

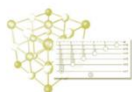
EMEC23

**23rd European Meeting
on Environmental Chemistry**
3–6 December, 2023, Budva Montenegro

Book of Abstracts



ASSOCIATION OF
CHEMISTRY AND THE
ENVIRONMENT



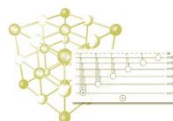
Chemical
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of Montenegro

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Dear Colleagues,

On behalf of Organizing Committee of the Conference and on my own behalf, it is my great pleasure to welcome you to the 23rd European Meeting on Environmental Chemistry.

This conference is organized by the Chemical Society of Montenegro, on behalf of the Association of Chemistry and the Environment (ACE).

EMEC23 continues the tradition of previous annual meetings providing a forum for the exchange of ideas on recent advances in research and development in environmental chemistry and technology for people from industry, research and academia concurrently.

We are looking forward to seeing you in Montenegro and we hope that you will spend nice days at the conference and in beautiful Montenegro

Welcome and enjoy the Conference!

*Yours Sincerely,
Željko Jaćimović,
Conference Chairman*

Organising Committee

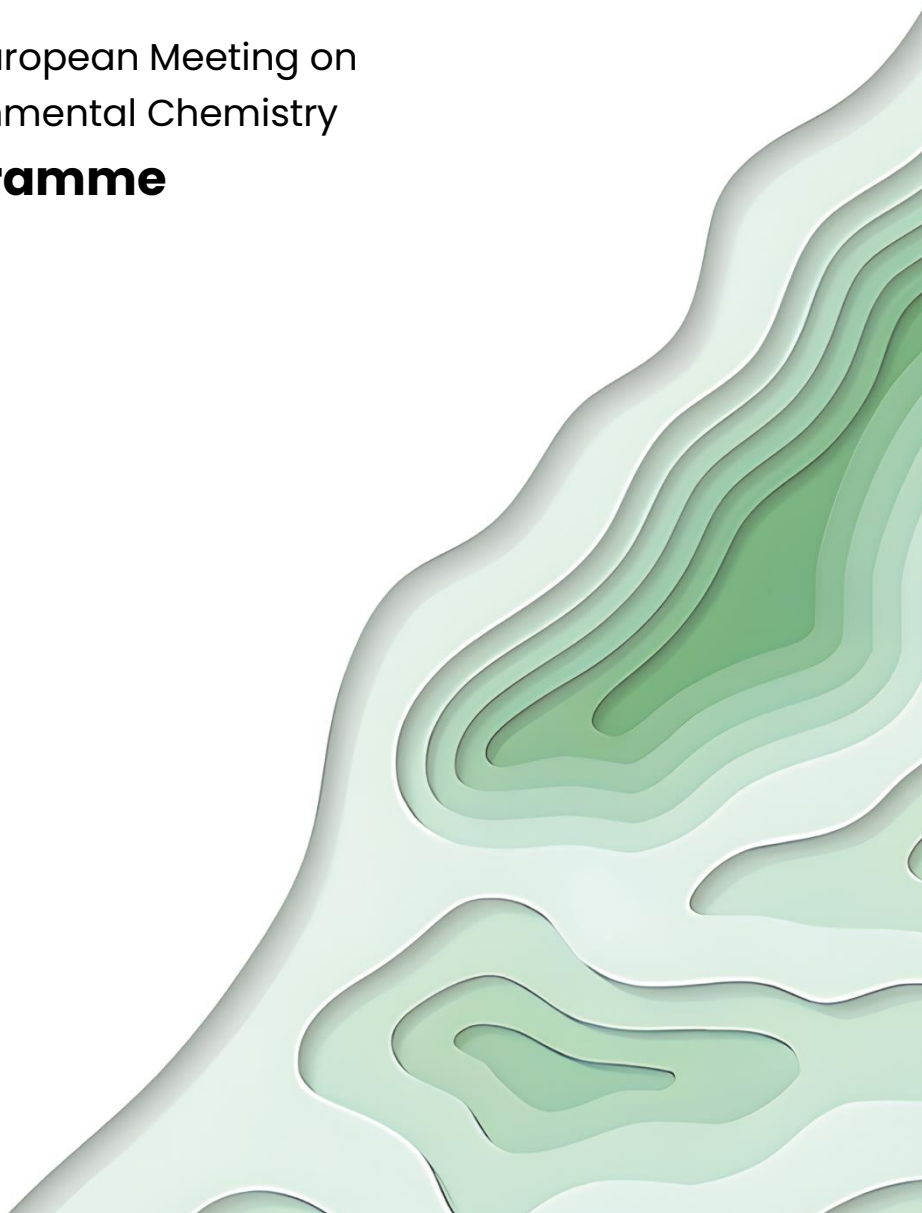
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23rd European Meeting on
Environmental Chemistry

Programme



Sunday, December 3 rd 2023			
12 ⁰⁰ – 18 ⁰⁰	Registration of participants (Hotel Avala)		
19 ⁰⁰ –	Welcome reception (cocktail)		
Monday, December 4 th 2023			
8 ³⁰ –9 ⁰⁰	Registration of participants (Hotel Avala)		
9 ⁰⁰ – 9 ²⁰	Opening ceremony		
9 ²⁰ – 10 ²⁰	Plenary lecture	Anthropogenic and Naturally Occurring Brominated Compounds	Prof. John Giesy
Chair	Nuno Ratola		
10 ²⁰ –10 ³⁵	Coffee break		
10 ³⁵ –11 ⁰⁵	Keynote lecture	Dynamic and Behavior of Ultrafine Particles in Urban Atmosphere: Toxicity and Deposition in Human Respiratory System	Prof. Pasquale Avino
Chairs	Polonca Trebše and Jan Schwarzbauer		
11 ⁰⁵ –11 ²⁵	Session: Atmosphere	Photochemical Fate of Polystyrene Photodegradation Products in the Environment: The Case of Benzene and Phenol in a Two-Compartment Scenario	Davide Vione
11 ²⁵ –11 ⁴⁵		Comprehensive Analysis of Micro- and Nanoplastics Using High-Resolution Mass Spectrometry with Enhanced Chromatographic Resolution	Dmitrii Mazur
11 ⁴⁵ –12 ⁰⁵		Calibration Samples for Heavy Metals Quantification in Particulate Matter by X-Ray Fluorescence Under Grazing Incidence	Paola Cirelli
12 ⁰⁵ –12 ²⁵		Impact of Agricultural Emissions on Rural and Urban Air Quality (IMAGE)	Vivien Pohl
12 ²⁵ –12 ⁴⁵		Airborne Microplastic Particle Concentrations and Inhalation Exposure	Ana Torres-Agullo
12 ⁴⁵ –13 ⁰⁵		Temperature Dependency of Fenton and Fenton-like Reactions in the Presence of Oxalate – Implications to Atmospheric Particle Aqueous Phase Chemistry	Daniele Scheres Firak
13 ⁰⁵ –14 ¹⁵	Lunch		
14 ¹⁵ –14 ³⁰	Sponsor presentation: Company Tara Resources Geochemical waste management and water management (incorporating our env videos) Richard Boffey, General Manager		
14 ³⁰ –15 ³⁰	Plenary lecture	Paraben Transport and Transformation in Wastewater and Bioaccumulation in the Brazos River of Texas, USA	Prof. George Cobb
Chairs	Željko Jaćimović and Branimir Jovančević		
15 ³⁰ –15 ⁴⁵	Coffee break		

15 ⁴⁵ –16 ¹⁵	Keynote lecture	Pollution by Microplastics in the Sea – the Case of the Gulf of Trieste and the Bay of Boka Kotorska.	Prof. Oliver Bajt
16 ¹⁵ –16 ³⁵	Session: Water	Fish Otoliths and Scales as Indicators of Long-term Metal Exposure in Wastewater Impacted River	Sara Šariri
16 ³⁵ –16 ⁵⁵		Biochar Produced from Sewage Sludge as an Adsorbent and Soil Conditioner: A Scottish Case Study	Szabolcs Pap
16 ⁵⁵ –17 ¹⁵		Alternative Forms of Solid-Phase Extraction for Ultratrace Analysis of Emerging Organic Pollutants in Water	Aleksander Kravos
17 ¹⁵ –18 ¹⁵	Poster session 1 (Water and Solid Matrices)		
18 ³⁰ –20 ⁰⁰	Early-career workshop		
19 ⁰⁰ –21 ⁰⁰	Budva by night /Old Town Budva/		
Tuesday, December 5 th 2023			
8 ⁰⁰ –8 ³⁰	Registration of participants (Hotel Avala)		
8 ³⁰ –9 ³⁰	Plenary lecture	Arsenic Contamination of Groundwaters and Novel Approaches for its Removal	Prof. Ioannis Katsoyiannis
Chairs	Davide Vione and Albert Lebedev		
9 ³⁰ –9 ⁵⁰	Session: Water	An initiative towards circular economy for water remediation employing hydrochar	Arshitha Madhusudhan
9 ⁵⁰ –10 ¹⁰		Metal and Metallothionein Concentrations in the Fish Intestine and Acanthocephalans in Relation to Environmental Metal Exposure in the Krka River	Tatjana Mijošek
10 ¹⁰ –10 ³⁰		Fish Intestine and Muscle as Bioindicators of Microplastic Exposure in the Aquatic Environment	Vlatka Filipović Marijić
10 ³⁰ –10 ⁴⁵	Coffee break		
10 ⁴⁵ –11 ¹⁵	Keynote lecture	Per- and polyfluoroalkyl substances – from challenges to potential solutions	Prof. Vladimir Beškoski
Chairs	Małgorzata Iwona Szykowska-Jóźwik and Stuart Gibb		
11 ¹⁵ –11 ³⁵	Session: Water	Microalgae-based Wastewater Treatment Process in the Presence of Microplastics and Pesticides	Urška Šunta
11 ³⁵ –11 ⁵⁵		Computational and Experimental Approach to the Development of Novel Test for Pathogen Detection in Water	Branimir Bertoša
11 ⁵⁵ –12 ¹⁵		Voltammetric Detection of Neonicotinoids in Surface Water and Honey by Activated In-House Screen-Printed Graphite:Glass Working Electrodes	Maksimiljan Dekleva
12 ¹⁵ –12 ³⁵		Use of Iron-bearing Waste Materials in Laundry Wastewater Treatment	Yara Arbid
12 ³⁵ –12 ⁵⁵		Bromides in Treated Wastewater: Limiting the use of Post-ozonation for Micropollutant Removal	Deniss Klauson

12 ⁵⁵ –14 ⁰⁰	Lunch		
14 ⁰⁰ –14 ¹⁵	Sponsor presentation – Analysis DOO Current analytical challenges in environmental analysis Luka Mihajlovič, PhD		
14 ¹⁵ –14 ⁴⁵	Keynote lecture	Toxicity vs. Biological Activity of Different Transition Metal Ion Complexes	Prof. Biljana Petrović
Chairs	Milica Kosović Perutović and Marian Olazabal Dueñas		
14 ⁴⁵ –15 ⁰⁵	Session: One Health	Nicotine release in saliva- effect of time, pH, alcohol and sugar content on nicotine release from pouches available on Slovene market	Polonca Trebše
15 ⁰⁵ –15 ²⁵		Environmental Pollution, Human Health Risk and Bioaccessibility Assessment of Potentially Toxic Elements from Agricultural Soils and Grapes	Tijana Miličević
15 ²⁵ –15 ⁴⁰	Coffee break		
15 ⁴⁰ –16 ⁰⁰	Session: Solid Matrices	Non-targeted Analysis of Household and Office Dust Using GCxGC–HRTOFMS	Albert Lebedev
16 ⁰⁰ –16 ²⁰		How bad Volcano–Clastic Badlands Actually are?	Nevena Antić
16 ²⁰ –16 ⁴⁰		Elemental Analysis of Rice in the Context of Safety and Authentication	Aleksandra Pawlaczyk
16 ⁴⁰ –17 ⁰⁰		Persistent Organic Pollutants in Surface Sediments from Portuguese Marine Estuaries and Coastal Environment	Luís Gomes
17 ⁰⁰ –17 ²⁰		The Agricultural Dilemma: Biodegradable vs. Conventional Plastics, Aging and MP Formation	Mojca Bavcon Kralj
17 ³⁰ –18 ³⁰	Poster session 2 (Sustainability, One Health and Atmosphere)		
18 ⁴⁵ –19 ⁴⁵	Board meeting		
20 ³⁰ –23 ⁰⁰	Gala dinner		
Wednesday, December 6 th 2023			
8 ⁴⁵ –9 ⁰⁰	Sponsor presentation – LECO Corporation		
Chairs	Miljan Bigović and Željko Jaćimović		
9 ⁰⁰ –9 ²⁰	Session: Sustainability	The Urban Water Cycle and its Modifications Through Time: Diachronic Approach based on Strontium Isotopes Study of Perched Aquifer Waters and Calcareous Deposits in Paris, France.	Edwige Pons Branchu
9 ²⁰ –9 ⁴⁰		Sustainable Food Protein and Water Purification Processes using Ionic and Porous Material Systems	Luís Branco
9 ⁴⁰ –10 ⁰⁰	Session: Water	A comparison Between Constructed Wetland Substrates and Impacts on Wastewater Treatment Performance	Ilgaz Cakin
10 ⁰⁰ –10 ²⁰		Emerging Pollutants in Greywater: is Laundry Wastewater Prone for Water Reuse?	Marta Turull
10 ²⁰ –11 ⁰⁰	Coffee break		
11 ⁰⁰ –12 ⁰⁰	Closing ceremony		

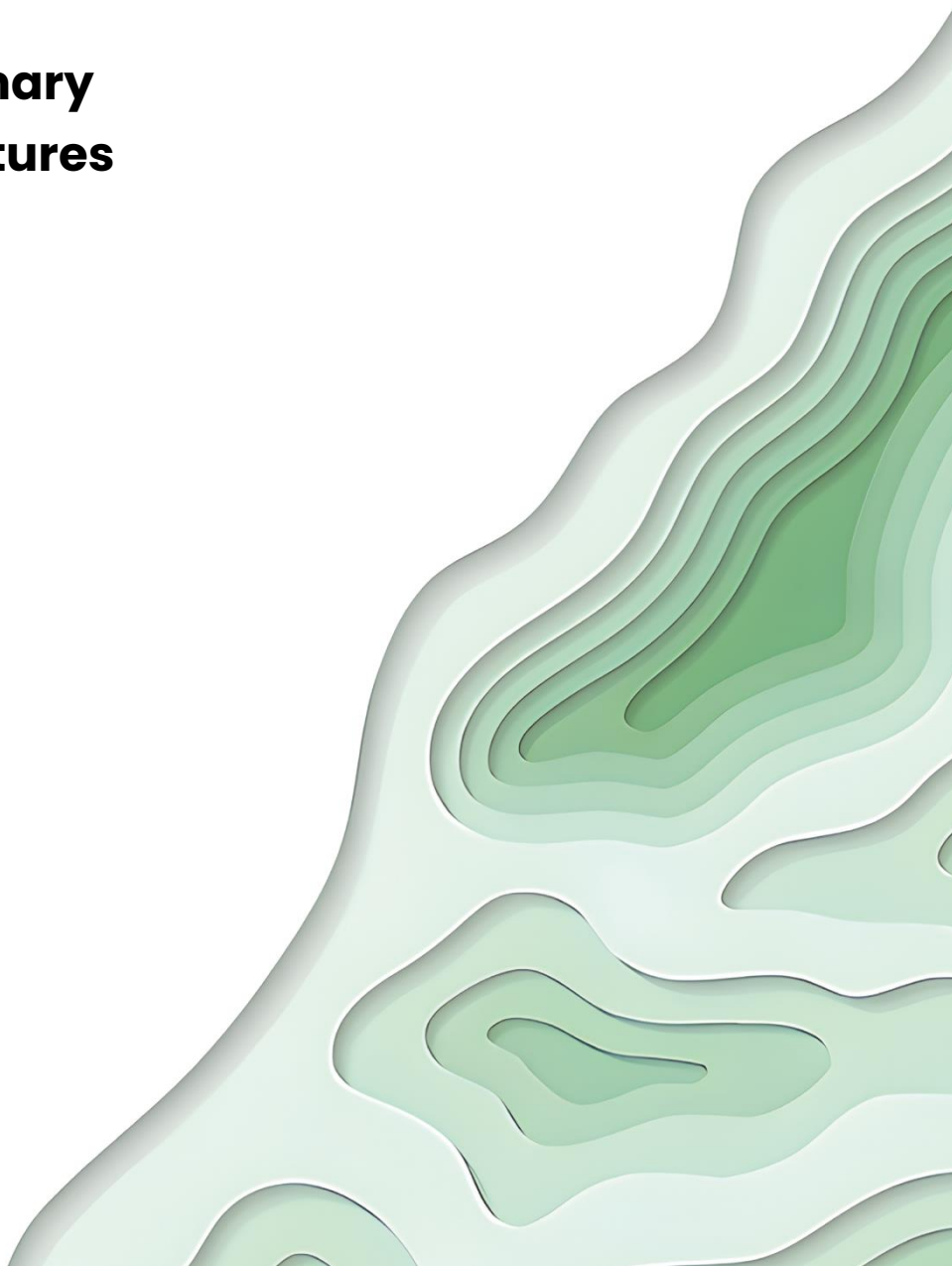
Poster Sessions

Presenting author	Title of presentation	Poster Board Number
Monday, December 4th 2023		
Session Topic: Solid Matrices		
Miljan Bigović	Comparing the Content of Heavy Metals in Peloids from Sutomore and Igalo (Montenegro)	SM1
Ilgaz Cakin	Designing a Biochar-Based Pretreatment Method for Acidic Cu-rich Distillery Effluents Entering Wetlands	SM2
Małgorzata Iwona Szynkowska-Jóźwik	Elemental Analysis of Surface Soil Collected from the Vicinity of the Waste Disposal Places in Lodz Region	SM3
Nives Matijaković Mlinarić	Antibacterial Activity of CuO and ZnO Treated Surfaces	SM4
Jernej Imperl	A Comparative Study of the Effectiveness of Possible Washing Agents for the Remediation of Sediment Contaminated with Heavy Metals	SM5
Dijana Đurović	Heavy Metals and PAHs Content in Agricultural Soil in the Vicinity of Thermal Plant in Pljevlja (Montenegro): Ecological Risk Assessment	SM6
Valentina Jauković	Environmental Risk Assessment and Risk Management of Polymeric Nanoparticles as Drug Carriers	SM7
Milica Balaban	The Influence of Agricultural Activity on the River Sediments of the Ukrina River	SM8
Sanja Pržulj	Biomarkers in River Sediments (Vrbaš, Bosnia and Herzegovina)	SM9
Giulia Fucile	Comparison Of Extraction Procedures of Organic Mercury in Soil and Sediments Reference Materials	SM10
Mira Pucarević	Instrumental Methods for the Microplastics Determination in the Environment	SM11
Gordana Gajica	Inorganic Composition of Serbia and Slovenia Peloids in Context Their Applicability as Therapeutic Agents	SM12
Nevena Prlainović	Bacterial Nanocellulose as a Potential Adsorbent for Strategic and Heavy Metals Removal	SM13
Darko Vuksanović	Identification of the Impact of the Quarry on the Environment	SM14
Jelena Ščepanović	Effects of Pollutants on the Quality of The Environment During the Operation of the Plant for The Production of Concrete-Concrete Base	SM15
Nevena Antić	Soil Degradation Indicators as a Tool for Climate-Smart Urban Forestry	SM16
Marian Olazabal Dueñas	Microplastics Risk as a Reservoir of Metallic and Organic Contaminants of Legacy and Emerging Concern on the Cantabrian Coast (Northern Spain)	SM17
Session Topic: Water		
Neda Bošković	Abundance, Distribution Patterns, and Identification of Microplastics in Bojana River Sediments in Montenegro	W1
Viktoriia Liapun	Versatile Application of BiVO ₄ /TiO ₂ S-scheme Photocatalyst: Photocatalytic CO ₂ and Cr (VI) Reduction	W2

Aleksander Kravos	Dispersive Micro Solid-Phase Extraction (DMSPE) for Water Analysis: Why, How, for What?	W3
Jelena Radonić	Selection of Significant Parameters for River Water Quality Monitoring by Multivariate Analysis	W4
Schwing Océane	Coagulation – Flocculation of Water by Green Wastes: New Insight in Mechanisms Involved	W5
Gordana Gajica	Determination of the Adsorptive Capacity of Biochars for Bioremediation of Petroleum-Type Pollutants	W6
Tijana Milićević	Human Health Risk Assessment of Endocrine Disrupting Herbicides Present in Waters from Croatia	W7
Tatjana Šolević Knudsen	Estimation of Surface Water Contamination by Pesticides in the Kovin Area, Serbia	W8
Nevena Prlainović	Reducing Wastewater in Textile Industry: Innovative Dying Approach	W9
Dragana Šunjka	Pesticide Residues in the Water of Nature Park Jegrička (Serbia)	W10
Luís Gomes	Evaluation of SeaFAST System as an Alternative to DigiSEP Cartridges in Pre-concentration of Trace Metals in Seawater Samples	W11
Bratislav Antić	Unravelling the Influence of Magnetite Nanoparticle Morphology on the Efficient Removal of As(III) and As(V) in Water Treatment Processes	W12
Lenin Thulluvan Valappil	Synthesis and Photocatalytic Performance of Cu-TiO ₂ Nanotube Powders Obtained via Rapid Breakdown Anodization	W13
Marian Olazabal Dueñas	A full optimization of the Anodic Stripping Voltammetric Determination of Pb and Cd in Seawater Using a Rotating Ring-Disk Electrode With an in situ Bi Film.	W14
Tuesday, December 5th 2023		
Session Topic: Atmosphere		
Aida Šapčanin	Levoglucosan In Biomass Combustion Products	A1
Thomas Schaefer	T- and pH-dependent OH Radical Kinetics of Lactic Acid, Glyceric Acid and Methylmalonic Acid in the Aqueous Phase	A2
Session Topic: Sustainable Development		
Miljan Bigović	Removal of Heavy Metals from Cigarette Butts in Different Ways and Their Recycling	SD1
Muhammad Bilal Hanif	Effect of Mo-doping on Proton-conducting BaCe _{0.9-1} Mo _x Y _{0.1} O _{3-δ} Electrolyte at Intermediate Temperature SOFCs	SD2
Nuno Ratola	Volatile Methylsiloxanes (VMSs) Profiles in Wastewater Originated from Different Sources	SD3
Miroslav Vrvic	From Sustainable, Through Suitable to Smart Development	SD4
Mirjana Radanović	Synthesis and Structure of New Polymeric Zn(II) Complex with <i>bis</i> (4-carboxy-benzyl)ammonium Chloride and <i>trans</i> -1,2- <i>bis</i> (4-pyridyl)ethene as Building Blocks of Potential Network Materials	SD5
Emilija Vukićević	Potential of Biochar as Fuel Obtained by Pyrolysis of Agricultural Waste	SD6
Nevena Mihailović	Green Synthesis of Silver Nanoparticles and Its Potential Antitumor Effect on HCT-116 Human Colon Cancer Cell Line	SD7

Branka Lončarević	Investigation of Biodegradability of Levan-polystyrene Graft Copolymers in Liquid and Solid Medium	SD8
Branka Lončarević	Starch Copolymers with Enhanced Biodegradability	SD9
Kristina Joksimović	Decolorization of Azo Dye Through the Utilization of Microbial Fuel Cells Connected in Parallel Configuration	SD10
Kristina Joksimović	Exploring the Potential of Plants for the Degradation of Perfluorooctanoic Acid	SD11
Paola Cirelly	A Green Sample Preparation Procedure for Elemental Analysis of Environmental Samples by X-ray Fluorescence Analysis with Smart Store®	SD12
Sanja Lazić	Influence Of Insecticides on The Photosynthetic Pigments Content in Peach Leaves	SD13
Marija Lješević	Reducing Adverse Effects of Copper on <i>Alivibrio Fischeri</i> Using Microbial Levan and Pullulan	SD14
Marija Lješević	Investigation of the Capacity of the Isolated Sulfate-reducing Bacteria to degrade PFOA	SD15
Dragana Šunjka	Behaviour of Herbicide Prosulfuron in Agricultural Soil	SD16
Jelena Isailović	Physicochemical Characteristics of Biofuel Obtained by Pyrolysis of Corn Waste	SD17
Ana Radović	Biological Effectiveness of Newly Synthesized $[CuL(H_2O)]$ on Fungy <i>Colletotrichum acutatum</i>	SD18
Session Topic: One Health		
Aida Šapčanin	Wild Mushrooms from Eastern Bosnia and Heavy Metals Accumulation	OH1
Jelena Radonić	Are the Residents of AP Vojvodina, Serbia, Exposed to Persistent Organic Pollutants and Polycyclic Aromatic Hydrocarbons Through Inhalation?	OH2
Lyubka Tancheva	Synergic Action of Citicoline and Standardized Snail Extract in Alzheimer's Dementia	OH3
Lyubka Tancheva	Antioxidant Potential of Myrtenal and its Adamantane Conjugates in Dementia Rat Mode	OH4
Elisaveta Mladenova	Investigation on Some Elements Content in White Wine After its Treatment with Different Dose Bentonite	OH5
Svetlana Vujović	Ecopharmacovigilance – Necessary Discipline for a Greener Future	OH6
Biljana Damjanović Vratnica	Effect of Vegetation Cycle on the Chemical Composition and Antimicrobial Activity of <i>Rosmarinus Officinalis</i> Essential Oil	OH7
Konstantin Ilijević	Relevant Parameters for Standardless Determination of TiO_2 in Food Samples by Portable X-ray Fluorescence Spectroscopy (PXRF)	OH8
Reni Kalfin	New Neurotensin Analogue: Effects on prosocial behaviour in experimental model of Parkinson's disease	OH9
Reni Kalfin	Induced by Toxin 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine Parkinson's Disease Model and the Effect of Helix Aspersa Extract In Vivo	OH10
Nenad Zarić	Micronutrient Effect on the onset of Chalkbrood Disease in Honey Bees	OH11
Nenad Zarić	Honey Bee Metal Accumulation: Midgut vs Bee Tissue	OH12

Plenary Lectures





John. P. Giesy, Ph.D., FRSC

John P. Giesy was born in Youngstown Ohio in 1948 and is currently a dual citizen of Canada and the USA. He obtained a B.S. Degree, *Summa cum laude* with honors in Biology from Alma College, M.Sc. and Ph.D. in Limnology from Michigan State University in 1971 and 1974, respectively.

