator AIBN (1 wt. %) were added, followed by the mixture of pore-forming solvents (tetradecanol and toluene), stirred for 18 h at the same elevated temperature.

LMS microspheres were characterized by zero charge point determination, FT-IR and SEM. The efficiency of pollutants (chromium(VI) and arsenic(V) ions) removal was analysed in terms of varying the experimental conditions: the mass of adsorbent, the pH of solution, the temperature of reaction and the contact time. The best sorption was observed for the pH between 5.0 and 7.0. Synthesized bio-adsorbents showed high efficiency, with capacities of 35.5 and 54.0 mg g^{-1} for the LMS adsorbents loaded with magnetite modified using methacyl functionalized silane (LMS-1) or methacryloyl chloride (LMS-2), respectively, obtained according to Freundlich isothermal model. Adsorption kinetics are described according to a pseudo-second order model. Based on the obtained results, both adsorbents showed excellent adsorption abilities.

Thermodynamic parameters, including the Gibbs free energy (ΔG^{Θ}), enthalpy (ΔH^{Θ}) and entropy (ΔS^{Θ}), proved that adsorption is viable, spontaneous and endothermic process (LMS-1) and exothermic process (LMS-2) at temperatures between 25 and 45 °C.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-9/2021-14/200066; 451-03-9/2021-14/200023; 451-03-9/2021-14/200135; 213-1/21-08-03-2021; 451-03-9/2021-14/200325 and 451-03-9/2021-14/200214).

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Mass Balance of Volatile Methylsiloxanes (VMSs) in Different WWTPs Methanogenic Digesters

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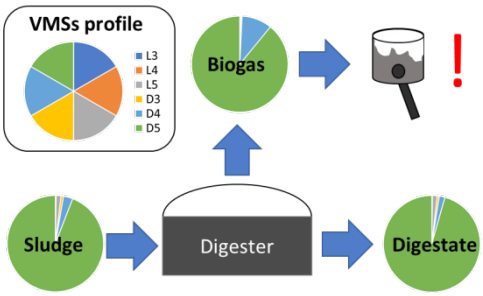

Volatile methyl siloxanes (VMSs) are a group of man-made compounds comprising a Si-O backbone saturated with methyl groups [1]. Nowadays, VMSs are extensively used as emollients in cosmetics and personal care products (PCPs) formulations. After their application, a significant part of these compounds arrives to wastewater treatment plants (WWTPs) via grey waters. Once there, VMSs congeners are distributed among the different matrices present in these installations depending on their chemical properties. The less soluble and less volatile compounds end up in the sludge, and once this material is digested, a part is transferred to biogas. VMSs hinder the quality of this renewable fuel by blocking and corroding different parts of engines after biogas is combusted. Therefore, monitoring these compounds within WWTPs is crucial to design strategies for their removal and treatment. Nowadays it is possible to find studies focused on monitoring VMSs in the water and sludge lines of different WWTPs, but there are no studies deepening on the dynamics occurring in biogas digesters [2]. The present work aims to surpass this gap by studying the partition of VMSs of digesters in different WWTPs. To accomplish so, samples of sludge (both pre and post digested) and biogas were collected in several WWTPs in Portugal. VMSs from sludges were extracted by liquid-liquid extraction with n-hexane, before GC-MS quantification. Biogas was directly analyzed from sampling bags by means of a GC-IMS-SILOX. Preliminary results show that the difference in VMSs mass between entry and digested sludge reach average values around 50%, being, in some, cases, close to 100%. Consequently, some locations showed levels of total VMSs above 5 mg/m^3 (limit recommended by some internal combustion engine manufacturers [3]). Decamethylcyclopentasiloxane (D5) was the prevalent VMSs regardless of matrix and WWTP analyzed.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - national funds through the FCT/MCTES (PIDDAC); (ii) Project LANSILOT (PTDC/CTA-AMB/32084/2017; POCI-01–0145-FEDER-032084) funded by FEDER through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) N. Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call - [CEECINST/00049/2018].

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Novel Technology with Solvent Extraction of Used Timber Railway Ties to Obtain Raw Material

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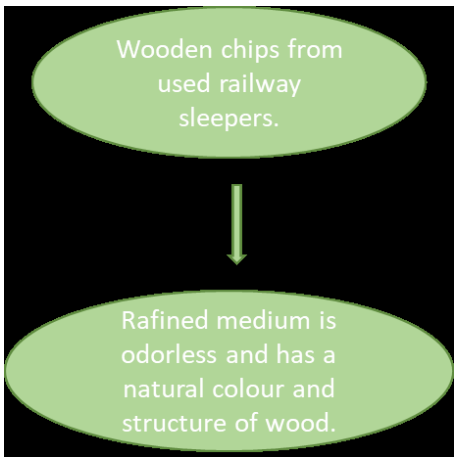

Wood is traditionally the primary construction material in human society. Wooden railway sleepers are commonly used in railway track systems. A specific source of pollutants in the railway are wooden railway sleepers impregnated with creosote.

When it comes time to replace the wooden railway sleepers, it becomes critical waste and carry a certain risk to the environment. The way in which the generated waste will be treated depends on the concentration of toxic compounds in the waste and hazardous characteristics. Limit values for concentrations of pollutants are prescribed by European Union legislation in the field of solid and hazardous waste management.The current practice is to incinerate or dispose of such waste [1].

Creosote is a distillation product of coal tar, thick, oily liquid and is one of the most widely used wood preservatives in the world. Chemical composition of creosote is a highly complex mixture that can contain up to 85% of polycyclic aromatic hydrocarbons (PAHs) together with 10% phenolic and 5% N-, S-, O-heterocyclic compounds. The sum of sixteen PAH compounds (US EPA) is used as an expression of its total creosote content [2]. Timber railway ties can be reused after removal toxic substances from wooden material. Toxic substances were removed after repeated solvent extraction with dichloromethane, hexane and deionized water. Cutting and grinding used wooden railway sleepers into wooden chips before solvent extraction gave high yields in PAHs recovery. Rafined medium is odorless and has a natural colour and structure of wood and can be used for other purposes as raw material. Chemicals (primarily polycyclic aromatic hydrocarbons) by which they are protected are released in pulses into the environment, either by inadequate storage, disposal or treatment [3]. The aim of this study is to reduce the concentration of pollutants in the wood to the point where the wood sleepers would cease to be hazardous waste and / or to completely remove the pollutants so that the wood material can be reused, e.g. as a raw material for the preparation of firewood, a substrate for growing plants and raising animals, a material for composting [4].

Acknowledgements

This study was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract number: 451-03-9/2021-14/200051.

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Design of Ceramic Materials Based on Industrial By-Products

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Ecological catastrophe, Ajka, Hungary
foto: Ris-restore summer school 2021

The rapid increase in alumina production is followed with a fast growing production of its by-products. One of them is the red mud (RM). Depending on the quality of the bauxite and its processing [1], around 15 – 40% of the processed bauxite ore is waste in the form of alkaline slurry – red mud [2]. It is estimated that 1.0–1.5 t of RM was generated during the production of 1 t of alumina. In reality the problem is not the red mud itself, but the residue storage and its utilization.

Over the years, extensive research work has been done worldwide to be developed various economic ways for utilization of red mud. From different applications of red mud that have been explored, among which are adsorbents for the removal of heavy metals, recovery of iron, stabilization material, there is also one additional promising approach: production of ceramic tiles and bricks which could be used for consumption of large quantities of this waste material[3]. Following the circular economy principles these alternative usages of the red mud in production of ceramic materials could have positive impact on the reduction of raw materials costs and the environment footprint. However, only small quantities of the red mud are currently used in building materials production due to high alkalinity of the red mud, therefore further investigation needs to be done.

The aim of the research presented in this paper was the valorisation of the red mud in order to be used as a useful raw material for the production of ceramic products. This valorisation included the chain of activities, from thermal, chemical-and mineralogical characterisation, morphological characteristics, particle size distribution, potential dangers to human health and environment to evaluation and valorisation of RM potentials to be used as a raw material for production of novel bricks and ceramic tiles.

The obtained results shown that it is possible to produce ceramic products of satisfied characteristics by using combination of red mud (up to 80 mass %) and local clay materials.

Based on the thermal characterisation, the maximal temperature of the thermal treatment was set at 980° C and the final products characteristics were evaluated including physic-chemical properties: porosity, microstructure, mechanical properties, colour, and leaching of soluble salts. The obtained results verified the suitability of red mud as a raw material for production of ceramic materials (at the amount up to 80 mass%).

Acknowledgements

The authors would like to acknowledge the support from Ministry of Education, Science and Technological Development (Serbia), project No.: 451-03-9/2021-14/200134 and to the project RIS-RESTORE – Evaluation of Red Mud Tailings in the ESEE region, EIT RawMaterials, Horizon, 2020.

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Siloxane Removal from Synthetic Sludge Using Air Stripping

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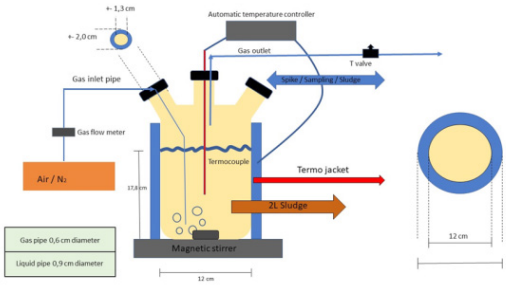

Siloxanes are chemicals formed by Si-O bonds with aliphatic chains attached to silicon [1]. Due to their properties, they are widely used in industrial processes and added in the formulation of numerous consumer products [2]. With the extensive use of siloxanes, it is expected a considerable release into the environment, with a large amount ending up in wastewater and partitioning into sludge [3]. During anaerobic digestion most volatile methyl siloxanes (VMSs) are released from the sludge and enter biogas composition, being oxidized during combustion into abrasive microcrystalline silica that damages equipments, exponentiating maintenance costs, reducing biogas yield and compromising its energetic and economic valorization [4]. In this context, the aim of this investigation was to design and build an air stripping unit to remove the siloxane content in synthetic sludge.

For the development of the synthetic sludge, 40 g of puppy dog food and 10 g of pasteurized egg white were used. 500 mL of the 10% total solid sludge was added with the 0.125 to 0.500 mg/L spike of the siloxane mix (L2-L4 and D3-D5), obtaining a total solids equivalent to 2.5% (to simulate the average conditions existing in sludge entering the anaerobic reactor). After loading the synthetic sludge in the air stripping unit, the air flow started at a flow rate varying from 0.5 to 4.0 L/min. At the beginning and at the end of each assay, samples of the simulated sludge were collected for analysis, to quantify the initial and final VMS content. The experiments had a total time of 5 hours. At 15, 30, 45, 60, 75, 90, 105, 120, 180, 240 and 300 min, air samples were collected with 1 L Tedlar gas bags. The gas bags were analysed using a dedicated GC-IMS-SILOX chromatograph. The sludge was extracted and later analysed in the GC-MS.

With the air flow fixed in 2.0 L/min and varying the siloxane mix spike (0.125, 0.250 and 0.500 mg/L), it was not observed a significant difference in VMSs removal (94.9%, 94.6% and 91.2%, respectively). On the other hand, when fixing the siloxane mix spike in 0.5 mg/L, the siloxane content removal achieved were of 54.1%, 76.8%, 81.8%, 91.2% and 97.4% when using an air flow of 0.5, 1.0, 1.5, 2.0 and 4.0 L/min, respectively.

Air stripping proved to be effective, with the reduction in total siloxane content of the simulated sludge achieving 97.4%.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - national funds through the FCT/MCTES (PIDDAC); (ii) Project LANSILOT (PTDC/CTA-AMB/32084/2017; POCI-01–0145-FEDER-032084) funded by FEDER through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) G. Pantuzza thanks FCT PhD programme for Grant 2020.07815.BD, supported by, under the Portugal 2020 Partnership Agreement and European Social Fund (ESF) (iv) N. Ratola thanks FCT for the financial support of his work contract through the Scientific Employment Stimulus - Institutional Call - [CEECINST/00049/2018].

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Possibilities of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes

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In 2022, a new Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products comes into force. It replaces Regulations (EC) No. 1069/2009 and (EC) No. 1107/2009 and Regulation (EC) No. 2003/2003. It is part of the EU Action Plan relating to the circular economy. This plan is one of the main blocks of the European Green Deal, i.e. the new strategy for the sustainable development of the EU economy. The new regulation on fertilizing products is intended to encourage economic operators to process waste into products containing valuable nutrients for plants, to develop new, innovative fertilizers from waste and to place them on the EU market [1].The new regulations make it possible to use waste phosphates from the production of polyols for fertilization purposes. This waste has not been used so far and it was necessary to dispose of it.

The waste phosphate solution is produced in the polyol production plant at the phase separation stage, where the organic phase (product), the water phosphate phase and the interphase containing the filtration aid are separated. Phosphates are formed as a result of the neutralization of sodium and potassium ions (from the polymerization catalyst) with disodium acid pyrophosphate and cannot be returned into the process and reused.

The carried out analysis show that waste phosphate from the production of polyols is a valuable source of plant nutrients. It contains phosphorus soluble in mineral acids, calculated as P_2O_5 in an amount close to 19%, potassium calculated as K_2O in an amount of about 8% and sodium in an amount of about 5%.

Since this waste is in a hydrated form, the best direction of its application are suspension fertilizers. The production of solid fertilizers from this waste would be expensive due to the need to evaporate large amounts of water.

The suspension form of the fertilizer offers wide possibilities of using various waste and raw materials of less purity, which reduces their costs. Moreover, the concentration of nutrients in these fertilizers is comparable to the concentration in solid fertilizers [2].

Suspension fertilizers are an important tool for agriculture that meets the set environmental and agronomic criteria. Their liquid formula and high concentration of fertilizing salts affect more effective absorption of nutrients by plants. These fertilizers are part of the sustainable management of mineral components, consisting in the possibility of balancing their distribution, and also create the possibility of utilizing waste [2].

Popularization of suspension fertilizers in common use is a response to the cur-rent and possible future problems related to the growing amount of waste and the depletion of natural resources.

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Removal of Mercury (II) from Wastewater Using Beech Charcoal

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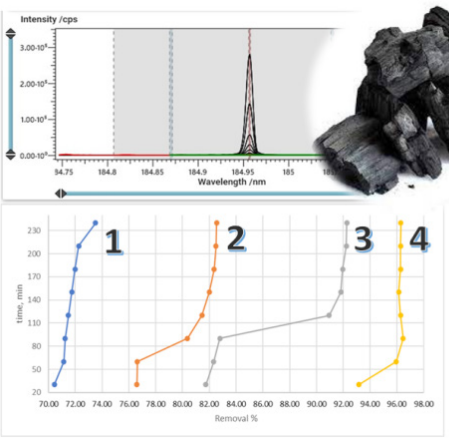

Beech charcoal (BC) as an adsorbent for the removal of Hg (II) from wastewater effluents was used. Batch adsorption experiments were conducted by using 1g of BC mix with 25 ml 10 ppm Hg (II) solution, where the pH was adjusted to ≤ 2, within contact time from 30 min up to 4 h. The adsorption capacity of charcoal and efficiency of mercury removal can be enhanced by the addition of various activators, so for this experiment KBr was used. In the second batch of solution 1 ml of 0.1g/L KBr solution was added, under the same adsorption conditions, while in the third batch 2 ml KBr of solution was added, and in the fourth batch 4 ml KBr of solution was added. Percentage removal (R, %) [1, 2, 3] was calculated by measuring the initial and residual concentrations of Hg (II) by inductively coupled plasma optical emission spectrometer (ICP-OES).

BC was a suitable adsorbent for removing Hg (II) from aqueous solution, where the removal efficiency grew exponentially from 70.43% to 73.51%. With the addition of KBr solution, the removal efficiency of Hg (II) was increased from 76.59-82.56%, 81.75-92.27 to 93.16-96.29%. The adsorption was found to be strongly increased by the addition of KBr solution. The adsorptive capacity (q_e) [1, 2, 3] was increased from 176.1 mg/g up to 183.8 mg/g without KBr solution. Adding KBr solution, q_e increase from 191.5 up to 232.9 mg/g. Quantitative and effective removal of Hg (II) from wastewater was demonstrated.

Acknowledgements

This research work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Agreement No. 451-03-9/2021-14/200122. This scientific research was done at 1) Mining and Metallurgy Institute in Bor; 2) University of Kragujevac Faculty of Science, Department of Chemistry.

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Identification of Banned Pesticide Residues in Municipal Solid Waste Landfills Leachate from Vojvodina Region

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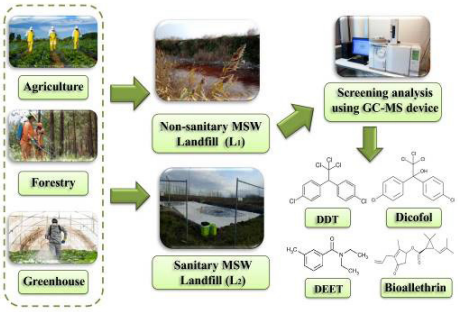

Introduction

Pesticides are widely used in agriculture and forestry, and in other plant production such as in greenhouses and gardens [1]. As a consequence of the above mentioned, they occur frequently in -domestic and organic waste. The handling and unselective application of pesticides may create an important waste fraction going to landfills, with the potential for transferring its residues into the environment, thus causing contamination [2].

Materials and methods

Leachate sampling campaigns were carried out in the autumn of 2019, at one non-sanitary (L_1) and one sanitary (L_2) municipal solid waste landfill in the region of Vojvodina. A total of 2 L of leachate were collected at each location for the purpose of the screening analysis. The samples were prepared by liquid-liquid extraction and concentrated in the Kuderna-Danish apparatus or evaporator. Previously prepared internal standard, Fenantren D10, concentration of 15 ppm in methanol, was applied, while dichloromethane was used as a solvent agent. P2010-Ultra GC-MS, Shimadzu, and Agilent HP-5ms column (30 m ×0.25 mm ×0.25 µm) were used for the screening analysis.

Results and Discussion

By performing screening analyses of leachate samples, two pesticides, pyrethroid ester, Bioallethrin, and organochlorine pesticide, Dichlorodiphenyltrichloroethane (DDT), were detected in the sample L_1, and other two, organochloride acaricide, Dicofol, and N,N-Diethyl-m-toluamide (DEET), were detected in the sample L_2.

According to the Pesticide Action Network (PAN), International Consolidated List of Banned Pesticides issued in March 2021, the application of Bioallethrin is banned in Switzerland. DDT and metabolites are banned in 144 countries worldwide, while Dicofol is banned in 50 countries worldwide. Since 2017, 100% of DEET products were withdrawn from the European market and are no longer available due to the EU Biocidal Products Regulations 528/2012 (BPR). Utilization of remaining stocks of banned pesticides on agricultural lands nearby landfill site L_1, as well as lack of primary separation of waste fractions on landfill sites L_1 and L_2, are some of the main reasons of contamination and pesticide residues identification in landfill leachate samples.

Conclusion

Due to long-range transport capacity, carcinogenic and endocrine-disrupting characteristics, pesticides can, adversely affect human health, livestock, and wildlife. In order to replace conventional pesticides with less toxic and easily biodegradable ones, preferably biological pesticides with high efficiency, farmers' awareness needs to be improved and enhanced. The development and selection of safe, on-farm disposal/treatment technique for agricultural pesticides is paramount for environmental protection.

Acknowledgments

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".

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Research on Developing a Sustainable Way of Neutralizing the Red Mud for its Further Exploitation

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Figure 2. Red mud tailings in Klisa (Zvornik, above) and Dobro Selo (Čitluk below), subject of the study

Bauxite residue or red mud (RM) is a solid caustic waste generated from the Bayer process during alumina production. Depending on the quality of the bauxite and its processing, about 15-40% bauxite ore presents the waste in the form of alkaline slurry. In Bosnia and Herzegovina there are two locations for RM disposal: Klisa near city of Zvornik (around 19M tons of solid red mud) and Dobro Selo near city of Čitluk (around 4M tons of solid red mud) shown in Figure 1. The utilisation and recycling of this material is currently serious environmental issue not only in Bosnia and Herzegovina, but in the whole Europe and it needs to be addressed as soon as possible. The alkaline constituents in the red mud impose severe and alarming environmental problems, such as soil and air pollution [1]. In particular, pH of RM is substantially higher than any other waste - different studies report that pH ranges from 10 to 13.5 regardless of the origin of RM.

However, red mud contains significant amount of iron oxide, aluminium oxide, silicon oxide and potentially rare earth metals which carry certain economic potential. In particular, red mud is discussed as valuable secondary raw material [2] has and it is studied for various industrial applications such in the field of building (geopolymers, clay material, cements, ceramics, fired and nonfired building materials, concrete industry), pollution control (in wastewater treatment, absorption and purification of acid waste gases), metal recovery (iron, titanium, aluminium, rare earths), coagulant, adsorbent, catalyst and in soil remediation (calcium silicon fertilizer) [3].

Further handling, disposal, and use of RM is the function of several properties, but at the first place pH value. Extraction of valuable constituents is interfered due to its alkalinity. To make the bauxite residue applicable finding a sustainable techniques for its neutralization is the must. This paper demonstrates research on developing an economical way of red mud neutralizing using simple centrifugation and rinsing with minimal quantities of water, all with purpose to extract hematite ultra microparticles for further use.