He is a world leading eco-toxicologist and environmental chemist with a total of over a quarter of a billion dollars (\$284,547,002 CAD) in funding for his career. He discovered the phenomenon of photo enhanced toxicity of organic compounds, such as PAHs. He was the first to report the occurrence of perfluorinated compounds in the environment. Recently he has been using e-DNA and e-RNA to assess presence and absence of aquatic species, including invasive species, and community structures as well as effects of chemical and physical stressors and measuring the virus that causes COVID-19 in domestic sewage. He was a Canada Research Chair and is a Fellow of the Royal Society of Canada and a member of National Academy of Science of Canada in the Division of Earth, Ocean and Atmosphere. He served two terms as a chartered member of the US EPA Science Advisory Board and served two terms on the US EPA Board of Scientific Counselors. He is included in 40 biographical listings, including Who's Who in Canada, Who's Who in America, and Who's Who in the World. He was rated the No. 1 environmental scientist in Canada by the Globe and Mail Newspaper. He is also the recipient of many national and international awards including three major awards from the Society of Environmental Toxicology and Chemistry (SETAC); the *Founders Award*, which is the highest award given globally; *Environmental Education Award* and *Global Capacity Building Award* as well as serving as president of SETAC and is now a *SETAC Fellow*. In 2014 he received *Miroslaw Romanowski Medal in Environmental Science* of the Royal Society of Canada. In 2019 he was made *Doctor Scientiarum Ambalium, Honors Causa*, by Masaryk Univ. He has published 1385 peer-reviewed works and is the most cited author in the world in Ecology and Environmental Sciences, and most cited author at the U of S, with an Hirsch (H) index of 137 (Google Scholar®: based on over 85,170 citations to his works. His i10 Index (number of papers cited more than 10 times) is 1021 publications. He is the most cited author in the world in the combined fields of Ecology and Environment and has published more papers in the Journal *Environmental Science and Technology* than any other author. He was the Editor of *Chemosphere* for 27 years.

Anthropogenic and Naturally Occurring Brominated Compounds

John. P. Giesy, Ph.D., FRSC

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There are nearly 3200 known naturally occurring organo-halogen compounds, and more than 1600 of these contain bromine. Little is known about the sources, transformations and biological activities of many of these compounds. Anthropogenic brominated compounds, especially brominated flame retardants (BFRs), have attracted recent interest due to their large production volumes and ubiquitous occurrence in the environment. Among the brominated compounds, polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are of major concern. Several recent studies have described the presence of naturally occurring organo-bromine compounds, such as methoxy-PBDEs (MeO-PBDEs), hydroxy-PBDEs (OH-PBDEs) bromo-phenols (BRPs), polybrominated dibenzo-p-dioxins (PBDDs) in the marine environment. These classes of naturally occurring compounds have in some cases been measured at concentrations greater than that of the anthropogenic brominated contaminants. Some OH-PBDEs and BRPs have been reported to be degradation products of anthropogenic organo-bromines. OH-PBDE's are of particular concern due to their greater toxicities relative to synthetic PBDEs. To clarify the relationships between anthropogenic and naturally occurring brominated compounds, environmental investigations and in vitro metabolism studies of these compounds have been conducted. The results demonstrated the metabolic production of OH-PBDEs from naturally occurring MeO-PBDEs as a previously unidentified mechanism that could be an important contributor for the occurrence of OH-PBDEs found in marine wildlife. To further assess the contribution of anthropogenic organo-brominated compounds to total bromine in samples, a mass balance of total bromine was conducted. Total bromine in samples and organic sample extracts was determined by neutron activation spectroscopy. Combined concentrations of PBDEs, MeO-PBDEs, OH-PBDEs, BRPs and PBBs accounted for 0.01-0.04% of total bromine present in the livers of tuna, albatross, and polar bears collected from marine environments worldwide. Furthermore, extractable organic bromine accounted for only 7.03-16.81% of total bromines in the samples. Ongoing studies are exploring the nature origins and toxicities of the predominant brominated compounds in these samples. These studies highlight the need to consider potential natural sources of organo-halogen compounds when assessing environmental and human health risk assessments of the marine environment.



Prof. George P. Cobb Ph.D.

Dr. George P. Cobb is a professor at *Baylor University*, where he serves as Chair of the Department of Environmental Science. Prof. Cobb is an *American Chemical Society* Fellow and a *Society of Environmental Toxicology and Chemistry* Fellow. He previously served as Chair of the *American Chemical Society's Division of Environmental Chemistry* and President of *SETAC North America*. He currently serves in various roles within the *American Chemical Society*. He is a member of the *United States Environmental Protection Agency's Science Advisory Committee on Chemicals* and an *ad hoc* member of the *Board of Scientific Counselors*. He holds a Ph.D. in Chemistry from the *University of South Florida*.

Throughout his career, Prof. Cobb has used novel sampling and analysis techniques for biotic and abiotic media to evaluate toxicant transport, transformation, and biological exposure processes. His exposure assessments within agricultural monocultures have also been integral parts of data packages for regulatory consideration of pesticide registration and reregistration. His research has also evaluated novel airborne transport processes that distribute synthetic anabolic steroids near concentrated animal feeding operations.

The Cobb research group has also performed novel exposure and effect assessments of nanomaterials, metals, chlorinate hydrocarbons, and explosives in the environment. His most recent work includes monitoring and evaluating paraben's chemical transformation in Texas wastewater.

Paraben Transport and Transformation in Wastewater and Bioaccumulation in the Brazos River of Texas, USA

Prof. George P. Cobb and Michael T. Penrose

Department of Environmental Science Baylor University
Waco, Texas, USA 79798

Parabens are commonly used preservatives that are weakly estrogenic. Wastewater effluent is the greatest contributor of parabens in surface waters. While previous studies indicate parabens are well removed in wastewater treatment plants (WWTPs) via transformation, little is known about paraben transformation products. We evaluated paraben transformation and release into the Brazos River of Texas, USA throughout a calendar year. Paraben concentrations were quantified in upstream and downstream reaches of the river, and in fish that inhabit the river. Influent concentrations and transformation rates varied seasonally at the two WWTPs. Para-hydroxy benzoic acid was present in greatest amounts in influent and effluent at both WWTPs. Parent paraben transformation rates were greater at plant 1 with concentrations of all three shorter chained parabens decreasing by over 50% after treatment. Dichlorinated transformation product formation was greater at WWTP 1 with concentrations of dichlorinated paraben increasing by 10X in some cases. Shorter chained parabens generally had a greater transformation rate, no correlations were found between decreases in methyl and ethyl parabens and the formation of their respective dichlorinated transformation products.

Once waste waters enter riverine systems transformations continued. River water downstream of wastewater treatment outfalls had lower concentrations of methyl paraben. Para-hydroxybenzoic acid was the compound present in greatest concentration at most sites. Dichlorinated paraben concentrations increased downstream of WWTPs. Concentration increases indicate that effluent contains dichlorinated parabens in high enough concentrations to effect concentrations in the river. Dichlorinated species also persisted, with no significant decreases at sites further downstream during any season. Methyl paraben concentrations decreased at the site furthest downstream while dichlorinated methyl paraben concentrations remained stable showing that the dichlorinated species degraded slower than their respective parent paraben. Due to the dichlorinated species being released in higher concentrations in effluent than parents and being more resistant to degradation, the dichlorinated parabens are more likely to be environmentally relevant than are parent parabens. The nuances of chemical profiles indicate that sorption and bioaccumulation processes are also important.

Parabens and their transformation products are differentially accumulated by fish species, smallmouth buffalo (*Ictiobus bubalus*) and gizzard shad (*Dorosoma cepedianum*). The two fish species evaluated were. Four parent parabens and mono and dichloro disinfection byproducts were found in fish. Uptake is dependent on both chemical speciation and the biological species that is exposed to the analytes. Assays to determine endocrine effects show the potential for effects that will be detailed further during the presentation.



Prof. Ioannis A. Katsoyiannis Ph.D.

Ioannis Katsogiannis is Professor of Environmental Technology at the Chemistry Department of the Aristotle University of Thessaloniki. He is President of the Hellenic Academy of Industrial Property and of the Association of Greek Chemists. He was a fellow of recognized international organizations such as the Alexander von Humboldt Foundation, the German Academic Exchange Service (DAAD), the Swiss National Science Foundation and has received a Marie Curie individual fellowship. He has conducted research at the Technical University of Berlin (TU Berlin), Hamburg University of Technology, ETH Zurich and EPF Lausanne, Switzerland. He is the author of more than 90 research papers, which to date have received more than 6800 citations with an H index of 40. He was scientific responsible in more than 20 research projects and has been invited more than 25 times to give lectures worldwide at international conferences and prestigious universities. In 2023, during the work of the UN conference on water, he gave a speech from the floor of the UN General Assembly in New York, on the global state of water.

Professor Katsogiannis currently serves as a member of the EuChemS Executive Committee, chair of the EuChemS Chemistry and Environment Department and editor of the journal Environmental Science and Pollution Research.

Arsenic Contamination of Groundwaters and Novel Approaches for its Removal

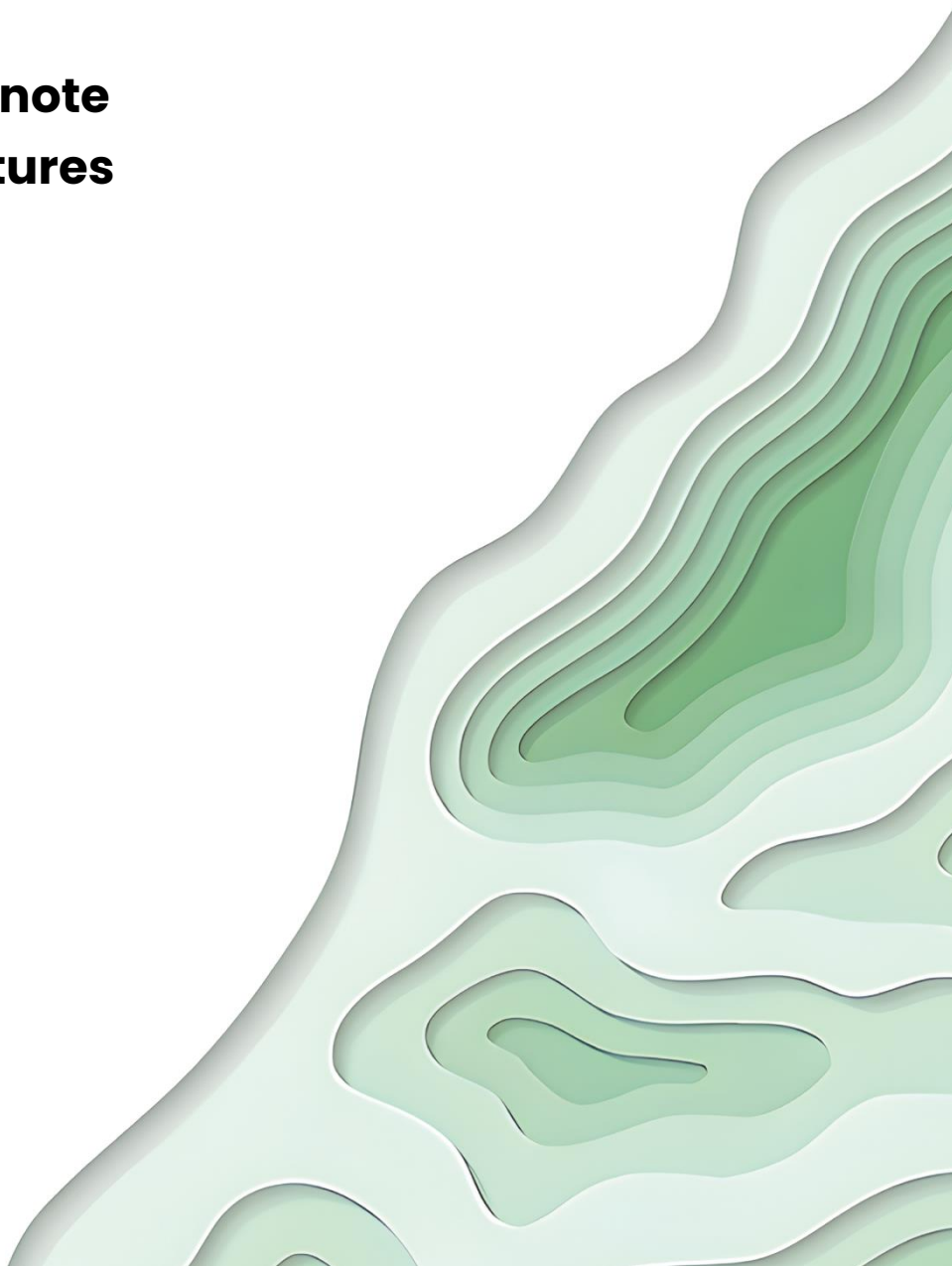
Prof. Ioannis A. Katsoyiannis Ph.D.

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Arsenic contamination of groundwaters is still a matter of concern in several countries across the world, among which also Balkan countries, such as Serbia and Greece. Treatment of drinking water for arsenic (As) removal has been implemented in centralized facilities worldwide, reflecting the increasingly stringent national and international drinking water standards for As, for which a standard of 10 µg/L has been widely adopted. On the other hand, in several countries in South East Asia, the problem of arsenic contamination is severe, and treatment of groundwater is based on low-tech technologies, which are efficient for arsenic removal but installed community filters lack the capacity to provide the required amounts of drinking water to the local population. A review of available information on installed treatment does provide some insight into the scale of implementation and difficulties that have arisen in practice (as a complement to more accessible information on bench-scale and pilot-scale studies).

In practice, the two most applied technologies for arsenic removal are coagulation using iron-based salts and adsorption based on iron or alumina based adsorbents. For both of these technologies, Furthermore, a detailed analysis of the mechanisms of arsenic removal from groundwaters will be discussed in relation the groundwater composition, knowledge which is very critical in the decision of the treatment option to be implemented.

Keynote Lectures



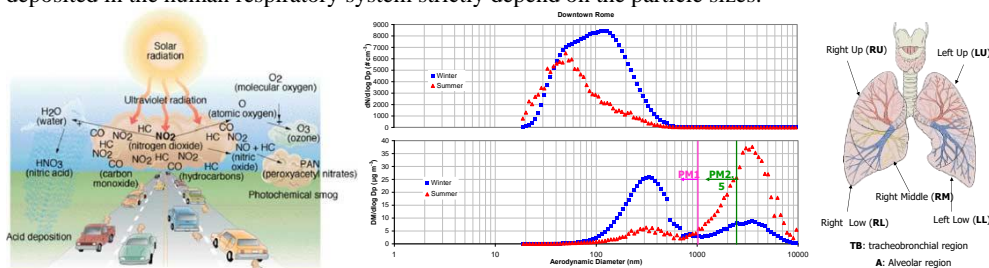
Dynamic and Behavior of Ultrafine Particles in Urban Atmosphere: Toxicity and Deposition in Human Respiratory System

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Aerosol pollution in urban environments has been recognized to be responsible of important pathologies of the cardiovascular and respiratory systems, it has also been associated to increased mortality and hospital admissions. New regulations state that for fine particulate matter (PM_{2.5}) there is yet no identifiable threshold below which PM_{2.5} would not pose a risk. Recently, the International Agency for Research on Cancer (IARC) has considered outdoor pollution as a leading environmental cause of cancer deaths. Furthermore, particulate matter has been classified as carcinogenic to humans (Group 1). Within this context, the importance of the measurements of aerosol size distribution resides in that the doses deposited in the human respiratory system strictly depend on the particle sizes.



In this perspective, great attention has been addressed to Ultra Fine Particles (UFPs, < 100 nm), since they efficiently penetrate into the respiratory system and are capable of translocating from the airways into the blood circulation [1]. Many studies show that particle toxicity increases with decreasing their size, emphasizing the role of submicrometric particles, in particular of ultrafine particles (< 100 nm). High aerosol size resolution measurements are important for a correct assessment of the deposition efficiency in the human respiratory system as well as time resolution is another important requisite. Starting from such considerations, time resolved aerosol particle number size distributions have been measured in downtown Rome. FMPS and SMPS measurements have been carried out in downtown Rome, in an area characterized by high density of automotive traffic. The two instruments have allowed to investigate deeply the urban aerosol in the range 5.6–560 nm and 3.5–117 nm, respectively. In particular, the FMPS measurements have confirmed the interpretation about the transition phenomena in the time interval of few seconds, time scale typically associated with the emission of gasoline and diesel.

Furthermore, moving from these data the total dose of particles and ultrafine particles deposited in the regions of the respiratory system (head, tracheobronchial and alveolar in the different lung lobes, have been estimated [2]. Doses are reported both as number of particles deposited for each tidal volume of air inhaled (instant doses) and as number of particles deposited at the end of an exposure period (cumulative doses).

This lecture will discuss the aerosol doses deposited in the respiratory system of individuals exposed in proximity of traffic. According to the greater dose estimated, right lung lobes are expected to be more susceptible to respiratory pathologies than left lobes.

Acknowledgements

The authors wish to thank dr. Maurizio Manigrasso for having shared their studies for a long time.

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Per- and Polyfluoroalkyl Substances - From Challenges To Potential Solutions



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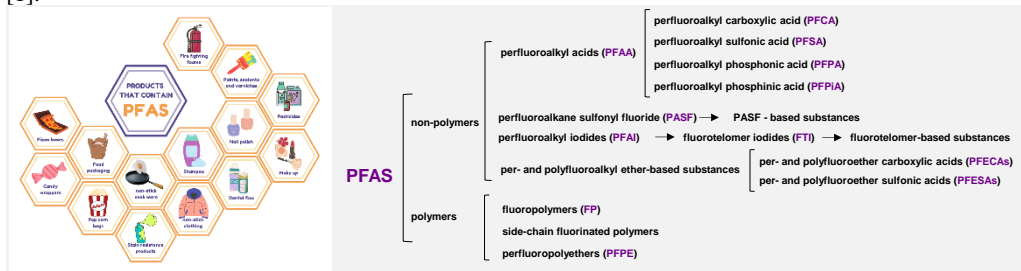
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Per- and polyfluoroalkyl substances (PFAS) have emerged as significant environmental pollutants with far-reaching implications for both the environment and public health. These synthetic chemicals have been in use since the 1940s, finding applications in both industry and consumer products. Consequently, they have become pervasive in the environment, contaminating water sources, soil, and even the human body [1].



The persistence, tendency to bioaccumulate, and harmful effects of PFAS on ecosystems and human health have prompted growing scientific and regulatory interest. The occurrence and fate of PFAS in drinking and wastewater, have become key areas of interest. In addition, PFAS-contaminated soil has been increasingly reported worldwide. When these chemicals infiltrate soil, there's a risk of contaminating groundwater, potentially affecting drinking water and food safety. This underscores the urgent need for tailored remediation technologies for PFAS-contaminated water and soils. In recent years, there have been efforts to find solutions for cleaning up PFAS contamination. These studies have led to the exploration of various technologies such as adsorption, filtration, thermal decomposition, oxidation/reduction, and soil washing. However, some of these methods can inadvertently interact with other pollutants, generating high-concentration waste. Others may disrupt the natural balance of soil and ecosystems. Additionally, some of these techniques can be costly to implement [2]. Our recent study focuses on treatment train technology in which advanced oxidation techniques should be followed by microbial treatment to reduce PFOA levels. Initially, we investigated abiotic and biotic PFOA degradation, using target LC-MS/MS for quantitative analysis and non-targeted LC-MS/MS for degradation products identification. In the photocatalysis experiments, we employed carefully selected Ti and Al-based photocatalysts. Microbial communities from PFAS-contaminated sites in Serbia, Japan, and Italy were enriched by culturing in media supplemented with PFOA [3]. Photocatalysis resulted in PFOA degradation ranging from 50% to 80%. Non-targeted analysis revealed the presence of shorter-chain PFOA homologs, and free fluoride were detected. In our biodegradation study, PFOA concentrations decreased by 21% to 36% using the most active microbial consortia. Future research will focus on optimizing and combining these techniques.

Acknowledgements

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Pollution by Microplastics in the Sea-the Case of the Gulf of Trieste and the Bay of Boka Kotorska



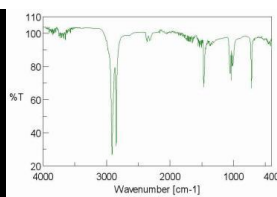
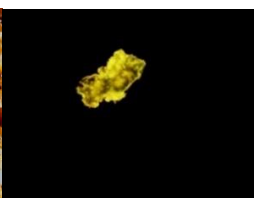
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Plastic products are being produced at ever-increasing rates, making plastic pollution one of the most important environmental problems. Plastic is a very practical material that is long-lasting, resistant to degradation, inert, and easy to shape, with very low production costs. Annual global production of plastic materials is about 300 million tons, increasing more than 20-fold in the last 60 years. About 10% of the plastic produced each year ends up in the ocean and about 8 million pieces of plastic escape into the oceans from land-based sources every day, mostly by rivers [1].



Microplastics (MP) are pieces of plastic measuring less than 5 mm in length which are divided into primary and secondary MP. Both types of MP have been found to accumulate and persist in natural aquatic ecosystems. MP particles can be harmful to marine life. Ingested plastic fragments can cause changes in feeding and reproductive behavior as well as increased mortality [2].

In this paper, we will address the problem of MP in the marine environment. The most important sources of microplastics, their degradation and transport processes and their impacts on marine organisms will be presented. The Gulf of Trieste and the Bay of Boka Kotorska are interesting areas for the study of marine pollution by various pollutants, including MP. Both bays are relatively enclosed marine areas with limited exchange of water with the open sea. They are also relatively shallow bays and are affected by many sources of pollution. To compare MP pollution, the distribution and basic characteristics of MP in marine sediments, mussels and some fish species were determined [3, 4].

All sediment samples contained microplastics, with higher concentrations near pollution sources (highly populated areas, wastewater discharges, areas with fishing and touristic activities) and in more enclosed areas (harbours, marinas). The most common forms were filaments (fibers), fragments and films, mainly of PP, PE and PET. More than 50% of the mussels and fish at both sites contained MP. Similarly to the sediments, the most common forms in the organisms were filaments and fragments, largely composed of PP, PE and PET. The results indicate a pressing problem of MP pollution in such coastal marine environments. Similarities between sediments and organisms in terms of particle shape and polymer composition were also observed, which is certainly related to the sources of pollution in the areas investigated.

Acknowledgements

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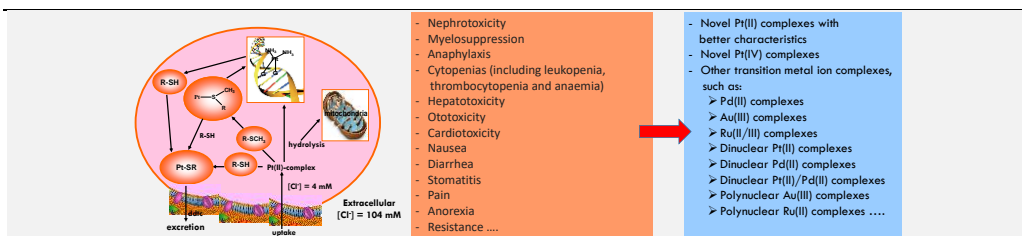
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Toxicity vs. Biological Activity of Different Transition Metal Ion Complexes



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The investigation of the potential antitumor activity of the huge number of platinum complexes starts after discovery of the antitumor activity of cisplatin, $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$, and later carboplatin and oxaliplatin. However, it is well-known that platinum complexes express toxicity, numerous side effects and resistance during the application in chemotherapy. This led to the increasing efforts of the scientist to synthesize other platinum as well as non-platinum compounds with potential antitumor activity, primarily Pd(II), Ru(II/III) and Au(III) complexes. The antitumor activity of platinum drugs is a result of the interactions between complex and DNA. Moreover, the interactions of complex with sulfur-containing biomolecules are associated with negative phenomena, such as nephrotoxicity, gastrointestinal toxicity, ototoxicity, etc. Considering this, here are summarized the results of the synthesis of novel potentially active transition metal mononuclear, homo- and hetero-polynuclear Pt(II), Pd(II), Ru(II/III) and Au(III) complexes and the results of their interactions with different sulfur- and nitrogen-donor biologically relevant nucleophiles to predict their potential activity or toxicity. Among mononuclear complexes, the compounds with *terpy* (terpyridine) or its 4'-[4-chlorophenyl] derivative, different pyrazole derivative, pyridine derivatives, *bpma* (*bis*-(2-pyridylmethyl)amine), *o-bqdi* (*o*-benzoquinone diimine), *nqdi* (2,3-naphthaquinonediimine), *bpy* (2,2'-bipyridine) and its derivatives, and aliphatic *dien* (diethylenetriamine) as nitrogen-donor inert ligands were studied. Different homo- and hetero-polynuclear complexes with *pz* (pyrazine) or 4,4'-*bipy* (4,4'-bipyridine) as bridging and mostly *en* (ethylenediamine), *bipy* (2,2'-bipyridine) and *dach* (*trans*-1,2-diaminocyclohexane) as inert ligands were studied as well. [1-4] The research was focused on the correlation between the structure of complexes, type of transition metal ion and mechanisms of their interactions with different biomolecules, such as L-Cys (L-cysteine), L-Met (L-methionine), GSH (glutathione), 5'-GMP (guanosine-5'-monophosphate), serum albumin and DNA (deoxyribonucleic acid). Some of the studied complexes were selected for further *in vitro* studies of the cytotoxicity on different tumor cell lines. These results could help a lot for the better understanding of structure-activity relationship (SAR) of different transition metal ion complexes.

Acknowledgements

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TOPIC 1
**SOLID
MATRICES**



Non-Targeted Analysis of Household and Office Dust Using GCxGC-HRTOFMS

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Humans spend most of their time at home and their place of employment where they are exposed to a wide variety of hazardous chemicals. These substances can be detrimental to human health. House and office dust is a repository of chemicals and can serve as an indicator of environmental exposure. However, there are certain difficulties with the analysis of their chemical diversity, trace concentrations, and sheer numbers of compounds present in this complicated mixture. Moreover, chromatographic separation and identification of pollutants are challenging due to a large number of congeners and spectral interferences between the pollutants and matrix compounds.

In this study, the non-targeted analysis of dust extracts was conducted using a multi-mode source GCxGC-TOFMS instrument from LECO (St Joseph, MI, USA), and the corresponding spectral analysis software tools from the same company. The multi-mode source was used to generate complementary electron ionization (EI), positive chemical ionization (PCI), and electron capture negative ionization (ECNI) high-resolution accurate mass spectra. The resolving power of the mass spectrometer was 50000, while 200 spectra/second were recorded. Data processing was carried out using both untargeted Peak Find for the screening of dust samples followed by Target Analyte Finding for the trace analysis and quantitation of specific pollutants found in the samples. The samples of dust were collected in the houses and in the offices. NIST SRM 2585 mixture was used as a standard.

Compounds were identified using a combination of spectral database searches (NIST, Wiley,

ChemSpider) and formula determinations for fragment, molecular, and adduct ions. In addition, scaled mass defect plots were used to facilitate dust constituent characterization. Over one thousand chromatographic peaks in two-dimensional maps were taken into account while the majority of them were identified as belonging to the most various classes of organic compounds. Legacy persistent organic pollutants (POPs) that were identified, included polycyclic aromatic hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated naphthalenes (PCNs), and polychlorinated paraffins (PCPs). Finally, polyfluorinated alkanes and alcohols were also discovered in the dust samples. Quantification of priority pollutants was carried out using the available NIST standards.

Application of three complementary ionization modes allowed increasing sensitivity, and the number of compounds with registered molecular ions. It also significantly improved the identification reliability using three types of spectra for the same compounds. When dealing with certain classes of pollutants the position of the related peaks in the particular site of the two-dimensional map was very helpful. That feature represents an additional tool for the correct identification of the compounds of interest.

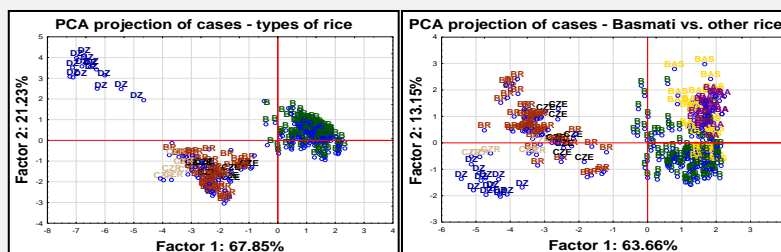
Significantly higher sensitivity of ECNI in the analysis of polyhalogenated species enabled identifying numerous congeners of the corresponding chlorinated, brominated, and fluorinated species. These compounds were mainly undetectable in classic EI mode.

Elemental Analysis of Rice in the Context of Safety and Authentication

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Rice is an excellent source of nutrients, and information on its elemental composition is important both from the point of view of nutrition itself, including possible toxicological risks, and in terms of conducting the so-called food authentication. Rice grain contains 12% water, 75%-80% starch and 7% protein with a full set of amino acids, and is also a source of vitamins (including B group) and minerals. Rice is a crucial part of the diet for over 50% of the world's population. About 90% of rice is produced in Asia (mainly in China, India, Indonesia, Bangladesh). The countries with the highest per capita rice consumption include Laos and Cambodia, where the consumption exceeds 250 kg/capita (in Poland is about 2.7 kg/person). The wide range of rice types available on the market makes higher quality rice varieties potentially susceptible to fraud. Some varieties, including Basmati rice from India (only 8 varieties) and Pakistan (only 4 varieties) are eligible for zero import duty. Therefore, there is a justified risk of an increase in adulterations. for aromatic rice [1-3].

The aim of this study was to assess the differences in the elemental composition of rice samples, including: wild rice (manomin), white and brown rice commonly available on the Polish market. Within each of the 84 packages, from 2 to 4 independent samples ($N = 281$) were tested. An additional aspect of this work was to determine whether individual type of rice (including Basmati rice and jasmine rice) could be distinguished from the other groups considered in this study based only on their elemental composition. Total mercury (Hg) content in rice samples was determined by the cold vapor atomic absorption spectroscopy

CVAAS technique (MA-3000, NIC). Arsenic (As) and selenium (Se) levels were measured using the graphite furnace atomic absorption spectroscopy technique GFAAS with Zeman background correction (Solaar M6, Unicam). The concentration of other elements (e.g. Ca, Cd, Cu, Fe, K, Mg, Mn, P, Pb, S, Zn) was assessed using the inductively coupled plasma optical emission spectroscopy technique ICP-OES (iCAP 7400, Thermo).

No sample exceeded the limits valid in China regarding the content of Hg (0.020 mg/kg) or the concentrations of Cr (1.0 mg/kg) and As (0.2 mg/kg). 40 samples exceeded international limits and EU standards for Pb concentrations (0.20 mg/kg). In 22 cases Cd concentrations were above the maximum allowed levels established in China (0.2 mg/kg) and in the EU requirements (0.15 mg/kg). Research has also proven that it is possible to distinguish individual groups of rice samples (wild, white and brown) based on their elemental composition. Basmati rice can be characterized by very low levels of Fe, K, Mg, Se, Hg and high concentrations of Mo and S compared to other groups considered.

Acknowledgements

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The Agricultural Dilemma: Biodegradable vs. Conventional Plastics, Aging and MP Formation

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Biodegradable plastics (BPs) have been created as alternatives to traditional plastics. Various types are available, such as poly (butylene adipate-co-terephthalate)/poly (lactic acid) (PBAT/PLA) and thermoplastic starch (TPS) films. These BPs are utilized to replace traditional polyethylene (PE) mulch films and other agricultural products crafted from polystyrene (PS) and polyethylene terephthalate (PET).

Our research aim was to compare the degradation rate of the agricultural foils made from BPs compared to conventional PE in real agricultural environment on fields of the Agricultural Institute of Slovenia and in the artificial weathering chamber with UV light at the Slovenian National Building and Civil Engineering Institute. Besides this, various forms of microplastics (MPs) originating from polystyrene (PS), polyethylene terephthalate (PET), and polyethylene (PE) were examined for their ability to adsorb pesticides and their potential as carriers.

To simulate one year of outdoor exposure, the tested plastic foils (TPS; PBAT/PLA; PE) underwent artificial weathering in the chamber with three air-cooled 1800 W xenon lamps for 1 month of UV light and another 1 month with alternating temperature from 80 °C to -20 °C. On the contrary, the same plastic foils were left in an outdoor environment for a duration of one year, allowing them to undergo natural weathering. The polymer changes after weathering were analysed with Agilent Cary 630 ATR-FTIR spectrometer. The ability of microplastics (MPs) to adsorb pesticides (acetamiprid, chlorantraniliprole, flubendiamide; K_{ow} 0.80, 2.76, and 4.2) was

investigated based on their shape (pellets, spheres, and foil fragments), and composition (PS, PET, PE). MPs were first extracted from soil samples using density separation with a saturated $ZnCl_2$ solution [1]. Subsequently, their capacity for adsorbing pesticides was analyzed using solid-phase extraction (SPE) followed by high-performance liquid chromatography with diode array detection (HPLC-DAD) [2].

The ATR-FTIR spectra of aged PBAT/PLA, TPS and PE films compared to pristine foils showed characteristic bands at 1710 cm^{-1} (the C=O stretching vibration) and wide bands at 3100–3600 cm^{-1} (the -OH stretching vibration) in all cases. During the artificial aging procedure, a weight reduction of 8.6% was determined for PBAT/PLA, 6.5% for TPS, and a mere 0.02% for PE. Samples from agricultural fields showed a similar pattern of MPs formation, starting from the most susceptible for degradation PBAT/PLA, 0.17 ± 0.03 mg macro MPs/kg_{soil}; followed by TPS, 0.08 ± 0.05 mg macro MPs/kg_{soil} and concluding with PE 0.004 ± 0.004 mg macro MPs/kg_{soil}. Statistical analyses have confirmed that fragments with specific shapes, such as pellets and spheres, exhibited a greater capacity for adsorbing and retaining pesticides. Additionally, PET-type microplastics displayed higher sorption rates for all pesticides compared to both PE and PS.

Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency, P3-0388 (Mechan. of health maintenance), and P4-0431 (Next Gen. Agriculture).

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How Bad Volcano-Clastic Badlands Actually Are?

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Badlands, often described as natural field laboratories, are landscapes of limited vegetation, with reduced or not existing human activity that are exposed to a wide range of geomorphological processes [1]. These areas are made of mostly soft and poorly consolidated terrigenous, lacustrine or marine sediments of different age that were developed under different climatic conditions due to specific combination of sediments physico-chemical properties that depend on their mineralogical composition.

However, badlands can also form in volcano-clastic materials. One of the most well-known landscapes of this type is Cappadocia in Turkey. Compared to Cappadocia, less known ones are Đavolja Varoš in Serbia and Kazár badlands in Hungary. Even though these two sites are geographically close and of the same, volcanic sediments origin, Đavolja varoš is in a form of the reddish earth pyramids built of erodible materials that are protected by the cap rock, while Kazár badlands are greyish white cliffs and white barren patches are not protected with the cap rock.

For these potential similarities and differences, eight sediments samples, four from Đavolja varoš and four from Kazár badland have been compared from the perspective of mineralogical composition, petrographic characterization, particle size distribution, pH, electrical conductivity (EC), and the sodium adsorption ratio (SAR).

Observing mineralogical composition, it is seen that both of these sediments are acidic to intermediate acidic volcano-clastic sediments, composed mainly of quartz, in case of Đavolja varoš, while in Kazár badlands feldspar, quartz and biotite dominate in its composition. As expected, that type of composition was confirmed by thin section of these samples, but more interestingly a

difference in terms of porosity, comparing these two locations was noticed. These samples share similarity in grain size distribution with already well-known badlands that are mainly silty, and both these volcano-clastics are actually sandy silt or silty sand sediments. Connecting particle size distribution to the previously mentioned porosity, noticed porosity pattern could be explained by secondary silification processes.

Observing pH, Đavolja varoš samples are acidic, while Kazár badlands are slightly alkaline with similar EC values that fall in the 35-80 $\mu\text{S}/\text{cm}$ range and both sites. According to the SAR, present potentially dispersive to dispersive material.

In conclusion, comparing Đavolja varoš and Kazár badlands, not only between each other, but to badlands generally, we can say that: grain size distribution is making both of these sediments erodible; different porosity and mineralogical composition as well as different origin are accelerating erosion processes in Kazár badlands; and the absence of real sedimentary minerals and presence of organic material is marking the difference to already, in the literature better known badlands.

Acknowledgements

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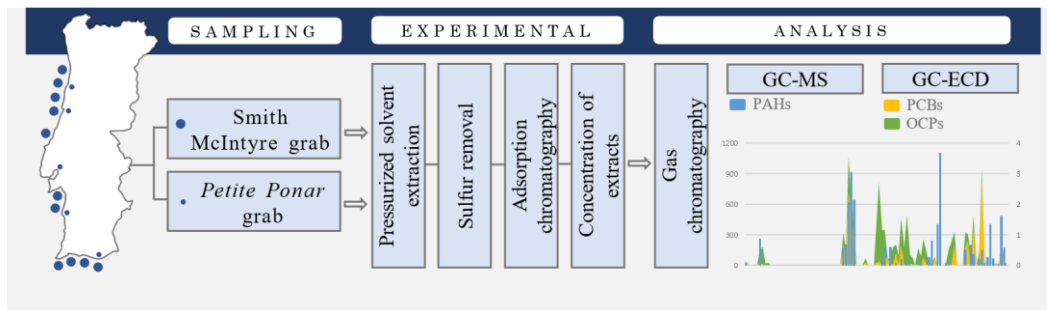
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Persistent Organic Pollutants in Surface Sediments from Portuguese Marine Estuaries and Coastal Environment

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Persistent organic pollutants (POPs) are ubiquitous chemical contaminants that persist in the environment for long periods after their release [1, 2] and are potentially transported over great distances and dispersed around the globe by air and ocean currents [3]. The concern around the presence of POPs in the environment has led to the adoption of an international treaty in 2001, the Stockholm Convention on POPs.

In order to monitor these compounds, the Hydrographic Institute (IH) collects and analyses samples of marine sediments and assesses the level of pollution in accordance to applicable international guidelines [4] and national legislation [5] related with dredged material which characterize the sediments in terms of levels of pollution present in the samples. In this work, IH evaluates levels of POPs, namely polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs), in surface sediment samples from project AQUIMAR collected in different sampling campaigns of five coastal areas and of four Portuguese inland waters: Ria de Aveiro, Ria Formosa and Mira and Mondego rivers. Results of the analysis of collected sediments in Tagus river estuary, from Valorsul, S.A. monitoring program, were also used. Samples from coastal areas were collected with a Smith-McIntyre grab sampler while samples from estuaries were collected with a Petite Ponar grab sampler.

POPs were extracted from sediment samples by pressurized liquid extraction (PLE) and the resulting extracts purified by adsorption chromatography using silica gel and deactivated alumina before analysis by gas

chromatography-mass spectrometry (GC-MS) mass spectrometry for PAHs detection and by gas chromatography-electron capture detector (GC-ECD) for PCBs and OCPs.

The results obtained were used to evaluate the spatio-temporal distribution of POPs and the levels of contamination present in the analysed sediments by comparison with applicable international guidelines and national legislation. The results from the AQUIMAR project indicate that sediments from the Portuguese marine environment are clean or, in the worst case scenario for some samples, with trace levels of POPs. Similar conclusions are drawn from the results from Valorsul, S.A. monitoring program.

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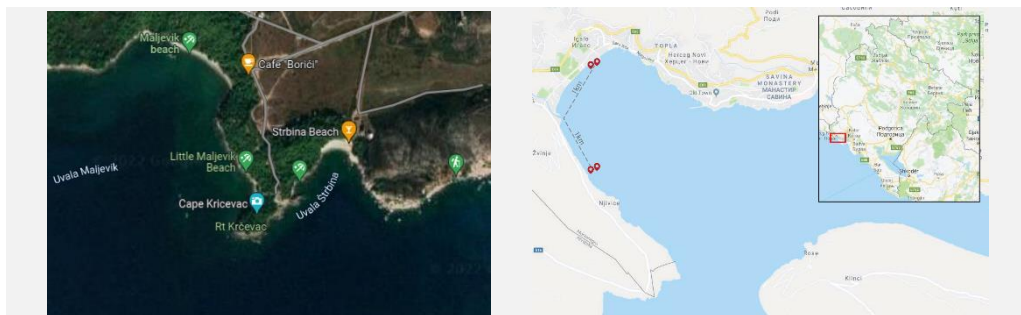
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Comparing the Content of Heavy Metals in Peloids from Sutomore and Igalo (Montenegro)

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Peloids are hydrothermal inorganic gels with optimal rheological and thermal properties, produced by process of mixing of clay minerals and mineral-medicinal waters. It has been used for recovering muscle–bone–skin pathologies and now such old practice has received applications also for wellness and relax purposes.

The final characteristics of peloids depend on: a) the chemical and mineral composition; b) the properties of water that participates in the processes of maturation and formation of peloids; c) the maturation process which is conditioned by numerous microbiological activities and the presence of organic matter. Samples for analysis were collected during 2020. , at the locations where they originate and three samples were taken, and then they were mixed.

Elements (primarily metals) of interest for peloid characterization are those that can harm our body in terms of toxicity or those that are essential for our survival. According to the effect that metals achieve in the living organism, they are divided into essential, useful and toxic, and these properties are related to their concentration. The element content in the sample (metals and non-metals) was determined by means of the induced plasma emission spectrometer (ICP-OES). The content of mercury was determined by Direct Mercury Analyser DMA-80.

We found that aluminium is by far the most abundant element in the both peloids, followed by

a significant amount of calcium, magnesium and iron. In our study we determined: the contamination factor (CF), the pollution load index (PLI) and the index of geoaccumulation (I_{geo}). These parameters are important and precise indicators of the state of the environment in terms of heavy metal pollution. By analyzing the obtained values, we can conclude that the examined peloids are uncontaminated which means that there is no contamination of the sediment with heavy metals.

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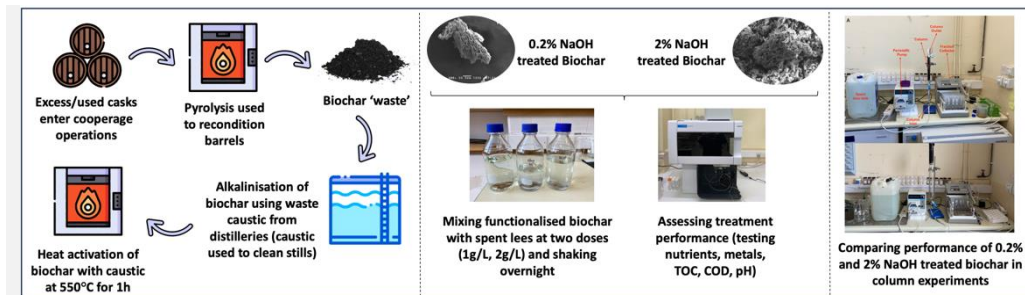
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Designing a Biochar-Based Pretreatment Method for Acidic Cu-rich Distillery Effluents Entering Wetlands

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Constructed wetlands have been an attractive approach for many years to remove dissolved copper (dissCu) and increase the pH of distillation effluents [1]. These systems are sometimes used to treat 'spent lees' in Scotland, a distillation by-product of whisky production. However, the acidic pH (pH < 4.5) [2] and high copper (Cu) concentration (up to 50 ppm) [3] in spent lees can induce high stress in wetlands (leading to failure) - unless it is pre-treated.

In this project, we modified biochar sourced from whisky cask cooperage (manufacture/reconditioning) - to pretreat spent lees by increasing its pH and decreasing its dissCu levels before it enters constructed wetlands.

Whisky cask cooperage-derived biochar underwent functionalization through overnight soaking in 0.2% or 2% NaOH, followed by activation at 550°C for 1 hour. These NaOH concentrations mirrored those used in distillery still washing processes. Performance evaluation, including nutrient and metal levels, TOC, COD, and pH, was conducted after mixing 1 g/L and 2 g/L of functionalized biochar with various distillery-sourced spent lees from Scotland and overnight agitation. Subsequently, column experiments compared the treatment efficiency of biochar treated with 0.2% and 2% NaOH. The final step involved optimising column treatment using biochar treated with 0.2% NaOH to enhance Cu recovery.

The 0.2% and 2% NaOH modified biochar increased the pH of a variety of undiluted spent lees by 1.5 (\pm 0.8) and 3.1 (\pm 1.5) pH units, and decreased dissCu by 17% (\pm 25) and 58% (\pm 41) respectively. Column experiments showed that

0.2% NaOH-treated biochar gave 32% more dissCu recovery than 2% NaOH-treated biochar (per gram). Optimisation increased recovery yield from 3.26 mg dissCu to 5.78 mg per gram of biochar.

Our study indicates that biochar could be used to pre-treat spent lees – increasing its pH and reducing its dissCu load. This in turn, would reduce negative (stress) impacts on the living wetland systems used to treat such waste effluent. Biochar produced using solid waste from cooperage operations could be highly sustainable, may have various uses, and may provide a low-cost water treatment option.

In future, scale-up will be considered. The laboratory column experiments proved the 'principal' of this process, and a field study with an industrial scale treatment column would now be needed to investigate process efficiency at scale, using effluent from a distillery.

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Elemental Analysis of Surface Soil Collected From the Vicinity of the Waste Disposal Places in Lodz Region

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The growing dominance of urban environment with heavy metals through natural and anthropogenic depositions and the potentially adverse health implications following environmental contaminations have focused attention on the disposal of municipal and industrial wastes. In the early 1990s, ecological awareness began to broaden and people started to discuss the problem of so called ecological bombs. They were identified as substances harmful to the natural environment accumulated in a given area, such as hazardous waste, which, if released into water or soil, may cause damage to the local environment. Many studies so far have proven that all forms of waste disposal have adverse effects on the environment, public health and local economies, which can be further intensified by poor management of municipal or industrial wastes leading to e.g. severe soil and groundwater contamination. Nowadays waste disposal is a problem that continues to grow with human civilisation and the determination of the impact of some dumpsites through soil analysis can be helpful in providing information needed for the development of proper programme and planned disposal/management strategies [1-2].

In the Lodz region, one of the cities with several landfills (containing e.g. dyes post-production wastes, hazardous wastes, gypsum and ashes wastes), located within significantly wide area is Zgierz. Dumpsites for years were not regularly inspected. Moreover, the failure to enforce the obligation to reclaim the area contributed to the illegal accumulation of waste. In this study analytical procedures to investigate the concentrations of some potentially toxic elements in soil material coming from Zgierz wastes disposal sites were employed.

The main objective of the research was to assess the impact of waste disposal places located in Lodz region based on the content of selected metals (e.g. Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn) in surface soil material. All samples were collected using soil stick from the closest vicinity of the waste disposal sites in Zgierz. Samples after collection were placed in a laboratory dryer and kept there for several days to obtain constant weight. Dry samples were sifted through a sieve with a mesh diameter of 2 mm and then grounded using agate mortar to obtain the appropriate grain size. In order to determine the total mercury content the Cold vapour atomic absorption spectroscopy technique (CVAAS) was applied. Before the multielemental analysis samples were treated with the mixture of concentrated nitric acid and chloric acid (3:1) and the extractable content of chosen elements was measured using Inductively Coupled Plasma Optical Emission Spectroscopy technique (ICP-OES). All gathered data was subjected to multivariate PCA analysis and places with the highest levels of chosen metals were identified.

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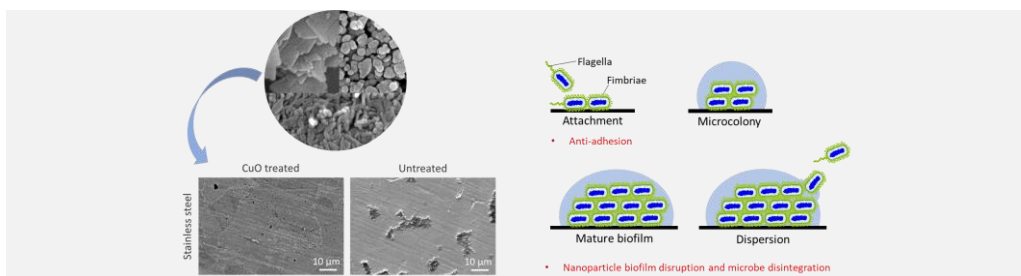
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Antibacterial Activity of CuO and ZnO Treated Surfaces

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Among the most serious medical problems are bacterial infections which most often originate from human bacterial flora [1]. *Escherichia coli* (*E. coli*) is a commensal strain present in the human gastrointestinal tract and usually coexists with its host in a mutually beneficial way, while immunocompromised people are susceptible to the development of disease. Bacterial cells can adhere and grow on different surfaces such as glass, various polymers, aluminum, and stainless steel. Organic coatings can influence the ability of bacterial adhesion on surfaces and the development of biofilms. Most bacterial cells are negatively charged, and a repulsive force is established between the bacteria and negatively charged coatings [2]. To date, ZnO and CuO NPs showed good antibacterial activity against both Gram-positive and Gram-negative bacteria. However, the comparison of the antibacterial activity between ZnO and CuO [3,4] lacks information on the effect of different nanoparticle (NP) morphology. To fill this gap we prepared ZnO and CuO NPs with different morphologies and sizes to compare their antibacterial effect. The study's main objective was to prepare polyallylamine hydrochloride (PAH), and alginate (ALG) multilayers doped with CuO and ZnO NPs with different morphology on the surface of stainless steel and determine their antibacterial activity on *E. coli*. Applying polyelectrolyte multilayers changed the hydrophobicity and zeta potential of the stainless

steel surfaces. PAH/ALG polyelectrolyte multilayers showed no antibacterial activity and did not lower the number of viable bacteria compared to untreated stainless steel surfaces. Polylayers with ZnO NPs exhibited excellent antibacterial activity against planktonic *E. coli*. They completely inhibited the growth of adherent cells where no viable cells were observed on the surface of the plates. CuO NPs did not significantly influence the number of planktonic cells, while in the case of adhered *E. coli* on the surface of the plates, the NPs caused complete growth inhibition. The influence of the last applied layer showed that the overall number of viable cells was much lower in the case of alginate. All prepared samples showed excellent cytocompatibility with HaCaT cells.