Acknowledgements

Authors thank the EIT RawMaterials association for financial support (project RIS RESTORE, agreement number: 1259051)

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Determination of Variety of Substances from Emptied Aerosol Containers

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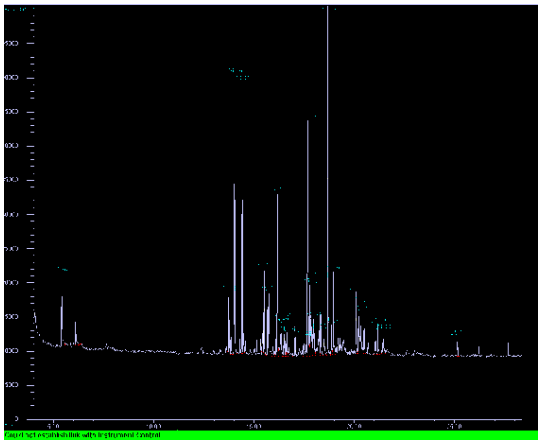

One of commonly used forms of product packaging is a pressure container. The consumable material is dosed under pressure using working gas. Currently, propane or butane, and less often carbon dioxide are the most commonly used propellants. These gases are flammable and pose a threat, especially in situations where a fully charged pressure container becomes a waste.

According to the European Aerosol Foundation (FEA), Europe is the largest producer of aerosol sprays. Following the 2017 FEA report, this is over 5.7 billion packages a year (in 16 billion worldwide). In 2017, Poland produced over 78 million units annually, which gives the 9th position among producers in Europe. The recovery of aerosol container materials is low. In Poland, it reaches 8.4% only in relation to the amount of materials used in the production of these containers, excluding the volume of the imported aerosol packages [1]. A complex structure of containers, involving many different materials is a reason. There is, therefore, a strong need for recycling and utilisation of the resulting waste in the form of empty containers or containers with different levels of the product and working gas filling, which has not been emptied as intended due to various reasons.

A review of patent databases has pointed to three solutions to the problem of pressure container utilisation, however none of them provides a complete and environmentally friendly technology for the utilisation and recycling of aerosol containers [2, 3, 5].

A group of scientists from the Lodz University of Technology and CSD-ECO Ltd. company have developed a new solution and a method that allow for emptying packaging and recycling materials in an environmentally friendly way [4].

The presentation includes results of preliminary investigations enabling one to determine different chemical substances coming from emptied aerosol containers. Results also cover detection of various metals, including heavy metals in those substances. Investigations were performed by means of the following methods: ICP-OES, ICP-MS, CV-AAS, GC-MS, TOC.

Acknowledgements

The work has been performed under the project POIR.01.01.01-00-0850/17cofinansed by National Centre for Research and Development.

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Preliminary Investigation of Origin of Aliphatic Compounds in Street Dust Samples, Pančevo, Serbia

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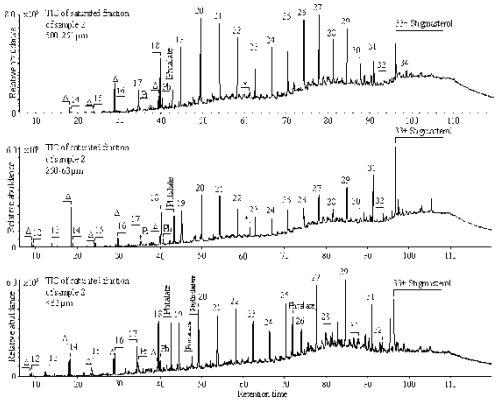

Figure 1. Representative total ion chromatograms of the saturated fractions isolated from different size fractions of the same sample.

The aim of this study was analysis of the origin of the aliphatic compounds in selected street dust samples. The samples were collected in the city of Pančevo, Serbia, within residential areas in close vicinity to heavy traffic roads.

In order to determine if there was a significant difference in composition of aliphatic fraction depending on particle size, the samples were sieved and separated in three fractions, 500–250 μm, 250–63 μm and <63 μm. The samples were extracted, and the extracts were separated to aliphatic, aromatic and polar fractions by column chromatography. The aliphatic fractions were further analysed by GC/MS. *n*-alkanes were identified using mass ion *m/z* 71, hopanes *m/z* 191 and steranes *m/z* 217 [1].

Concentrations of total hydrocarbons in the street dust samples were in the range from 34.5 to 280.0 μg/g. It is generally accepted that total hydrocarbons content higher than 50 μg per 1g of sediment can be considered as a potential anthropogenic pollution [2]. According to these results, presence of organic pollutants in almost all samples can be presumed.

Concentrations lower than 50 μg/g were observed in coarser fractions (500-250 μm). Higher concentrations of total hydrocarbons were observed in the finest fraction (< 63 μm). With only few exceptions, concentration of total hydrocarbons increases with decrease of grain size of samples indicating greater affinity of these compounds for the smallest particles.

In all samples analysed, the most abundant compounds were *n*-alkanes, followed by n-alk-1-enes, regular isoprenoids and hopanes. No significant compositional changes were observed in different size fractions of the samples.

n-Alkane distribution in all samples is bimodal, with *n*-alkane maximum at C_{20} in the range C_{13}-C_{23}, and with maximum at odd number *n*-alkanes in the range C_{24}–C_{34}. Carbon Preference Index (CPI) [2] for the whole range of *n*-alkanes (CPI C_{13}-C_{33}) is in the range of 1.07 – 2.40, CPI C_{13}-C_{20} is close to 1, and CPI C_{25}-C_{34} is in the range from 1.0 to 3.9. These results and distribution of *n*-alkanes in the chromatograms (Figure 1) indicate that the investigated *n*-alkanes in the C_{13}-C_{23} range originate from a mature organic matter source while those in the C_{24}–C_{34} range originate from the native terrestrial organic matter.

Definite proof that the aliphatic fractions of the street dust samples contain petroleum pollutant can be seen by distributions of hopanes, steranes and diasteranes, which have typical distributions found in crude oils.

It can be concluded that the aliphatic compounds in the street dust samples investigated in this study are mixtures of a natural terrestrial source (indicated by presence of even alk-1-enes and odd higher *n*-alkanes) and a petroleum pollutant (indicated by CPI values and presence of typical crude oil biomarkers)

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract numbers: 451-03-68/2020-14/200168 and 451-03-9/2021-14/200026 and Project No. 451-03-01039/2015-09/05) for supporting this research.

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Preliminary Investigation of Origin of Polycyclic Aromatic Hydrocarbons in Select Street Dust Samples, Pančevo, Serbia

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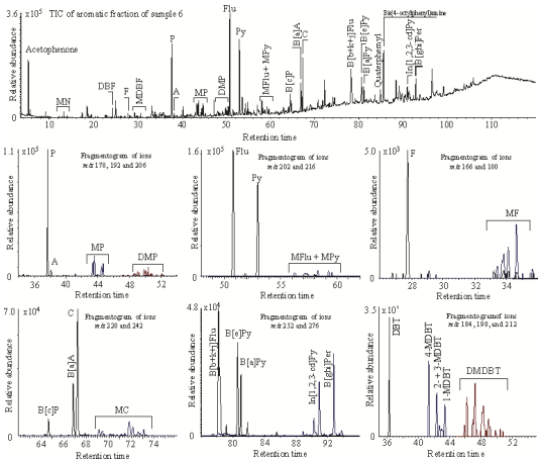

Figure 1. Representative GC-MS chromatograms showing distribution of all PAHs analyzed in this study.

The aim of this study was to investigate the origin of polycyclic aromatic hydrocarbons (PAH) in street dust samples from a small industrial city Pančevo in Serbia. The samples were collected in different parts of the city and sieved to separate the <250 μm fraction. Aromatic hydrocarbons were isolated by extraction and column chromatography. In these extracts, PAH were analysed by gas chromatography - mass spectrometry (GC/MS) using total ion current (TIC) and single ion monitoring (SIM) methods. Monitored ions were: *m/z* = 128 (naphthalene; N), *m/z* = 152 (acenaphthylene), *m/z* = 154 (acenaphthene), *m/z* = 166 (fluorene; F), *m/z* = 178 (phenanthrene and anthracene; P and A), *m/z* = 202 (fluoranthene and pyrene; Flu and Py), *m/z* = 228 (benzo[a]anthracene and chrysene; B[a]A and C), *m/z* = 252 (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j] fluoranthene,

benzo[e]pyrene and benzo[a]pyrene; B[b]F, B[k] F, B[j]F, B[e]Py and B[a]Py), and *m/z* = 276 (indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene; In-[1,2,3-cd]Py and B[ghi]Per). All these compounds were quantified (using the reference standard Z-014G PAH mix) and characteristic molecular ratios were calculated.

The concentrations of non-methylated (parent) PAH in the street dust samples were found to be in the range from 175 to 2746 ppb. Content of PAHs in street dust samples is not regulated by the Serbian National legislation. However, some of these values are higher than the limit values for soils as set by Serbian National legislation [1].

All samples contain smaller amounts of lower, 2-3 ring, PAH (13 - 347 ppb), in comparison to the higher, 4-5 ring, PAH (175 - 2399 ppb) indicating pyrogenic origin of these compounds in the samples investigated [2].

Low abundance of methylated PAHs, as seen in ratio ΣMP/P (lower than 1 in all samples) indicates pyrogenic origin of these compounds. Similar conclusion can be drawn from Flu/(Flu+Py) ratio which, depending on the sample, indicates source from petroleum or biomass and coal combustion. Furthermore, PAH origin from traffic emissions, for samples collected closer to busy roads, and from biomass and coal combustion, for samples collected within residential areas, is shown by values of B[a]A/(B[a]A+C), B[a]Py/(B[a]Py+B[ghi]Per) and In[1,2,3-cd]Py/(In[1,2,3-cd]Py+B[ghi]Per ratios [3].

It can be concluded that the dominant source of PAHs in the selected street dust samples is combustion of petrol, diesel, biomass and coal which agrees with the results for similar samples in other cities in the world [2, 3].

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract numbers: 451-03-68/2020-14/200168 and 451-03-9/2021-14/200026 and Project No. 451-03-01039/2015-09/05) for supporting this research.

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Comparison of Heavy Metal Content in Peloids from Igalo and Sutomore (Montenegro) and Assessment of the Environment State

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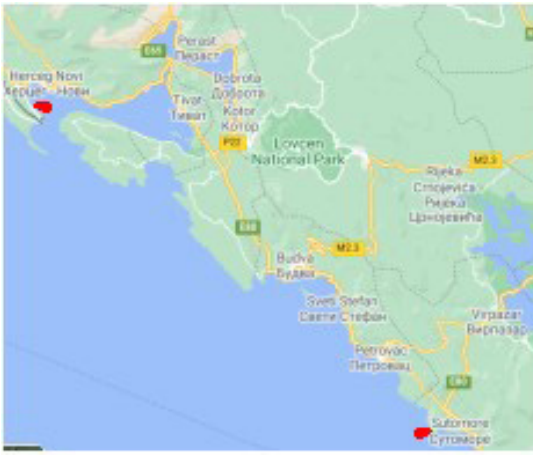

Peloid is mud, or clay used therapeutically, as part of balneotherapy, or therapeutic bathing. Peloids consist of humus and minerals formed over many years by geological and biological, chemical and physical processes. For the development of many biological processes, the presence of various organic and inorganic substances is necessary. When it comes to inorganic substances, water is one of the main factors, but content of metals have great importance as well. In Montenegro, there are three locations with natural peloids: Igalo, Ulcinj and Sutmore. In our work, we analyzed the content of heavy metals (Pb, As, Sb, Cr, Mo, Mn, Fe, Co, Ni, Cu, Cd, Hg) in Sutomore and Igalo peloids in order to compare the value, quality assessment and ecological status of these two peloids. In general, metals have some important roles in biological processes: structural role (construction of structures, skeletons, stabilization of nucleic acids…), transferred the charge (concentration gradient through the membranes, transmission of electrical impulses through neurons), function, metabolism and degradation of organic molecules). Some of these metals are present in the body in high concentrations (such as sodium, potassium, calcium, magnesium), while others are necessary in significantly smaller quantities (iron, zink, cobalt, copper). Twenty-five elements are necessary for the normal functioning of the human organism and the maintenance of homeostasis.Also, we determined the physical and chemical characteristics of peloids from Igalo and Sutomore (the peeling temperature at the sampling site, pH-value, density, electrical conductivity). Analyzed heavy metals are known as major pollutants of water and soil, so determining their amount is an important indicator of the state of the environment and soil. Afterwards, we have determined some environmental indicators based on the data of the content of metals such as: contamination factor (CF), pollution load index (PLI) and index of geoaccumulation (Igeo). These three indexes can provide important information about the level of pollution by a particular potentially toxic element, the amount of toxic element that is accumulated on a certain sampled surface as well as the total level of pollution by potentially toxic elements. Based on the obtained results, we can conclude that our two peloids do not contain high concentrations of heavy metals, that they are quite safe to use and do not exhibit any toxic effects on their own.

Acknowledgements

We thank the Ministry of Science of the Republic of Montenegro for financing several projects that dealt with testing the physical and chemical properties of peloids from Igalo.

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GC/MS and TOC Analyses of Ibuprofen after Degradation in Waterusing Chlorine Dioxide

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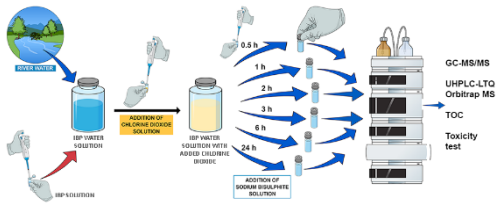

Figure 1. IBP degradation using ClO_2.

Drinking water and wastewater treatment facilities often have a chemical oxidationstep for disinfection, the removal of organic micropollutants, color removal and taste andodor control. Among the most commonly used oxidants are chlorine dioxide (ClO_2), chlorine, and ozone.ClO_2 has been increasinglyemployed as disinfectant in water treatment due to its antibacterial and antiviral properties. As a powerful oxidant, ClO_2 can remove many organic and inorganic pollutants [1,2].

The aim of the present study was to assess thepotential of ClO_2 to oxidize pharmaceutical during water treatment. Therefore, degradation of ibuprofen (IBP) using ClO_2in water was investigated.The degradation under different reaction conditions (concentration of ClO_2: 5, 10, 15 mg/L; concentration of ibuprofen: 10, 20, 35, 60 mg/L; reaction time: from 0.5 to 24 h; pH values: 3, 7, 10) was monitored using high performance liquid chromatography (HPLC) analysis, while mineralization degree was detemined by total organic carbon (TOC) measurements. The highest degree of IBPdegradation in deionized water was obtained by treatment with 15 mg/L ClO_2, using 10 mg/L ibuprofen, at pH = 10, after 24 h of treatment. The obtained degradation degree value under optimal conditions was 99%.

TOC analysis of ibuprofen showed reduction in content of organic carbon in the solution. Before degradation TOC content was 7.8 mg/L and after 5.6 mg/L. This showes that degradation and mineralization of ibuprofen occur during this process.

The degradation products obtained under optimal conditions were analyzed and confirmed by gas chromatography–mass spectra (GC–MS) and the reaction pathwayswere proposed.From GC chromatograms, degradation products of ibuprofen appeared at following retention times: 4.35 min, 5.12 min, 6.76 min, and 7.05 min. After the analysis of mass spectra, based on the spectral characteristics and the ratio of mass and charge (m/z), it was determined that there are four main degradation products of ibuprofen, after treatment with ClO2.The first characteristic ion appeared at 6.76 min and has m/z 163 (2-(4-methylphenyl) propionic acid). In further degradation path, two products are formed, one of which is a characteristic ion with m/z 57 (2-methylpropane) at 4.36 min, while the other product is further decomposed to give two new products, one of which is also a characteristic ion with m/z 57 (acetic acid) at 5.21 min. Another characteristic ion having m/z 161 (1-ethyl-4-isobutylbenzene) appeared at 7.05 min.

ClO2 treatment is an efficient method for IBP degradation.The findings of the present study are very useful for the treatment of drinking waters contaminated with pharmaceutical.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-9/2021-14/200026; 451-03-9/2021-14/200168).

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Influence of Geological Settings and Land Use on Physico-Chemical Properties of Soils in the Fruška Gora Mt., Serbia

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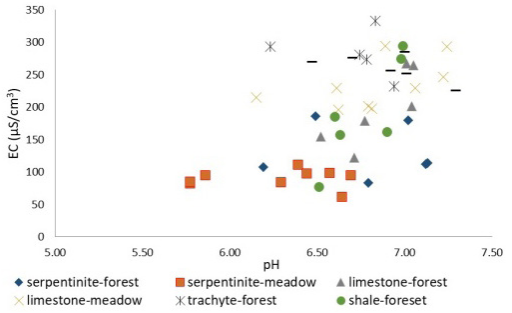

Figure 1. Correlation between pH and electrical conductivity (EC) for forest and meadow soils on different bedrock.

During the last few decades there has been an increase of the land degradation and unsustainable land management recognized as one is one of the key drivers of this process **[1]**. Increased agricultural exploitation of pastures and forests and changes in land use often leads to land quality degradation and can be a cause of land loss through erosion. Therefore, the protection of land, as an important non-renewable natural resource, is recognized as one of the priorities **[2]**.

The objective of this study was to determine the impact of geological substrate and land use on: physico-chemical properties of soil and size and stability of soil aggregates. Seventeen soil samples of forest soil and 30 samples of meadow soil developed on different bedrock from Fruška Gora slopes were analyzed: forest soil on serpentinites, marls and trachytes, and meadow soil on serpentinites, marls, shale and loess. The Fruška Gora is located in the northern part of Serbia and stretches between the Sava and the Danube rivers. The maximum length of this mountain is 75 km along the east-west direction, and along the north-south direction the maximum width is about 15 km, while the total area is 500 km^2. After air drying following parameters were determined on all soil samples: grain size, electrical conductivity (EC), pH, available ions (Na^+, K^+, Ca^{2+}, Mg^{2+}), sodium adsorption ratio (SAR) **[3]**, and organic carbon (Corg). Aggregate stability was determined using the aggregate size of 2-4 mm. Five grams of material was immersed in water and after 10min water was drained with a pipette and the soil was dried. Percentage of stable aggregates was determined from the weight difference. Analysis of variance was used to determine whether the relationship between tested parameters exists.

The highest sand content was found in the trachytes soil (35.15%), while the clay content was the highest in the forest marl soil (27.84%). The content of silt is highest in the soil sample above forest serpentinites (76.61%). Most abundant size fraction of soil aggregates was 8-4 mm. The most stable aggregates are 4-2 mm over loess and trachytes, and the least stable soil aggregates are over forest serpentinites. Furthermore, meadow soil aggregates are more stable than forest soil aggregates. It can be concluded that the stability of soil aggregates is associated with high pH and EC values, because the most stable aggregates, above the loess, have the highest average pH value (6.90) and high EC (259.8), and others in stability aggregates, above trachytes, have the highest EC (282.4 µS/cm^3) and high pH value (6.70) (Fig. 1).

There is no statistically significant difference in pH, Eh, EC, and SAR values between the analyzed forest and meadow soils, but there is a statistically significant difference in the Corg content. Therefore, it can be concluded that the land use does not have a significant influence on the pH, Eh, EC and SAR values, but that the content of Corg largely depends on the presence of vegetation and the degree of land use.

Taking into account all results it can be concluded that the analyzed physico-chemical properties of the soil depend more on the geological setting, and less on land use.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant No: 451-03-9/2021-14/200026) for financial support.

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Heavy Metals Distribution, Environmental and Health Risk, Sources, and Origin in Soil from European Beech Forests

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Figure 1. Sampling sites across European mountain beech forests.

Forests cover about 40% of Earth's surface, while is 42% of the European Unions' total land area is covered by forests and wooded land [1]. Forest ecosystems are open and dynamic systems that exchange matter with other systems such as the atmosphere, hydrosphere, and biosphere [1]. Nowadays, in addition to the exchange of substances necessary for its functioning, there is also an exchange of polluting substances. Heavy metals in forest soil can originate from natural and anthropogenic processes and their high concentration can be toxic for ecosystems and humans [2]. The aim of this study is to determine: (i) heavy metal distribution in forest soil; (ii) environmental and health risk; (iii) the source of heavy metals; (iv) the origin of heavy metals; and (v) influence of the geological substrate on heavy metal contents.

Soil samples were collected from European mountain beech forests in 11 countries: Bosnia and Herzegovina, Bulgaria, Czech Republic, Germany, Italy, Poland, Romania, Serbia, Slovakia, Slovenia, and Spain. Since European beech forests grow on a wide range of geological settings, during this research terrestrial ecosystems that lie on five major bedrock groups (andesite, carbonate, conglomerate, granite, and sandstone) were investigated.

The average abundance order of heavy metal contents in forest soil samples is Cr > Zn > Ni > Pb > Cu > Co > Cd. According to geo-statistical analysis soil samples with the lowest heavy metal contents belong to cambisol soil type, on sandstone, and granite substrate, and with the highest contents belong luvisols and rendzina soil types on limestone and dolomite substrate. The concentration of most heavy metals doesn't show a systematic pattern with depth. Considering enrichment factor (EF) Pb, Sb, Cd and As, have moderate enrichment, or moderately severe enrichment in the surface soil layer. Mercury has severe enrichment. The highest values of hazard quotient pathways are noticed for ingestion in the children population, especially in the case of Pb. The Pearson correlation coefficient revealed a positive correlation among most of the elements indicating one or more common sources of heavy metals. Based on the Positive Matrix Factorization (PMF) V, Ni, Cu and Th were provided the highest percentage contribution for Factor 1, As, and Se for Factor 1 and Factor 3, Hg for Factor 4, and Cd for Factor 5. Principal Component Analysis (PCA) showed that Principle Component 1 (PC1) was mainly loaded with V, Ni, Cu, As, Se, and Th with similar high values, and Cd and Hg were strongly correlated in the Principle Component 2 (PC2).

Taking into account all results it can be concluded that heavy metal concentrations in European beech forests soil are mainly determined by the geological substrate.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-9/2021-14/200026) and COST Action CA15226 for financial support.