Acknowledgements

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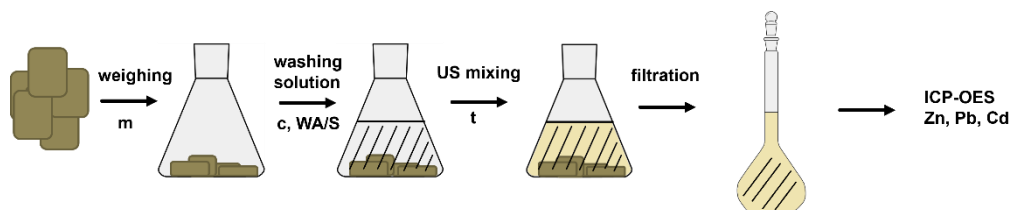
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A Comparative Study of the Effectiveness of Possible Washing Agents for the Remediation of Sediment Contaminated with Heavy Metals

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Sediments are known to accumulate different inorganic and organic substances that are present in or released into the environment. Of these, heavy metals are persistent contaminants, as they cannot be further degraded. While not an immediate threat if the sediment is stable, any disturbance (i.e., flooding, dredging) can cause the release of the contained heavy metals [1,2].

One possible remediation method for heavy metal contaminated sediment is sediment washing whereby chemical washing agents are used to extract heavy metals from the sediment. Many chemicals were tested for this purpose with varying degrees of success. These chemicals include inorganic and organic acids, chelating agents, and surfactants [3-5].

The presented study included two dredged sediment samples from Lake Ptuj, a manmade lake on the River Drava in Slovenia. These sediments have elevated levels of zinc (Zn), lead (Pb), and cadmium (Cd) [2]. The total mass percentage of these heavy metals were determined by microwave assisted acid digestion with *aqua regia* and were approx. 1100 ppm Zn, approx. 300 ppm Pb, and approx. 7 ppm Cd. Concentrations of heavy metals were measured by ICP-OES.

Speciation of the selected heavy metals was performed using a sequential extraction procedure, with which 5 fractions were described based on the elemental form and its stability.

Many chemicals including but not limited to those already described in literature (e.g., HNO₃, EDTA, citric acid, malic acid, humic acid, saponin) [1,3-5] were used as potential washing agents for

the extraction of the heavy metals from the sediment samples to be able to compare their remediation effectiveness.

The sediment samples were washed by solutions of chemical agents using ultrasound mixing. The extracted heavy metals in the leachate were determined using ICP-OES.

The sediment washing results are reported as heavy metal removal effectiveness, calculated as the percentage of the total heavy metal content removed by washing. Some of the tested washing agents were able to remove significant amounts of heavy metals (removal effectiveness up to 70 %) with different values for zinc, lead, and cadmium, which is the result of the elements being differently distributed among described fractions and the difference in the total amount of each element. Some of the washing agents removed only slight amounts of heavy metals or failed to remove any heavy metals entirely.

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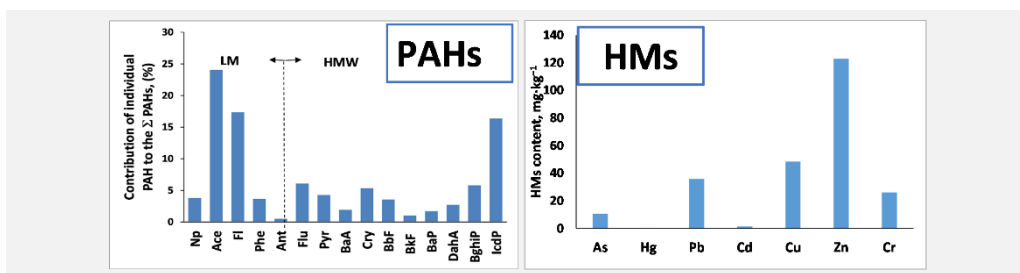
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Heavy Metals and PAHs Content in Agricultural Soil in the Vicinity of Thermal Plant in Pljevlja (Montenegro): Ecological risk assessment

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Although pollution of agricultural soil has always been considered a major challenge in the scientific community, studies based on observing the state of the environment through monitoring pollutant concentrations in the soil are considered important to prevent additional loads on agricultural soils [1].

Heavy metals (HMs) and PAHs are common pollutants present in soil as a result of different industrial activities [2,3].

This research aimed to investigate agricultural soil pollution caused by the activity of thermal plant located in Pljevlja (North Montenegro) and to access the ecological risk of soil pollution by heavy metals (As, Hg, Cd, Pb, Cu, Zn, Cr) and PAHs (sum of 16th priority PAHs).

The results have shown that mean concentration of HMs in agricultural soil following the descending order as follow: Zn(119.9 mg·kg⁻¹)>Cu (47.69 mg·kg⁻¹)>Pb(33.77 mg·kg⁻¹)>Cr(25.43 mg·kg⁻¹)>As(10.33 mg·kg⁻¹)>Cd(1.48 mg·kg⁻¹)>Hg(0.08 mg·kg⁻¹). Among the all investigated HMs, only content of Pb excided the maximum allowable concentration by Montenegrin legislation [4]. Mean concentrations of ΣPAHs and Σ7carcPAHs in soil were calculated to be 271.49 μg·kg⁻¹ and 99.73 μg·kg⁻¹, respectively.

Based on the mean concentrations of ΣPAHs, soil was classified as uncontaminated according to Montenegrin legislation [5].

Ecological risk of soil pollution my HMs based on ecological risk index (RI) is characterised as moderate while according to PLI, soil is classified as unpolluted.

Ecological risk of the ΣPAHs based on the risk quotient (RQ) was characterised as low.

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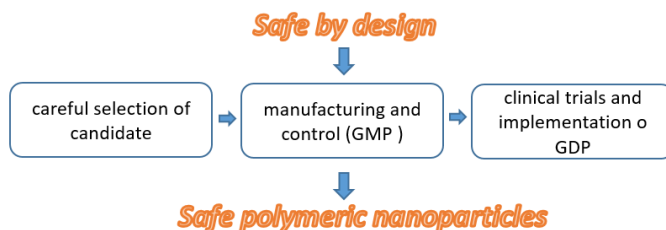
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Environmental Risk Assessment and Risk Management of Polymeric Nanoparticles as Drug Carriers

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Significant research activities in the field of biomedicine are focused on the development of polymeric nanoparticles as drug carriers to improve drug bioavailability and to achieve sustained and/or targeted drug release. However, the increasing use of polymeric nanoparticles in the pharmaceutical industry raises questions of their potentially harmful effects on the environment due to their large surface area to volume ratio.

Toward better understanding of nanoparticle safety, risk assessment and risk management should be carried out. To assess the potential risk of nanoparticles on environment, their behavior in human body must be evaluated. Like medicines, polymeric nanoparticles are eliminated through urine and feces. If they are not completely biodegradable, they reach water, soil and air.

To assess the environmental risk of polymeric nanoparticles, two indicators can be useful tools. First indicator is predicted no effect concentration (PNEC). PNEC is the highest concentration of nanoparticles at which no hazard effects are obtained on the ecosystem. Whereas, the second indicator is a concentration of nanoparticles in the environment, known as predicted environmental concentration (PEC). PEC/PNEC ratio above 1 indicates potential harmful effect of nanoparticles on the ecosystem, which requires further environmental risk analyses or risk management [1].

Since exposure to nanoparticles occurs during their development, manufacturing, storage and application, implementation of safe by design approach is suggested (SbD). Concept of SbD integrates safety through each phase mentioned

above [2]. Firstly, careful selection of adequate nanoparticle candidate must be done based on available literature data and conducted characterization studies regarding its toxicity. It should be noted that toxicity of polymeric nanocarrier also depends on potential toxicity of incorporated drug substance. Once the suitable candidate is chosen, GMP standards should be considered during manufacturing and control phases. Results of clinical trials of polymeric nanocarriers reveal information regarding their efficiency and stability, allowing the implementation of Good distribution practice.

To enable the application of polymeric nanoparticles as drug carriers, their potential risk on environment should be considered. Through risk assessment and risk management, development and manufacturing of safe nanocarriers can be ensured.

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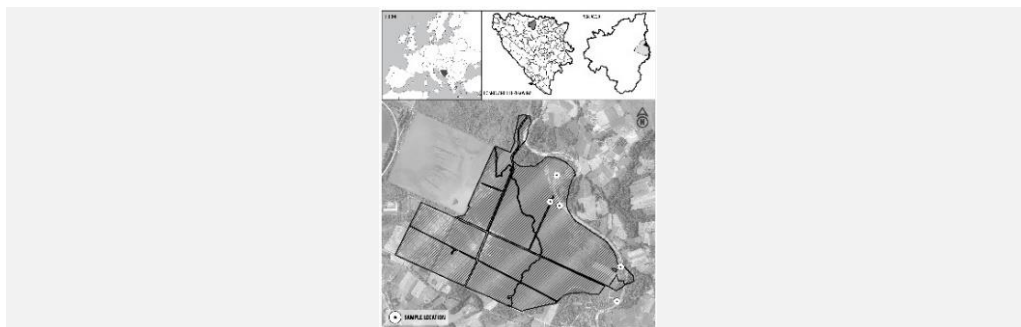
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The Influence of Agricultural Activity on the River Sediments of the Ukrina River

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Agricultural soil rich in organic matter can influence the carbon cycle and contribute to greenhouse gas dynamics, as the breakdown of organic matter can release carbon in various forms. Agricultural production in the field contributes about 15% of total greenhouse gas emissions. The production of pesticides, fertilizers, irrigation, and the fertilization process also contribute to greenhouse gas emissions [1].

In this work, river sediment samples of the Ukrina River, a right tributary of the Sava River, which were taken in the immediate vicinity of an agricultural plot intended for the production of vegetables and medicinal plants, were analyzed. In the researched area, an increase in temperatures was observed on an annual basis, as well as an evident trend of temperature increase during the growing season, and an increase in days without precipitation [2]. The aim of this work is to examine not only the impact of agricultural activities on the content and origin of organic matter, but also the possible effect proven intense climate changes on their composition and migration routes.

Five river sediment samples of the Ukrina River were collected in close proximity agricultural plots. Samples were extracted using the Randall apparatus for four hours and fractionated in four fractions by using column chromatography. Fractions were analyzed using gas chromatography-mass spectrometry (GC – MS).

Selected ions, 71, 217, and 191, representing the *n*-alkanes, steranes, and terpanes were observed [3], as biomarker compounds whose interrelationships can contribute to a better understanding of the organic-geochemical status of river sediments under conditions of intense environmental stress. Apart from certain parts of the Vrbas River, other river systems in Bosnia and Herzegovina were not examined from the aspect of organic geochemistry [4].

Acknowledgments

This work was supported by the Ministry of Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska, "Synergy" Grant (19.030/961-20-1/21): A multidisciplinary approach to support the expansion of the raw material base of a domestic food produce

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Biomarkers in River Sediments (Vrbaš, Bosnia and Herzegovina)

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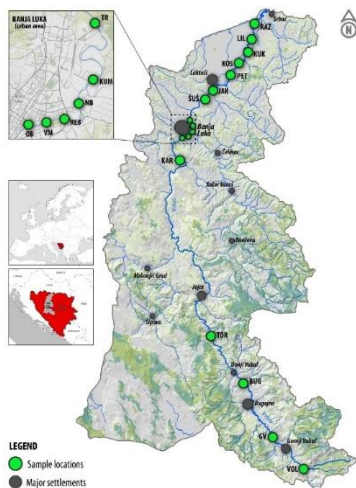


Fig 1. Sample locations (Vrbaš River basin).

This study aims to determine the presence and type of organic pollutants in river sediments using molecular fossils (biomarkers) that are stable under geological conditions and mainly originate from biological lipids. Organic compounds can be adsorbed on the sediment surface by physical or chemical bonds, depending on the geological composition of the river sediment.

Vrbaš River sediments were collected in 18 locations (Fig. 1), and the soluble organic matter of river sediments was extracted using the Soxhlet apparatus for 36 h with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixture. The extraction was followed by the bitumen preparation for column chromatography. First, the samples were saponified using a 5% solution of KOH in CH_3OH , neutralized with a 10% solution of HCl, and transferred with a $\text{CHCl}_3:\text{CH}_3\text{OH}$ (1:1) solution. After that, in the dried samples the required volume of CH_2Cl_2 (with 1% CH_3OH), *n*-hexane, and anhydrous Na_2SO_4 was added. The prepared sample was evaporated in a nitrogen stream to 2 mL and used for further separation by column chromatography. Saturated, aromatic, alcohol fraction, and fraction of fatty acids were

separated by column chromatography. Further, fractions were analysed by gas chromatography-mass spectrometry (GC-MS) in a selected ion monitoring (SIM) mode. The monitored ions were m/z 71 (*n*-alkanes); m/z 217 (steranes); m/z 191 (terpanes), m/z 69 (alcohols); and m/z 74 (fatty acids). [1] The *n*-alkane distribution in most samples is bimodal and is characterized by evident abundances of higher odd *n*-alkane homologs with a maximum at C_{29} (characteristic for native terrestrial input), while even homologs with a maximum at C_{16} dominate among the lower ones. Domination of lower *n*-alkanes may point to the presence of the mature organic substance, as well as the presence of microorganisms, but since the deposition environment in examined samples is not typical for the microorganism growth, it can be assumed that there is the presence of oil-type compounds that results in an increased abundance of lower even *n*-alkanes. The distribution of the steranes and terpanes, as well as the GC-MS analysis of the aromatic fraction, indicates the presence of oil-type pollutants. The detections of lower even *n*-fatty acids and alcohols (C_{14} , C_{16} , C_{18}), as well as cholesterol, confirm that for the synthesis of new even *n*-alkanes are responsible dinoflagellate algae grown on oil substrates. [2]

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No: 451-03-68/2023-14/200026 and 451-03-9/2023-14/200168) and by the Ministry of Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska, "Synergy" Grant (Grant No: 19.030/961-20-1/21)

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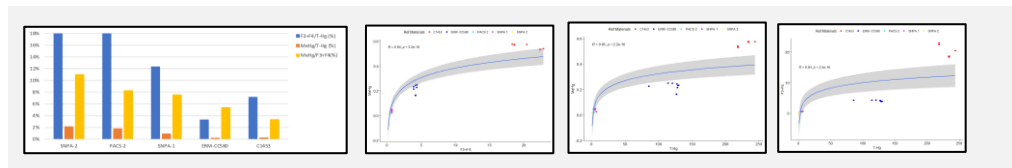
Comparison Of Extraction Procedures of Organic Mercury In Soil And Sediments

Reference Materials

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Mercury is the most worrying pollutant globally: the World Health Organization lists it as one of ten chemicals hazardous to global health. However, not all mercury species are equally harmful. As known from the Minamata disaster, the organic forms are the most dangerous because of the accumulation in organisms and transfer in the aquatic food chain up to man [1].

The study of contaminant total concentration does not indicate the actual availability of the metal to bioaccumulate in the organisms and consequently the potential toxicity of metal in the sediment studied, therefore, it is important to indicate the temporal variation of the metal quantity.

IUPAC (International Union of Pure and Applied Chemistry) defines the SEP (Sequential extraction procedures) as a fractionation that is the process by which elements can be extracted based on their mobility, physical and chemical characteristics [2]. The term SEP was firstly given by Tessier et al. (1979) [3] to indicate the analytical procedure developed for partitioning the metals bound to sediment/soil in terms of different chemical fractions (F1-F5) by means of appropriate reagents to selectively extract the specific fractions.

Beyond sequential extraction procedures, single chemical species of mercury can be determined by means of selective extraction methodologies. The methylmercury extraction is an example of this [4]. Thus, in this work a SEP [5] and the selective extraction of methylmercury in soil and sediment samples were compared to verify if it is possible to correlate the methylmercury concentration with the metal fraction bound to the organic matter (sum of F3 and F4) determined by a SEP.

Five reference materials, different by their origin (soils, marine sediments) and by the concentration of total mercury, are analyzed. The statistical tests

of chemical results show a significant correlation between the content of methylmercury and the organic fraction extracted in the third and fourth step. Also, the data of methylmercury, compared to the total, decrease from the material with the lower content of total mercury to the material with the higher content.

We can estimate the amount of MeHg starting from the total content or from the organic fraction, through a simple approach, without resorting to complex instruments. In this way it would be possible to evaluate the quantity of mercury in the organic form, without further investigations. Hence it offers the advantage of making the speciation methods comparable by considering the ratios between organic content and total content, and also organic mercury content over quantity of mercury bound to the organic fraction. It has been seen that the trend is general based on the concentration of mercury and the specific characteristics of the material being investigated.

Acknowledgements

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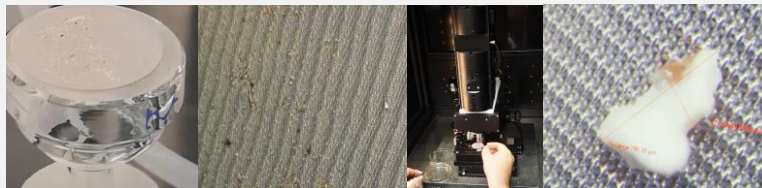
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Instrumental Methods for the Microplastics Determination in the Environment

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Microplastics are tiny plastic particles and fragments that are less than 5 millimeters in size. These particles can be found in various environmental compartments. They are a growing concern due to their potential environmental impact and the challenges they pose for ecosystems and human health. Microplastics can vary in shape, composition, and size, with some being so small that they are not visible to the naked eye (nano dimensions). This diversity makes the detection and analysis of microplastics a complex scientific field.

When conducting microplastics analysis, it is essential to choose the appropriate combination of instruments and techniques based on the sample type, and expected particle sizes.

Additionally, methods for the analysis of microplastics are still being developed and have not been brought to the level of standards. Like all other methods of analysis, this procedure involves the extraction of particles from the matrix [1] and then an analysis that enables the confirmation of the identity of the polymer from the point of its particle composition. Particles that are mixed polymers also often appear. That is why it is most practical, and at the same time the most expensive, to have several different techniques to determine the type of particles. Everything gets complicated when applied to micro and nano particle sizes.

Today, different instrumental techniques are used for the detection of microplastics, depending on the dimensions of the particles to be identified.

FTIR Spectrometer works by measuring the absorption of infrared light by the sample, providing information about the types of polymers present. Raman Spectrometer is uses the scattering of laser light to provide information about the molecular structure and composition of microplastics. SEM with Energy-Dispersive X-ray Spectroscopy (EDS) capable to visualize the surface morphology of particles and when coupled with EDS, it can also provide information about the elemental composition of the particle. Micro-Raman spectrometers are specialized for micrometer sizes particles. Pyrolysis instrument and GC-MS system that burns microplastics and this products are analyzed using GC-MS.

None of these techniques have been accepted as standard so far. And this will probably be decided for a long time, because the particle sizes are in a very wide range and not all of these techniques are sensitive and reliable enough for particles of micro and nano size. The choice of technique will also be influenced by the way the results are expressed

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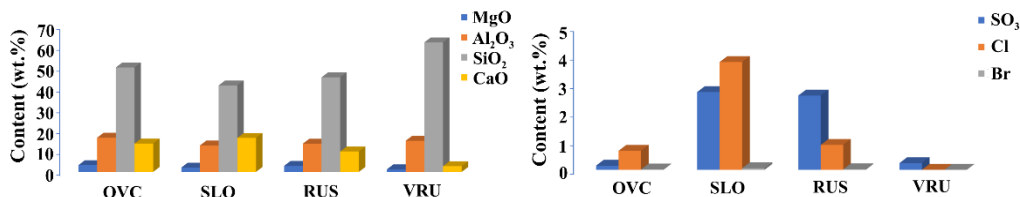
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Inorganic Composition of Serbia and Slovenia Peloids in Context Their Applicability as Therapeutic Agents

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Therapeutic (spa) muds or peloids are widely recognized as natural materials comprised of solid (a mixture of minerals and organic matter) and liquid (mineral-medicinal water) phases [1-5]. Their specific physical and (bio)chemical properties allow their wide application as therapeutic agents for humans and animals.

One of the critical aspects influencing or benefiting their quality and application relates to concentrations of harmless or hazardous inorganic forms (e.g., metal oxides, ions etc.) [3,4]. The importance of investigating their contents lies in the interplay between perspiration and mobility/absorption processes of toxic ions through the skin, subsequently entering the bloodstream [1-4].

In this context, X-ray fluorescence analysis of four collected from Ovča (OVC), Rusanda (RUS) and Vrujci (VRU) in Serbia and Sečovelje (SLO) in Slovenia was performed. Dried samples, prepared as pressed pellets, were analyzed on a Rigaku, ZSX Primus II X-ray fluorescence spectrometer (Rigaku, Tokyo, Japan).

By inspecting the contents of major elements, higher concentrations of CaO and MgO (up to 16.29 and 3.21 wt.%, respectively) are detected in OVC, SLO and VRU samples. Their presence usually relates to the precipitation of carbonate minerals, which may have positive physiological effects by stimulating subcutaneous blood circulation and epidermal renewal [2,4]. Besides, the highest value of the Si/Al ratio is registered in the VRU sample (4.17 wt.%), which is probably attributed to the presence of quartz. In contrast, somewhat lower values of the Si/Al ratio are observed for OVC, SLO and RUS (under 3.36 wt.%), potentially indicating higher participation of clay minerals. Peloids rich in clay minerals may retain a large amount of moisture but can also

absorb hazardous elements from the environment [2,3]. Additionally, higher concentrations of sulfite, chloride and bromide ions are noticed in SLO and RUS samples, probably originating from salts that may have the keratolytic effect of an antiallergic and anti-inflammatory nature [2,4,5].

The preliminary investigation shows that investigated peloids may possess the potential for application as therapeutic agents. However, more experiments must be carried out for optimum material characterization.

Acknowledgements

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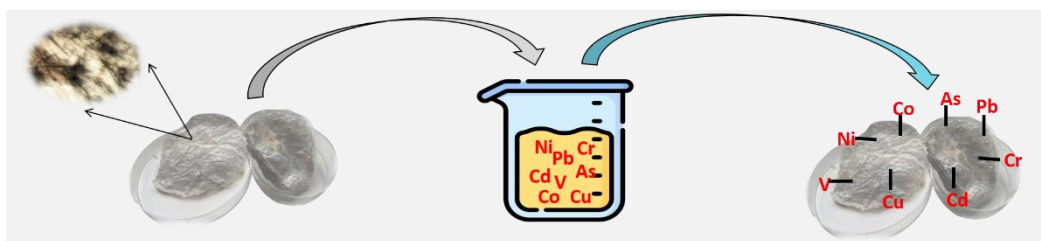
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Bacterial Nanocellulose as a Potential Adsorbent for Strategic and Heavy Metals Removal

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Bacterial nanocellulose (BNC) is a homopolymer of β -1,4 linked glucose, synthesized by aerobic bacteria using simple culturing methods, allowing inexpensive and environmentally friendly production. BNC is a semi-transparent, mechanically highly resistant, but soft and elastic, with a large capacity for water storage and gas exchange. As a biomaterial with exceptional physico-chemical and biological properties, BNC has found practical application in medicine and pharmacy as therapeutic dressings and drug carriers [1]. The ability to adsorb different classes of pollutants, organic and inorganic, opens up possibilities for application in environmental protection [2]. Adsorbents based on nanocellulose represent an environmentally acceptable platform for the removal of strategic (rare elements of the Earth's crust - lanthanoids) and heavy metals [3].

In this work, BNC was used as adsorbent for removal of (V^{51} , Cr^{52} , Co^{59} , Ni^{60} , Cu^{63} , As^{75} , Cd^{111} and Pb^{208}) from a slurry of fly ash originating from a thermal power plant. Prior to adsorption studies, BNC was analyzed by various methods in terms of structure confirmation (FTIR analysis), thermal properties (DSC/TG analysis) and degree of crystallinity (XRD analysis) [4]. The FTIR spectrum shows all characteristic peaks that confirm the carbohydrate structure of BNC. Analysis of thermal properties confirmed three stages of degradation, and XRD analysis confirmed that BNC is a highly crystalline biopolymer. The adsorption capacity of BNC for strategic metals from fly ash, suspended in a solution of water and

0.1 M acetic acid, was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) by varying pH, contact time, and adsorbent contact surface. The highest adsorption capacity (Q) was obtained overnight for As, with the maximum value of $553 \mu g g^{-1}$, which represents efficiency of 73%. The results also showed that BNC have higher adsorption capacity for selected metals in the form of thin film, than in the shredded form. Mechanical treatment of nanocellulose disrupt complex nanofibril network, thus leading to reduced capacity of nanocellulose to capture metal ions within its structure.