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Finding Meso- and Micro-Plastics in 'Waste-to-Resource' Agriculture

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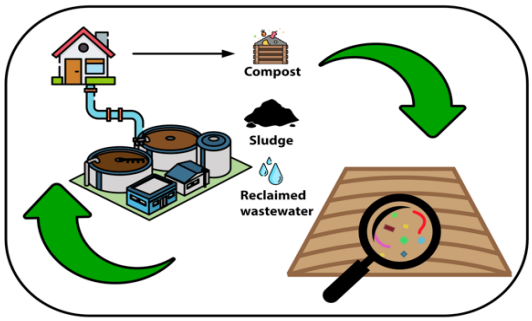

Continuing population growth and increasing consumption are driving global food demand, with agricultural activity expanding to keep pace.This results in ever increasingexploitationof natural resources, such as water and nutrientsentering the food chain and being disposed as waste. The linear functionality (take-use-dispose) is causing irreversible environmental problems and negatively affects economies and societies [1] therefore a transition to circular economy is encouraged. In this context, the cycling of nutrients and water needs to be restored to keep resources in use. E.g., treated municipal wastewater can be used for irrigation and by-products of wastewater treatment and bio-waste processing are used as fertilisers and soil amendments [2]. Plastics is widely present in these resources as personal care products and synthetic textiles release plastic particles to wastewater, where they may persist even after treatment. Organic fertilisers, such as waste activated sludge and compost are particularly rich in plastic contaminants [3]. Lately, algal biomass from algae-based wastewater treatment is being explored as a potential soil amendment [4], however, plastic contamination in this resource has not yet been investigated. Micro-plastics has been found to affect soil microorganisms and nutrient cycling; however, the effects are varying depending on their size, concentration, shape, and composition [5].

Toevaluate realistic micro-plastic effects on soil health and agricultural production,quantification and classification ofplastic contaminants is needed in these alternative resources applied to soil as well as the agricultural soil amended with them.

In this study, meso- and micro-plastics were isolated and quantified in samples of soilirrigated with mechanically pre-treated municipal wastewater for 5 years, and soil fertilised with biowaste compost for 20 years at approximately 10 tonnes/ ha of land every 2 years. In addition, control soils were investigated in both cases, to determine plastic contamination not originating from applied resources. Meso- and micro-plastics were also investigated in bio-waste compost, waste activated sludge, and algal biomass. Sieving was used to isolate meso-plastics, while density separationemploying saturated $ZnCl_2$ solution was used to extract micro-plastics.

Organic fertilisers, compost, and sludge had the highest number of meso- and micro-plastics. Algal biomass, on the other hand, contained no meso-plastics, and a low concentration ofmicro-plastics. Soil irrigated with wastewater and soil fertilised with compost had some plastic contamination, but whether this was solely due to application of these resources is yet to be determined.

The results of this study contribute to our understanding of plastic streams in 'waste-to-resource' agriculture and managingassociated risks.

Acknowledgements

The authors acknowledge the project (Agri-iM-Pact: Microplastic prevalence and impact in agricultural fields, Z2-2643) and the research core funding No. P3-0388 were financially supported by the Slovenian Research Agency.

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Metal Accumulation in Honey Bees: Workers vs Drones

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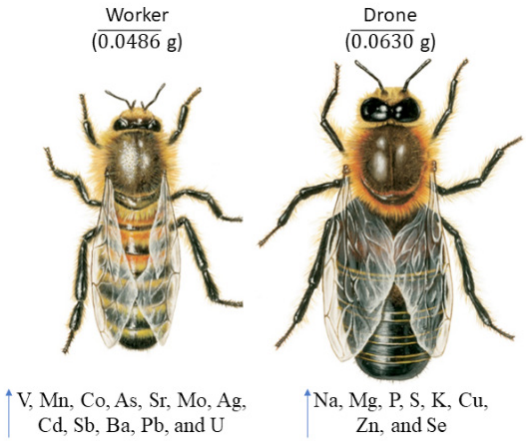

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Forager honey bees reflect pollution that is present in all aspects of the environment. Direct deposition of particulate matter from air on the hairy body of the bee or water through drinking are direct sources. Elements from soil are either taken up by plants and transferred to flowers (pollen and nectar) and are then consumed by bees or are transported into the air by resuspension of soil into the air and are consequently directly deposited on bees and on plant organ [1]. Although honeybees are used for monitoring of metal pollution for a couple of decades, until now worker bees (dominantly foragers) were never compared to their male counterparts – drones. The aim of our study was to evaluate differences in elemental concentrations in worker bees and drones.

Both, worker bees and drones were collected from the same hive, located on a rooftop in Gries, Graz in June 2021. Elemental analysis was done on individual worker bees and drones. After microwave-assisted digestion with conc. HNO_3, element concentrations were determined using inductively coupled plasma mass spectrometry (ICPMS).

The average dry weight of the drones (0.0630 g) was higher compared to worker bees (0.0486 g). Elements that had significantly higher concentrations in drones were Na, Mg, P, S, K, Cu, Zn, and Se. Higher concentrations for V, Mn, Co, As, Sr, Mo, Ag, Cd, Sb, Ba, Pb, and U were detected in worker bees.. No significant differences were observed for B, Al, Ca, Fe, Ni, and Rb.

The main differences between foragers and drones in regard to environmental exposure is that drones do not forage at flowers and don't consume pollen. So, metals accumulated by drones are only those present in the hive, or brought to the hive by forager bees, through food or water. These are naturally occurring in the environment. They aremost likely part of the larval or adult food prepared by workers for the drones. Hence it can be speculated that elements with higher concentrations in drones do not originate from direct environmental pollution.

Metals with higher concentration in foragers are most likely a consequence of direct pollution accumulated by bees during their flight or food consumption. However, to be able to draw decisive conclusions further investigation is needed on elemental composition the food consumed by drones.

Acknowledgements

This work was made possible throughMinistry of Education, Science and Technological Development of the Republic of Serbia contract number 451-03-9/2021-14/ 200178, and CEEPUS network CIII-SI-0905-07-2021.

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Metals Pollution of Surface Flowing Water in Timiș County, Romania

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Metals are considered pollutants in the environment, due to their toxicity and bioaccumulation. They can be of natural origin, through the weathering of rocks as well as a consequence of a variety of human activities such as mining, fossil fuel burning, smelting, electroplating, andindustrial processes that have metal residues in their waste streams. Fertilizers and metal-containing fungicides and pesticides used in agriculture were recognized as another potential source of metal pollution [1]. Metal pollution of surface flowing water represents a problem both for the region crossed by these waters and for the discharge area. As the most of the rivers in Timiș County, Romania flow into Serbia, the metal content of these waters is a cross border problem.

The purpose of these study was to determine the content of metals and some elements with toxic potential in surface flowing water, in order to identify the best methods to prevent degradation of their quality. The samples were taken in the autumn of 2020, from 19 sites from Timiș County, Romania (Dragșina, Chevereșu Mare, Biled, Becicherec, Checea, Bobda, Cenei (2), Uivar(2), Otelec, Foeni(2), Grăniceri, Toager, Denta, Moravița, Jamu Mare, located on the banks of rivers Timiș, Bega, Bârzava, Moravița and streams Ierici, Jeru, Timișăț and Șimița).

Using an ICP-MS method, we determined the following pollutants from water samples: Cr (0 ÷ 5.136 ppb), Ni (0 ÷ 3,09 ppb), Cu (0 ÷ 5,30 ppb), Zn (0,28 ÷ 50,60 ppb), Fe (0 ÷ 1653 ppb), Mn (0,854 ÷ 707,5 ppb), Pb (0,064 ÷ 0,661 ppb), Sr (7,91 ÷ 329 ppb), Ba (0 ÷ 36 ppb).

In order to avoid the degradation of the quality of these waters, a permanent monitoring is necessary in order to act immediately in case of detecting the increases of the metal content.

Acknowledgements

This work was made possible through Interreg IPA CBC Romania – Serbia Programme, project RORS – 279 "Cross-border network for education and research of natural resources".

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Health Risk Assessment for Residents and Workers Based on Toxic and Carcinogenic Element Content from $PM_{2.5}$ in Belgrade Suburban Area

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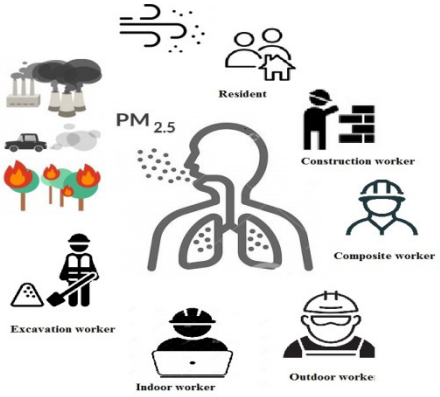

Particulate matter of diametar <2.5 μm ($PM_{2.5}$) pollution is recognized as one of primary pollution contaminant which directly affect human health. Toxic and carcinogenic elements originating from different pollution sources can be constituents of $PM_{2.5}$. Because of their small size, particles can penetrate deeper into the lungs and enter the bloodstream causing different disorders and threats to human health [1].

We performed elemental characterization of $PM_{2.5}$ samples collected during the spring/summer season 2019 in a suburban part of Belgrade (in the inner courtyard of Institute of Physics Belgrade). The spring/summer period was characterized by the industrial or different outdoor activities with several Saharan dust episodes. In addition, April and October were partly characterized by heating sources.

The quartz filters with $PM_{2.5}$ were digested by the microwave digestion system using 7 mL 65% HNO_3 and 1 mL 30% H_2O_2. The concentrations of Al, B, Ba, Bi, Ca, K, Fe, Mn, Ni, P, S and Sr were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES), while concentrations of Ag, As, Be, Cd, Co, Cu, Cr, Hg, Pb, Se, Sb and Tl were measured using inductively coupled plasma mass spectrometry (ICP-MS).

The non-carcinogenic and carcinogenic risks for residents and for five different types of workers (outdoor, indoor, composite, construction and excavation workers) in this ambient were assessed by equations provided by The Risk Assessment Information System – RAIS [2].

Comparing the investigated scenarios, the highest non-carcinogenic and carcinogenic risks were observed for the residents. There were observed non-carcinogenic (HI>1) and carcinogenic ($R \geq 1 \times 10^{-5}$) risks for the residents from this area. The residents spent the most of their time in this ambient and they are most at the risk caused by the measured $PM_{2.5}$ pollution ($HI_{median:}$ 2.28; R_{median}: 1.25×10^{-4}). Observing the scenarios for workers, the risk mostly depends on the time that workers spent outside during working hours. Similar non-carcinogenic risks were observed for outdoor, indoor and composite workers, slightly higher risk was observed for construction workers, while the lowest risk was obtained for an excavation worker who is less exposed to the $PM_{2.5}$ atmospheric deposition than soil dust resuspension. The same was observed for the carcinogenic risk, while the similar risks were observed for all workers. Only for an excavation worker, the carcinogenic risk was significantly lower than for other workers. The most significant contributor to the non-carcinogenic risk in all scenarios was the concentration of Mn, and then the concentration of Be, while the most significant contributor to the carcinogenic risk was Cr^{6+}.

Observing the risks among the investigated period the highest non-carcinogenic and carcinogenic risks were observed in April and October based on the toxic and carcinogenic elements in $PM_{2.5}$. In these months beside the influence of the industrial activities, dust episodes or activity of heating sorces possibly caused the increase of the toxic and carcinogenic elements in $PM_{2.5}$.

Acknowledgements

The athors received funding by Institute of Physics Belgrade (No. 0801–116/1) and Faculty of Chemistry (No. 451-03 68/2020–14/200168) supported by Ministry of Education and Science of the Republic of Serbia.

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Development of Colorimetric Sensor for Surface Water Quality Monitoring

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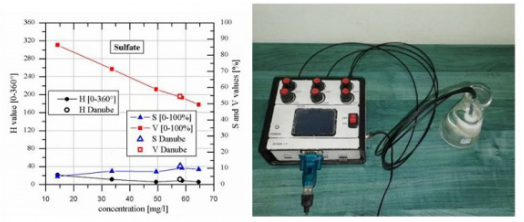

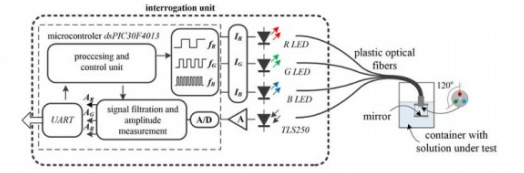

Common natural and anthropogenic activities lead to contamination of the environment. A high-quality monitoring program requires reliable, realistic and timely information about the state of the observed medium to prevent the occurrence and spread of contamination. The standard laboratory methods are generally accepted and reliable; however, they have certain limitations due to: expensive and specific chemicals, the complexity of the analysis, inability to obtain immediate results, and the loss of the analyte in the process of sampling, transportation, extraction and storage [1, 2]. The existing limitations of laboratory analysis require new, improved and cost-effective devices for monitoring the quality of aqueous media [3, 4].Colorimetric sensor used in this research represents new, innovative and original laboratory method for measurement of inorganic chemical parameters in surface water [5]. When selecting key parameters the simplicity of sample preparation for analysis, the influence of elevated concentrations on surface water contamination, as well as rapid variations in concentration due to degradation and transformation processes were taken into account. Multiparameter sensor device was used for the measurement of concentration of following five parameters in surface water: orthophosphate, nitrite, sulfate, cation of chromium (VI) and total chlorine. Sensor converts RGB (Red-Green-Blue) color model to HSV (Hue-Saturation- Value) color model. S and V values were used for determination of analyte concentration. H parameter was used for the calculation of wavelength at which applied sensor measures the concentration of selected chemical parameters [5].

Optimization of sensor was achieved by analyzing the sample of Danube surface water near Novi Sad and comparing the results obtained by standard laboratory methods. Sensor is adapted for applications in the analysis of environmental media, primarily surface water by this procedure. Comparative analyzes were conducted to confirm the efficacy, precision, and reproducibility of results obtained by sensor. The relative deviation is in the range of 2.31 % for sulfates to 6.20 % for total chlorine. Sensor can be effectively used in experimentally controlled conditions, with the ability to replace expensive standard analytical equipment. Device is adapted to the analysis of pollutants in surface water and provides the possibility of fast, simple, reliable and high-quality monitoring program of the surface water.

Acknowledgements

This research has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: “Innovative scientific and artistic research from the FTS (activity) domain”.

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PM Emissions Generated During Pork Meat Frying

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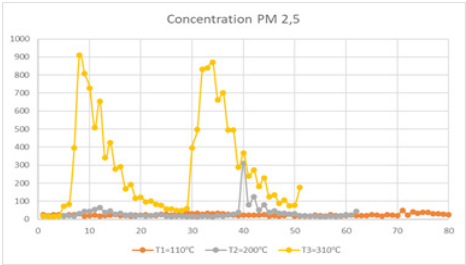

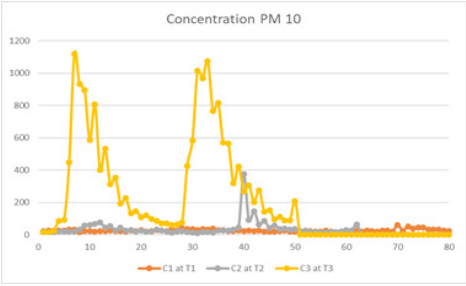

It is widely accepted that indoor environments air pollutants have adverse effects on humans' health. Poor indoor air quality is a causative agent of premature death and disease, above all respiratory and cardiovascular diseases [1]. A variety of air pollutants are generated in indoor spaces. In households, cooking causes airborne particulate matter (PM), black carbon, carbon dioxide (CO_2), polycyclic aromatic hydrocarbon (PAHs), formaldehyde (HCHO), nitrogen oxide (NOx), and other pollutants which can harm occupants' health [2]. Fine particles ($PM_{2.5}$, PM_{10}) significantly contribute to poor indoor air quality and violate human health.

The particles formed during the food preparation are inhaled into the respiratory system and deposited in the airways [3]. In addition, numerous consequences happen in contact with other organs. Meat frying at high temperatures is threatening to people who implement this action. In addition to the adverse impact on directly exposed people, PM emitted during frying also harms people in the immediate environment [4].

The present research analyzes the effect of the frying process on indoor air quality through the on-site measurements of frying-generated fine particles (PM2.5 and PM10).

For this purpose, the experiment was performed in the summer period, for three days, in a household located in a rural environment. There were no other internal activities other than frying meat were performed during the research. During the experiment, the room was ventilated naturally to bring the experimental conditions closer to the real situation and prepare food in the usual way.

For this research, pork was used, as the most often used kind of meat in nutrition, in the Republic of Serbia.

The meat was fried at three different temperatures T_1 = 110 ºC, T_2 = 200 ºC, and T_3 = 300 ºC. Temperatures were measured with a thermocouple and a thermal imaging camera.

The sensors used for the PM concentration measurements belong to the group of low-cost sensors, which can provide interesting complementary data. Sensors were set at 1.7 m, which represents the average human breathing zone. They recorded PM concentration levels every 2 minutes.

The measurement results indicate that the concentration levels of PM increase with the increasing temperature at which the meat is fried. PM is within the recommended values of 50 μg/m^3 for PM10 and 25 μg/m^3 for the PM2.5 fraction at temperature T1. However, we can also notice that the concentrations are often higher than the recommended values at higher temperatures.

With numerous factors that influence the generation of PM, additional research will be focused on establishing the optimal conditions of food preparation to minimize the formation of harmful pollutants during food preparation.

Acknowledgements

This paper has been supported by the Ministry of Education, Science and Technological Development through the projects no. 451-03-68/2020-14/200156.

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Achievements to Date and Perspectives of Passive Sampling: Organic Contaminants Bioavailability in Sediments

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Polluted sediments pose an ongoing, ubiquitous global challenge for environmental managers, because sediments can reflect the legacy of contaminations that can diminish the beneficial uses of aquatic bodies [1]. Recent developments in passive sampling offer a promising approach to measure bioavailability parameters of lipophilic organic contaminants in sediments [2].

To provide contaminant concentrations on a defined basis, surface layer of bottom sediment samples collected in 2012 at ten localities along the Danube stretch in the territory of Serbia, starting from upstream location Apatin and ending downstream at Dubravica, were *ex-situ* equilibrated with silicone passive samplers of constant accumulative properties, using the multi-ratio equilibrium passive sampling approach.

A formidable challenge in assessing the risks of contaminated sediments has been the elucidation and measurement of contaminant bioavailability, expressed as the freely dissolved concentration (C_W) of lipophilic organic contaminants in interstitial water, which serves as a surrogate measure of the substance's chemical activity. The applied passive sampling method allows the C_W of sediment-associated contaminants to be quantified at the trace level.

At all investigated sites, C_W concentrations of organochlorine pesticides ranged from 0.001-0.040 and 0.05-0.2 ng/L for penta- and hexa-chlorobenzenes, respectively. In all analysed samples p,p'-DDT was not detected. The method quantified only the metabolites concentration levels, p, p'-DDD and p, p'-DDE, which were within the measurable range (up to 0.5 ng/L). The highest total concentration of the organochlorine pesticides in pore water, calculated as the mean value of four samples, was recorded at locality Ratno ostrvo in the vicinity of Novi Sad (D6: 1.25 ng/L), and the lowest at Dubravica (D10: 0.29 ng/L). Based on the registered situation, it is concluded that there is no current new intake of tested pesticides in the investigated area. Registered concentrations of PAHs in pore water ranged from 0.02 to 15 ng/L, while the detected sum of PAHs was highest at Belegiš (D8: 199.54 ng/L) and lowest at Dubravica (24.44 ng/L). For concentrations of organophosphate flame retardants, C_W ranged from 0.1 ng/L, in the case of the most hydrophobic tri (2-ethylhexyl) phosphate, to 50 ng/L, for highly hydrophilic tri (1-chloro-2-propyl) phosphate. For concentrations of OPFRs, C_W ranged from 0.14 ng/L (D10) to 85 ng/L (D6), while the polycyclic aromatic musks detected concentration levels were the lowest at site Pančevo (D9: 0.79 ng/L), and the highest at Belegiš (D8: 5.55 ng/L).

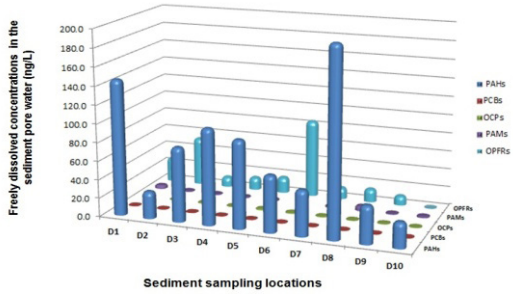

Figure 1. Freely dissolved concentrations in the sediment pore water

Sediments with high *Cw* values represent diffusion sources of contamination in surface waters which is the opposite of the obtained values. Data on free dissolved lipophilic organic contaminants concentrations provide valuable insight into the fate of the compound and to the surrounding biotic and abiotic matrix exposure.

Acknowledgements

This research was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (III46009 and TR34014), the Czech Ministry of Education, Youth and Sports (LM2015051).

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Determination of Extractable Organic Matter Type from Urban Sediments of Vrbas River (Banja Luka, Bosnia and Herzegovina)

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The Vrbas River is an important river ecosystem in Bosnia and Herzegovina with a length of 250 km and catchment areas of 5900 km^2. Before reaching Banja Luka, the Vrbas River passes through a canyon and numerous gorges, which are from 1955 protected by the Law on the Protection of Natural Values. This river flows through many towns and villages along the entire course, but the main anthropogenic influence comes from Banja Luka, one of the largest cities in Bosnia and Herzegovina.The aim of this research was to characterise extractable organic matter of sediments from the Vrbas River in the city area of Banja Luka.

Six samples were collected at locations which were selected based on the vicinity of potential sources of anthropogenic pollution: 1 and 3 – sites near bridge and frequent traffic, 2 – city's promenade, 6 – site in the vicinity of the thermal power plant, 7 – site close to Banja Luka Brewery and the bridge on frequent road, and 8 – site close to the food industry "Vitaminka". Extractable organic matter was isolated with dichloromethane/methanol mixture using a Soxhlet apparatus. Hydrocarbons were isolated from the extracts using a column chromatography and analyzed by gas chromatography – mass spectrometry (GC-MS). Detailed analysis of *n*-alkanes (*m/z* 71), diterpanes (*m/z* 123), hopanes (*m/z* 191) and steranes (*m/z* 217) was done. The individual peaks were identified by comparison with literature data [1] and based on their mass spectra (library: NIST11).