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Effects Of Pollutants On The Quality Of The Environment During The Operation Of The Plant For The Production Of Concrete-Concrete Base

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The production of concrete can lead to certain negative impacts on the environment, depending on the technological process of work, as well as on the location of the location where the process takes place. Impacts that can occur during the operation of the concrete production plant are emissions of substances into the air, which can cause changes in the air quality at the site and in its surroundings, the impact of increased noise levels, the impact of waste water from the area of the concrete mixer, as well as the impact in the event of an accident. Air pollution in the atmosphere can be viewed through:

- negative impact on man and his health,
- endangering other elements of the environment (water, soil, and other living things).

Emission of pollutants: gases, dust, smoke, etc. into the surrounding area is its pollution. In this particular case, the sources of air pollution are the concrete production plant, as well as the machines and trucks that service the operation of this plant. Accidental situations can occur due to malfunctioning filters on silos during their filling, which can affect the existing air quality. This impact is temporary and local.

During the operation of the concrete production plant, noise from the operation of the mixer, trucks that bring stone aggregates, loaders, concrete mixers and cement tankers is a source of noise. Noise emissions generated by the operation of machines operating outdoors are determined by EU Directives (2000/14/EC and 2006/42/EC). Also, valid legal regulations were applied: Law on the Protection against Environmental Noise ("Official Gazette of Montenegro", No. 28/11, 28/12 and

1/14) and the Rulebook on Noise Limits in the Environment, Method of Determining Indicators of noise and acoustic zones and methods of assessing the harmful effects of noise, limit values of noise in acoustic zones ("Official Gazette of Montenegro", no. 60/11).

Wastewater can also have a negative impact on the quality of the environment, if it is not adequately treated. Namely, when washing the equipment of the concrete mixer and the machinery that serves its work, waste water appears that can be contaminated with fuel used for the engaged machinery (loader, trucks, etc.), lubricants for said machinery, as well as cement dust that can have a limited impact on the turbidity of surface waters in the environment, if the same would reach them carried by the wind. For these reasons, in order to protect the environment from the negative impact of waste water from the area of the concrete mixer, systems are being built for the reception of this water and its further treatment (clarifiers, separators, etc.), before its further discharge into the recipient.

The aim of this work is to show through the process of concrete production which all influences can be present, and which can have a negative impact on the quality of the environment in the area where such a plant exists.

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Identification Of The Impact Of The Quarry On The Environment

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The environment is a source of natural values and natural resources, and therefore also a source of existence, so we must accordingly treat this fact responsibly. The quality of the environment depends on the sustainable management of natural values and natural resources. In relation to the level of industrialization, urbanization and widespread use of resources, the need for sustainable resource management is also growing.

One of the instruments for achieving these goals is the environmental impact assessment (Environmental Impact Assessment-EIA), which mostly originated in the developed countries of the West, as a result of growing awareness of the need to protect the environment.

Quarries that perform direct activity in space and intensive use of natural resources (stone) represent potential environmental pollutants.

Impacts on the environment that occur as a consequence of the regular operation of the quarry represent particularly significant impacts from the point of view of the relationship to the environment, that is, endangerment and preservation from further degradation, as well as the time dimension of duration. Finally, there are impacts in emergency, right-of-way or accident situations with their characteristic that they occur in a short time interval with great intensity. In this sense, the priority is always to define them in relation to basic natural factors (climate, water, air, soil, flora, fauna, landscape) which, seen through the prism of ecosystem theory, represent a completely ordered and balanced self-regulating mechanism.

Surface exploitation in the area of excavation, loading, transport and auxiliary works is evident in numerous forms of environmental damage, which amount to damage to the biosphere (lithosphere, atmosphere and hydrosphere), so that there is a possibility of the occasional release of harmful substances into the biosphere. This emission of harmful substances into the biosphere can be related to the applied technical solutions, both from the technological aspect and from the aspect of environmental protection.

Based on the parameters, during the preparation of the environmental impact assessment, all the impacts of quarry operations can be clearly identified. The biggest impact that is present during the exploitation of stone at the quarry location is the appearance of dust and fuel combustion products due to the operation of engaged machinery, as well as the effects of noise and blasting. Therefore, on the basis of these identified impacts, all necessary measures to protect people and the environment must be clearly defined, so that all identified impacts are minimized.

The aim of this work is to clearly define and specify appropriate measures for the protection of people and the environment through the identification of the negative impacts of the quarry on the environment, which will minimize all negative impacts.

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Soil Degradation Indicators as a tool for Climate-Smart Urban Forestry

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Climate-Smart Forestry (CSF) is sustainable adaptive forest management aimed to protect and enhance the potential of forests to adapt to and mitigate climate change (CC). The CFS aim is to sustain ecosystem functions and to assure the continuous delivery of ecosystem goods and services while minimizing the impact of climate-induced changes on forests. Soil, an essential resource and the base for fulfilling social and ecological human needs including soil condition is one of the important indicators for assessing CSF management.

Urban forests (UF) are defined as forests located in cities that provide residents with a continuous level of economic, social, and environmental benefits. Managing UF to achieve sustainability is a long-term goal of all stakeholders and relevant institutions. However, the concept of sustainability in UF is a poorly defined concept, both in terms of scope and application. The CSF concept, designed for mountain forests, can be implemented, but not fully translated to UF due to the high intensity of anthropogenic pressures. For this reason, arises a need to develop a new concept the Climate-Smart Urban Forestry (CSUF) concept. Each UF differs in tree species, size, and age. Compared to traditional forestry, urban context forestry focuses on additional services to advance urban sustainability. They are the driving force for providing ES such as air pollution removal, stormwater pollution capture, and urban heat regulation, and as such are essential parts of green infrastructure. UF contribute to the green infrastructure, i.e., natural or engineered ecological systems that conserve ecosystem values and functions. However, UF face significant pressure including difficult growing conditions, insufficient resources for proper care, pollution, encroachment from development, and generally incomplete public understanding of the benefits provided by them. The direct negative impact between CC and anthropogenic pressure in UF is particularly reflected in soil degradation, and this problem

requires special attention. Despite the extensive scientific literature, the understanding of factors influencing natural and anthropogenically induced degradation processes in UF is still limited.

The main objective of the project “Urban Forest Soil Indicators as a tool for Climate-Smart Forestry” (UrbanFoS) is to define soil degradation indicators in UF to adapt to and mitigate CC and anthropogenic pressure in urban areas. This goal will be achieved by determining the key sensitivity soil properties through physico-chemical analyses and climate simulation experiments; and defining ecosystem services (ES) of UF. Defined indicators will be used to test existing soil degradation indices applicable to forest soils and a suitable soil degradation index for UF under CC conditions will be proposed. Finally, based on previous steps, UrbanFoS will define restoration measures based on the principle of ecological engineering and Nature-Based Solutions (NBS).

UrbanFoS tackles gaps in knowledge on UF soil conditions, pressures, and degradation processes and aims to define key information to support decision-making toward climate and sustainability goals. UrbanFoS also tests soil behavior under various climates aiming to mitigate UF degradation and sustain the provision of various ES essential for sustaining biodiversity and human livelihoods and wellbeing. Furthermore, determining the properties of soil sensitivity to CC, coupled with ES, will open an avenue to create a soil degradation index that will focus on the dynamics of the soil properties identified as valuable indicators.

UrbanFoS incorporates novel methodologies and expert knowledge of analytical techniques, soil properties, climate simulation experiments, ES, ecological engineering, and NBS. It develops tools for soil monitoring, and predictions of soil behavior under CC, and improves forecasting of soil-based mitigation, adaptation, and ES.

Acknowledgements

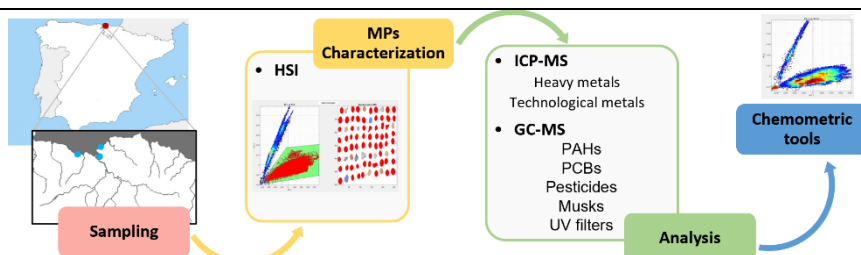
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Microplastics Risk as a Reservoir of Metallic and Organic Contaminants of Legacy and Emerging Concern on the Cantabrian Coast (Northern Spain)

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Several investigations demonstrate that microplastics (MPs) present a risk as a contaminant's reservoir, being able not only to release their manufacturing additives along the different environmental compartments, but also to adsorb the pollutants present. Thus, they are a clear route capable of increasing the distribution, bioavailability, bioaccumulation and ecotoxicity related to them. Nevertheless, the MPs potential as environmental indicators have not been yet exploited, as most of the studies are often focused on their monitoring to identify and quantify which type of plastics are present instead of what they carry [1].

The work here addressed aims to identify and quantify the MPs that are arriving to the Spanish northern coast beaches, and furthermore, which is the level of metallic and organic pollutants that is adsorbed into them. For this purpose, a bi-annual sampling campaign was performed in three significant points of the Cantabrian Coast (Bay of Biscay) to cover pristine, touristic and urban scenarios. As the MPs role as reservoirs depends on their surroundings but also on the nature of the plastic matrix, firstly, a non-destructive characterization based on Hyperspectral Imaging (HSI) was used to classify and quantify the MPs collected. Subsequently, extraction methods for metals and organic pollutants were optimized, and the extracts were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Gas Chromatography Coupled with Mass Spectrometry (GC-MS), respectively. Finally,

chemometric tools were used to deeply study the results by Principal Component Analysis (PCA).

According to the results, 3 types of polymers were found as main components of the MPs matrices: polyethylene (PE), polypropylene (PP) and polystyrene (PS). Besides, the presence of several metals such as Pb, Sb and Co, as well as different families of organic contaminants (PAHs, PCBs, pesticides, UV filters and fragrances) were quantified as the most predominant pollutants in the area. Thus, this research evidenced the role of MPs as vectors for transport and release of organic contaminants in aquatic environments, and the potential of their use as indicators of the environmental risk of the compartment studied.

Acknowledgements

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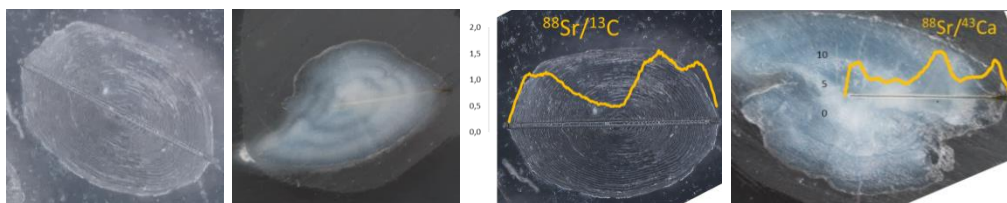
WATER



Fish Otoliths and Scales as Indicators of Long-term Metal Exposure in Wastewater Impacted River

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When assessing long-term metal exposure in dynamic ecosystems such as rivers, it is useful to use indicator organisms. Fish otoliths (ear stones) and scales are calcified structures, increasingly used as natural markers. Because they grow gradually in layers they provide a time resolved record of metal exposure over the life span of a fish and can therefore be used as pollution indicators. Moreover, especially otoliths are metabolically inert, with permanently stored records, while scales can be partially reabsorbed by the fish during stress periods [1, 2].

In this study, we present the preliminary results of metal analysis in otoliths and scales of brown trout (*Salmo trutta* Linnaeus, 1758) from the karst Krka River in Croatia. Most of the river is protected as a national park due to high biodiversity, but the upper part is affected by industrial (screw factory) and municipal (town of Knin, 8300 inhabitants) wastewater discharges.

Therefore, fish samples ($n=18$) were collected at three sites: 1) KRS, the reference site at the source of the Krka River, 2) KRK, a site near wastewater discharges, and 3) KNP, a downstream site in the National Park. Metal concentrations were measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), taking a continuous cross-sectional line scans through the samples. The otoliths were previously ground to expose their core, which contains chemical information about the first years of a fish's life.

Trends in metal content profiles along ablation lines were similar for all elements in the scales, confirming continuous metal exposure over the life of the fish. Metal incorporation differed among elements in the otoliths, showing various patterns along ablation lines. These trends in the otoliths were most pronounced for Sr, Ba, Zn, Mn, and Tl. When compared between locations, levels of Sr and Ba followed the same pattern in otoliths and were highest in samples from KNP, while Tl levels

were highest at KRS. These results were comparable to the differences in concentrations of these metals between sites in the water [3].

Another finding of this study was the presence of abnormal otoliths (different shape and composition, no annual rings) and replacement scales (formed after the loss of scales) in many fish individuals. These abnormalities are indicative of stocked fish, as they are much more common in farmed fish than in wild populations due to rapid growth, constant environmental conditions, and more frequent injuries. Therefore, in these individuals, only the outermost part of the otolith is representative of conditions in the river.

Presented data will be further processed and categorized, resulting in the first record of water chemistry over the life history of a freshwater fish in Croatia. These data will contribute to interpretation of metal accumulation in fish soft tissues, and to the protection of trout population in the sensitive karst Krka River.

Acknowledgements

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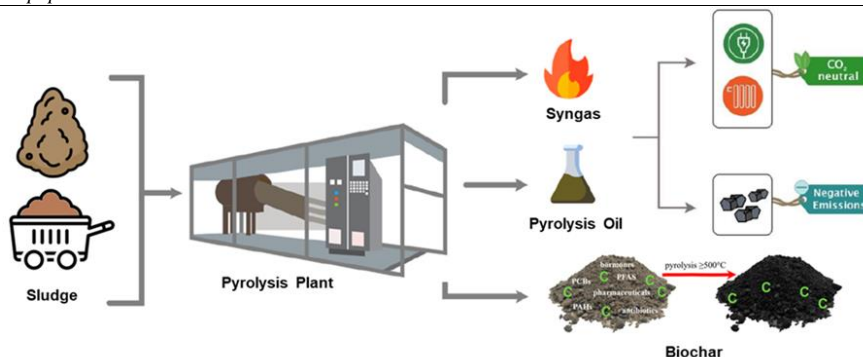
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Biochar Produced From Sewage Sludge as an Adsorbent and Soil Conditioner: A Scottish Case Study

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The production of ‘biochar’ from sewage sludge (SS) is consistent with the goal of sustainable resource recovery and promotes a circular economy. Pyrolysis of SS to biochar resolves two issues simultaneously, as it minimises the cost of disposal and creates a new product that can be cleaner than its predecessor.

SS is produced in hundreds of millions of tonnes globally each year. Historically, SS has often been applied to agricultural land to recycle nutrients and carbon. However, untreated sludge contains pathogens and a myriad of potentially harmful organic and inorganic compounds, many of which are unregulated, e.g., flame retardants, microplastics and pharmaceuticals (Figure) [1]. As these may be taken up by plants and enter food chains, such practices are becoming unfavourable. Treatment of SS by pyrolysis to biochar offers great potential for the destruction of many pollutants, and the concurrent generation of highly valuable adsorbent material and fertiliser that may be rich in nutrients such as phosphorus (P). Such biochar can also be used in the production of materials for the construction industry, in anaerobic digestion, environmental remediation, energy storage, and can act as a long-term sink for carbon storage. At present, such biochars are under lab/pilot scale development and their utility has not been exploited, in part due to restrictive regulatory frameworks (i.e., in the UK). The key benefits of SS biochar are:

- Pyrolysis destroys pathogens (> 350 °C for several minutes).
- Pyrolysis can eliminate many micropollutants (e.g., pharmaceuticals, personal care products, per- and polyfluoroalkyl substances – PFAS) (500-850°C) and microplastics (~ 500°C).
- Biochar can act as an organic soil improver and P-fertiliser (i.e., if P is loaded onto biochar through adsorption during water treatment application).
- It can contribute to the agricultural carbon sink and reduce GHG emissions.
- It is deployable and scalable, with a fast-growing market and significant technological development/innovation potential.

This work presents the first pilot scale P recovery application from wastewater using SS biochar (in the FILTRAFLO™-P reactor). Future work will include P plant uptake studies to observe how the biochar influences soil health and plant growth.

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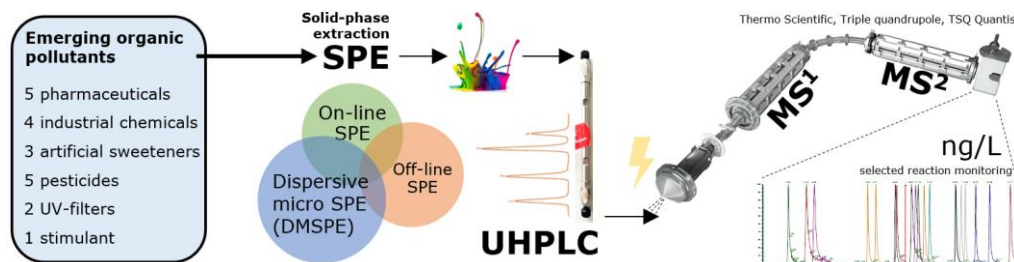
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Alternative Forms of Solid-Phase Extraction for Ultratrace Analysis of Emerging Organic Pollutants in Water

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Modern water analysis is striving towards simple yet effective analytical procedures for multiresidual determination of organic pollutants within only one single run. Quest for lower limits of detection (LODs) has moved frontiers in chromatography and mass spectrometry (MS). But nonetheless, LC-MS systems are in practice still very susceptible to matrix effects and are unable to directly determine sub-ng/L levels. This calls for proper clean-up and pre-concentration steps.

Among many, solid-phase extraction (SPE) has reached success due to its effectivity, capacity, and commercial availability. Conventional off-line SPE using packed cartridges has become the first choice. But the need to increase multiplexing capacity and simplicity has in recent years spread the interest to alternative forms of SPE [1].

This work tries to unveil potential uses of two alternative SPE forms: (1) direct-connection on-line SPE and (2) dispersive micro SPE (DMSPE) coupled with UHPLC-MS/MS. Method development was performed on 20 emerging organic pollutants with different polarities: pharmaceuticals, food additives, industrial chemicals, personal-care products. Effectivities were compared with (3) conventional off-line SPE.

(1) *On-line SPE*. Is a promising and highly automated SPE technique. However, due to complex dual-pump LC instrumentation, we were interested in its simplified direct-connection on-line SPE [2]. Using hydrophylic-lipophylic balanced (HLB) column, analytical pump, and 200 μ L sample load *via* autosampler, we developed a method that can determine 12 (mostly polar)

analytes with LODs 0.5–5 ng/L and $< \pm 30\%$ matrix effects for samples of river water.

(2) *Dispersive micro SPE (DMSPE)*. This novel approach has been receiving progressively more attention due to its simplicity and possibility to use mixtures of different sorbents [3]. By extracting analytes on C18/C8 sorbent mixture from 40 mL water sample (pH 7.5), DMSPE-UHPLC-MS/MS leads to effective determination of 14 analytes with 1–12 ng/L LODs and minimal matrix effects.

(3) *Off-line SPE*. Using HLB sorbent and 250 mL acidified sample, 0.1–1.2 ng/L LODs are reached for most of the 14 analytes. As so, sensitivity can be compared with on-line SPE, while only 10-times higher LODs are achieved with DMSPE.

In summary, all three modes of SPE coupled with UHPLC-MS/MS reach environmentally-relevant LODs for the majority of selected pollutants and exhibit low susceptibility to matrix effects. However, the modes differ in simplicity and time-consumption. In 8 h, 5 parallel off-line SPEs can be done, while up to 2x4 and 10 samples can be the subject of DMSPE and on-line SPE, respectively, showing their plausible applicability.

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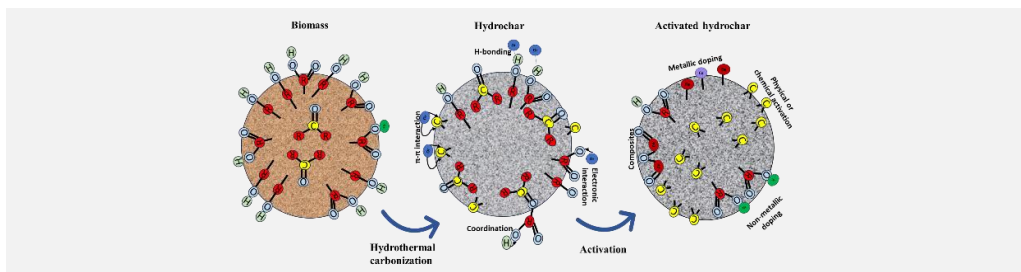
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An Initiative Towards Circular Economy for Water Remediation Employing Hydrochar

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On the Earth, there is 71% of water, in that just 3% is fresh water and only 1% of it is accessible. As populations rise and natural habitats deteriorate, it is becoming increasingly difficult to ensure that everyone has safe and sufficient water supplies. Emerging pollutants include pharmaceutical compounds but also personal care products, and they accumulate in the natural environment, thus harming both the ecosystem and human health. Different technologies for wastewater treatment and purification have been extensively investigated in the literature where the design and operation of affordable methods are yet to be achieved. The adsorption technique has been recognized as a practicable technology for water remediation due to the economic and technological feasibility. This technique is influenced by a variety of criteria such as adsorbent type, targeted pollutants, and operating conditions (pH, T, etc) [1].

Carbonaceous materials contain high porosity and interesting surface properties that promote molecule adsorption to their surface, thus such materials being studied to a greater extent for adsorption applications [2]. Activated carbons (ACs) stand out due to their ease of synthesis, which does not necessitate a highly sophisticated experimental setup when compared to other approaches, and the ability to use heterogeneous sources such as biomass as starting materials. Pyrolysis is a thermochemical process of conversion of biomass into carbon-based material and is carried out at temperatures higher than 300°C and in the absence of oxygen and the solid output is called 'biochar,' which has been

extensively discussed in the literature. Because of the increased energy input required for pyrolysis and the high cost of pretreatment, hydrothermal carbonization (HTC) has surpassed pyrolysis as the preferred thermochemical method for waste biomass. HTC is performed at lower temperatures, typically ranging from 80 to 240°C, and under subcritical water pressure. This method produces "hydrochar" as a solid byproduct.

Here, we present an efficient approach to synthesize hydrochar (HC) using orange peels which is activated using an oxidizing agent (ACHC) for water remediation. Caffeine (CAF) is a psychoactive drug which is of concern due to its presence in the environment, especially surface water[3]. Hence it was chosen as the pollutant for this study. The morphology and chemical composition of ACHC and HC were studied. Different parameters such as pH, temperature and concentration studies were carried out. Interestingly, it was found that physisorption played a vital role. This study shows a promising direction for efficient wastewater treatment.

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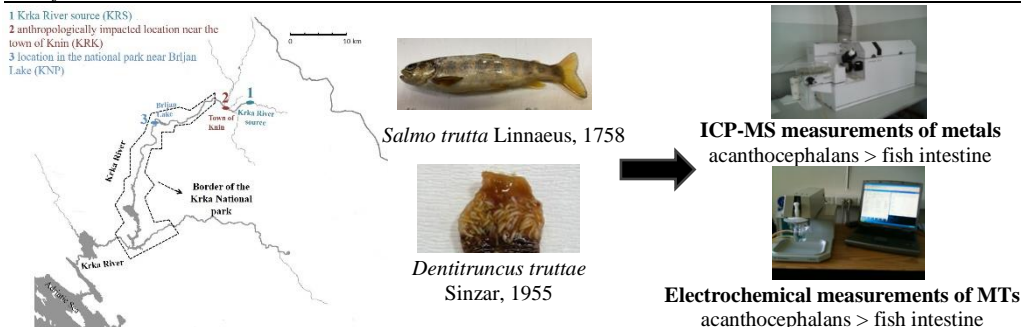
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Metal and Metallothionein Concentrations in the Fish Intestine and Acanthocephalans in Relation to Environmental Metal Exposure in the Krka River

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Due to persistence and low biodegradability, metals are a serious threat for organisms, especially in karst freshwater ecosystems. Thus, different bioindicator organisms are used in metal exposure assessments and parasites have been considered as good indicators of water quality in recent decades. Among them, acanthocephalans are recognized as promising bioindicators of metal exposure [1,2] due to high efficiency of metal accumulation [2,3].

To investigate the effects of industrial and municipal wastewaters and agricultural activities in the protected karst Krka River, but also to describe the complex relation of the host-acanthocephalan system, we measured concentrations of 15 metals and metallothioneins (MTs) in the intestine of brown trout *Salmo trutta* and for the first time, in acanthocephalan *Dentitruncus truttae* from three sites (reference site – river source upstream of the wastewaters, KRS; contaminated site near the Town of Knin – downstream of the effluents, KRK; and the most downstream site in the Krka National Park, KNP) in two seasons (spring and autumn). Levels of metals were measured by ICP-MS, and of MTs by differential pulse voltammetry.

The highest accumulation of Ca, Cu, Fe, Pb, and Zn was observed mainly in organisms from KRK, of Cd, Rb and Tl from KRS, and of Hg, Mn, Sr, and V from KNP, which partially corresponded to metal exposure through water and sediments, but also indicated relation to the ecology of species, dietary habits, and number of acanthocephalans in fish. Acanthocephalans showed significantly higher accumulation of most elements than fish, especially of toxic elements like Cd, Tl and Pb. MT

levels were often higher in acanthocephalans and fish from KRS and KNP compared to KRK, confirming possible threats for this area. MT values were also higher in acanthocephalans than in fish. Seasonally, MT and metal concentrations were often higher in spring than autumn, probably related to elevated fish feeding rates. Another finding was that higher number of acanthocephalans per fish intestine often caused so-called biodilution process and resulted in lower concentrations of many elements.

Presented data indicated that wastewater impact is still moderate, but also showed concerning trends of higher concentrations of some elements or MTs in organisms from the national park. Since concentrations of metals and MTs depend on ecological, chemical and biological conditions, in addition to environmental exposure, continuous monitoring is recommended to distinguish effects of these factors from the effects of environmental exposure and to successfully preserve the Krka National Park in future.

Acknowledgements

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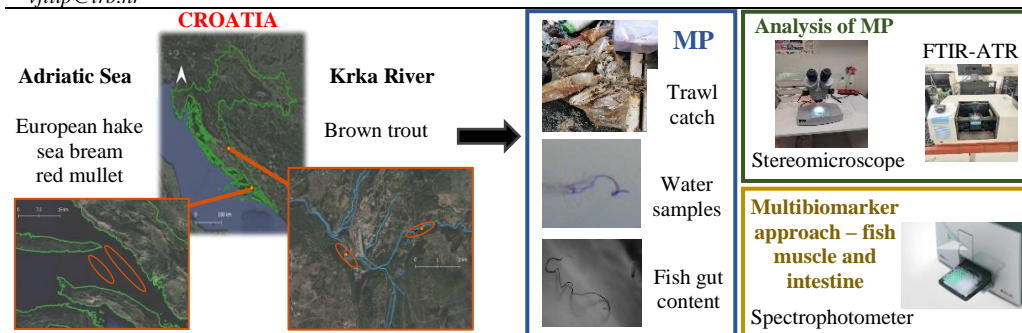
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Fish Intestine and Muscle as Bioindicators of Microplastic Exposure in the Aquatic Environment

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Modern life is characterised by continuous input of various pollutants into aquatic environment, of which microplastic (MP) is considered a serious environmental problem. Important sources of pollutants in the sea are tourism, agriculture, industry, ports, but also freshwater ecosystems, especially from wastewater outlets. Therefore, our research estimated the impact of MP on marine and freshwater environments, using fish intestine and muscle as bioindicator tissues.

The application of fish intestine in the MP exposure assessment gives insight into dietary uptake routes and of muscle connection to human diet. The aim of our study was to compare biomarker responses in native fish as an indication of antioxidant activity (catalase, CAT; glutathione, GSH), oxidative stress (malondialdehyde, MDA) and neurotoxicity (acetylcholinesterase, AChE), as a first warning signs of pollution impact on biota. Moreover, the presence of MP was analysed in the water and fish gut content, by applying four different methods and selecting the most appropriate one for MP isolation from biota.

The study was conducted in the Adriatic Sea near the Port of Ploče and Neretva River mouth, using three fish species, European hake, sea bream and red mullet, as representative bioindicators. In the freshwater ecosystem, we investigated upstream watercourse of the Krka River influenced by municipal and industrial outlets, using brown trout as a bioindicator. MP analysis in the water and fish gut content involved filtration over 0.45 µm pore size filters and analysis on the stereomicroscope and FTIR-ATR, with additional digestion step for

3.5 hours at 85°C for the gut content using four methods: HNO₃, HNO₃+H₂O₂, HNO₃+HF and 10% KOH. Biomarkers were analysed by colorimetric methods on spectrophotometer (Tecan Infinite 200 Pro).

The results showed that 10-17 % of the total trawl catch contained waste, mainly plastic. Regarding water, all freshwater and marine samples contained MP, regardless of the sampling sites. Although Adriatic Sea was reported as the third location in Europe by plastic waste abundance [1], our results pointed that fish species still don't show significant differences in biomarker responses in muscle between nearshore and offshore area. Contrary, biomarkers in intestine of brown trout pointed to pollution impact from the wastewater outlets.

In all fish species, MP were isolated from the gut content, confirming its presence in fish diet and HNO₃+HF was selected as the most suitable digestion procedure. Therefore, presented data highlights the importance of continuous biomonitoring and assessment of plastic accumulation in marine and freshwater environment and organisms.

Acknowledgements

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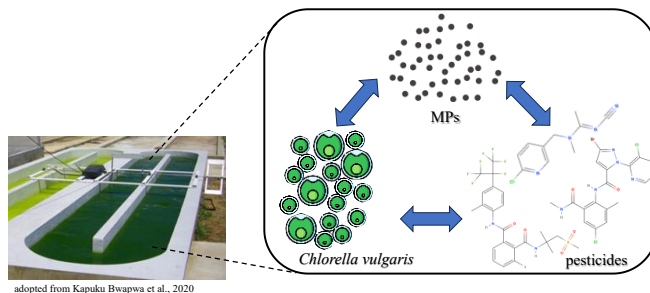
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Microalgae-based Wastewater Treatment Process in the Presence of Microplastics and Pesticides

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Finite sources of crucial nutrients in fertilisers – nitrogen and phosphorus – are finite, therefore closing their nutrient loops are needed to preserve them in the environment [1]. Microalgae-based wastewater treatment systems are one of the nature-based solutions that enable the reuse of nutrient-rich biomass and treated wastewater, as well as offer a more sustainable wastewater treatment alternative to current extensive treatment technologies with activated sludge [2,3]. Wastewater is not only a source of nutrients but due to anthropogenic activities also a source of contaminants of emerging concern such as pharmaceuticals, pesticides, and microplastics (MPs) [4]. Their presence in the wastewater may affect the efficiency of wastewater treatment with microalgae. Furthermore, MPs are known to act as a vector for pesticides and other contaminants [5].

The aim of the research was to study the effects of the presence of MPs' polymer mixture (polyethylene terephthalate, polystyrene, and polyethylene) and/or a mixture of three model pesticides (acetamiprid (ACE), chlorantraniliprole (CAP) and flubendiamide (FLU)) on the growth and nutrient uptake of microalgae *Chlorella vulgaris* in the wastewater.

Microalgae culture of *C. vulgaris* was inoculated in samples of primary treated wastewater from Central Wastewater Treatment Plant Ajdovščina. The MPs (80 mg/L) and the mixture of ACE, CAP, and FLU (1 mg/L) were added to those samples. Growth of *C. vulgaris*, physicochemical parameters, concentration of chlorophyll A and B, pesticides, as well as concentrations of nutrients

were monitored for 10 days in triplicates.

MPs presence in wastewater showed no significant impact on the growth of *C. vulgaris*, chlorophyll production or nutrient uptake from wastewater. The microalgae culture exhibited no growth effects in the presence of the pesticides; however, contrasting observations were noted for other parameters, such as an increase in the chlorophyll content of *C. vulgaris*, pH, and electrical conductivity, as well as in the ammonium and Kjeldahl nitrogen concentration. Additionally, lower uptake efficiency of orthophosphates was observed in the presence of pesticides. Whereas, the status of microalgae remained unaffected by the presence of MPs, whether in the co-occurrence of pesticides or in the control samples with *C. vulgaris* only.

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Computational and Experimental Approach to the Development of Novel Test for Pathogen Detection in Water

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The fast and cost-efficient detection of pathogens in water is highly important in many sectors such as healthcare, agriculture, food industry, and many others. However, current technologies for pathogen detection in water samples are limited, and significant advances are required to develop low-cost (<10 €) detection assays that can detect a few bacterial cells (<10 cells/ml) within less than one hour.

In an attempt to develop novel test for pathogen detection in water, a new detection concept for the fast and low-cost identification of human pathogens in water samples is proposed. Such concept relies on protein-protein and protein-DNA interactions which were studied computationally and experimentally. The choice of protein that is the key part of the novel test, depended on its possibility to be split in two parts which produce a functional enzyme when are reconnected. Horseradish peroxidase (HRP), an enzyme with high potential for biotechnology applications, has such ability and it was in the focus of the study. Interdisciplinary study was used to study its structural and dynamical properties [1], as well as its interaction with oligonucleotides [2]. Computational and experimental methods, that were used in the frame of the study, complemented each other and their synergy enabled deeper understanding of the results. In addition, CATANA a novel computational tool that facilitate study of large biochemical systems, was developed [3].

Results of study showed that glycosylation has large influence on different HRP properties. In presence of glycosylation, structural stability of HRP enzyme is significantly increased. Further, electrostatic properties, including electrostatic potential of enzyme active site, are significantly different in presence comparing to the absence of glycosylation. Finally, glycosylation has different effect of fluctuation of protein regions (i.e. propagated effect was observed - glycosylation from the protein surface influenced fluctuations of the inner core regions of protein). In addition, it was shown that oligonucleotide attachment does not influence enzyme activity and HRP-DNA system can be used for the development of novel test for pathogen detection in water.

Acknowledgements

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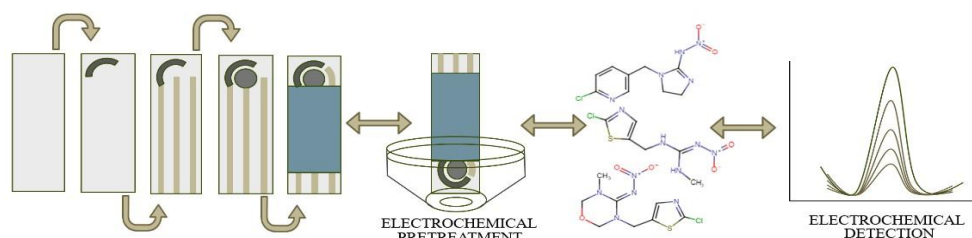
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Voltammetric Detection of Neonicotinoids in Surface Water and Honey by Activated In-House Screen-Printed Graphite:Glass Working Electrodes

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Neonicotinoid pesticides (NNIs) are synthetic systemic pesticides, notorious for their toxicity against non-target organisms, such as different species of pollinators. Although the use of certain NNIs is prohibited outdoors in the EU, the presence of these pesticides in soil, rivers, and even some foods remains a serious problem, especially in third world countries. The development of electrochemical sensors in the form of screen-printed three electrode systems (TESs) therefore offers an inexpensive, portable, time-efficient, environmentally friendly, and simplified method for reliable pollution monitoring [1]. The electrochemical response can be further enhanced by activation of the working electrode (WE) surface by electrochemical pretreatment [2].

In this work, we present the use of activated TESs with a graphite:glass composite thick film working electrode for the detection of imidacloprid, clothianidin, and thiamethoxam in a model solution as well as in real samples. First, a Pt auxiliary and Ag reference electrode on alumina were prepared by screen-printing of commercial Pt and Ag pastes followed by post-annealing. WE paste was prepared from a graphite:glass powder mixture, dispersed in ethyl cellulose and α -terpineol. The paste was screen-printed on alumina, followed by annealing at 850 °C in argon atmosphere. Prior to electrochemical characterisation, the TESs were thoroughly rinsed with ultrapure water. An optimization study of electrochemical surface activation was performed. For the detection of NNIs, WE was activated by performing cyclic

voltammetry (CV) in 0.1 M H₂SO₄ in the potential window between -0.6 and +2.0 V for 10 cycles. To magnify the cathodic current peak, corresponding to the reduction of the nitro group, several experimental parameters, such as accumulation time, temperature, and pH were evaluated. Using adsorptive differential pulse voltammetry (AdDPV), a study of linearity was performed. Two linear ranges were observed for all three pesticides of interest. Limits of detection (LODs) were found in the range 12 – 26 nM, depending on the analyte. Several inorganic ions as well as glucose and fructose were tested as possible interferences and none of the selected species were found to interfere with the signals of the analytes. Samples of river water from Ljubljana, Slovenia and Slovenian honey were spiked with known concentrations of the three NNIs and the developed method was successfully applied to detect all three pesticides in a real sample matrix.

Acknowledgements

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Use of Iron-Bearing Waste Materials in Laundry Wastewater Treatment

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The industrial laundry sector in the European Union (EU) is experiencing an increase in wastewater volume due to the escalating water demand, necessitating wastewater treatment. Specifically, the EU industrial laundry sector washes approximately 2.7 billion kg of textiles annually, using 42 million m³ of water [1].

The advanced oxidation processes (AOPs) hold promise for the removal of persistent chemicals. Among the various AOPs, photo-Fenton oxidation is an eminent treatment due to its high efficiency to remove recalcitrant compounds [2].

Magnetite is a prominent iron source vastly studied in heterogeneous photo-Fenton reactions for water and soil remediation [3]. However, most deal with synthetic or commercial magnetite for its ability to catalyze Fenton reactions but there is limited knowledge on the efficiency of magnetites produced from ferrous wastes. The utilization of ferrous/steel wastes has the potential to lower treatment expenses and provide an avenue for waste valorization; especially that the stainless-steel industry is one of the fastest-growing sectors of the manufacturing industry [4].

We investigated the use of magnetite produced from steel wastes as an iron source in photo-Fenton reactions for laundry wastewater (LWW) treatment. The efficiency of waste-derived magnetite (WM) was compared to that synthetic magnetite (SM) and zero-valent iron (ZVI). Their capacity to adsorb metals co-existing in LWW was also assessed.

Experiments were conducted in LWW by spiking 20 µM of ciprofloxacin (CIP), an antibiotic, or

phenol, a model pollutant, followed by the addition of magnetite or ZVI (0.1 g/L) and H₂O₂ (25 mM). Irradiation took place under UVC (254 nm) or UVA (365 nm) lamps. Degradation and total organic carbon (TOC) removal were followed by HPLC-UV and TOC meter respectively, whereas metals concentration was determined by ICP-OES.

Effective CIP and phenol degradation was achieved using WM. UVC was more efficient than UVA in promoting degradation. The presence of ZVI greatly enhanced the degradation efficiencies. The ZVI/UVC/H₂O₂ system was the most effective system in mineralization in LWW. A 70% TOC removal was obtained with ZVI/UVC/H₂O₂ vs. 55% in the WM/UVC/H₂O₂ and SM/UVC/H₂O₂ systems. The magnetite and ZVI used in this study acted as adsorbents to heavy metals present in the LWW. This highlights the importance of waste valorisation in wastewater treatment.

Acknowledgements

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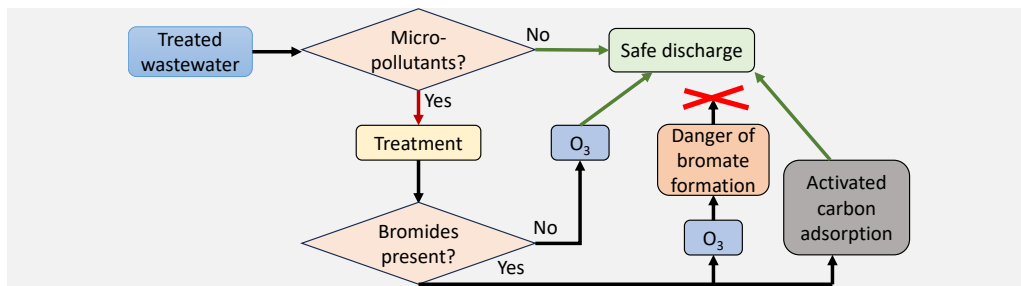
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Bromides in Treated Wastewater: Limiting the Use of Post-Ozonation for Micropollutant Removal

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A major challenge in wastewater treatment is the presence of various micropollutants. Being different in nature and sources, they all end up in the wastewater, and can largely pass wastewater treatment plants intact.

Wastewater treatment plant (WWTP) effluents appear to be a proper place for the removal of micropollutants, with ozonation and activated carbon adsorption being primary choices.

Ozonation has been long shown to possess the potential of oxidising bromide anions to carcinogenic bromates. Previous research suggests [1] that ozonation of 0,15 mg/L bromide and more could produce sufficient amounts of bromates.

Additionally, bromate may be formed upon WWTP effluent disinfection when using high doses of hypochlorite [2], or when using chloride dioxide under illumination [3, 4].

Thus, before choosing a suitable method to remove micropollutants from WWTP effluents, a research is needed to map the bromide situation in the WWTP catchment area. In Estonia, around 2/3 of water supply comes from groundwater, including coastal areas. The research results show that among 20 analysed locations throughout Estonia, five measuring points are clearly over the 0,15 mg/L Br⁻ threshold, another 6 are just under it. Consequently, for over half of the analysed WWTP effluents throughout Estonia ozonation as the means to remove micropollutants is precarious.

The main outcome of this research is mapping areas where ozonation cannot be applied for the degradation of micropollutants in treated WWTP

effluents due to the threat posed by bromate formation; also, their possible disinfection by chlorination would not be possible. The research also results in the general awareness of potential problems caused by bromide in wastewater. The continuation of this research shall be aimed at experimental applicability of ozonation as the post-treatment technology for those wastewaters where ozonation may be considered to be safe.

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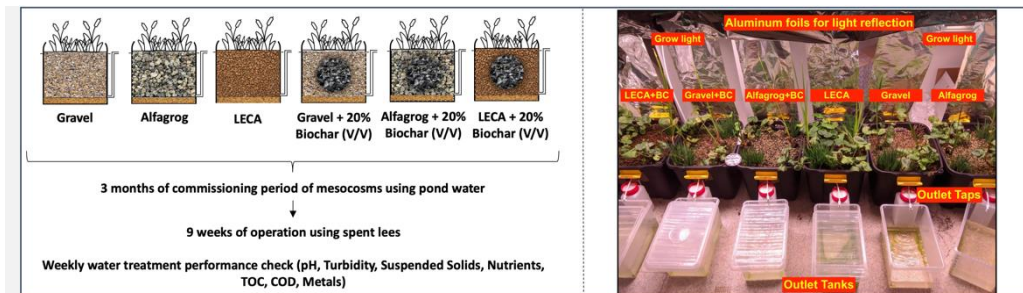
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A Comparison Between Constructed Wetland Substrates and Impacts on Wastewater Treatment Performance

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Constructed wetlands (CWs) are man-made systems that harness wetland plants, substrates, and microorganisms to treat wastewater [1]. Substrates play a pivotal role in CW performance. They serve as a platform for biofilm development, support wetland plant growth, and adsorb pollutants, significantly influencing CW effectiveness [2].

In this project, we compare substrates in terms of their ability to treat whisky wastewater (spent lees) using mesocosms built with pea gravel, alfagrog (a foamed ceramic) and LECA (a clay aggregate) – each with or without 20% (V/V) of 6-12mm biochar.

Six 42L plastic containers were used for the mesocosms. Each container had a 2 cm layer of silver sand at the bottom, followed by a 25 cm substrate layer (gravel, alfagrog, LECA, etc.). Two each of *Caltha palustris*, *Juncus ensifolius*, and *Acorus calamus* were then planted into each mesocosm. Growth lights were used indoors and for 8 hours daily (9 am to 5 pm). Pond water from a nearby town park was used to feed the system for three months, allowing plant and microbial growth/establishment. Subsequently, spent lees was treated for nine weeks, with weekly water quality checks, and a hydraulic retention time (HRT) of seven days.

During the nine weeks, the average inlet pH of spent lees was 5.1 (± 0.1). The highest pH increase (desirable) occurred in the LECA-biochar mesocosm, reaching pH 6.0 (± 0.2), followed by LECA alone at pH 5.8 (± 0.1). Gravel-biochar, gravel, and alfagrog mesocosms had pH's of 5.6 (± 0.1), 5.5 (± 0.1), and 5.5 (± 0.2), respectively. The least pH increase was in the alfagrog-biochar mix outlet at 5.3 (± 0.1).

The average dissolved Cu (dissCu) in inlet spent lees was 55.8 mg/L (± 11.7). The most effective dissCu removal again occurred in the LECA-biochar mesocosm, with outlet results of 1.7 mg/L (± 1.5), followed by gravel-biochar at 1.9 mg/L (± 1.6). Gravel, LECA, and alfagrog-biochar outlets were 2.5 mg/L (± 2.1), 4.2 mg/L (± 3.7), and 5.2 mg/L (± 4.2) (dissCu, respectively). The least effective substrate was alfagrog with an outlet of 36.1 mg/L (± 9.5).

The initial total organic carbon (TOC) in inlet spent lees was 737 mg/L (± 126). TOC removal ranked from highest to lowest was as follows: gravel-biochar (336 mg/L ± 66), LECA-biochar (361 mg/L ± 64), alfagrog-biochar (386 mg/L ± 112), LECA (526 mg/L ± 82), alfagrog (556 mg/L ± 94), and gravel (564 mg/L ± 94), at the outlet.

Our study shows that substrate choice impacts treatment performance in constructed wetlands. The biological community within each mesocosm is also critical, and this will be elucidated by analysing the bacterial and fungal biofilms formed in each mesocosm using DNA metabarcoding.

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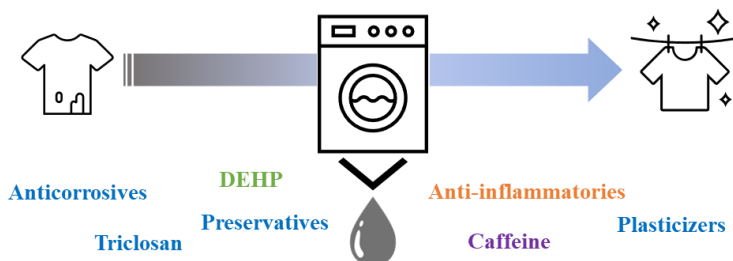
Emerging Pollutants in Greywater: is Laundry Wastewater Prone for Water Reuse?

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Water scarcity is an increasing problem in several areas worldwide and greywater treatment and reuse could represent an alternative water source. Greywater is wastewater generated in households, excluding that which comes from toilets. It encompasses wastewater from various sources like laundries, washbasins, dishwashing, bathrooms, and kitchen sinks. Depending on its source, greywater can contain various types of contaminants. For instance, greywater from laundry may contain softeners, plasticizers, emulsifiers, preservatives, surfactants, phthalates, pharmaceuticals, and microplastics, along with many other emerging and priority contaminants [1]. Due to the complex nature of the laundry greywater and the lack of adequate analytical methodologies, there is a very limited knowledge on the presence of plastic additives and other emerging micropollutants. This study aims at characterizing and comparing greywater from two laundries in Catalonia (Spain), which differ in size, clients, and services, exploring their future water reuse.

The study focused on selected emerging organic contaminants, including pharmaceuticals and endocrine disrupting compounds (EDCs), which were extracted from laundry greywater using solid-phase extraction followed by UHPLC-MS/MS analysis [2,3]. In addition, the di(2-ethylhexyl) phthalate (DEHP) was analysed by on-line headspace solid-phase microextraction coupled to gas chromatography tandem mass spectrometry (HS-SPME-GC-MS/MS). The sampling was conducted by collecting daily composite samples throughout one week.

In the case of pharmaceuticals, acetaminophen, ibuprofen, diclofenac and ketoprofen exhibited the

highest concentrations among the 88 compounds analysed in both laundries. For EDCs, preservatives, triclosan, anticorrosives, plasticizers and caffeine were detected among the 30 compounds analysed. DEHP, the most prominently identified compound, was present in both laundries, with a concentration range of 29-173 µg/L.

Complementary, a wide-scope screening will be conducted using LC-HRMS to broaden the spectrum of micropollutants, thereby providing a more comprehensive characterization of laundry greywater.

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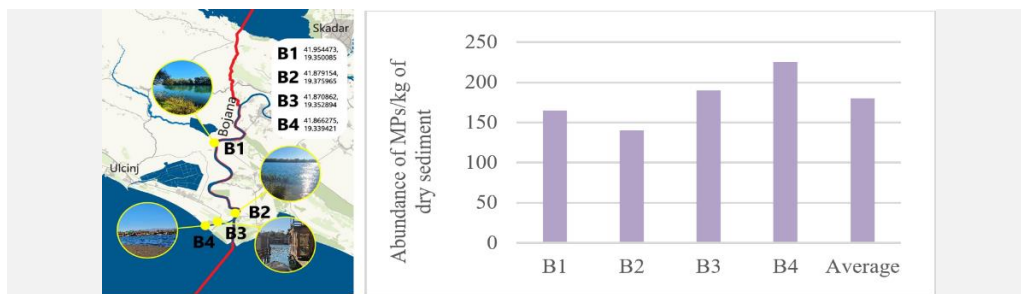
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Abundance, Distribution Patterns, and Identification of Microplastics in Bojana River Sediments in Montenegro

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Microplastic (MP) pollution (particles smaller than 5 mm) represents a scientific topic that has received increasing attention over the last decade, due to the constant increase in plastic production and its subsequent disposal and accumulation in environment. Freshwater is considered one of the sources of MPs flowing into the seas, and rivers are considered the main transport vector of plastic debris from terrestrial sources [1]. The objective of the present study is to determine MPs abundance, distribution, and identification in surface coastal sediments of Bojana river as well as to assess whether the Bojana river is a significant source of MPs on the Montenegrin coast.