Among saturated hydrocarbons diterpane, 16α(H)phyllocladane is the most dominant component in almost all samples (Fig.1). The exception is a sample 7. This diterpane is followed by *n*-alkanes with a predominance of higher odd homologues. It indicates predominately native organic matter of Vrbas river sediments, originated mostly from terrestrial plants. That was noticed the predominant presence of native organic material in noticed in samples 2, 3, 6, while the presence of oil type pollutants was confirmed in other samples (1, 7, 8), which are near the bridge and frequent traffic roads.

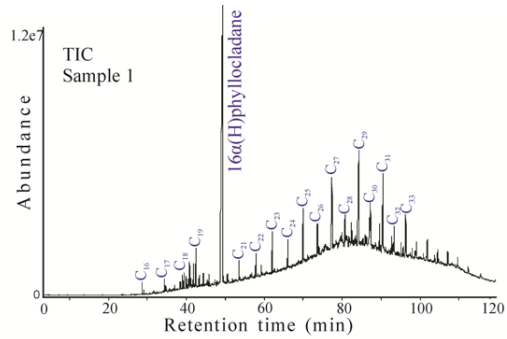

Fig 1. Total ion current (TIC) of saturated fraction.

The previous study regarding the contents distribution of heavy metals in these sediments showed that most contaminated samples are at sampling points 2 and 6 [2]. That is not the case with oil contamination pointing to probably different sources of anthropogenic pollution.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grants No: 451-03-9/2021-14/200026 and 451-03-9/2021-14/ 200168) for financial support.

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Toxic Metals in 3 Fractions (d<63µm, d63-250µm and d250-1000µm) of Dust Collected on Roads of Industrial Town Kostolac, Serbia

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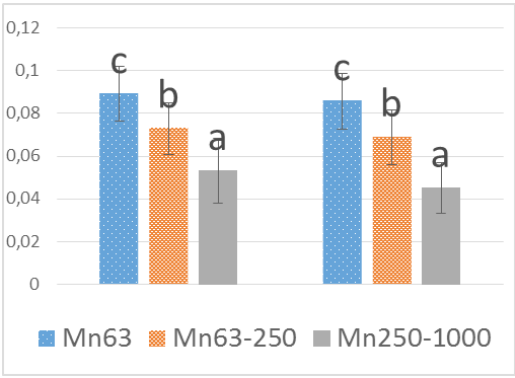

Kostolac is a town exposed to several serious sources of toxic metals and other inorganic pollutants. They arrive from sources typical for urban environments such as traffic, but also from various heavy industry sources: coal mining, burning of coal in power plants, ash landfills, and steel factory.

Toxic metals in the air are concentrated in particulate matter. Their transport and health risks depend strongly on the size of dust particles.

Goals of the research were to estimate: 1. how much does traffic contributes to the total pollution load compared to the natural sources and the industry; 2. how is pollution distributed in different fractions of the dust; 3. are there any spatial trends present and is there any correlation between vicinity of pollution sources and concentrations of toxic elements in different fractions of the dust.

Samples of dust were collected from 10 locations in July and in September. Each location had one sampling site on a major road with intensive traffic and the other site on auxiliary road with much less traffic, located 10-20 m away from the major road.

The dust was dried, sieved through sieves with 3 different apertures (d=63µm, 250µm and 1000µm) and pressed into 32 mm diameter pellets. The samples were analysed by WD-XRF standardless method.

The results showed that Al, P, K, V, Mn, Fe, Co, Zr, Rb and Ti have the highest concentrations in the smallest fraction (d<63µm) and the lowest concentrations in the most coarse fraction with stat. significant differences among concentrations. Concentrations of: Mg, S, Zn and Cu have the same trend as previous group of elements but no stat. significant differences, wile conc. of Si and Ca have the opposite trend.

Neither the time of the year nor the intensity of the traffic have had any significant effect to the concentrations, therefore it can be concluded that industrial sources of pollution have significantly higher attribution to the total pollution load than traffic.

The trend that toxic elements are more concentrated in the smallest fraction of the dust indicates that the source of the pollution is rather anthropogenic than natural.

Concentrations of elements in dust collected on sites from our research were compared to concentrations of the same elements in the soil collected by SEPA (Serbian Environmental Protection Agency). Although locations from both researches were in close proximity, no significant correlation between concentrations was observed. The lack of correlation can be explained by several hypotheses which should be further investigated in future researches.

Acknowledgements

This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-68/2020-14/200168) and GEF-funded project *Enhanced Cross-sectoral Land Management through Land Use Pressure Reduction and Planning* implemented by the Ministry of Environmental Protection and Serbian Environmental Protection Agency with the support of UNEP.

Levels of Volatile Methylsiloxanes (VMSs) Entering an Urban WWTP in Portugal

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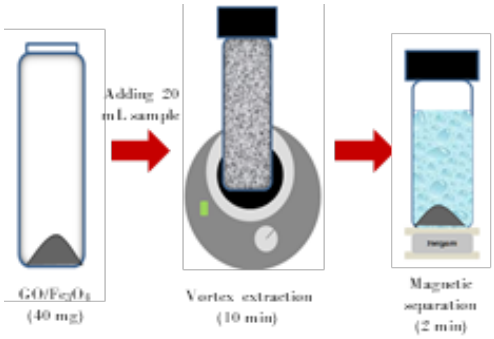

Wastewater treatment plants (WWTPs) are major receivers of the volatile methyl siloxanes (VMSs) load after their use in numerous consumer and industrial products [1]. Their impact can be severe, particularly in cogeneration units fueled by biogas produced by anaerobic digestion of the sewage sludge. But WWTP managers have no power over the wastewater load arriving each minute to their facilities. In order to have a more efficient control of the VMS level inside the WWTPs it is important to know from where and when these chemicals are coming from. Usually, WWTPs are served by a network of collectors from different origins which can give an indication of the main contributors. In the case of an urban facility from Portugal serving about 300,00 inhabitants-equivalent, four collectors from domestic/urban activities, industries, landfills, hospitals, and agricultural sources were targeted and sampled.

The strategy focused on a weekly and monthly assessment, collecting grab samples (250 mL) in polypropylene, and also in the main entrance collector of the WWTP. Looking for more specific contributions to the domestic/urban activities, individual tests will be done in the future in effluents from hotels, supermarkets and in household activities such as washing water from showers and from clothing machines. All this can be of crucial importance when events like when events like a pandemic can alter drastically peoples' way of life, which can in turn affect greatly the loads of siloxanes (and other chemicals) arriving at WWTPs for long periods of time.

To the analysis of seven VMSs (L3, L4, L5, D3, D4, D5, D6) in wastewater, two methods were employed: liquid-liquid extraction of 30 mL sample with hexane and magnetic dispersive solid-phase microextraction of 20 mL of sample using graphene oxide as sorbent [2]. Both were followed by GC/MS quantification.

Preliminary results showed a prevalence of VMSs in the summer, likely due to the increased use of personal care products related to tourist activities and the typically lower wastewater flows due to the scarce presence of rain.

Acknowledgements

This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - national funds through the FCT/MCTES (PIDDAC); (ii) Project LANSILOT (Ref. PTDC/CTA-AMB/32084/2017; POCI-01-0145-FEDER-032084), funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; (iii) COST Action CA16215 – portASAP; (iv) Spanish Ministry of Economy and Competitiveness and European Union (FEDER funds) (project n. CTQ2016-79991-R); (v) Generalitat Valenciana (Spain) (project n. PROMETEO/2018/087). The authors extend their appreciation to MCIU for granting the Spanish Network of Excellence in sample preparation (RED2018-102522T). The authors wish to thank Milton Fontes from Águas do Centro Litoral (Portugal) and the workers of the Aveiro Sul WWTP for their help in collecting the samples.

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Anthropogenic and Climate Influence on Land Degradation

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Badlands are areas with scarce or completely absent vegetation formed in a wide range of lithologies in different climate conditions and exposed to a wide range of geomorphological processes [1]. Generally, rapid evolution governed by erosion processes is a consequence of complex mineralogical and physico-chemical sediment composition and climate conditions. Because of that, badlands are often described as natural field laboratories and, furthermore, badland material is suitable for laboratory experiments that can, in controlled conditions, provide insight of changes that occur in the field.

As indicated above, beside lithology, climate is one of the most significant factors in badlands forming. Since human activities have great impact on the environment and since climate changes present one of the biggest environmental pollution problems nowadays, in this research badland material was exposed to different conditions with the aim of monitoring changes caused by extreme climate conditions and acid ice.

Three samples from badlands in China organized in six sets were treated with ice (representing snow) and acid ice (frozen acid rain) during fifteen cycles, dried in the oven for three cycles and afterwards again threated with ice and acid ice for additional five cycles. After each cycle samples were photographed, so that physical changes can be tracked, while leachate was collected and analyzed for monitoring changes in its volume, pH, electrical conductivity (EC) and cation concentration.

Beside slight oscillations in parameters through cycles of samples treated with acid ice, extreme changes in observed parameters were not noticed neither between samples, nor between treatments. Leachate EC were a bit higher in samples treated with ice, leachate volume was higher for samples treated with acid ice, while pH was similar in both cases. Cation concentrations are similar in the leachate of all tested samples. In most of cases, the highest concentrations were measured at the beginning of the experiment, during the first two cycles or during the first "ice" cycles after drying. This indicates the high cation concentrations originate from the sediment surface or washing along the crack that appeared after drying.

Physical changes that occurred through cycles implied that heat/drought is more aggressive agent of sediment decay. Decay caused by ice is slower, not as aggressive as drought, but not negligible, causing noticeable and significant cracks and fissures of fragments.

This experiment confirmed that drought has high impact on sediment weathering, but more importantly, pointed out the impact of ice and its thawing, opening new questions about climate impact on forming, erosion processes and evolution of badlands which need to be further examined.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant No: 451-03-9/2021-14/200026) for financial support.

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Natural Attenuation of Petroleum Hydrocarbons in Karst Aquifers (Bowling Green, Kentucky)

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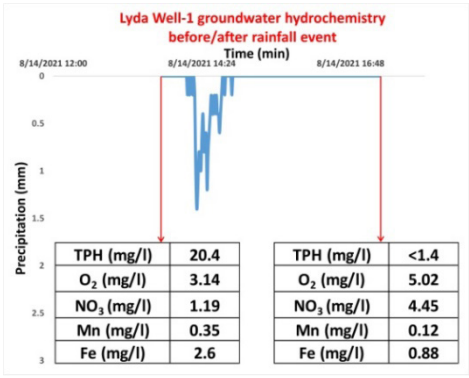

Lyda Well-1 groundwater hydrochemistry

Karst landscapes form by the dissolution of carbonate rocks. Karst groundwater systems, also referred to as karst aquifers, are prone to contamination due to poor filtration and rapid infiltration from the surface. On the other hand, the leakage of petroleum hydrocarbons from underground storage tanks was apparent as a major source of groundwater contamination in the United States in the early 1980s [1]. Today, it is widely recognized that the fate and transport of hydrocarbons in non-karst aquifers are impacted by natural attenuation processes. U.S. EPA [2] lists biodegradation, dispersion, dilution, sorption, radioactive decay, and chemical/physical mechanisms resulting in contaminant reduction, as the key components of natural attenuation processes. However, the natural attenuation processes in karst aquifers are still understudied.

This study has been conducted in the City of Bowling Green, KY which is an urban karst environment with a subterranean river system flowing throughout its bedrock. To be more precise, the study site is a newly discovered natural hydrocarbon seep in this groundwater system (Lyda Well-1). This is an ongoing study of natural attenuation processes that affect hydrocarbon contamination in karst. Hereby, we present the initial data and conclusions of the study. The groundwater hydrochemistry of two sampling campaigns conducted before and after rainfall event are shown in the Figure. As can be seen, an intense rainfall event on August 14 (17 mm of precipitation from 14:10 to 14:53) caused the flushing of the hydrocarbon-contaminated well. Thus, the concentrations of total petroleum hydrocarbons (TPH) in groundwater decreased from an initial 20.4 mg/l to <1.4 mg/l. Moreover, this shift towards uncontaminated conditions revealed an insight into the geochemical fingerprints of hydrocarbon biodegradation. The groundwater before the rainfall event was characterized by the decreased content of O_2 and NO_3 (electron acceptors), and increased concentrations of Mn and Fe (biodegradation metabolic products). After the freshwater recharge, Mn and Fe concentrations decreased following a similar trend as TPH. The concentrations of previously reduced electron acceptors (O_2 and NO_3) have increased after this freshwater recharge.

Overall, the sampling campaign before the rainfall event reveals hydrocarbon-contaminated groundwater with a low electron-acceptor, high biodegradation by-products content. The second sampling campaign reflects a shift towards uncontaminated conditions. These results emphasize the need for a more detailed study on the role of dilution and biodegradation in hydrocarbon-contaminated karst aquifers.

Acknowledgements

This research was supported by the Fulbright Visiting Scholar Program (Grant No. PS00304275).

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BPA-free Epoxy–Silica Hybrid Materials of Natural Origin for Stone Conservation: Inhibition Potential Against Biocolonization

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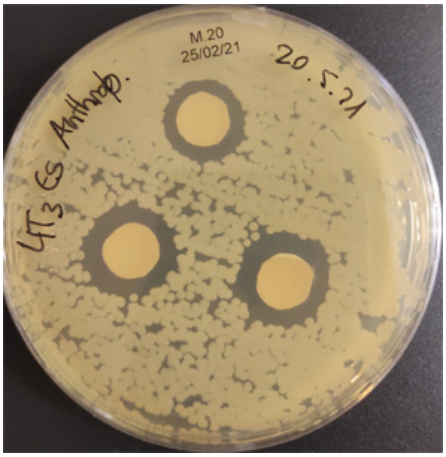

In this work, epoxy–silica hybrids based on a BPA-free bio-based cycloaliphatic diol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), were tuned and tested as multifunctional products with consolidating, water-repellent and biocide capacity to be used for stone recovery. For that purpose, sol-gel technology was applied to carry out the epoxy hardening reactions, via triethylenetetramine (TETA), in the presence of (3- glycidyloxypropyl)trimethoxysilane (GPTMS) and octyltriethoxysilane (OcTES), as silica-forming additives to acquire the flexibility and hydrophobic base requirements [1]. Then, the formulations were enriched, using different synthetic strategies (i.e., as such ionic liquids, essential oils and nanoparticles), and checked to gain an inhibition potential against biocolonization while keeping the main properties unchanged. Thus, the effect imparted on the hybrid network by various blends of dimethyloctadecyl[3(trimethoxysilyl)propyl] ammonium chloride, tetradecyl phosphonium, thyme oil encapsulated in mesoporous SiO_2 nanoparticles and cerium-doped TiO_2 nanoparticles was investigated by a combination of Scanning Electron Microscopy/Energy-Dispersive X-ray spectroscopy (SEM-EDS), Fourier Transform Infrared (FTIR) and Attenuated Total Reflection Infrared (ATR-FTIR) measurements. Moreover, the thermal, hydrophobic, and chromatic properties of the hybrids were determined by thermogravimetry/differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), contact angle, and color measurements. Furthermore, the antimicrobial growth inhibition capacity was studied by agar disk-diffusion method using sowing strains of *Micrococcus luteus*, and *Anthrobacter spp.* bacteria and, the most promising formulations were final tested on lithic samples by accelerated aging tests in acidic chambers.

Acknowledgements

This work has been financially supported by the project PHETRUM (CTQ2017-82761-P) from the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) and by the European Regional Development Fund (FEDER). P. Irizar and A. Pintor-Rial gratefully acknowledges their predoctoral grant from the MINECO (PRE2018-085888) and UPV-EHU (PIF19/81) respectively. O. Gomez-Laserna is grateful to the projects IT-742-13 for Consolidated Research Groups, funded by the Basque Country Government, and PHETRUM (CTQ2017-82761-P) from the MINECO for her post-doctoral contract. The authors are grateful to the technical support provided by the Raman-LASPEA laboratory, the Nuclear Magnetic Resonance laboratory and to the Macrobehaviour, Mesostructure, Nanotechnology: Unit of Materials and Surfaces of The Advanced Research Facilities of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF).

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Aqueous Multivalent-Ions Electrolyte for Electrochemical Supercapacitors: Boosting Electrochemical Performances

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Since the electrochemical capacitors are one of the most important electrochemical energy storage devices, they have found numerous applications in different power sources. Nowadays, different electrode material and different electrolyte formulation have been development in order to increase energy density. The widely used electrode materials are porous carbon materials due to high values of specific capacitance. Also, different electrolyte formulations have been development with large potential windows. These electrolytes include conventional electrolyte such as KOH, H_2SO_4 and different non-conventional (non-aqueous) electrolytes such as organic electrolytes ($TEABF_4$/ACN), ionic liquids ([EMIM][BF_4]) and their mixtures ([EMIM][BF_4]/ACN). Non-aqueous electrolytes are usually toxic, flammable, expensive and non-suitable for industrial production of electrochemical supercapacitors. The future of electrochemical supercapacitors represents new aqueous electrolytes based of multivalent ions such as Mg^{2+}, Al^{3+}, etc.

The aim of this work is to synthetize porous carbon/MWCNT hybrid material and investigates the charge storage mechanism of prepared carbon electrode in aqueous multivalent-ions electrolytes. The carbon/electrolyte interface will be studied and adjusted to achieve the large capability of carbon to store multivalent ions. Investigated material showed better energy storage behavior in multivalent-ions electrolyte, compare to conventional electrolyte such as H_2SO_4. New strategy aimed at improving the multivalent capacity of carbon will be presented and elaborated.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, PROMIS, #6062667, HISUPERBAT.

Photocatalytic Self-Cleaning Properties of Mo: TiO_2 Loaded Zn–Al Layered Double Hydroxide for the Application on Mineral Substrates

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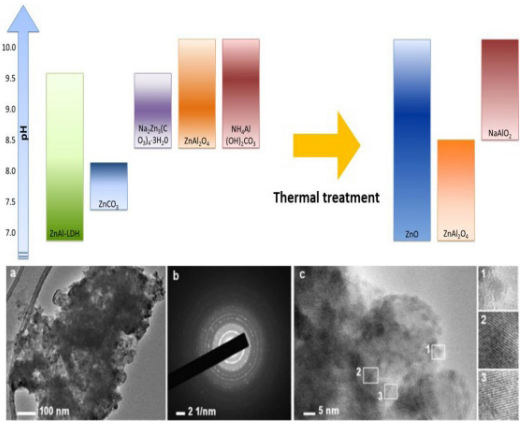

Layered double hydroxides (LDH) are, due to their lamellar nano-sheet structure, known as materials suitable for carrying of certain active, functional molecules [1]. In order to evaluate the dependence of the photocatalytic self-cleaning properties of layered double hydroxides (LDH) with intercalated active substances among their ultrathin nano-sheet layers on the synthesis parameters, particularly on the pH value, a series of ZnAl-LDH suspensions were synthesised using a modified low supersaturation co-precipitation method at various pH values between 7 and 10. The optimal pH value was found to be 8. The molybdenum doped TiO_2 nanocomposite LDH suspensions (Mo:TiO_2–ZnAl-LDH) were synthesised at the optimised pH value. The Mo/Ti mass ratio was systematically varied between 0 and 0.03 in order to cover the region below 0.03 which had been found to be optimal in our previous work [2] but it was at the limit of the investigation range (0.03–0.12). Systematic material characterisation study was performed.

The photocatalytic self-cleaning properties of the optimally synthesised Mo:TiO2–ZnAl-LDH suspensions were characterised when applied on stone, brick and glass substrates and after having been illuminated only by using LED visible light. The best results were obtained when the newly developed suspension was applied on the stone substrate due to the combined influence of surface roughness, textural characteristics and pH value of the mineral substrate [3].

Almost all synthesis routes of LDHs, both direct and indirect, employ some kind of thermal treatment, if not during the synthesis then after it aiming to improve the crystallinity of the products. Therefore, systematic thermogravimetric (TG) and dynamic scanning calorimetry (DSC) measurements were performed for all synthesized samples. Detailed microstructure analysis by X-ray powder diffraction (XRD) was conducted before and after the thermal treatment. From XRD analysis, supported by measured Fourier-transform infrared spectroscopy (FTIR), the crystal phases in synthesized ZnAl-LDHs were identified and the results of samples microstructure were compared in order to define thermally induced zinc and aluminium crystal phase transition pathways in dependence of the reaction medium's pH value.

Acknowledgements

The authors would like to acknowledge the support from Ministry of Education, Science and Technological Development (Serbia), project No.: 451-03-9/2021-14/200134 and from the EUREKA project E!13085 CAPTAN.

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Design of Ceramic System Based on Cement Kiln Dust as a Byproduct of Portland Cement Manufacturing

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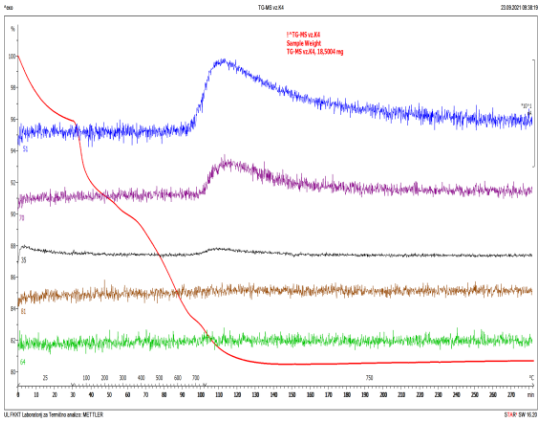

Novel practices of using alternative fuels by burning wastes in cement kilns have increased significantly during the last decade reaching almost 100% of the total energy consumption in some cement industries. These impacts in our research referrer to cement kiln dust (CKD) valorization obtained after the burning process of the alternative fuels (ordinary polyvinyl chloride). Organic compounds of these materials are completely destroyed during the thermal process and the obtained chlorine combines with sodium or potassium, both constitutive elements of the clay minerals used for the production of cement clinker, form ordinary salts like table salts (sodium or potassium chloride). One of the solutions, presented in our paper, is the use of cement kiln dust (CKD) as a secondary component in the production of ceramic systems.