Bojana flows through Albania and Montenegro, it originates from Skadar lake. The length of the Bojana river is 41 km, of which about 24 km belongs to Montenegro. Bojana is the largest tributary of the Adriatic Sea in Montenegro [2]. Surface coastal sediments of Bojana river were collected at 4 selected locations. For MPs density separation, was used concentrated NaCl solution [3]. Samples were visual analyzed under a microscope, while their chemical structure were analyzed using ATR-FTIR and μ FTIR spectroscopy.

MPs were identified in all examined samples of coastal sediment of the Bojana river. In the coastal sediment of the Bojana river at all investigated locations, the abundance of MPs ranged in the following sequence: B4 > B3 > B1 > B2, with a total mean abundance of 180 MPs/kg of dry

sediment. The results indicate that sediments of Bojana river in the present study are moderately polluted with MPs compared with literature data.

In coastal sediment of the Bojana river the primary MPs shape types by number were: fibers > fragments > films > granules; the primary MPs size class by number were: 0.5–1 mm > 1–3 mm > 0.1–0.5 mm > 3–5 mm; while the primary MPs color by number were: blue > clear > red > black > yellow > green > white. The representation of polymer types in the coastal sediment of the Bojana river moved in the following sequence: PP > PE > PET > PA > PS > PTFE > Acrylate cop.

Population density, tourist, fishing and agricultural activities, wastewater discharge, inadequate solid waste management and cross-border pollution were identified as the main sources of MPs pollution in Bojana river in Montenegro. Bojana river carries plastic from the territories of Montenegro and Albania and that it is the second largest terrestrial source of plastic in the entire Adriatic [4]. Bojana river represents one of the significant sources of MPs on the Montenegrin coast.

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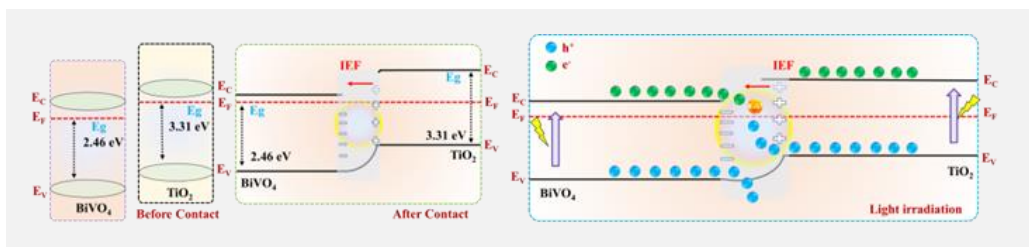
Versatile Application of BiVO₄/TiO₂ S-Scheme Photocatalyst: Photocatalytic CO₂ and Cr(VI) Reduction

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In recent decades, semiconducting materials have been widely investigated for photocatalytic applications [1]. TiO₂ plays a significant role in photocatalysis owing to its low, superior efficiency, high chemical stability, and excellent redox ability [2]. However, its photocatalytic properties, such as charge carrier generation and separation, are not suitable for commercial use because of their low efficiency (band gap of ~3.2 eV for anatase TiO₂ limits its use). A promising approach for preparing efficient photocatalysts is the combination of TiO₂ with other semiconductors such as BiVO₄ [3].

In this study, a versatile TiO₂/BiVO₄ nanocomposite was successfully prepared using a simple wet-impregnation method. The addition of BiVO₄ significantly promoted charge separation, leading to an enhanced photocatalytic activity for the reduction of Cr(VI) to Cr(III) and CO₂. The morphology, structure, composition, and optical properties were evaluated using transmission electron microscopy (TEM), X-ray diffractometry (XRD), laser-induced breakdown spectroscopy (LIBS), and diffuse reflectance spectroscopy (DRS), respectively. Significantly enhanced photocurrent densities (by 3–15 times) were obtained for TiO₂/BiVO₄ compared to those of pure TiO₂ and BiVO₄. The reduction of toxic Cr(VI) to Cr(III) was assessed, including the effect

of pH on overall photocatalytic efficiency. Under acidic conditions (pH ~ 2), Cr(VI) reduction efficiency reached 100% within 2 h. For photocatalytic CO₂ reduction, the highest yields of CH₄ and CO were obtained using TiO₂/BiVO₄. A higher efficiency for both applications was achieved because of the better separation of the electron-hole pairs in TiO₂/BiVO₄. The excellent stability of TiO₂/BiVO₄ over repeated runs highlights its potential for use in versatile environmental applications. The efficiency of TiO₂/BiVO₄ is due to the interplay of the structure, morphology, composition, and photoelectrochemical properties that favour the material for the presented herein photocatalytic applications.

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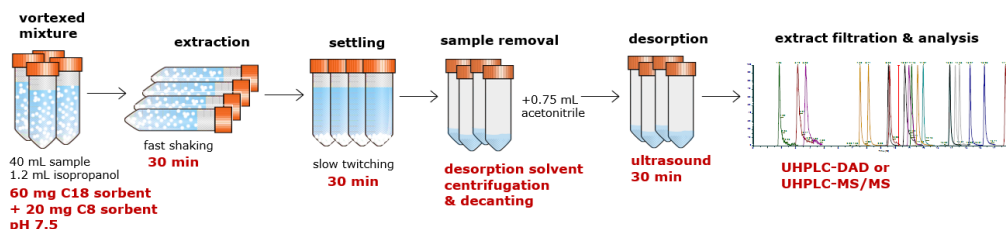
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Dispersive Micro Solid-Phase Extraction (DMSPE) for Water Analysis: Why, How, for What?

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Understanding pollution is crucial for safe coexistence with and synthetic chemicals in an increasingly chemicalized world. Herein, environmental analytical chemistry takes an important role, as there is a constant need for ultrasensitive analytical procedures to control organic pollutants in complex water samples.

Regarding environmental applications, solid-phase extraction (SPE) coupled with LC-MS/MS seems to have become a well-established technique for multicomponent analysis. Off-line SPE, performed in sorbent pre-packed columns, is by far the most used mode. However, it lacks simplicity, versatility, and rational consumption of solvents. So, reaching back to basics of SPE, dispersive micro SPE (DMSPE) experiences an onset of intensive research. Like dSPE used as a clean-up step in QuEChERS, DMSPE is instead used for pre-concentration of analytes onto freely dispersed sorbent directly in the sample. For example, Nascimiento et al. successfully developed DMSPE procedure for determination of PAH [1] and multiclass pesticides [2], while Vivas et al. dealt with endocrine-disrupting compounds [3].

In this study we aim to unveil practical aspect of DMSPE coupled with UHPLC-MS/MS for ng/L-range analysis of selected 17 emerging pollutants, for example, sartans, statins, herbicides, insecticides, UV-filters, industrial reagents, artificial sweeteners, etc. They vary significantly in polarities; some being acidic, others basic, or even zwitterionic, which has made method development especially challenging. Method optimization included screening of commercial sorbents (mixtures of C18, C8, Florisil, styrene-

divinylbenzene, graphitized carbon black, ion-exchangers), sample load, pH, composition of desorption solvent, mode of sample removal, extraction time, etc. Lastly, the method was subject of validation process and was applied on spiked real river water samples.

With the optimized conditions, extraction is done from 40 mL sample (pH 7.5) by adding 60/23 mg mixture of C18/C8 sorbent. Then, the sample is removed by centrifugation and decanting, while analytes are desorbed from the remaining sorbent. In brief, DMSPE has shown moderate effectivity for 14 polar and non-polar studied pollutants, reaching pre-concentration factors of about 5–50. With UHPLC-MS/MS, LODs were 1–12 ng/L within < 15% RSD repeatability (determined at 50 and 100 ng/L). Moreover, the procedure was not susceptible to major matrix effects, using samples of river water. All mentioned parameters make DMSPE-UHPLC-MS/MS an attractive novel method for fast and rational sample preparation due to its versatility, possibility of mixing various sorbents, simplicity, time-efficiency, and low consumption of organic solvents.

Acknowledgements

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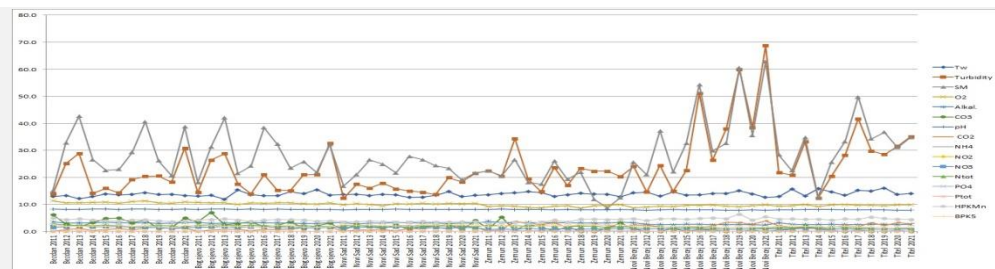
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Selection of Significant Parameters For River Water Quality Monitoring by Multivariate Analysis

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Understanding how changes and factors affect river water quality is crucial for managing water quality in river basins [1]. For this reason, the emphasis in this article is focused on the analysis of key factors affecting water quality, as well as temporal and spatial variation of Danube and Tisza River water quality.

Within the research, the data set contained 19 significant physico-chemical parameters quantified at 6 localities along the Danube River basin in Serbia (Bezdan, Bogojevo, Novi Sad, Zemun, Novi Bečej, and Titel) from 2011 to 2021 [2].

The lowest values of key parameters such as suspended matter (SM), O₂, saturation of O₂, NO₂⁻, NO₃⁻ and COD were recorded at the Zemun location, while the lowest values of NH₄⁺ and BOD₅ were recorded at the Bezdan site. Conversely, the highest values of O₂, saturation of O₂, pH, NO₃⁻, Ntot and Ptot were recorded at the Bezdan locality, while COD and BOD₅ were highest in Novi Bečej and Novi Sad, respectively.

Also, this study investigates the potential of using multivariate techniques, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA), to evaluate water quality data gathered from natural watercourses. With this goal in mind, a comprehensive water quality data set was used for the analysis, gathered on a rich of the Danube River over the period of eleven years.

Applying the PCA method to the set of all parameters at all localities, significant parameters - turbidity, SM, O₂, saturation of O₂, alkalinity, HCO₃⁻, NH₄⁺ and PO₄³⁻ were singled out. In this

way, the reduction of many parameters and the selection of parameters that could and should be monitored in these localities were made possible.

Hierarchical cluster analysis using the Ward method was applied to the analysis results. On the dendrograms, four clusters were distinguished. The last, fourth cluster indicated the highest loading in the site Bezdan (during all periods), and in the localities Titel, Bogojevo, Novi Sad, and Zemun only in 2011, initiation the fact that the quantified values and concentrations of the examined parameters decreased in these areas over the years.

Furthermore, the presented results indicate that these measurements, combined with some multivariate analysis methods, especially the principal component analysis, could be a promising approach for investigating the water quality tendencies of alluvial rivers.

Acknowledgments

This research was supported by the Science Fund of the Republic of Serbia, grant number 6707, REmote Water quality monitoRing and INtelligence – REWARDING and the Ministry of Science, Technological Development and Innovation through project no. 451-03-47/2023-01/200156 “Innovative scientific and artistic research from the FTS (activity) domain”.

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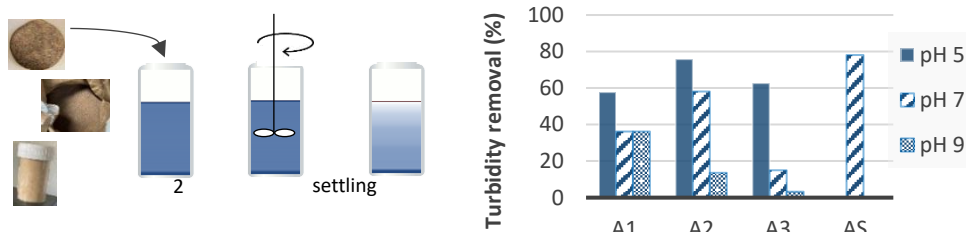
Coagulation – Flocculation of Water by Green Wastes : New Insight in Mechanisms Involved

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Graph : Removal turbidity of three agricultural by-products (A) 1 at 5 mg/L, 2 at 50 mg/L, 3 at 100 mg/L and sulfate aluminum (AS) at 150 mg/L as function of pH



Conventional coagulants (metallic or synthetic) in coagulation–flocculation processes for water treatment and sludge conditioning are increasingly being questioned. As organic and biodegradable compounds are considered as health or environmental friendly, to avoid the drawbacks of conventional coagulants and restrict their impacts, many studies are looking for substitutes using coagulants of natural origin, also known as biocoagulants – bioflocculants. It concerns natural polymers such as starch, polysaccharides, chitin or phenols originating from animal, plant or microorganism sources [1]–[3].

This work is focused on the search for new biomolecules as substitutes, using green waste or agricultural by-products, to reach circular economy objectives. To achieve this, eight kind of biomasses were selected and their flocculent properties were investigated. A screening was carried out to evaluate the dose and pH effects in Jar-tests on a synthetic water (colloidal suspension). The coagulation – flocculation efficiency is assessed by measuring the decrease in turbidity and dispersion stability (Turbiscan) after Jar-test experiments. These experiments enable to identify three active biomasses as bioflocculant with turbidity removal ranging from 57,76 % to 75,76 % (pH 5 – dose 5 to 100 mg/L). These results are promising as their performance are comparable to those of aluminum sulfate (used as reference coagulant: 75,60 % at pH 7 – 150 mg/L).

In a second time, jar tests experiments were conducted on three different synthetics colloidal suspensions: clay, sodium-exchanged clay, alumina and silica. Mechanisms involved in

biocoagulation - bioflocculation process are scarce in the literature. In this study, investigations on the mechanisms involved during biocoagulation - bioflocculation experiments were conducted. The results obtained revealed a non-negligible impact of calcium ions on the coagulant-flocculation process.

Further experiments are needed to identify and to evaluate the calcium-related coagulation-flocculation capacity of the active fractions from the bioresources. Eco extractions are in progress on the three selected biomasses to improve their turbidity reduction rate.

Acknowledgements

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Determination of The Adsorptive Capacity of Biochars for Bioremediation of Petroleum-Type Pollutants

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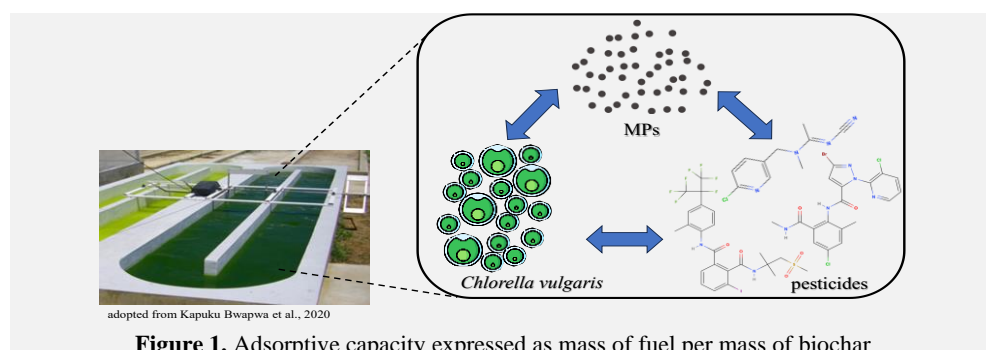


Figure 1. Adsorptive capacity expressed as mass of fuel per mass of biochar

Since the beginning of the 21st century, the importance of biochar has expanded from agricultural to remediation purposes. Its large active surface area and the presence of both organic and inorganic active sites make it a potentially very good binding agent for a wide range of pollutants [1].

On the other hand, the constant growth of the population and the number of transport vehicles demand the need for greater consumption of fossil fuels, the main source of energy for more than a century. Coal mining leachates, oil spills, and fossil fuel emissions can take an enormous toll on the environment.

As biochar is a product of pyrolysis of organic waste, which can originate from various sources, in this study, the adsorptive capacity was examined for biochars obtained from rice husks (RH), mixed softwood pellets (SWP), sewage sludge pellets (SS), oil seed rape straw (OSR), miscanthus straw pellet (MSP) and wheat straw pellets (WSP), at two pyrolysis temperatures (550 and 700 °C).

Adsorptive capacity was determined by immersing previously measured mass of biochar in fossil fuels. After half an hour, the biochar was removed from the fuel and dried. Adsorption capacity is expressed as the ratio of the mass of the adsorbed matter and the mass of the sorbent [2],[3].

The adsorption capacity depends on the properties of the initial biomass and pyrolysis conditions. As can be seen from Figure 1, all

biochars, except for the biochar produced from the rice husk, have a higher adsorptive capacity when obtained at a lower pyrolysis temperature. This is important because of the energy demand, lower temperatures use less energy. Furthermore, all biochars showed higher adsorptive capacity when crude oil than for diesel. This can be explained by the fact that biochar contains both polar and non-polar groups and therefore absorbs better crude oil, which is composed of a mixture of non-polar, aromatic, and heterocyclic compounds, unlike diesel, which is composed exclusively of non-polar compounds. If these biochars would be used in the bioremediation of water environments contaminated by petroleum-type pollutants, these adsorptive capacities studies should be considered.

Acknowledgements

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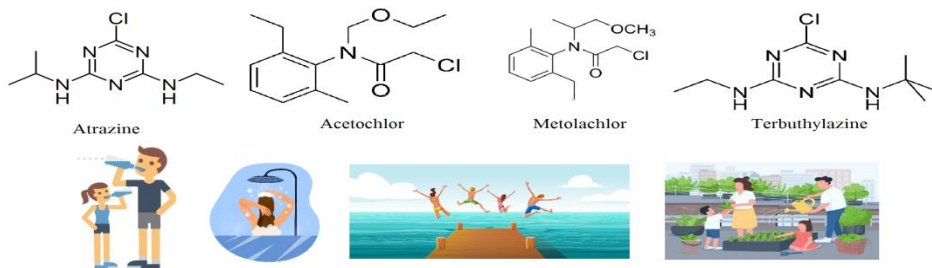
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Human Health Risk Assessment of Endocrine Disrupting Herbicides Present in Waters from Croatia

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The concern over certain herbicides being identified as endocrine disruptors has prompted apprehensions due to their capability to disrupt the normal function of the endocrine system. The aim of this study was to evaluate the potential risks to human health linked with terbutylazine and endocrine-disrupting herbicides such as atrazine, acetochlor, and metolachlor in tap, surface, and groundwater in Zagreb city region, Croatia [1]. To assess human health risk (HHR), we examined diverse exposure scenarios. These scenarios encompassed the risk of direct exposure to the herbicides through drinking water, bathing, and recreational activities e.g. swimming in rivers, streams, and lakes. Furthermore, we quantified risks of indirect exposure by consuming fruits and vegetables growth on land irrigated with the surface and groundwater.

Multivariate analysis identified atrazine and acetochlor as the predominant herbicides, compared to the other investigated, in drinking and groundwater samples. During the summer months, the presence of metolachlor and terbutylazine influenced the surface waters, particularly when they are used for recreation. However, the HHR results, based on the herbicide concentrations, did not indicate significant risks of either carcinogenic ($TR \leq 1 \times 10^{-6}$) or non-carcinogenic ($THI < 1$) illnesses. Anyhow, the oral exposure risk from drinking and groundwater is higher than the dermal risk compared to surface water. Surface waters have higher dermal than oral exposure risk. This is expected since human skin is dominantly exposed by swimming, while oral exposure by accidentally

swallowing the water is negligible. The dermal risk associated with acetochlor is higher from tap water used for bathing or showering.

Consumption of fruits and vegetables watered with the analysed surface and groundwater does not pose either non-carcinogenic ($THQ \ll 1$) or carcinogenic risks (TR values are lower than 5×10^{-7}) to human health. In addition, even when considering the combined impact of herbicide exposure across different water sources, an aspect often referred to as the "cocktail" of herbicides in the investigated waters.

Acknowledgements

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Estimation of Surface Water Contamination by Pesticides in the Kovin area, Serbia

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Kovin is a town and a municipality located in the South Banat District of the autonomous province of Vojvodina, Serbia. In the industrial zone of this city there are factories that produce alcohol and animal yeast, pet food, cutting and finishing of steel, production of syringes and packaging for vaccines and medicines, as well as the largest mushroom farm in the Balkans. In addition, 11 km from Kovin there is a mine that extracts coal from the bottom of a lake that is connected to the Danube, and represents a unique underwater coal mining in the world. Despite the mentioned numerous activities that can have an impact on the quality of surface waters, a systematic laboratory monitoring of the surface waters in this area has not been conducted so far. The present study represents the extension of our earlier work aimed at the preliminary characterization of the degree of loading of surface waters with the total and specific, most prevalent hydrocarbon polluting substances [1]. In the current research, the aim was investigation of the presence and concentration level of pesticides in these surface waters.

The water samples analysed in this study were sampled during November 2022, from five representative locations in the Kovin area (Figure 1). In the water samples, pesticides were analysed with gas chromatography - mass spectrometry (GC-MS) technique in the selected ion monitoring mode using one target and three qualifier ions for each analyte. Also, a series of samples with spikes was used to confirm the extraction efficiency of the method.

The results confirmed presence of pp-DDE (in concentration range from not detectable (ND) to 28.92 $\mu\text{g kg}^{-1}$), fludioxonil (from ND to 166.81 $\mu\text{g kg}^{-1}$), metalaxyl (from ND to 164.03 $\mu\text{g kg}^{-1}$), azinophos ethyl (from ND to 334.02 $\mu\text{g kg}^{-1}$), tetrahydrophthalimide (from ND to 38.07 $\mu\text{g kg}^{-1}$), difenconazole (from ND to 75.23 $\mu\text{g kg}^{-1}$), resmethrin (from ND to 54.23 $\mu\text{g kg}^{-1}$), fenvelarate (from ND to 263.20 $\mu\text{g kg}^{-1}$), diazinon (from ND to 145.56 $\mu\text{g kg}^{-1}$), linden (from ND to 74.2 $\mu\text{g kg}^{-1}$), carbaryl (from ND to 30.61 $\mu\text{g kg}^{-1}$), cypermethrin (from ND to 159.62 $\mu\text{g kg}^{-1}$), delta HCH (from ND to 37.48 $\mu\text{g kg}^{-1}$), myclobutanil (from ND to 275.53 $\mu\text{g kg}^{-1}$), krezoxym methyl (from ND to 185.47 $\mu\text{g kg}^{-1}$), azoxystrobin (from ND to 16,32 $\mu\text{g kg}^{-1}$), and hexachlorobenzene (from 10,02 to 23,12 $\mu\text{g kg}^{-1}$).

The number of the pesticides detected and their amounts indicate that these waters are exposed to a serious input of these pesticides and point to the need for continuous monitoring of the pesticides in this area.

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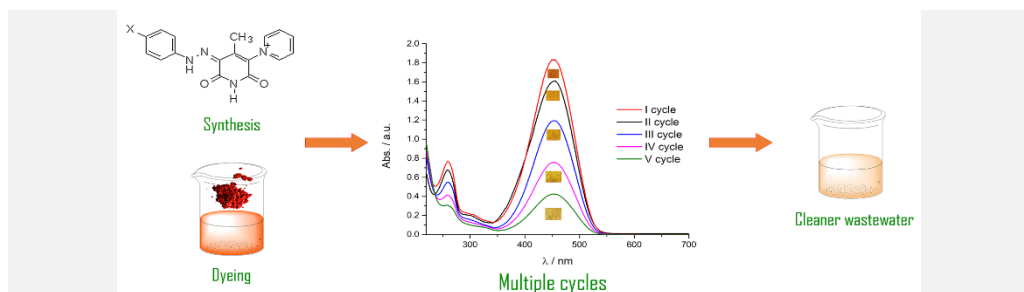
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Reducing Wastewater in Textile Industry: Innovative Dyeing Approach

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The reduction of water pollution represents one of the priority topics of the EU's goal to achieve climate neutrality by 2050. Herby textile industry is focused on developments in numerous environmental and social issues, including high emissions, high water and/or energy consumption and heavy pollution [1]. Coloured effluents from this industry disposed into natural ecosystems are responsible for about 20% of global clean water pollution [2]. The European Union aims to reduce textile waste and increase the life cycle and recycling of textiles as part of the plan to achieve a circular economy by 2050 by sustainable products and empowering consumers to participate in the green transition [2]. One of the main research topics connecting textile industry and waste water reduction is found in synthesis of eco-friendly dyes which are superior to their natural analogues due to the excellent dyeing capabilities and colour fastness properties. Among these, azo pyridine dyes gained attention for the simplicity of their preparation, good colour fastness, high tinctorial strength, thermal and optical stability [3]. Traditionally, applied as disperse dyes, they have low water solubility and are used for colouring mostly synthetic fibres. Recent findings showed that the introduction of the pyridinium ring into pyridone molecule resulted in enhanced water solubility of the dyes and improved affinity towards various natural and synthetic fibres, especially wool and cellulose diacetate fibres [4].

For the purpose of addressing environmental issues in the textile industry, in this work, two pyridinium-based azo pyridone dyes with improved solubility and affinity towards different fibres, are used for dyeing wool fabric. The results show that the same dyebath can be efficiently used multiple times, therefore reducing waste in the water while securing the optimizing dyeing. The obtained fabrics from different cycles are further characterized by K/S values while the residue of the dye in the wastewater was recorded using UV-Vis spectra.