The aim of our research was evaluation of solutions for CKD reuse as a secondary raw material for environmental-friendly building materials (lightweight aggregate, bricks and ceramic roofing tiles). It included the chain of activities, from thermal and chemical-mineralogical characterisation, evaluation and valorisation of the CKD potentials).

The paper analyses the compatibility of chemical and thermal characteristics of the basic clay mineral mixture (clay minerals, feldspars, mica, carbonates) used for the production of bricks, with the characteristics of cement kiln dust (CKD) samples in the presence of melting agents. Five mixtures based on clay materials, with different mass % of the cement kiln dust (CKD), from 30 % to 90 %, in the presence of a melting agent, were designed. Formation of new phases during the thermal treatment up to 950 °C was followed by thermo-gravimetric with mass spectroscopic analysis (TG-MS) and by DSC analyses. Based on the thermal characterisation, the maximal temperature of thermal treatment was set at 750 °C (Figure) as a frontier parameter aiming not to exceed the temperature of the salt decomposition what could lead to evaporation of harmful gasses in the atmosphere. The silica phase obtained during the thermal collapse of the clay minerals in the presence of the used melting agents bounded the released gases after the decomposition of the salts.

The final products characteristics were evaluated including thermal expansion, weight loss, porosity, microstructure, compressive strength, morphology and colour as well as leaching of soluble salts.

Key words: Cement kiln dust, environmental impact, ceramic materials, thermal treatment, new crystal phases

Acknowledgements

The authors are grateful for the support of The Ministry of Education, Science and Technological Development (Serbia), project No.: 451-03-9/2021-14/200134 and Serbia-Slovenia bilateral project [337-00-21/2020-09/49].

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Contribution to Water Resource Recovery Facilities: Influence of Magnetic Functionalization on Green Single and Hybrid Systems

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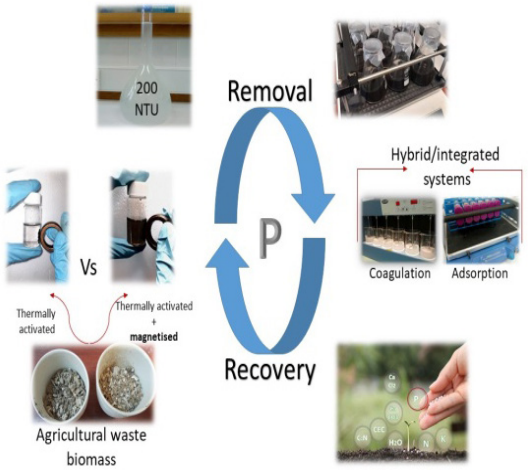

Resource recovery, as one of the major initiatives in the wastewater treatment field, aims to divert useful substances/pollutants and end-of-life materials away from the waste streams so they can be used to create valuable new products or outputs. In order to ensure long term sustainability in different wastewater technological operations, we need to rethink the way we deliver more sustainable and circular solutions. One of the challenges facing today's environmental engineers is phosphorus (P), as an irreplaceable nutrient and a scarce resource [1]. Different technologies including adsorption were investigated for potential P recovery from wastewater. This work emphasise the differences between magnetic and non-magnetic adsorbents applied in the single and hybrid/integrated purification systems. Further, magnetic adsorbents could be obtained from waste biomass by incorporation of different metal oxides/hydroxides (e.g., Al, Ca, Ce, Fe, La, Mg etc.) which are considered as fast, selective and efficient phosphate adsorbents [2].

Orthophosphates ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) are the most common form of P in waters and wastewaters, hence, present the main object of its recovery [2]. Magnetised adsorbent was obtained by thermochemical conversion (on 500°C in the absence of inert atmosphere) of agricultural biomass (apricot kernels) previously immersed in 20% $FeSO_4 \times 7H_2O$ solution. Non-magnetised adsorbent was prepared by the same procedure, but without impregnation step. Firstly, a single system were examined on a model solution of 10 mg/L orthophosphate (O-P) concentration. Tests were performed for different adsorbent dosages (1.25 - 12.5 g/L), pH values (2 -10) and contact times (5 min – 24 h). In order to better understand adsorption mechanism different isotherm and kinetic models were applied. Furthermore, the surface functional groups of both adsorbents were analysed using Fourier transform infrared spectroscopy (FTIR) analytical technique.

Under optimal pH (near neutral), adsorbent dosage (5 g/L) and contact time of 2 h high O-P removal (%) was achieved by magnetic adsorbent (> 90%), while significantly lower was obtained by non-magnetic adsorbent (< 40 %).

Finally, in the systems with elevated levels of suspended and colloidal particles, adsorption of P could be weakened. In order to overcome this problem adsorption was combined with coagulation/flocculation (e.g., green coagulant from common beans). The two technologies were applied simultaneously and successively in order to determine the most beneficial combination. The hybrid system was able to significantly reduce P from the water.

The results showed great potential, however, more research is needed in order to optimise P recovery in integrated systems and explore potential reuse of the recovered material in agriculture.

Acknowledgements

This research has been supported by Innovation Fund, Republic of Serbia, ID 5156 through project Proof of Concept and by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".

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Discovery of Polyesterases Able to Degrade Various Plastics

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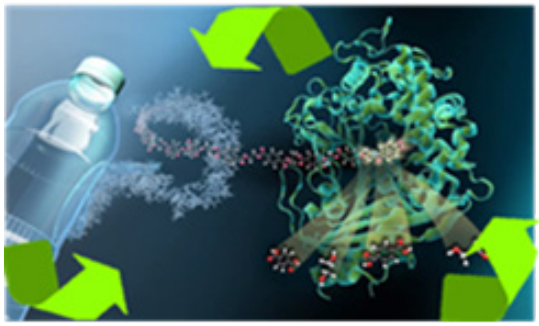

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Global demand for polymers has rapidly grown over the last decade, but more than 40% of total plastic production ends up in the environment, burdening it significantly [1]. Polyethylene terephthalate (PET) is synthesized by chain polymerization of terephthalic acid and ethylene glycol. Its properties have made PET the main material for bottle production adopted by the beverage industry. Despite the fact that most people are aware of recycling benefits, PET bottles are insufficiently recycled, as less than 28% of them were reused in the United States in 2018, while 57% of the produced bottles were disposed in landfills. Biodegradable polymers were proposed as a green alternative, despite the fact that their production remains low. Nonetheless, biodegradable polymers proved to not be a sustainable solution, as their natural degradation can take many decades, depending on the environmental conditions [2]. Moreover, compared to the existing plastic recycling processes, which demand high energy requirements and/or toxic reagents, biodegradation is considered an eco-friendly alternative, which can achieve depolymerization under mild reaction conditions.

In the present work, esterolytic enzymes with putative polyesterase activity were selected through genome mining and tested on different polyester-based plastics. PETases such as cutinase from fungus *Humicola insolens* [3], as well as the leaf-branch compost cutinase (LCC) [4] were used as benchmark enzymes. In our study, we also included enzymes mentioned in literature, which are referred as potential polyesterases, as well as commercial enzymes with proteolytic activity. The polymers tested include the biodegradable polybutylene succinate (PBS), polyhydroxy butyrate (PHB), polylactic acid (PLA) and polycaprolactone (PCL), as well as the non-biodegradable amorphous & crystalline PET and polyester polyurethane (PU).

The yield of degradation was evaluated by measuring plastic weight loss, variation in molecular weight by performing Gel Permeation Chromatography (GPC) or by detecting hydrolysis products by HPLC analysis.

Almost all the enzymes tested showed high depolymerase action in most materials. At this point, it should be mentioned that in some cases the tested polyesterases could hydrolyze more effectively different plastics than benchmark enzymes, a fact that could offer a vital solution in controlling plastic accumulation.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 870292.

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Regression Modelling of Ambient $PM_{2.5}$ Concentrations Sampled by Reference and Low-Cost Devices in Urban Environment

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Measurement and modelling of fine suspended particle ($PM_{2.5}$) concentrations are of great importance for health risk assessment and air quality management and control [1].

Our research aims to develop the Land Use Regression (LUR) model for Novi Sad, as one of the widely used models for air pollution assessment [2].

In order to better understand $PM_{2.5}$ pollution, as the first step in model development, sampling campaign was conducted at 20 measuring/sampling sites in Novi Sad municipality, during the summer and winter seasons in 2020 and 2021. Measuring / sampling sites were in urban, near urban and industrial areas. $PM_{2.5}$ were sampled using reference gravimetric pumps (Leckel Model LVS3) collocated with low-cost sensors. Duration of sampling was 48 h, providing five samples per site. Each low-cost sensor was calibrated in a separate collocation campaign which was conducted in the vicinity of the monitoring station of the Serbian Environmental Protection Agency in Rumenačka street, Novi Sad. Average daily $PM_{2.5}$ concentrations detected by low-cost sensors ranged from 19.86 – 43.80 μg/m^3 during winter and from 6.97 – 18 μg/m^3 during summer season. Concentration levels of $PM_{2.5}$ were in the range from 27.50 – 41.42 μg/m^3 during winter, heating season at 7 urban and near urban locations with low traffic frequency. Measured values are above daily limit value according to World Health Organization (WHO) of 25 μg/m^3, 24-hour mean. $PM_{2.5}$ levels at 10 urban / near urban locations with medium or high traffic frequency during heating season were even higher and ranged from 26 – 43.80 μg/m^3. Concentration level at industrial site, with high traffic frequency, during heating season was 33.69 μg/m^3. During summer, average daily $PM_{2.5}$ concentrations at all urban, near urban and industrial sites did not exceed daily limit values proposed by WHO.

The LUR modelling process will use geographical information system (GIS) and statistical analyses to quantify multivariate relationships between geographic features and measured concentrations of air pollutants [3, 4].

LUR model for Novi Sad will be developed using measured $PM_{2.5}$ concentrations at monitoring sites, as dependent variables, and data on the surrounding environment (traffic variables, population density, meteorology, land usage, and coverage), as potential predictors variables (PVs).

Having the LUR model for Novi Sad will provide a better insight into the air quality, enable useful guidance to local authorities, and many other benefits.

Acknowledgements

This research (paper) has been supported by the Ministry of Education, Science and Technological Development through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".

European Union's Horizon 2020 Research and Innovation programme under grant agreement No 952433.

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Chemometric Techniques Applied in Distribution and Characterisation of Polycyclic Aromatic Hydrocarbons (PAHS) in Krepoljin Coal Basin

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The variations in geochemical properties of organic matter in the sediments can be the result of the source input variations and/or diagenetic reactions in the sediment during and after the deposition. The characteristics of the early diagenetic processes which influenced the composition of the aromatic fraction of soluble organic matter, were assessed by the chemometric techniques: statistical correlation analysis and multivariate principal component analysis. After a mineralogical analysis (conveyed on the basis of the abundance in mineral calcite, Ct and sorptively active minerals of clay ilite and monmorionite, IM) had shown the existence of two hydrochemical environments [1].

The 16 PAHs on the U.S. EPA priority list have been determined in 10 sediment samples set, from Krepoljin coal Basin, Serbia, using Soxhlet extraction and GC-MS.

All the 16 PAHs were detected in the analyzed sediments. The first two primary factors of principal component analysis define over 77.5% of total variance in the set of results analyzed and included carcinogenic PAHs and low molecular weight PAHs. The total abundance of carcinogenic PAHs ranged from 165.55 to 550.42 μg kg−1. The most carcinogenic being benzo[a] anthracene, benzo[a]pyrene, and dibenzo[ah]anthracene, indicating a higher possibility of occurrence of adverse ecological effect. The PAHs are divided into three groups according to their molecular weight, i.e. low-molecular-weight (LMW-PAHs), medium-molecular-weight (MMW-PAHs), and high-molecular-weight (HMW-PAHs). Concentrations of LMW-PAHs (2-3 ring PAHs) constituted 26.25% of the 16-PAH content, followed by MMW-PAHs 54.25% and then lowest content of HMW-PAHs 19.50%.

The third factors includes Corg, atomic ratios H/C and O/C, Sorg and total S. This factor is expressing reduction, i.e. oxidation degree of sediment organic matter, which is result of diagenetic and /or maturation processes. Molar ratio of H/C play a leading role in the changing process in the PAHs, followed by the molar ratio of O/C. The average Corg-content in the calcitic sediments (Ct) seems to be lower than in the clay-matrix I-M sediments but the difference is not statistically significant due to the wide ranges of individual values. Carbonatic sediments have a weaker preservation capability for OM. Aapparent difference could contribute both: (i) an initially differing rate of organic precursor material supply affected by the hydrogeological events which paralelly changed the source of mineral materials (introduction of carbonates instead of clays) and/ or, (ii) the higher oxidative activity of humic electron-acceptors in the Ct environment [2]. In the both environment, Sorg directly depended om total sulphur content, hydrogeological conditions and the amount of Corg.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development (Grant No: 146008).

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Multibiomarker Responses in the Liver of the Northern Pike (*E. lucius*) from the Mrežnica River as an Indication of Water Contamination

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Mrežnica River is karst Croatian river included in ecological network of European Union NATURA 2000 which protects important areas for preservation of species and types of habitats. However, its lower course has been exposed to the impact of cotton industry for more than one hundred years, including release of metal polluted ash and slag material from coal burning [1].

To evaluate the current pollution status of the Mrežnica River and possible early toxic effects in organisms which occur due to exposure to industrial wastes, we have applied multibiomarker approach in the liver of the northern pike (*Esox lucius*), as a representative fish species. Analyzed set of biomarkers included the activity of enzymes catalase (CAT) and acetylcholinesterase (AChE), and concentrations of malondialdehyde (MDA), glutathione (GSH), total cytosolic proteins (TP) and metallothioneins (MTs). Additionally, we have measured cytosolic concentrations of several metals. Fish sampling was performed at the reference site, upstream of the known pollution source, and near the former cotton industry facility as the presumed site of historical contamination.

Some significant differences in biological responses between the fish from two sites, when we analyzed all sampled fish, were observed. However, strong impact of historical contamination was not confirmed when only fish with similar body masses were compared, which indicated the influence of body size. Still, trend of higher accumulation of some metals (Bi, Cs, Cu, Fe) at the contaminated site was evident, but not followed by biomarker responses. Higher levels of GSH and MT, as well as Mn and Tl, and lower AChE activity, were recorded at the reference site, possibly due to agricultural practices.

Two liver colorations, probably due to different feeding habits, were observed at both sites; „green“ in most of smaller and probably more invertebrate-feeding individuals, and „yellow“ in bigger fish which are almost completely piscivorus [2]. Green livers in fish can be caused by lower fish meal diet due to the deffiiciency of specific proteins involved in excretion of bile pigments [3].

Differences betwen green and yellow livers within each site were small for biomarkers. For metals, higher levels in fish with yellow liver were observed for Bi, Cs and Fe, and in fish with green liver for Mn, Mo and Co, suggesting different metal availability depending on the diet.

Differences between sites for metals were more obvious in fish with yellow liver, with significantly higher Bi, Cu and Fe accumulation at the former factory site, and Tl at reference site. Among biomarkers, significant difference between sites was observed only for AChE activity in fish with yellow liver. Beside water and sediments as contamination sources, our research showed the importance of feeding habits for fish biological responses. Diet of fish with yellow liver is probably more diverse, which contributes to variations in biomarker and metal levels between two groups of northern pike.

Our results point to moderate impact of former factory and contribute to evaluation of the influence of long-term historical contamination, but also of feeding behavior on condition of fish in the Mrežnica River.

Acknowledgements

This work has been fully supported by Croatian Science Foundation under the project METABIOM (IP-2019-04-2636).

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Photoactivity of Immobilized Titanium Dioxide (TiO_2) in Lindane Degradation

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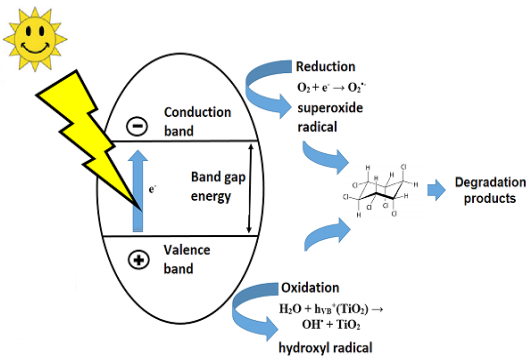

Introduction and study objectives

Lindane is a generic name for γ-hexachlorocyclohexane, one of the isomers from the group of Hexachlorocyclohexanes (HCH) [1]. Due to its neurotoxic activity, it had a very wide application, from agricultural to non-agricultural purposes.

As a result of its lipophility, lindane can easily pass through the blood-brain barrier. The reason of his neurotoxicity is that it can interact with $GABA_A$ receptors and obstruct GABA neurotransmitter signaling in nervous system. People who have been exposed to lindane for a long time can experience serious health problems, such as: poor liver function, cardiac arrhythmias, and irregular menstruation. Due to its adverse health effect, lindane is classified as a "pregnancy category C" chemical [2]. It is also one of the Persistent Organic Pollutants (POPs) that were listed under the Annex A (elimination) of the Stockholm Convention with a specific exemption for use as a human health pharmaceutical [3].

The aim of this paper was the assessment of the immobilized titanium dioxide photocalytic properties in lindane degradation.

Methodology

Spray pyrolysis method was used for a synthesis of thin titanium oxide films on the foils of the stainless steel [4]. The lindane solution was incubated with TiO_2 and exposed to UV/VIS light. Aliquots were taken from the reaction mixture after 0, 2, 4, 6, 8, 10 and 12 hours. Lindane was extracted according to the EPA method 505 [5], and analyzed using an Agilent 7890A gas chromatograph (GC) connected to an electron capture detector (ECD). The GC was equipped with a Thermo Scientific™ TraceGOLD™ TG-5MT capillary column (60 m × 0.25 mm ID × 0.25 µm). The temperature program used for gas chromatography was: Initial heating temperature: 50 °C for 3 minutes, then heating at a rate of 30 °C/min to 210 °C for 20 minutes. Hydrogen with a flow rate of 60 mL/min was used as the carrier gas.

Results and conclusions

Photoactivity of immobilized titanium dioxide in the degradation of lindane was measured as a percentage of lindane's degradation compared to its initial concentration.

The obtained results demonstrated that after two hours 45.32 % of lindane was degraded, while after twelve hours the percentage of degradation increased to 98.20 %.

In this study we proved that the immobilized titanium dioxide can be used as a productive and fast photocatalyst for lindane photodegradation.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant No: 451-03-9/2021-14/200026) for financial support.

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Deeper Insight into the Metallome of the Digestive Glands of *Unio crassus* Mussels at Different Metal Exposures: Distribution of Metals among Cytosolic Biomolecules

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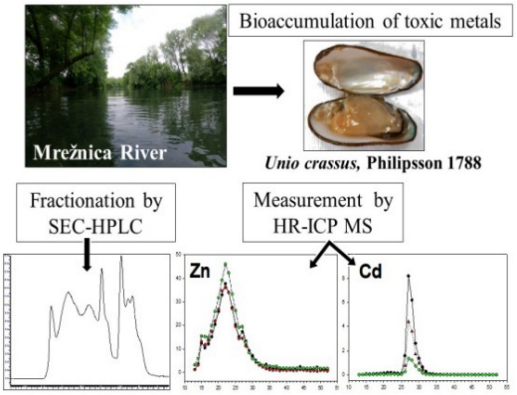

Metallomics, a recently developed field of metal and metalloid research, focuses on the determination the distribution of metals in cells and tissues and their interactions with cellular components, in addition to the quantification of metals [1]. Mussels are generally recognised as useful biological indicators of aquatic pollution at both the organic and cellular levels, while the digestive gland is the central detoxifying organ of the organism. The cytosolic fraction of the tissue metallome contains a metabolically active and therefore potentially toxic fraction of metals, while cytosolic metalloproteins are one of the most common targets of toxic metals [2].

The combination of size-exclusion liquid chromatography (SEC) and inductively coupled plasma mass spectrometry (ICP-MS) is a useful tool for screening metal distribution among the different molecular mass biomolecules [3]. Using the above methodology, the focus of this study was to establish cytosolic profiles of several essential (Cu, Fe, Zn) and non-essential elements (Ag, Cd, Pb) and to define the masses of metal-binding biomolecules in the digestive gland of the freshwater mussel *Unio crassus* from two sites of the Mrežnica River with different anthropogenic influences: the industrial area of the city of Karlovac (KAR) as a polluted site and location upstream of the city of Duga Resa as a reference site (REF). Cytosolic Ag, Cd and Pb were mostly bound to components of cytosol eluting in the high molecular mass (HMM; >300 kDa) and low molecular mass (LMM; 10-40 kDa) regions, but with greater elution in the LMM peak, which presumably contained metallothioneins (MT). The distribution profile of essential metal Cu was similar to the previously mentioned highly toxic metals. This suggests that MT plays a crucial role in the homeostasis of essential metals as well as in the detoxification of toxic metals. Iron had a peak in the HMM area, which roughly coincided to ferritin, the major Fe storage protein in almost all organisms. Zinc eluted in a wide range of molecular masses (10-750 kDa), indicating the binding of Zn to a large number of proteins, which is consistent with its importance in many biological processes. In general, the chromatographic profiles obtained at both sites were comparable for all elements studied, suggesting that the same cytosolic biomolecules are involved in metal binding at different levels of metal accumulation.

Quantitative differences in element profiles between the two sites, visible as different peak heights, were found for Cd, Cu, Fe and Pb and were consistent with significant differences in total cytosolic element concentrations between sites. These results suggest that the distribution of selected essential and non-essential elements among different cytosolic ligands may serve as a potential indicator of metal exposure. Therefore, further separation and characterization of cytosolic metal-binding biomolecules would be useful.

Acknowledgements

This work has been fully supported by Croatian Science Foundation under the project METABIOM (IP-2019-04-2636).

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Biodegradation Assessment of Poly(Urethane-Dimethylsiloxane)/Organoclay Nanocomposites under Environmental Conditions

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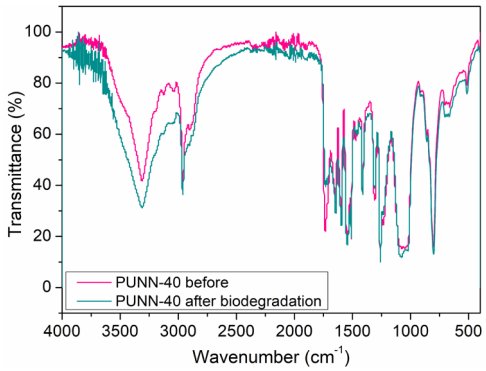

Figure 1. FTIR spectra of selected PUNN.

The first series of polyurethane network nanocomposites (PUNN) was prepared by *in situ* polymerization [1,2] from poly(dimethylsiloxane)-based prepolymer as the soft segment and 4,4'-methylene diphenyldiisocyanate and hyperbranched polyester of the third pseudo generation as the hard segment, in the presence of organically modified montmorillonite nanofiller (Cloisite 30B; 0.5 wt.%). The second series of pure polyurethane networks (PUN) without organoclay was also prepared. The composition of prepared materials in both series was varied through variation of soft segment content from 30 to 60 wt.%. Biodegradability of prepared materials was measured using mixed cultures of microorganisms that originated from soil. This test used soil bacteria and fungi to assess the impact of the environment on polymer compounds. This test is intended to determine which polymer compositions are best suited for coating other materials that must endure lengthy exposure to harsh environmental conditions while retaining their principal functionalities.

The biodegradation test was performed under aerobic conditions in the dark condition and in a thermostat at 28 °C. Bacterial and fungal mixed cultures were alternated monthly. After 3 and 6 months of the test, the materials were washed with water, dried in a vacuum oven to constant weight, and used for gravimetric measurements of weight loss. The prepared materials before and after biodegradation test were characterized by FTIR spectroscopy.

The results showed that pure PUNs (18.35-18.66 wt.% after six months) possess the highest weight loss as compared to PUNNs (from 7.53 to 14.78 wt.% after six months) after incubation of up to six months. PUNN films had lower biodegradation degree as compared the pure PUN films. Biodegradability was lower for materials with lower soft segment content.

In FTIR spectra of PUNN after biodegradation differences were noted at approximately 1700-1735 and 3324 cm^{-1}. The structures contributing to strong hydrogen bonds were partially destroyed during the biodegradation process. The results showed that PUNN with 40 wt.% of soft segment (PUNN-40) is the most resistance material to biodegradation. The reason was probably due to more hydrogen bonding between the polymer and Cloisite 30B organoclay and its better mechanical properties of PUNN-40 sample as compared to other prepared PUNN materials. The obtained materials are good candidate as top coating materials exposed to the environmental conditions.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-9/2021-14/200026; 451-03-9/2021-14/200168).

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Elemental Profile of Hashimoto's Thyroiditis: Thyroid Tissue, Blood, and Urine Analysis

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Fig 1. Map of Serbia. The shaded fields represent the capital (Belgrade) from which patient samples were collected, as well as the areas more exposed to toxic metals.

Hashimoto's thyroiditis (HT) is the most prevalent autoimmune disorder of the thyroid gland [1]. As a result of the continuous deterioration of the gland caused by HT, more than 90% of patients develop thyroid insufficiency and hypothyroidism [2]. It has been noted that genetic and/or environmental factors play an important role in the etiology of HT [3]. The most prevalent environmental and hazardous risk factors that were linked to the pathogenesis of HT include Se deficit, pollutants, and irradiation [4].

The focus of this research was to determine which trace elements could have a role in the pathophysiology of HT. In this regard, the essential trace elements for thyroid homeostasis (Mn, Cu, Zn, Se) and the main hazardous toxic trace elements (Ni, As, Pb, Cd, U) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) in the thyroid tissue, blood, and urine samples of patients with diagnosed HT. Control samples of blood and urine were collected from healthy donors. Moreover, the effects of relevant parameters on element profiles were examined and addressed in terms of environmental concerns.

This investigation discovered a variation in the elemental profile of HT and control samples. Thyroid tissue and HT blood samples had significantly increased As and Pb levels. The obtained negative correlations between As and Pb and Se potentially indicates the antagonistic influence of As and Pb on the extrusion of essential Se from the HT tissue.

The absence of Se in HT could be further explained by the obtained lower levels of Se in blood and higher Se in urine samples. Importantly, the findings could provide the understanding of the as-yet unresolved molecular basis of HT, and also highlight the role of these elements on thyroid homeostasis.

Acknowledgements

This research was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Contract Number: 451-03-9/2021-14/200288.

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Soil Contamination by Petroleum Products in the Urban Environments: Belgrade, Serbia

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Environmental pollution with petroleum and petrochemical products has attracted much attention in recent years. The present study is focused on the investigation of urban soil pollution in the area of thermal plant New Belgrade with more than 200000 residents. Thermal Power Plant New Belgrade is located on the left bank of the Sava, about 1 km from the Sava's confluence with the Danube. The Thermal Power Plant complex consists of storage tanks for crude oil and oil products and it was contaminated due to break-down of the mazut reservoirs (2009, during a gas crisis) and NATO bombing of the reservoirs (1999).

A total of 45 soil samples were collected in May, 2015, and in total 8 geochemical parameters were determined by using official or recommended methods [1].

Statistical data processing includes application of multivariate statistical methods to previously systematized data on geochemical parameters in soil samples from Belgrade city. Two multivariate statistical methods have been applied – hierarchical cluster analysis (HCA) and factor analysis – analysis of the main components (PCA).

From the output of the hierarchical cluster analysis, a total of three clusters of the soil samples were recognized according to the level of clustering. Cluster A and B are linked at a shorter distance and are together linked to Cluster C at a longer distance. Component 1 of the PCA dominated in group A. Samples of group A contained the maximum amounts of total aliphatic hydrocarbon (TPH) (71.85±17.9), and Unresolved/Resolved complex mixture (U/R) (3.02±1.8) higher than the other groups. The results of the soil analyses indicated that most samples classified as C1 may reflect anthropogenic contamination of the urban environment. The results showed that the top soil contained high concentration of TPH (90.65 mg kg^{-1}). This may be a result was caused by crude oil spills and leaks which continuously occured for long periods of time. According to the "Regulation on the program of systematic monitoring of land quality, indicators for According to the "Regulation on the program of systematic monitoring of land quality, indicators for assessment of the risk of land degradation and the methodology for making remediation programs "(Official Gazette of RS, No. 88/2010-Annex 13) are not higher than" values that may indicate significant contamination "-remediation values, but are higher than "limit values", which means that this area must be programs "(Official Gazette of RS, No. 88/2010-Annex 13)) are not higher than" values that may indicate significant contamination "-remediation values, but are higher than" limit values ", which means that this area must be under permanently monitoring.

Group B is represented by a principal component 2 related to the highest CPI (3.48±1.32), Low/High alkanes (0.299±0.45), and ACL (the average number of carbon atoms per molecule based on the abundance of odd-carbon-numbered higher plant *n*-alkanes) (29.67±0.40). The analyzed samples have similar ACL contents in all groups. Distribution of these parameters suggesting predominant biogenic sources rather than petroleum related input.

The component 3 of the PCA2, loaded by *n*-C17/ Pr, and *n*-C18/Phy, also constituted a strong cluster C, *n*-C17 and *n*-C18 are more abundant than the isoprenoids pristane and phytane. Comparatively, isoprenoid hydrocarbons are more resistant to biodegradation than *n*-alkanes [2], leading to the increase of Pr/ *n*-C17 and Ph/*n*-C18 ratios to a value of much higher than 1 when they have been deeply degraded [3]. The distribution of Pr/*n*-C17, and Ph/*n*-C18 ratios for almost all samples are small than 1, indicate biogenic contribution, except of some samples are around 1, points to petroleum contamination source in urban area of Belgrade city.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development (Grant Nos. III 43004).

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Effect of Poly-3-Hydroxybutyrate Microparticles on the Aquatic Organism *Daphnia magna* and the Plant *Lemna minor*

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Due to the superior properties of plastics, such as low cost, light weight, durability, waterproof, etc., plastic production has been growing rapidly for application in agriculture, industry, packaging or medical treatment [1]. Plastics accumulate in the environment due to their durability, improper disposal of plastic waste, and widespread use of plastic products [2]. In the environment, larger plastic fragments (macroplastics) are gradually broken down due to weathering, degradation, and microbial-mediated factors, into small plastic particles – microplastics [3]. Microplastics can be defined as solid synthetic particles or polymer matrices with regular or irregular shape and with a size in the range of 1 µm to 5 mm. These particles are insoluble in water [4].

Biodegradable plastics (BDPs) have an appeal in ensuring the safe return of carbon to ecosystems by complete assimilation of the degraded product as a food source for soil or aquatic microorganisms [5]. The material to produce BDPs can be renewable raw materials, petrochemicals, or mixtures [6]. Biologically based BDPs are made from natural materials derived from plants, animals, or microorganisms, such as polysaccharides (starch, cellulose, lignin, and chitin), proteins (gelatin, casein, wheat gluten, silk, and wool), and lipids (vegetable and animal oils). This category also contains rubber and certain polyesters produced by microorganisms or plants, eg, polyhydroxyalkanoates (PHAs), including poly-3-hydroxybutyrate (P3HB). BDPs have found applications in medicine, agriculture, and packaging materials. The advantage is that most of the modified conventional polymer processing techniques can be used to process BDPs [7].

One of the most important groups of biobased and biodegradable polymers are PHAs. In our work, we focused on the influence of P3HB microparticles on the aquatic organism *Daphnia magna* through acute and reproductive ecotoxicity tests (48 h of exposition, resp. 21 days of exposition). Based on the first results of the acute toxicity tests it can be concluded that P3HB microparticles have a very small acute toxic effect on the organism *D. magna*. The highest observed mortality was 25%, which was a statistically significant result. In reproduction tests, the average number of juveniles decreased significantly with increasing concentration of P3HB microparticles, and significantly lower birth rates were observed for particles from 63 to 125 µm size than for those smaller than 63 µm. The results of the growth inhibition test with *Lemna minor* showed a low effect on the test organisms after 7 days of exposition.

Acknowledgements

The financial support of project FCH-S-21-7398 of the Ministry of Education, Youth and Sports is acknowledged.

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Assessing the Potential Toxicity Effects of Microplastic Particles of Poly-3-Hydroxybutyrate on Terrestrial Organism *Eisenia fetida*

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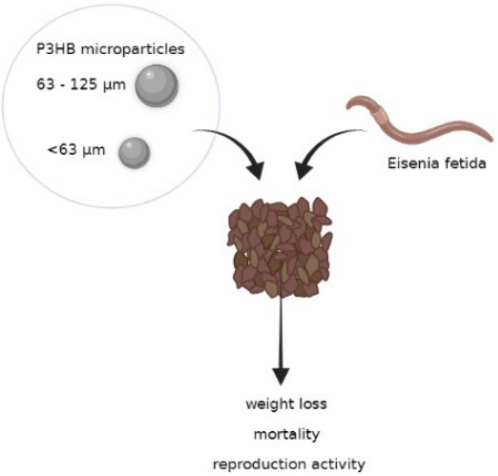

Microplastics are recognized worldwide as a threat to soil ecosystems. Soils can be contaminated with microplastics through the application of sewage sludge applied as fertilizers and wastewater, plastic mulching, littering, tire abrasion, and atmospheric deposition [1]. The microplastics present in the soil could affect its physical properties, such as the water retention capacity (WHC), processes such as soil agregation, the performance and composition of the soil microbial community, the soil fauna, and the flora [2]. Many plastics items are manufactured from durable polymers, such as polyethylene, which is not considered biodegradable and can persist in the environment for decades [3].

Soil fauna is critical for maintaining healthy soil. Earthworms are one of the most important and are considered key ecosystem engineers and bioindicators of environmental quality [4]. Microplastics can be easily ingested by soil-living organisms, potentially affecting their fitness and survival. Furthermore, microplastics could absorb harmful contaminants from soil solution and locally concentrate them in the soil [5].

Biodegradable polymers (BDPs) are becoming a common alternative to conventional plastics, but the degradation of many BDPs under ambient conditions has proven to be lengthy or incomplete [3]. Among the various biopolymers, poly-3-hydroxybutyrate (P3HB) is a preferable one due to its high thermoplastic properties like traditional polymers and has the most suitable physical, mechanical, and immunological properties, which promotes that P3HB is a suitable alternative for traditional polymers [6].

In our study, we focus on the influence of P3HB microparticles on the terrestrial organism *Eisenia fetida* through acute and reproductive ecotoxicity tests (14 days, resp. 8 weeks exposition). We tested two size fractions of microparticles, smaller than 63 µm and particles of size from 63 to 125 µm. For the biotest, we used artificial soil. Our first results show that P3HB microparticles have almost non acute effect on earthworms *E. fetida*. In reproduction tests, the number of juveniles and the number of cocoons decreased with increasing concentration of P3HB microparticles in the tested soil.

Acknowledgements

The financial support of projects FCH-S-21-7398 and Kvalitní interní granty VUT EF19_073/0016948 of Ministry of Education, Youth and Sports are acknowledged.

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The Effects of Microbial Polysaccharides on the Copper Accumulation in *Daphnia magna*

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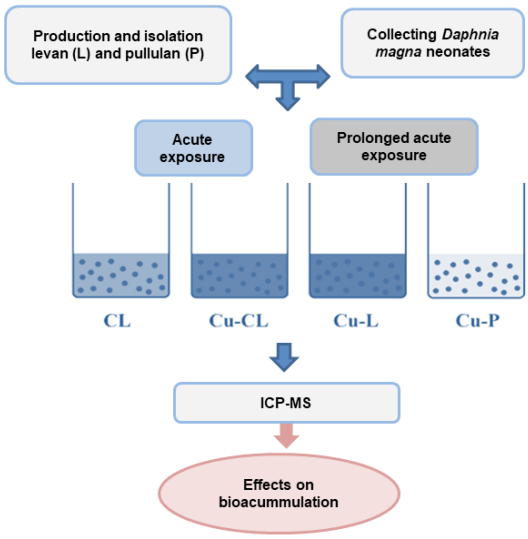

Copper is one of the leading metal pollutants in the water, which can cause adverse effects when present in high concentrations. The *Daphnia magna* is a model organism usually used for the determination of ecotoxicological effects of various compounds since it is highly sensitive to toxic compounds [1].

The aim of this work was to investigate the potential application of microbial extracellular polysaccharides (EPS), levan and pullulan, as agents for reducing the copper toxicity to *D. magna*. The protective effects of EPS were estimated based on the accumulation of copper in the D. magna cells.

Levan is a branched fructane EPS [2] and the one used in this study was produced by *Bacillus licheniformis* NS032. Pullulan, a linear glucan EPS [3], was produced by *Aureobasidium pullulans* CH-1. The *D. magna* were exposed to 50 μg/dm^3 of Cu (II) or a combination with 50 mg/dm^3 and 100 mg/dm^3 of levan or pullulan for 48h in the acute test. Additionally, the prolonged test was performed, where the daphnia were exposed to a 10 μg/dm^3 of Cu (II) with or without 50 mg/dm^3 of levan or pullulan for 5 days. After the exposure period, the samples were digested and the accumulation of copper in *D. magna* was analysed using the iCAP Qc ICP-MS (Thermo Scientific, United Kingdom).

The results showed that animals exposed to Cu (II) only, accumulated Cu (II) in a greater amount after the prolonged test compared to the acute one, despite the lower concentration. The treatment with EPS during the acute test increased the copper accumulation for both EPS concentrations tested, whereas during the prolonged exposure test, the Cu (II) accumulation was inhibited.

Considering that protective effects of levan and pullulan were observed only with lower copper concentrations and 5 days of exposure, additional experiments are necessary to determine the mechanism of EPS action in order to confirm their possible use as protective agents.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development (MoESTD) of Republic of Serbia (Grants No: 451-03-9/2021-14/200168 and 451-03-9/2021-14/200026).

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Metabolomic Study of the Biodegradation Pathway of Sodium-Benzoate in *Pseudomonas aeruginosa* san ai

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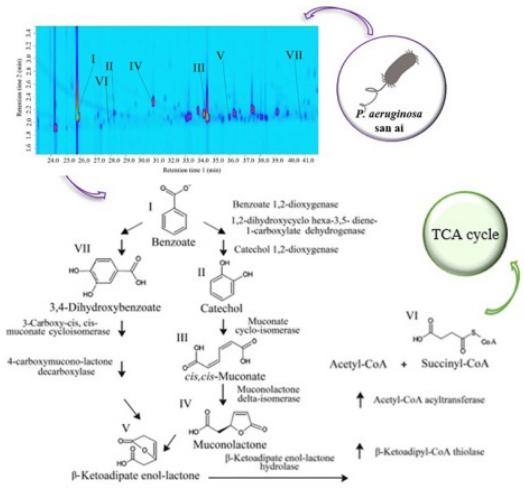

Many aromatic compounds are considered to be environmental pollutants that can adversely affect flora and fauna, resulting in the entry of toxic compounds into the food chain causing serious health problems and genetic damage in humans.

Fourteen different pathways of aromatic catabolism in *Pseudomonas* have been confirmed [1]. Benzoate is often used as a model compound to investigate the possibility of microbial degradation of aromatic compounds because it is the simplest known aromatic intermediate in the biodegradation of various complex polyaromatic compounds. The obtained information on the bacterial degradation of benzoate can be further used to understand and predict the degradation pathways of more complex aromatic compounds.

Analytical omics methods enable the study of early molecular changes in the organism to sources of pollution and as such can be used to identify a specific metabolic response to a toxic substance, detect new biomarkers and predict the effects of pollutants on organisms and the environment [2].

The goal of this study was to analyze the products of benzoate degradation by polyextremophilic, hydrocarbonoclastic *Pseudomonas aeruginosa* san ai [3] using targeted metabolomic analysis in order to determine the specificity of the metabolic pathway of sodium-benzoate. The metabolites of benzoate degradation, after 11 h, 24 h, 48 h and 7 days of incubation, were analyzed using a GC x GC-MS approach. The mass spectrum and retention time of compounds clearly confirmed presence of seven benzoate metabolites such as: 3,4-dixydroxybenzoate, catechol, *cis, cis*-muconic acid, muconolactone, β-ketoadipate enol-lactone and succinic acid as the end product of the benzoate transformation. Our results indicate the degradation of NaB through the catechol branch of β-ketoadipate degradation pathway, followed with *ortho*- cleavage of catechol. Furthermore, the identified protocatechuate implies the existence of the second branch of β-ketoadipate pathway.

Metabolomic study showed that almost 99% of benzoate was removed / metabolized within 48 hours and clearly indicates that aromatic degradation occurs via β-ketoadipate. *P. aeruginosa* san ai can be considered as a good candidate for application in bioremediation of environments polluted by different aromatic compounds.

Acknowledgements

This study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, Projects III 43004 and 176006.

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Ecotoxicological Effects of Methylnitrocatechols

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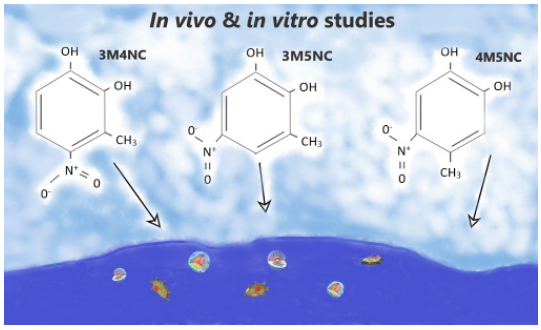

Nitrated monoaromatic compounds (NACs) are considered as indicators of secondary organic aerosols in the atmosphere mainly formed from biomass burning (BB) and anthropogenic sources [1]. MNCs are compounds determined in high concentrations in ambient particles contributing (with other less represented NACs) ~ 1% to their total organic mass [2]. These compounds are atmospheric pollutants that can easily enter aquatic ecosystems through atmospheric deposition [3].

We investigated the ecotoxicological effects of the selected model methylnitrocatechols (MNCs) 3-methyl-4-nitrocatechol (3M4NC), 3-methyl-5-nitrocatechol (3M5NC) and 4-methyl-5-nitrocatechol (4M5NC) as well as their mixtures. Acute and chronic toxicity was determined by measuring the cytotoxic effect *in vitro* on PLHC1 fish cells (MTT test) and chronic toxicity was determined *in vivo* by measuring the growth inhibition of unicellular green algae of the species *Scenedesmus subspicatus* (AlgalTox) over a 96-hour period.

In vitro bioassays were performed to determine the interaction with phases 0 and I of cellular detoxification mechanism. The inhibition of phase 0 membrane transporters, organic cation transporter Oct1 and organic anion transporting polypeptide Oatp1d1 was determined using Flp-In-293-drOct1 and Flp-In-293-drOatp1d1 stable cell lines. The results of measuring the inhibition of Oct1 transport of ASP+ model substrate after simultaneous incubation with model compounds showed inhibitory effect on model substrate uptake. Individual compounds and their mixtures inhibited in the range of 23.9 - 43.2 uM. We determined the inhibition of the transport activity of Oatp1d1 by measuring the inhibition of the uptake of the model substrate lucifer yellow (LY) after simultaneous incubation with model compounds. Individual compounds and their mixtures inhibited in the range of 28.8 – 53.6 uM. Phase I induction of CYP1A1 detoxification enzymes by EROD bioassay revealed that neither the model MNCs nor their mixtures were typical inducers of the CYP1A1 enzyme.

The observed significant toxic effects of individual MNCs and their mixtures will be discussed in the view of their structure and in relation to their concentrations found in aerosol samples affected by BB and mixed antropogenic sources.

Acknowledgements

This research was financed by the Croatian Science Foundation project BiREADI (IP-2018-01-3105) We also acknowledge financial support from Marie Curie FP7-PEOPLE-2011-COFUND (GA No. 291823) through the NEWFELPRO project AERONAR (Contract No. 47).

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Preliminary Results of the Evaluation of Lead Exposure in Adolescents: Should We be Concerned?

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Heavy metals, especially lead, have a growing hazard potential to human health due to the common occurrence in different environmental compartments (air, water and soil). Continuous emission from different sources such as industrial plants, vehicle exhausts, thermal power stations etc. present a global problem, due to the bioaccumulation potential and high persistence of lead in the environment [1]. Children are exceptionally sensitive to lead exposure due to outdoor activities and unproper hygienic habits [2]. Lead could interfere with different metabolic processes and consequently disrupt normal growth and development. Hence, human biomonitoring studies present an efficient tool for estimation of possible adverse effects of lead on health by measuring its levels in body fluids [3].

Considering the fact that lead was frequently detected in soil in Vojvodina Province (Serbia) and that the average levels in analyzed food samples (potato and carrot) exceeded the maximum allowable concentrations established by European and Serbian regulation [4], the aim of this preliminary study was to determine the prevalence of lead in urine samples among adolescents.

In this study 20 healthy adolescents of both genders (aged from 10-21) were randomly enrolled. After the microwave system digestion, lead was determined in morning urine samples by inductively coupled plasma-mass spectrometry, ICP-MS.

Lead was detected in 14 out of 20 samples (70%) above limit of the detection (0.02 mg/L). The higher frequency of the detection was obtained in girls (73%) in comparison with boys (67%). The obtained results confirmed that adolescents are ubiquitously exposed to lead in this region.

Lead is recognized as powerful endocrine disruptor due to the ability to impair normal synthesis, transport and/or metabolism of different hormone in a dose-dependent manner. By binding to the erythrocyte membrane, this heavy metal triggers the oxidative stress and causes adverse effects on locomotor, cardiovascular, gastrointestinal and urinary systems and significantly reduces cognitive abilities in children [5].

Bearing in mind all above mentioned, the special attention should be paid on urinary lead levels in children and young adults in Vojvodina, in order to evaluate the health risks that may be associated with the obtained high frequency of detection (70%). Further studies which include more adolescents of both genders are needed.

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Delineation of Light Non-Aqueous Phase Liquids (LNAPLs) Using Laser-Induced Fluoresence (LIF) Probe - Pennsylvania, United States

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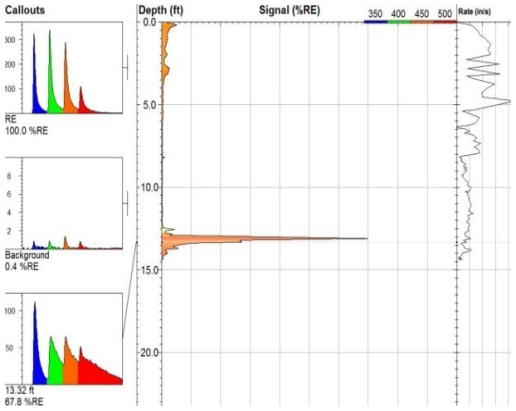

LIF Log Example from the Pennsylvania Site

An understanding of non-aqueous phase liquid (NAPL) distribution in the subsurface is a fundamental component of any hydrocarbon-contaminated site remediation strategy. This study emphasizes the potential of Laser-Induced Fluorescence sensor/probe (LIF) in the investigation of contaminated sites. The use of LIF advanced into the subsurface via direct push drilling technology enables the screening of residual and free-phase NAPLs by detecting polycyclic aromatic hydrocarbons (PAHs). Compared to traditional drilling and excavation methods, LIF investigations are faster and provide instantaneous output. Moreover, the direct push drilling technology without conventional core sampling provides highly accurate contaminant readings.

The LIF system utilized, at this diesel-contaminated site predominantly made of fine-grained sandstones in Pennsylvania, is the latest generation ultraviolet optical screening tool (UVOST) system developed by Dakota Technologies, Inc. Typical LIF/UVOST log from this study is shown in above-listed figure. It consists of a primary graph of total intensity fluorescence versus depth, and an information box with waveform "callouts". The depth is plotted on the Y axis and the combined total fluorescence intensity of the four monitored wavelengths is plotted on the X axis as a percentage of the normalized 100% Reference Emitter (RE) performance standard. Since different PAHs do not exhibit a linear correlation between fluorescence and increase in concentration it should be emphasized that the system response should be considered only qualitative and not quantitative. However, in some cases a change in PAH concentration may be inferred from the shift towards red waveform/channel on the LIF log. The current LIF sensors can be used to help identify the petroleum products including but not limited to gasoline, diesel, fuel oil, jet fuel, motor oil, cutting fluids, hydraulic fluid, and crude oil, but not individual chemicals present at the site [1].

The results of the LIF/UVOST investigation indicated that LNAPL was detected in 6 of 17 total LIF borings, with the RE responses ranged between 45% and 225%. This variation in signal response could be attributed to differing lithology or pore saturation values. The depth of contamination ranged from 3.9 to 4.6 m, with the exception was boring LIF-10 (3.2 and 3.5 m). The waveforms/channels(blue, green, orange, and red) likely differ due to variances in LNAPL saturation. The LNAPL readings were sporadic along the LIF investigation line (adjacent to a culvert), and indicated limited vertical extent of LNAPL concentrated mainly at the soil-groundwater interface. It was concluded that no substantial amount of LNAPL existed around the LIF investigation line along which contamination could migrate further. The use of LIF in the weathered portion of this fractured sandstone aquifer was limited to determining individual locations and depths of contamination along the presumed LNAPL migration path. In soils with intergranular porosity this technique can provide detailed insight into spatial distribution, and enable contouring of contamination occurrence.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, Program DIASPORA, #Grant No. 6455306, GRACE.

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Metabolic Responses of *Pseudomonas aeruginosa* san ai to Nanoceria

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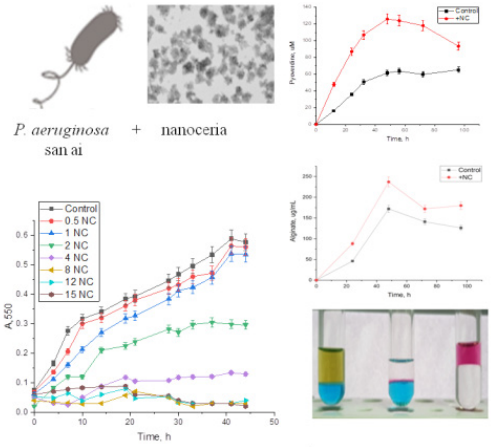

Among numerous available nanomaterials, nanoceria (NC) has a particular importance based on its redox properties which are considered as a cause of antibacterial activity [1]. *Pseudomonas aeruginosa* is Gram-negative bacteria, well known for its ability to grow in diverse environments due to great potential for adaptation and its metabolic diversity. Its ability to overcome the challenges lies on bacterial cell-cell communication mechanism, known as quorum sensing (QS) system, which regulates expression of numerous genes [2].

To reveal effects of NC on metabolism of environmental isolate of polyextremophile *P. aeruginosa* san ai, production of exopolysaccharide, pigment – pyocyanin, siderophores – pyoverdine and pyochelin, as well accompanied changes related to QS, biofilm formation, and redox homeostasis were investigated.

The minimal inhibitory concentration of NC against *P. aeruginosa* san ai is 8 mg/mL, which classifies it in a group of highly resistant *Pseudomonas*.

P. aeruginosa san ai exhibited an important formation of biofilm, with OD590 readings of 0.21 for culture grown in LB and in range from 0.26 to 0.57 for culture from LB amended with increasing concentrations of NC (from 0.5 to 5 mg/mL). Accordingly, *P. aeruginosa* san ai can be classified as moderately adherent strain.

Changes in alginate formation with increasement of 37% in the presence of NC, which have been detected, imply its engagement in the cell protection. An improved biofilm formation and production of alginate in the culture exposed to nanoceria clearly indicates their role in the first line of defence, according to previous data [3].

The up-regulation of both siderophores pyoverdine and pyocheline, was detected in cultures amended with NC, suggesting strong effect of NC on the iron homeostasis. The siderophore biosynthesis and transport require tight regulation, particularly in case of exposure to the toxic threat of ROS generated. Free radical species can trigger Fenton reaction further compromising the maintenance of intracellular iron levels. An improved production of pyoverdine- highly iron-specific siderophore, obtained in this study clearly documents how promptly and efficiently the bacteria reacts to overcome exhaustion of iron.

Production of pyocyanin is almost 3 times higher in nanoceria amended culture than in control, clearly suggesting redox homeostasis disturbance caused by NC. Although NADH/NAD redox couple plays a major role in central metabolism of *P. aeruginosa*, another characteristic feature of *P. aeruginosa* is the ability to produce redox-active pyocyanin, which can react with NADH suggesting that electron transfer to pyocyanin may represent an adaptation that allows bacteria to modulate their intracellular redox state.

Acknowledgements

This study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, Projects III43004 and 176006.

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Microbial Recovery of Copper and Zinc from Wasted Electronic Parts

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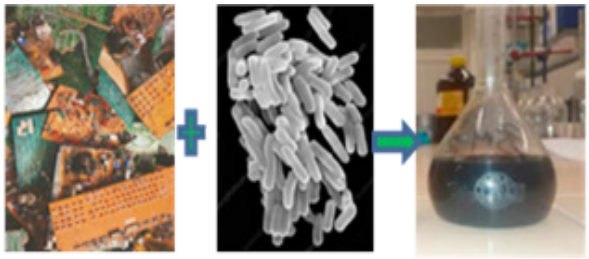

Recycling of electronic waste is crucial not only from the viewpoint of waste treatment but also from aspect of the recovery of valuable metals [1].

The aim of our study was to investigate the potential of using the *Acidithiobacillus* sp. B2, to solubilize metals (Cu and Zn) from electronic waste.

Methodology

Chemical analysis of electronic waste and pyrite

The electronic waste (after separating of the plastic parts) and pyrite were pulverized and sieved through a 63 μm stainless steel sieve in preparation for chemical and leaching studies.

Electronic waste preparation for the leaching experiment

The presence of alkali components in electronic waste is considered inconvenient for the reaction between the electronic waste and the acidic iron(III) sulphate solution. Hence, it is necessary to neutralize the electronic waste before adding the bacterial culture which would generate the oxidant. Before the leaching experiment, electronic waste was dispersed in 0.05 M H_2SO_4 solution, shaken for 48 h, filtered from the solution, washed out with deionized water and dried at 110 °C [2].

Preparation of pyrite for the leaching experiments

The pyrite concentrate for the leaching experiments was prepared by treating with a 0.5 mol/dm^3 sulphuric acid solution (pH ~ 0.5) (solid to liquid phase ratio 1:5 m/V), and mixing with a mechanical stirrer at a room temperature overnight. Then, the solution was decanted, washed with deionized water and dried at 80 °C to a constant mass [2].

Leaching experiments

The leaching experiments were carried out with bacterium *Acidithiobacillus* sp. B2. Experimental conditions were: leaching period of 20 d, 50 ml leaching solution (g/dm^3): $(NH_4)_2SO_4$ (3), K_2HPO_4 (0.5), $MgSO_4$ x $7H_2O$(0.5), KCl (0.1), $Ca(NO_3)_2$ (0.01), at a pH of 2.5 in 150 mL Erlenmeyer flasks at a pulp density of 10% (m/V) (5 g leaching substrate in 50 ml solution). The pH of the leaching solution was maintained at a constant value during the leaching process. One half of the substrate was pyrite and the other was an electronic waste. The initial number of microogranisms was 10^7 per mL, determined by the Most Probable Number method. The control suspension had the same chemical content and pH value as the suspension with *Acidithiobacillus* sp. B2 but the *Acidithiobacillus* sp. B2 culture had been inactivated by sterilization. The study was realized on a horizontal shaker. The incubation temperature was 28 °C [2].

Results and conclusions

The results of the effective metal leaching (calculated by subtraction of percentage metal leaching in the control suspension from that in the *Acidithiobacillus* sp. B2 suspension) are as follows: Zn (38%)>Cu (35%). The obtained results demonstrate that *Acidithiobacillus* sp. B2 was able to grow in the presence of electronic waste and may be "green" agents in the area of circular economy and sustainable development.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant no. 451-03-9/2021-14/200026, Grant no. 451-03-9/2021-14/200023 and Grant no. 451-03-9/2021-14/200168).

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Quantification and Qualification the Benefits of the Urban Protected Areas in Belgrade (Serbia) using PA Benefits Assessment Tool +

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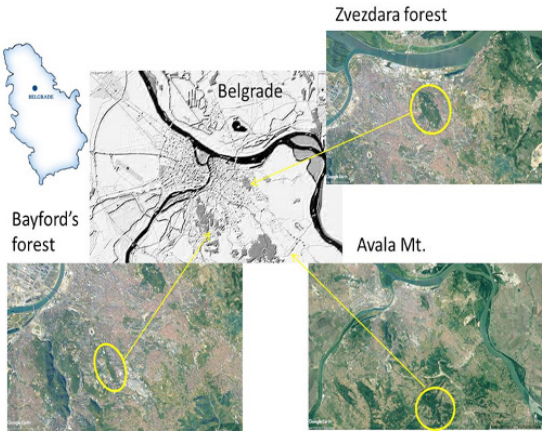

Figure 1. Study area

Urban protected areas (UPAs) are protected areas situated in, or at, the edge of larger population centers. Protected areas are a clearly defined geographical space, recognized, dedicated, and managed, through legal or other effective means, to achieve the long-term conservation of nature with associated ecosystem services (ES) and cultural values. The Millennium Ecosystem Assessment (MEA) recognized four categories of ES: cultural, provisioning, regulating, and supporting.

The main objective of this paper is to find the answers to the question: Which non-economic, economic, and potential benefits can be provided by UPAs in the city of Belgrade?

The study was developed in Belgrade (Serbia) in three UPAs under different protection regimes: Byford's and Zvezdara forest, and Avala mountain. To quantify and qualify the benefits of PAs the Protected Areas Benefits Assessment Tool + (PA-BAT+) was used [1]. The PA-BAT+ consists of three main generic elements: benefits - a list of benefits likely to come from the PAs; the flow of benefits - a list of stakeholders who could receive the benefit; and value of benefits - the assessment of each benefit and who it flows to against the assessment criteria of economic, non-economic, and potential benefit. Benefits were grouped through 29 questions based on the ES and related good. The flows of benefit were distinguished between different stakeholders: local people, local businesses, government, civil society organizations (CSO), and the academic community.

The results show that ES in all three study areas does not have flow economic benefits. Only in the Avala mountain, certain economic benefits are recognized from food provisioning. However, for all three UPAs, there are major potential economic benefits in providing cultural ES. Research and education, mental well-being, and health, as well as cultural and historical values of the PAs, are seen as possibilities for income. Local products and services PAs should ensure further opportunities for the development of sustainable tourism, especially in the field of branding of the local products. The academic community should be more engaged for the purpose of better management of the PAs and not for the sake of sheer research. The local community should be educated on the main ES values in order to understand the role of the PAs. Collaboration with the business public company" Zelenilo Beograd" is helpful for the implementation of management plans and monitoring the UPAs.

Based on the results it can be concluded that the most important future activity would include connecting three investigated UPAs with city green areas and establishing green corridors. The Byford's and Zvezdara forest have the role of a regulator of further development of the city in the direction of the Avala mountain, and represents a link between urban and suburban greenery. In this way, the sustainability of the ecosystems in UPAs will be preserved.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No: 451-03-9/2021-14/200026) for financial support.

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Application of Nature-Based Solutions in Serbian Protected Area Management for the Attainment of Sustainable Development Goals

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Healthy natural ecosystems, such as protected areas (PA), support and sustain biodiversity and human well-being by providing essential ecosystem services and health benefits. However, maintaining such ecosystems to provide these environmental benefits becomes a more and more challenging issue with climate changes, biodiversity loss, land degradation and the continued erosion of the natural capital, particularly in the developing world. The main objective of this research is to establish a methodology for achieving the United Nations Sustainable Development Goal 15 "Life on Land". The methodology will include the determination of heavy metals in soil and needle samples, and questioners for different stakeholders: local people, local businesses, government, civil society organizations (CSO), and the academic community.

Soils are integral components of protected area ecosystems. Soil health has been defined as "the capacity of soil to function as a vital living system, within an ecosystem and land-use boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and animal health" [1]. This definition speaks to the importance of managing soils, so they remain sustainable for future generations. On the other hand, the conifer needles are good bioindicators of ecosystem conditions. The questioner will allow obtaining data about the social and economic benefits of the PAs.

The soil and needle samples from four protected areas in Serbia (Zlatibor, Golija, Tara, Đerdap) were analyzed using Inductively coupled plasma –optical emission spectrometry (ICP-OES) and X-Ray Fluorescence (XRF). Quantitative pollution indices were calculated (Enrichment factor (EF), Contamination factor (Cf), Geoaccumulation index (Igeo), Pollution load index (PLI), and Degree of contamination (Cd)), since they are effective tools for converting the raw environmental data into information relevant to support decision-making [2]. Results of this study provide a scientifically-based overview of the conditions of soil health and health of the forest ecosystem and help to propose nature-based solutions (NBS) for enhancing the sustainability of management, especially in the context of improving ecosystem services and climate change adaptation and mitigation. NBS provide affordable, sustainable, and feasible benefits that contribute to improving soil quality and support several ecosystem services relevant to support public health and social well-being [4].

Results of this study use the United Nations Sustainable Development Goals 15 "Life on Land" as a global framework for establishing the partnership between PA managers, conservationists and local authorities that would enhance health and increase environmental, social and economic benefits of the PAs.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Grant No. 451-03-9/ 2021-14/200026 and 451-03-9/2021-14/ 200168) for financial support.

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Could Triclosan Excessive Use Make Covid-19 Pandemic Even Worse?

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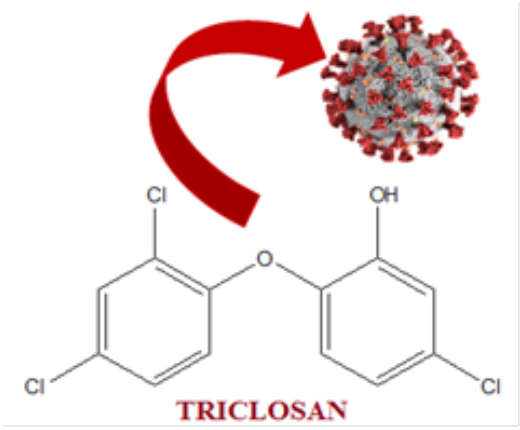

World Health Organization has reported, 232,636,622 confirmed globally cases of coronavirus disease 2019 (COVID-19), caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and 4,762,089 deaths until the 29th September 2021. Although different types of vaccines are available to deal with SARS-CoV-2 virus, the infection rate is increasing continuously, and disinfection remains the crucial measure to prevent the virus spread. Various chemical compounds are used on daily basis in the control and prevention of SARS-CoV-2. Hence, the large-scale use is resulted in the increased concentrations of disinfectants in wastewater and surface water [1].

Triclosan is a synthetic, multi-purpose antimicrobial agent which could be found in different commercial products (mouthwashes, toothpastes, soaps, disinfectants, deodorants, clothing textiles, furniture and other materials) [2]. Before the outbreak of COVID-19 pandemic around 1500 tons of this disinfectant were globally produced per year and more 130 million liters of triclosan-containing products were used only in the United States [3]. Consequently, it is believed that triclosan production and consumption rate has increased in the last year especially regarding the suggested triclosan virucidal efficacy against SARS-CoV-2 strain.

Besides the direct use, the exposure to triclosan via air, water and soil is also possible and wastewater are identified as the main source of triclosan in the aquatic environment [4].

The widespread use and disposal of triclosan should raise concerns about its negative effects on human health and environment. It is documented that the chronical exposure to triclosan can cause alterations of the skin and gut microbiome as well as *Staphylococcus aureus* and *Escherichia coli* increased resistance to antibiotics [5]. Additionally, based on *in vitro* and *in vivo* studies, triclosan could be associated with neurodevelopment and metabolic disorders, cardiotoxicity and even with the increased incidence of cancer. Also, in the environmental studies, triclosan acute toxicity and mild genotoxicity in aquatic organisms were demonstrated [4,6].

Although triclosan use in the over-the-counter antiseptic wash products has been banned by the United States Food and Drug Administration, the non-alcohol-based sanitizers and wipes are not yet regulated. Moreover, triclosan application in personal care products is still allowed in European Union.

Having in mind all of that, there is an urgent need for global precautionary and preventive measures that will minimize negative impact of triclosan on the environment. International guidelines for the application of disinfectants are necessary and of utmost importance in order to ensure the control of SARS-CoV-2 virus transmission but also to prevent harmful effects of excessive use of triclosan like disinfectants on both human health and environment.

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On the Desirable Relationship Between Chemistry and the Environment from the Point of View of Legal Science and Legislations

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As we know The Association of Chemistry and the Environment (ACE) is scientific association founded with the main aim to preserve the environment, as much as possible, from pollutions and residues resulting from the use of chemical processes and substances during businesses. In such efforts we need, at the same time, scientific and practical knowledge oriented toward commercial sectors as well as adequate regulatory approaches to the possible and observed problems. In order to achieve the best results in environmental protection we need adequate ethical-political and legal approaches formed at two mutually and hierarchically connected levels: international and national. Such approach logically starts from the formation of the most general, at the same time legally-logically and hierarchically highest, elements and develops towards a narrower and more detailed. In the poster we will concisely explain some of the most important elements from the levels of International Public Law, starting from the Universal Declaration on Human Rights [5], going toward to its elements which are building fragments of Public Law special part: The Environmental Law. Elements incorporated in international law documents, such are many conventions, but also EU documents, for example: Convention on Long-range Transboundary Air Pollution [1], Rotterdam Convention [2], Stockholm Convention [4], Regulation (EC) No 1907/2006 [3], and many others.

It should be pointed out that the legislature of the Republic of Serbia is strongly harmonized with the elements of international and European Union law. Our special attention is paid toward protection of mediums (water, air and soil) from negative technogenic effects produced at the levels of: 1. energy producing activities, 2. mining, 3. chemical industries - oil industry, pharmaceutical industry, plastic production, chemical producing of importance to agriculture, 4. constructing, and 5. legal frameworks for protection of the environment from negative technogenic impacts of production and treatment of wastes.

All those previously mentioned elements should be properly known and applied, each in its own way, both by engineers during construction and the application of economic facilities and processes, but also by the successors of the necessary state, primarily supervisory services. Hence, this is the basic reason and goal of forming the work that will be presented at the EMEC21.

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Multiclass Multipesticide Residue Analysis in Hake on the Market in Serbia

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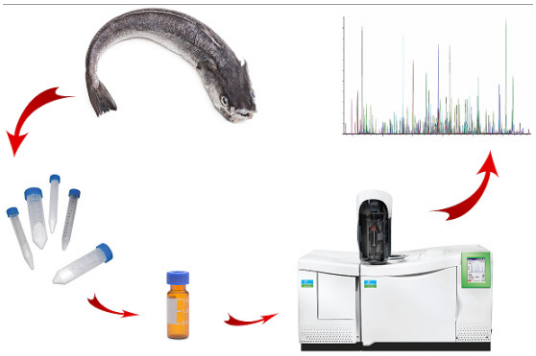

The aim of this study was an assessment of pesticide residues in hake (*Merluccius merluccius*) on the Serbian market.

The fish samples were comminuted, extracted and cleaned by a modified QuEChERS method. The prepared samples were analysed by gas chromatography – mass spectrometry (GC/MS) technique in the selected ion monitoring mode (SIM) using one target and three qualifier ions for each analyte. 59 pesticide compounds were analyzed in the samples using the Oregon pesticide standard mixtures. The identified compounds were quantified against the authentic standards. More than 100 samples were analysed in this study.

The results confirmed presence of carbaryl (in concentration range from not detectable (ND) to 7.4 μg kg^{-1}), cyfluthrin (sum of isomers; from ND to 107.5 μg kg^{-1}), cypermethrins (from ND to 14.3 μg kg^{-1}), metalaxyl (from ND to 8.6 μg kg^{-1}), diazinon (from ND to 11.2 μg kg^{-1}), bifenthrin (from ND to 11.6 μg kg^{-1}), imazalil (from ND to 15.0 μg kg^{-1}), methyl parathion (from ND to 18.2 μg kg^{-1}), *p,p′*-DDT (from ND to 40.7 μg kg^{-1}), chlorpyriphos (from ND to 12.7 μg kg^{-1}), and endosulfan (from ND to 19.7 μg kg^{-1}) in nine fish samples.

Cyfluthrin and *p,p′*-DDT had the highest frequencies of occurrence and were detected in 4 samples. Cypermethrins, imazalil, methyl parathion, and endosulfan were found in two samples each while carbaryl, cypermethrins, metalaxyl, diazinon, bifenthrin, and chlorpyriphos were found in one of the samples each.

Except from carbaryl and metalaxyl, all other pesticides quantified in this study were found in concentrations higher than a maximum residue level (MRL) of 0.01 mg/kg as set by EU legislation on MRLs [1]. Considering the fact that most of these pesticides are not on the EU pesticide Watch List, these results point to the need for expansion of this list.

p,p′-DDT belongs to a group of organochlorine pesticides - the group of compounds that are highly toxic to mammals, resistant to degradation and prone to bioaccumulation [2]. Because of that, its presence in food is usually a cause for increased concern. However, the *p,p′*-DDT concentrations measured in this study are lower than 5 ppm which is the action limit (the threshold at or above which the product should be removed from the market) set by FDA [3] and because of that it is not expected to pose any health risk to the humans consuming these products.

According to the results of the quality testing of hake on the market in Serbia, it can be concluded that these analyses were proven justified and that they should be continued in the future, as well as the control of the application of all pesticides that were found in this study in concentrations higher than the MRL.

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract numbers: 451-03-9/2021-14/200026 and 451-03-68/2020-14/200030) for supporting this research.

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Determination of Anthropogenic Gadolinium and Correlation of Elements between Vineyard Soil, Vine, and Wine

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Gadolinium is a transition metal, ferromagnetic element, the lanthanide group's eighth member, and a rare earth element (REE) [1,2]. It is used in various fields, such as industry (e.g. petrol industry, electrotechnical industry, iron industry, etc.), agriculture (e.g. phosphate fertilisers, growth stimulator in farm animal feed), and medicine (gadolinium-based contrast agents) [2,3,4]. Due to this wide use, it enters the environment from many sources through anthropogenic activities, e.g. disposal of household equipment and subsequent Gd leaks from landfills, flushes from agricultural land, and Gd emissions from hospitals with MRI services [2,3,5]. The specific environmental conditions and properties of Gd compounds determine the fate of anthropogenic gadolinium in the environment [6]. Subsequent ecotoxicological effects of REE may be reduced plant growth, reduced or insufficient nutrient metabolism, genotoxicity, and neurotoxicity in animals, trophic bioaccumulation, chronic and acute toxicity in soil organisms [5,7]. Another negative effect may be the entry of this emerging contaminant into the food chain, which can have a dangerous effect on human health. For these reasons, monitoring anthropogenic gadolinium in food is important to prevent potential risks [8].

Symptoms of deficiency or excess of some elements, already visible in the vineyard on the vine leaves, may not be the cause of the actual deficiency of plant nutrition. The element may be blocked in the soil by another element and thus inaccessible to the vine. Knowledge of the correlation of individual elements between soil, vines, and wine is an important part of nutrition, fertilisation, and plant care [9].

The aim of this work was the elemental analysis of soil, vine (leaves and berries), and wine samples from the Czech Republic to monitor the content of anthropogenic gadolinium and the correlation of selected elements between these types of samples. 33 elements were monitored, of which Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, and Zn were determined using the ICP-OES method and As, Cd, Co, Cu, Ni, Pb, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, and Yb using the ICPMS method. The procedures for preparing samples for analysis were optimized. The reliability of the proposed methods was verified through the analysis of certified reference materials, monitoring of long-term repeatability, recovery, and veracity of analytical results. The correlation relationships of individual elements between soil and leaves, between leaves and berries, and between berries and wine were monitored. These correlations were positive, negative, strong, weak, and also insignificant. The content of anthropogenic gadolinium was evaluated for individual types of samples and the gadolinium anomaly was examined as an indicator of human activity in the environment. The values found were compared with the available literature.

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The Determination of Heavy Metals and Ochratoxin A in Wine Products in Montenegro

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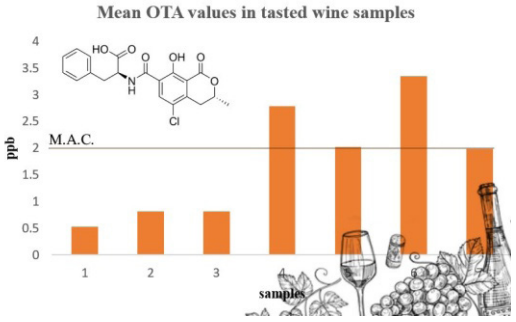

The quality, origin, general parameters, aroma characteristics and health safety of wine consumption are influenced by environmental and anthropogenic factors and can be identified by variable contents of inorganic and organic substances forming its chemical composition [1]. Level of Fe, Mn, Cu, Cd, Zn, Pb, Hg and As in five brands od wine from Montenegro were investigated. In these samples, as well as in seven new samples selected from Montenegro vineyards with great and long tradition, the content of Ochratoxin A (OTA) was examined.

By consuming wine, one enters sufficient amounts of some essential elements into the body (K, Ca, Mg ...), but at the same time brings into the body toxic metals and metalloids (As, Pb, Cd). International Organization of Vine and Wine has found the maximum allowable amounts of certain elements in wine [2]. The metal content was determined using the ICP-OES technique. The concentrations of metals in wines were below their M.A.C. in each analyzed sample.

In wines, OTA is the most studied mycotoxin, and the European Commission (by regulation 1881/2006) established as the maximum tolerable level in wines destined for human consumption a concentration of 2 µg/l. OTA contamination can occur during any stage of the winemaking process, but the primary contamination of the finished product comes from the carryover of mycotoxins from grapes [3]. Analyses for the determination of OTA were performed by ELISA (Enzyme - linked immunosorbent assay) method. The maximum concentration of OTA (3.34 µg/l) was above the regulatory limit. Three more samples are in the group with a slightly higher concentration of Ochratoxin A than allowed. More than a half of sampled wines contained OTA in quantifiable amounts, but below the regulatory limit.

Considering the threat, it poses the presence of ochratoxins in wines and long-term health problems that can cause in wine in people who drink, these results indicate that the level of ochratoxins in domestic Montenegrin wines should be examined more regularly.

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Pyrazole Derivative L and its Cobalt Complex for the Control of Fungi *Phomopsis viticola Sacc*. Patent Number 03496*

Ž. Jaćimović[1], N. Latinović[2], J. Latinović[2], M. Kosović-Perutović[1]. (1) Faculty of Metallurgy and Technology, University of Montenegro Cetinjski put, 81000 Podgorica, Montenegro, (2) Biotechnical Faculty, Center for Plant Protection, Mihaila Lalica 1, 81000 Podgorica, University of Montenegro Montenegro*contact_zeljkoj@ucg.ac.me.*

Pyrazole-based compounds and their transition metal complexes have attracted considerable research interest because of their potentially beneficial biological properties (anticancer, antimicrobial, antiviral, anti-inflammatory, antifungal and others). This patent is a part of our continued work with pyrazole based complex compounds.

Research related to the effectiveness of newly synthesized compounds in the control of black spot of grapevine is particularly relevant in order to obtain new active and environmentally friendly compounds to which fungi have no resistance.

In the study inhibitory effects of pyrazole ligand and its cobalt(II) complex (Patent number 03496) were examined to the mycelial growth of *Phomopsis viticola* (pathogenic fungi that causes Phomopsis cane and leaf spot disease) in vitro. The compounds were applied in five 5 different concentrations in the range of C1-C5 starting from the lowest to the highest. Obtained results were compared with the commercial fungicide Cabrio Top with active ingredient pyraclostobin that belongs to pyrazole derivates.

Tested compounds of appropriate concentrations (C1) showed 100% efficacy in preventing the growth of the fungus *P. viticola Sacc*. This result is at the level of the efficiency of the action of the commercial fungicide used in the experiment.

Therefore, the essence of the invention is in the preparation of compounds which can be used as effectively commercially for the protection of the grapevine from the said disease as the commercial product currently on the market.

Acknowledgements

Thanks to the Ministry of Science of the Republic of Montenegro for financial support (Innovative Project-Bioextra)

* **Patent number 03496** (11)03496, (51)A01N 3/00, (21)P-2019-204, (54)Pyrazole derivative and its cobalt complexes for the control of fungi Phomopsis viticola, SACC, Bioextra, Pz, Intellectual property gazette of Montenegro, published 20.01.2020, ISSN 1800-8003

Determination of the Iodine Value – Novel Environmental Friendly Insights

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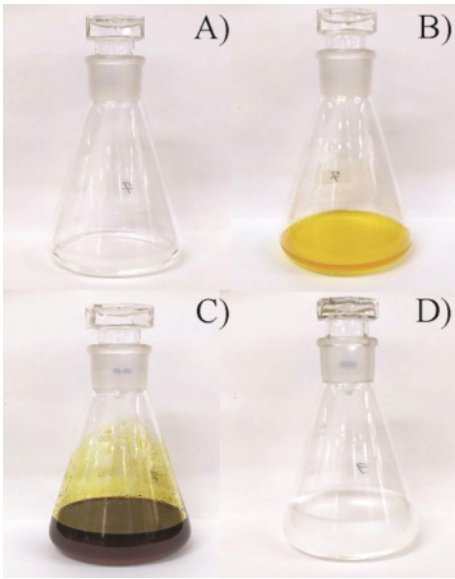

The iodine value (iodine number) is characteristic for the content of unsaturated fatty acids in fats, fixed oils, emulsifiers and solubilizers. The determination of the iodine value is of significance for pharmaceutics, food chemistry and cosmetics. Standard methods for the iodine value determination approved by the Association of Official Analytical Collaboration (AOAC) International, the American Oil Chemists' Society (AOCS), the International Organization for Standardization (ISO) and the European Pharmacopoeia (Eur. Ph.) [1-3] use hazardous solvents for fat samples such as cyclohexane/glacial acetic acid mixture or chloroform, whereas glacial acetic acid is unique solvent for iodine monochloride or iodine monobromide that serves as iodination agent. Certain earlier proposals for more environmental friendly and faster iodine value determination considered utilization of 1,3-dibromo-5,5-dimethylhydantoin and potassium iodide instead of iodine monobromide, however also in glacial acetic acid as a solvent [4,5]. Recently, combining data from American and ISO standards, the Metrohm (2019) [6] proposed utilization of glacial acetic acid as a solvent for the fat sample and addition of magnesium acetate as catalyst to significantly reduce the reaction time, from 1 h to 5 minutes.

In the current study we report certain novelties, which may contribute to development of less hazardous and environmental friendly method for the iodine value determination. Our method considers utilization of ethyl acetate as a solvent for the sample instead of cyclohexane/glacial acetic acid mixture or chloroform, whereas iodine monochloride in glacial acetic acid has been replaced by water solution of iodine monochloride (stabilized by small amount of hydrochloric acid). In the presence of ethyl acetate, starch solution does not yield the characteristic blue colour with iodine. Nevertheless, the titration end point can be recognized clearly and precisely without indicator. The method was tested on the following samples: coconut oil, olive oil, sunflower oil and linseed oil, covering a wide range of the iodine value from ~8 to ~180. Comparison of the average iodine values for studied samples obtained by the proposed and standard AOAC method indicates standard deviation less than 0.60, whereas repeatability limit for the proposed method is bellow 1.7 that is in line with statistical results for the precision of the Wijs method reported in ISO 3961 (2018) standard [2].

Acknowledgements

This study was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract number: 451-03-9/2021-14/200168).

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Development of a Technology of Innovative Microbiologically Enriched Mineral Fertilizers (BIOFERTIL)

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Fig. 1 *Installation 1/2 technical scale for the production of microbiologically enriched fertilizers.*

Nowadays, a vast number of commercial biofertilizers are available worldwide. However, the quality and efficacy of many of them are not proven or tested. Thus, the availability of high-quality biofertilizers must be priority particularly in countries where crop plant production plays a key role in the economy and food security [1]. The BIOFERTIL project aims to reduce the amount of mineral fertilizer input without decreasing yield of crops, by using function of beneficial microorganisms in biofertilizer, which increase availability of plant nutrients from soil.

The purpose of the project is to develop the innovative microbiologically enriched biofertilizers and to assess the effects of their use in crop production and in improving the bio-physico-chemical properties of arable and degraded soils. At the first stage of the project, the biofertilizers were produced by combining urea, NPK mineral fertilizers with precisely characterized beneficial microorganisms. At the next stages of the project, the biofertilisers will be manufactured with the use of beneficial microorganisms and natural humic acids.

The project is organized into 6 work packages: WP1 - Production technology of microbiologically enriched fertilizers, WP2 - Effectiveness of biofertilizers in improving bio-physico-chemical properties of degraded and agricultural soils, WP3 - Effect of biofertilizers on growth and yield of horticultural plants and on soil microbiology, WP4 - Effect of biofertilizers on growth and yield of arable crop plants and on improving soil fertility, WP5 - Assessment of the impact of biofertilizer use on water potential and macro- and microelement content in the soil and plants, WP6 - Preparation for implementation, dissemination and commercialization of research results and newly developed biofertilizers.

The production of biofertilizers by the method of coating the mineral fertilizer granules with an external layer containing a neutral carrier seems to be the most appropriate direction for the production of this type of products. During the production process, it is advantageous to use low temperatures and to avoid using water as much as possible, because in the presence of moisture, especially at elevated temperatures, as during drying, rapid growth of live bacteria from their spore forms took place. It is also beneficial to physically separate the bacteria from the fertilizer granules, so that they are not exposed to high local concentrations of mineral salts formed during the dissolution of the fertilizer in the soil under the influence of moisture. Diversification of the dissolution rate of both these layers by creating a readily soluble outer coating containing microorganisms may favourably affect the effectiveness of the use of biofertilizers.

In the carried out laboratory tests, the method of incorporation of bacteria into granulated fertilizers was developed by applying the coating in the form of an external layer of bacteria deposited on an organic carrier (carbohydrate) using different binder formulations. Trial batches of microbiologically enriched fertilizers were produced on a 1/2 technical installation. The produced fertilizers were sent for field and environmental research. Moreover, the biofertilizer application on maize at field trials carried out in 2018-2020 shows the positive effects on its production.

Acknowledgements

The project is co-financed by the National Centre for Research and Development of Poland within *BIOSTRATEG Programme under Grant No. BIOSTRATEG3/347464/5/NCBR/2017.*

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Determination of Selected Metals in Wine and Ciders by Spectroscopic Techniques

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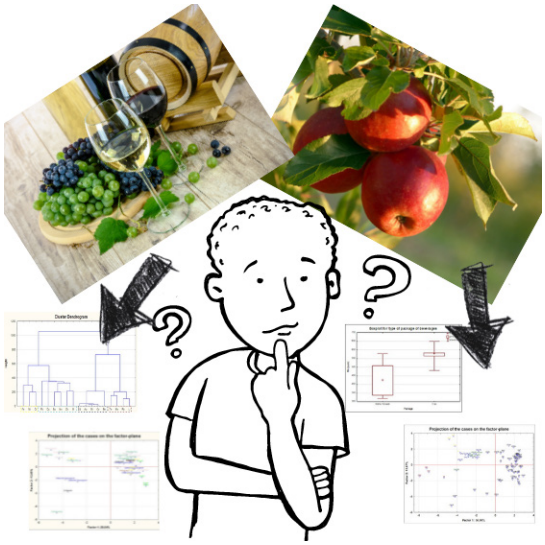

The determination of metals in different types of food and beverages samples has drawn significant attention due to several reasons, with the most important one being the nutritional and toxic effects of these elements or their compounds. The knowledge of certain elements content in wines or other products of alcoholic fermentation as ciders, is of special interest due to their toxicity in case of excessive intake and also the effect they seem to have on the organoleptic properties of alcoholic beverages [1]. Most of the scientific studies on these alcohols focus on the analysis of volatile compounds, sugar content, colour or the presence of polyphenolic compounds, and the most frequently used analytical techniques for this purpose are chromatographic methods. However, an important element of a comprehensive discriminant analysis, quality control or the much-desired authentication of alcohol products may be the elemental and isotope analysis, which so far is not a common solution in the case of alcohol products [2,3].

The aim of the study was:

to performed elemental characteristics of selected alcohol groups (wine and cider) available on the Polish market.

to determine the influence of selected factors (type, grape variety or country of origin) on the content of determined elements in alcohol samples.

to compare of the obtained concentrations with the applicable standards for products of alcoholic fermentation

The concentrations of the examined elements were determined by the ICP-MS and ICP-OES methods.

The performed tests have shown that the elemental profile of the final product is defined by such elements as: the ingredients used, the technological process, the equipment used by the manufacturer, and the type of packaging, therefore discrimination between commercial and home-made alcohols was possible [2]. Relatively low levels of many of studied elements in Polish wines should be treated as a beneficial information from the consumer point of view. Moreover, this study revealed that also wine samples from USA and Australia can be potentially discriminated from the rest of studied wines. For USA the most characteristic metal for positive identification of the country of origin seems to be uranium, whereases for Australia–strontium and manganese. The location of the grape-growing plays a key role in characterizing the chemical composition and distinguishment between wine samples. In a lesser extent, it was related with the grape variety [3].

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Organizations that supported the EMEC21

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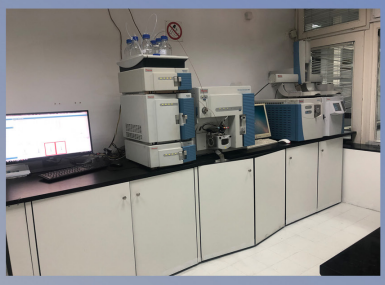

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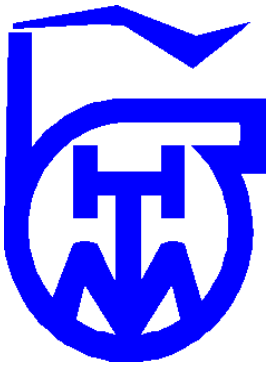


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CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(048)

EUROPEAN Meeting on Environmental Chemistry (21 ; 2021 ; Novi Sad)
Book of abstracts / 21st European Meeting on Environmental Chemistry, EMEC 21, November 30 - December 3, 2021, Novi Sad, Serbia ; [editors Ivana Ivančev-Tumbas, Vladimir P. Beškoski, Aleksandra Šajnović]. - Belgrade : Serbian Chemical Society, 2021 (Belgrade : RIS Studio). - 197 str. : ilustr. ; 25 cm

Tekst štampan dvostubačno. - Tiraž 150. - Str. 5: Predgovor / Branimir Jovančićević. - Bibliografija uz većinu apstrakata. - Registar.

ISBN 978-86-7132-078-8

а) Животна средина -- Апстракти

COBISS.SR-ID 52064521