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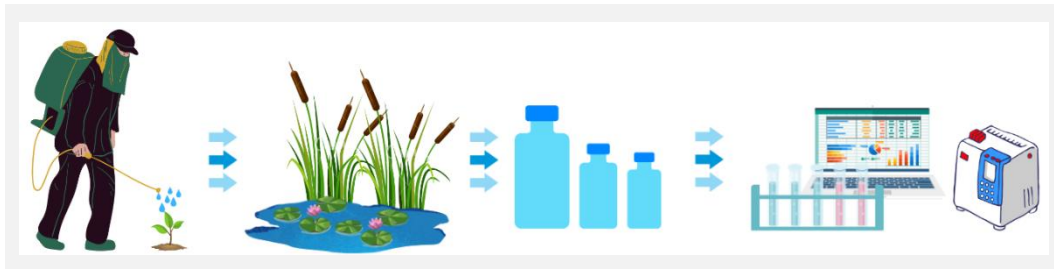
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Pesticide Residues in the Water of Nature Park Jegrička (Serbia)

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With the aim to restore ecosystems damaged from agriculture, reducing the use and risk of chemical pesticides by 50% until 2030, has been suggested [1].

This implies the evaluation of the current status of water bodies through the monitoring of priority pollutants, including pesticides. The current legislation in the proposal for amending WFD lists 70 substances as the priority pollutants of surface water, mainly pesticides, industrial chemicals, and metals for surface water [2, 3]. The list includes some currently used pesticides (acetamiprid, deltamethrin, esfenvalerate, nicosulfuron, glyphosate).

This study focuses on the monitoring of pesticide residues in the Jegrička River located in the Nature Park, in the Vojvodina province (Serbia). Jegrička extends in the area under intensive agricultural production, where water from Jegrička is used to irrigate arable land, posing a risk of contamination of soil and agricultural products. Due to the intensive use of pesticides, the concern about their presence in the water of this protected area is raised.

Sampling was performed at 12 sites along the river, during June and July 2022. A volume of 1.5 l of water samples was collected into HD polyethylene, transferred to the laboratory, and analyzed. Solid-phase extraction with ENVI-C18 (47 mm) disc, followed by gas chromatography/mass spectrometry was used for the analysis of pesticides in water samples.

In the water samples of this study, insecticide chlorpirifos and herbicide atrazin were predominant. In the Republic of Serbia, in recent years, many active substances of pesticides have been banned from use, including those based on chlorpirifos and atrazin. However, due to their persistence and potential application, they still can be present in the environment.

Acknowledgements

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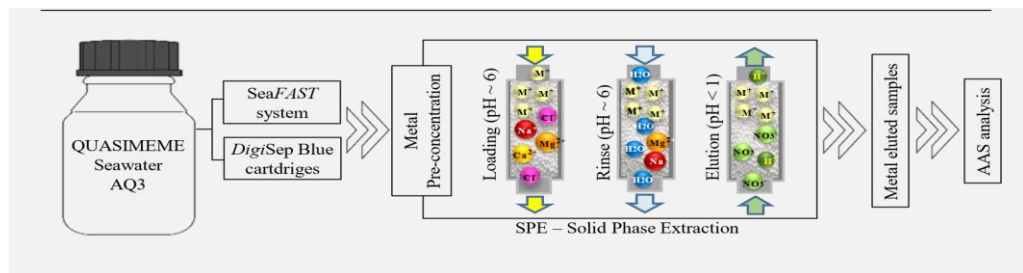
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Evaluation of SeaFAST System as an Alternative to DigiSEP Cartridges in Preconcentration of Trace Metals in Seawater Samples

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Analysis of trace metals in seawater is challenging due to the complex matrix ($\sim 35 \text{ g L}^{-1}$ total dissolved solids) and low dissolved concentrations (in $\mu\text{g L}^{-1}$) which requires a preliminary separation of the matrix and a preconcentration of the analyte.

In this study we compare results of trace metal concentrations from seawater samples, analyzed by Atomic Absorption Spectrometry (AAS) after analyte pre-concentration using either an automated offline seaFAST device or DigiSEP cartridges technique.

Both seaFAST and DigiSEP cartridges approach are based on solid phase extraction (SPE), where metals are chelated on the pre-concentration column, while matrix elements are flushed from the column. Nevertheless pre-concentration seaFAST methodology is becoming more prevalent as it is a fully automated system that eliminate very laborintensive and prone to contamination sample preparation steps inherent to the DigiSEP cartridges technique.

For comparison purposes, both methodologies were used to analyze eight seawater test materials of QUASIMEME proficiency program (R2022-1 and R2023-1) [1,2].

An off-line automated pre-concentration seaFAST SP3 system (Elemental Scientific - ESI) [3] equipped with two $200 \mu\text{L}$ low-pressure columns and DigiSEP Blue label cartridges (SCP Science) [4] were used in matrix separation and metal pre-concentration.

Eluted samples were analysed for Cu, Fe, Mn and Zn by AAS using a Thermo Scientific iCE 3000 series equipment [5].

Results of trace metals determined by AAS/seaFAST methodology were submitted to QUASIMEME programme and the z' -scores obtained compared to those of AAS-DigiSEP cartridges calculated afterwards by the authors.

In general, better results were obtained with combined AAS-seaFAST methodology compared to those of AAS-DigiSEP cartridges. For the eight seawater test materials results for Fe, Mn and Zn were rated with satisfactory performances, with z' scores $< |2|$, for both Interlaboratory Studies. For Cu three of the results were rated with z' -scores between $|2|$ and $|3|$ and the other five results were rated with z' -scores $< |2|$.

Despite the early phase of our study, these preliminary results appear very promising as an alternative to the time-consuming DigiSEP cartridges technique, as shown by these first results. Further studies are still required particularly in what concerns other trace metals analysis.

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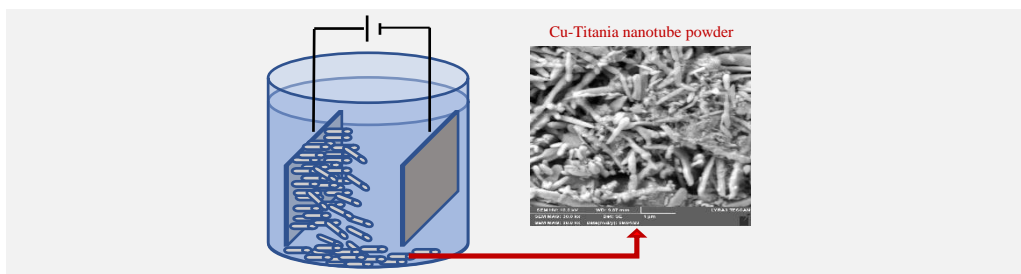
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Synthesis and Photocatalytic Performance of Cu-TiO₂ Nanotube Powders Obtained via Rapid Breakdown Anodization

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In recent decades, extensive research has been conducted on the development of titania nanotubes (TNTs) for a wide range of applications. These studies have unveiled the distinctive characteristics of TNTs, including their substantial surface area, exceptional chemical stability, and ability to facilitate rapid electron transfer [1]. These attributes position TNTs as highly promising candidates for utilization in fields such as photocatalysis, dye-sensitized solar cells, gas sensors, energy storage, and biomedical applications [2]. Among the numerous techniques employed to create TNTs, the anodization method stands out as one of the most commonly employed methods. This method provides a high degree of precision in controlling the dimensions and shape of nanotubes, rendering it remarkably versatile [3]. However, concerns have arisen due to the environmental hazards associated with fluorides, and the tendency for the oxide layer formed in fluoride-containing electrolytes to detach easily. The advantages of using fluoride-free electrolytes over fluoride-based ones include ease of application, environmentally friendly waste disposal, and the potential unique characteristics [4, 5].

Here, we present an efficient approach for the synthesis of Cu-TNTs powder via rapid breakdown anodization (RBA). Cu-TNTs powders were fabricated via electrochemical anodization of titanium (Ti) foil in an electrolyte containing (0.1-0.5) M of copper chloride dihydrate (CuCl₂·2H₂O) and 100 mL deionized water. Anodization was conducted at different potentials (from 15 V to 60

V) for 2 hours at room temperature. The as-prepared Cu-TNTs were annealed at 450 °C for 3 hours to obtain crystalline TiO₂ and subsequently comprehensively characterized in terms of morphology, structure, and composition. The photocatalytic activity of Cu-TNTs was evaluated through the photodegradation of Rhodamine B (RhB) as the model organic pollutant using a UV light source.

The most promising Cu-TNTs were obtained in 0.1 M CuCl₂ electrolyte anodized at 20 V for 2 hours. Well-defined tubes with an outer tube diameter of approx. 100 nm and 1 μm thick layers were obtained. The results indicate the successful modification of TiO₂ by copper with enhanced photocatalytic properties. The degradation efficiency of Cu-TNTs photocatalyst was investigated using RhB under UV and VIS light irradiation, respectively.

Acknowledgments

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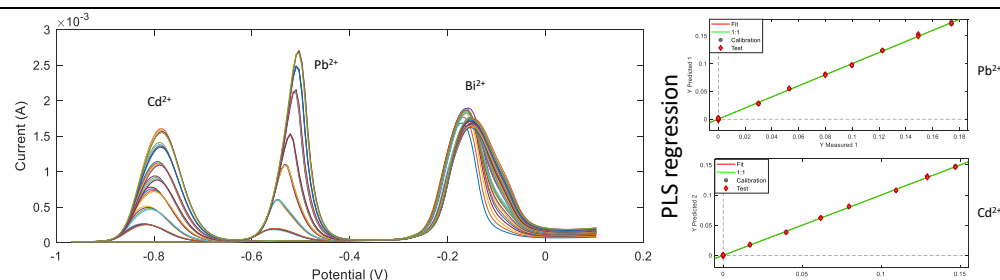
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A full optimisation of the anodic stripping voltammetric determination of Pb and Cd in seawater using a rotating ring-disk electrode with an *in situ* Bi film

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The presence of heavy metals in marine environments is of general concern since they tend to accumulate in aquatic organisms [1,2].

These compounds are usually found at trace levels and, therefore, it is crucial to use techniques with very low limits of detection (LOD). In this sense, electrochemical techniques offer a suitable way for both qualitative and quantitative analysis of heavy metals with also very low LODs being reported [3,4]. Moreover, electrochemical techniques benefit from low initial investment cost, unnecessary dilution of high salinity samples and the potential of complete automation.

Pb and Cd are very commonly measured heavy metals due to their high toxicity. However, the methodology to measure them differs greatly amongst authors.

This work focusses on the optimisation of the determination of Pb and Cd by means of Anodic Stripping Voltammetry (ASV) using a glassy carbon/Pt rotating ring-disk electrode (RRDE) with an *in situ* formed bismuth film on the carbon surface.

Since the number of variables affecting these measurements is quite large, first a two-level factorial design was performed to study their effect. In summary, the variables that showed an effect were: rotation speed, step potential, frequency, and amplitude. Considering these variables, a central composite design was performed to obtain the response surfaces and optimise those variables. The optimisation was performed using both the signal values (area and height) and the relative standard deviation of the repeated measurements. To study the combined responses, the Origin 2023

software (OriginLab Corporation, Northampton, MA, USA) was used. Results showed a straight correlation between the signal and the RSD of the repeated measurements, meaning that the higher the signal the higher RSD values were obtained. Therefore, a compromise had to be made between those two responses.

Although simple univariate regressions are typically used for metal quantification employing the peak areas or heights, this work studied the use of the full voltammogram as a signal, exploring the possible advantages of multivariate data analysis. Finally, since RRDE has two different working electrodes (glassy carbon and Pt, in this case), data fusion strategies were studied to see if lower LODs could be reached.

Acknowledgements

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Unravelling the Influence of Magnetite Nanoparticle Morphology on the Efficient Removal of As(III) and As(V) in Water Treatment Processes

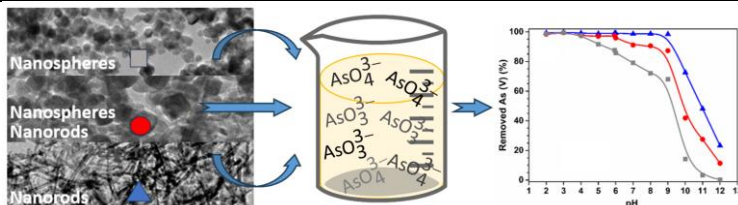
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The treatment and purification processes of waste and drinking water play a crucial role in economic development and in the preservation and enhancement of health and the environment. It is imperative to explore diverse technologies in water treatment. The advent of nanotechnology has introduced a novel realm of research focused on detecting and eliminating water pollutants through innovative procedures utilizing nanomaterials [1,2].

We are developing nanoplatforms for various applications, including their use in electrochemical sensors for pollutant detection (e.g., [1,2]), electrocatalysis applications (e.g., [1,2]), as magnetic sorbents (e.g., [3]), and in catalytic processes for the degradation of emerging organic contaminants (EOCs) utilizing advanced oxidation processes (AOPs) in a magnetic field (work in progress).

Using nanoplatforms based on magnetite (Fe_3O_4) makes possible their magnetic separation, recycling, and reuse due to their magnetic nature. Using the precipitation method in a microwave field, we synthesized magnetic nanoparticles based on magnetite. The synthesized Fe_3O_4 nanoparticles display a pseudospherical shape. However, introducing yttrium into the magnetite structure through partial substitution of iron ($\text{Fe}_{2.958}\text{Y}_{0.042}\text{O}_4$) induces morphological heterogeneity. Specifically, nanorods emerge alongside a broader distribution of pseudospherical nanoparticles. With an increased concentration of yttrium ($\text{Fe}_{2.916}\text{Y}_{0.084}\text{O}_4$), the presence of nanorods becomes more pronounced, leading to the formation of aggregates of pseudospherical nanoparticles. In all produced samples, porosity is evident, with pore diameters predominantly falling within the mesopore range [3].

Our work was focused on tailoring magnetite-based sorbents for the efficient removal of inorganic arsenic(III) and arsenic(V) from water. The introduction of Y^{3+} in Fe_3O_4 nanoparticles ($\text{Y}:\text{Fe}_3\text{O}_4$) significantly enhances their adsorption capacity for As(V), broadens the optimal pH range for maximum As(V) removal, and reduces the contact time required for such removal. The study explores the affinity of $\text{Y}:\text{Fe}_3\text{O}_4$ for adsorbing inorganic arsenic species, revealing that increased Y^{3+} content correlates with changes in sample morphology, leading to decreased efficiency in As(III) removal and enhanced efficiency for removal As(V) [3].

$\text{Co}:\text{Fe}_3\text{O}_4$ is being investigated for use as a self-heating heterogeneous nanocatalyst for the degradation of Emerging Organic Contaminants (EOCs) in alternating magnetic fields (AMF). XPS studies indicate the presence of catalytically active centres $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ on the nanoparticle surface, which could be remotely activated by AMF for the degradation of EOCs (work in progress). The specific loss power (SLP) value was approximately 50 W/g ($H_{AC} = 15.91$ kA/m and $f = 252$ kHz), making the sample potentially suitable as a heating agent in the application of magnetic hyperthermia in catalysis.

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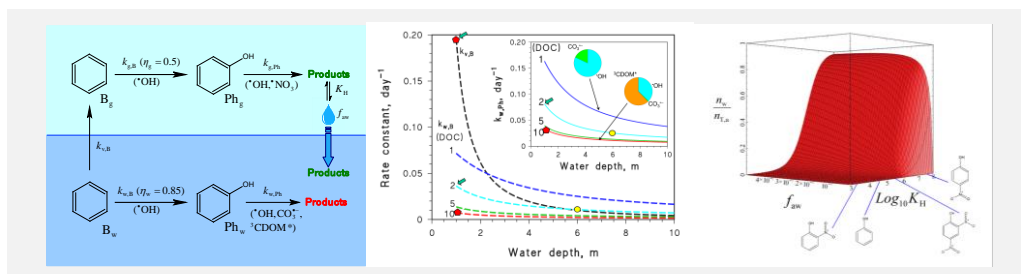
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Photochemical Fate of Polystyrene Photodegradation Products in the Environment: The Case of Benzene and Phenol in a Two-Compartment Scenario

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Micro- and nanoplastic particles are a considerable emerging problem in the environment, because their small size facilitates interaction with living organisms with harmful effects. Exposure of water-suspended plastics to sunlight may cause fragmentation, which is a source of microplastics and nanoplastics, but it may also induce formation of dissolved compounds [1]. The latter phenomenon is interesting because it could end up in eventual removal of plastic particles from environmental waters, thus its details deserve investigation. We have previously shown that exposure of polystyrene aqueous suspensions to sunlight produces a range of aromatic and aliphatic compounds that could derive either from the polymer skeleton, or from additives and plasticisers [2]. This presentation will introduce an approach to predict the fate of two toxic/carcinogenic photodegradation products of polystyrene, i.e., benzene and phenol, using a two-compartment model that considers both surface waters and the atmosphere.

Most benzene produced by irradiation of aqueous polystyrene would end up in the gas phase, where it would react with the hydroxyl radical (•OH); phenol is the main product of the reaction between benzene and •OH in both water and air. In water, phenol would mainly react with the triplet states of chromophoric dissolved organic matter (³CDOM*) [3]. In the gas phase, the main removal pathways of phenol would be reaction with •OH in daytime and with the nitrate radical (•NO₃) during the night [4].

The reaction between phenol and •NO₃ yields nitrophenols, which can undergo partitioning to atmospheric waters (e.g., cloud water), whence they could reach surface-water environments by precipitation (especially, 4-nitrophenol and 2,4-dinitrophenol). This scenario was modelled by considering a gas-water partitioning equilibrium, as described by the Henry's law constants (K_H) and by the volume fraction of liquid water in the atmosphere (f_w = 5 × 10⁻⁷) [4].

We could thus model the time evolution of aqueous phenol from benzene + •OH_(w), followed by phenol degradation with ³CDOM*_(w), as well as phenol formation in the gas phase followed by liquid-water partitioning and precipitation of its transformation products.

Acknowledgements

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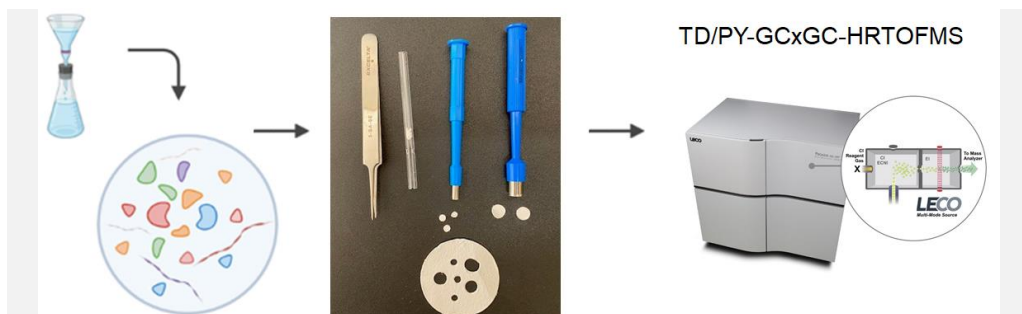
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Comprehensive Analysis of Micro-And Nanoplastics Using High-Resolution Mass Spectrometry With Enhanced Chromatographic Resolution

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Plastic production started early in the 20th century and has dramatically changed the materials we use every day. Enormous quantities of plastics are produced globally each year. These materials can be tailor-made for specific applications by adjusting their composition to increase strength, durability, etc. Breakdown products of plastic waste, micro- (Diameter 100 nm – 5 mm) and nanoplastic (Diameter < 100 nm) are of particular concern because of the ease of their distribution in the environment. These materials result from the breakdown of larger plastic particles such as fibers from synthetic fabrics in washing machines, detergent pods, and microbeads in personal care products. Micro- and nanoplastics are ubiquitous, and chronic exposure via inhalation or ingestion can be detrimental to human health. This is compounded by the fact that persistent pollutants can adsorb these materials and cause further harm.

The goal of this study was to identify micro- and nanoplastics in the environment, as well as characterize adsorbed persistent organic pollutants (POPs) associated with these dangerous materials. Unfortunately, the characterization of these pollutants is challenging due to their chemical diversity and trace concentrations in complex plastic samples. Many POPs are present in different forms (i.e., congeners, structural isomers, and stereoisomers). Furthermore, analysis by conventional GC-MS or LC-MS methods is hampered by overlapping chromatographic peaks and isobaric interferences. In this study, we

implemented the use of thermal desorption and pyrolysis to identify adsorbed compounds, as well as characterize the plastic materials. Sample analyses were carried out in two steps: 1) Thermal desorption followed by 2) pyrolysis with chromatographic separation and detection using comprehensive two-dimensional gas chromatography, a novel ionization source, and high-resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS). The enhanced chromatographic resolution and high resolving power of the HRTOFMS minimized sample component coelutions and isobaric interferences.

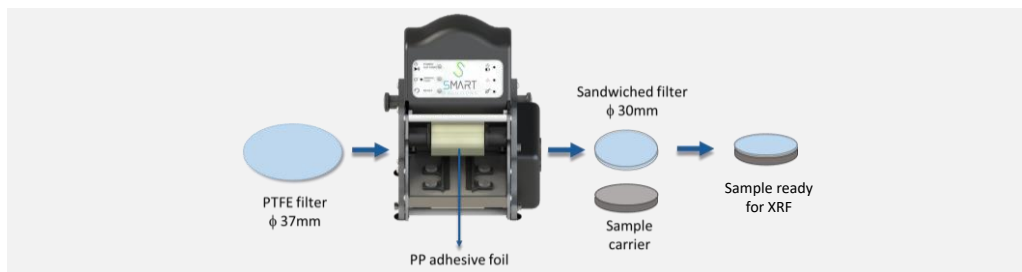
The technology resulted in comprehensive data with exceptional peak alignment between ionization modes, better S/N, and an increase in the total number of compounds identified. Electron Ionization (EI) data were utilized to identify compounds through untargeted processing which consisted of spectral similarity searches of large databases, and formula determinations from molecular, adduct, and fragment ions. Positive Chemical Ionization (PCI) and Electron Capture Negative Ionization (ECNI) spectra provided complementary molecular formula information to increase confidence in compound annotation. Advanced software tools allowed for both untargeted data processing as well as retrospective targeted analysis of the comprehensive data. The analyses resulted in the identification of polymers and annotation of adsorbed materials such as aromatics, polyaromatics, and bisphenols.

Calibration Samples for Heavy Metals Quantification in Particulate Matter by X-Ray Fluorescence Under Grazing Incidence

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The consequences of air pollution are extensive, affecting not only people's cardiovascular and respiratory system but also degrading the environment, impacting biodiversity, and causing climate change. Despite a decrease in the emissions of particulate matter (PM) of around 30% from 2000 to 2021 in Europe, air pollution is still a major health concern for people [1]. To further decrease the emissions of PM, the identification of its sources and composition of is of great importance.

Recent studies demonstrated that it is possible to determine the elemental composition of PM thanks to the analysis of air filters using Total reflection X-ray fluorescence (XRF) spectrometers [2, 3]. Air filters that collect PM can be effectively analysed using TXRF spectrometers, provided they undergo a suitable preparation procedure such as the Smart Store[®] method. This procedure consists in enclosing the filter between two polymeric foils, to avoid contaminations and to preserve the sample. Quantitative analysis is performed applying the external calibration approach, based on the analysis of reference materials, which are currently almost non-existent in the case of PM filters.

Therefore, calibration samples that can be employed as reference materials for PM filters were realized nebulizing a solution of known elemental concentration with a particle generator and collecting the obtained aerosol onto a filter. The concentration range of the calibration samples was selected considering the limits imposed by the European Commission (EC) for the protection of health in the two Air Quality Directives (2004/107/EC, 2008/50/EC). Samples were

analysed with several X-ray based instrument, to perform a complete characterization.

The presented results prove the applicability of the direct analysis of air filters with TXRF techniques for air quality monitoring purposes. In addition, it is demonstrated that the realized calibration samples are suitable to develop calibration curves for the quantification of PM elemental content by means of all the XRF based spectrometries in a faster, cheaper, easier, and more sustainable way than conventional methods, proposing a green alternative for air quality monitoring. The data obtained in this study were used to support the proposed analytical approach to the International Standard Organization (ISO) as part of the project 23971, entitled "Analysis of Air PM Filters by XRF under Grazing Incidence".

Acknowledgements

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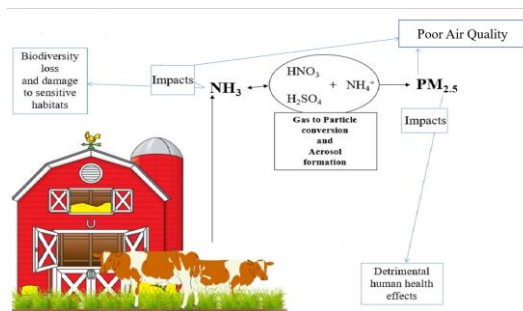
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Impact of Agricultural Emissions on Rural and Urban Air Quality (IMAGE)

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Air quality is of paramount importance to human health. This is recognised by numerous agencies, most notably the World Health Organisation. Adverse health impacts result from air pollutants, many of which are linked with anthropogenic/agricultural activity, including particulate matter (PM), nitrogen oxides (NO_x) and ammonia (NH₃). These pollutants also lead to the secondary formation of deleterious compounds and aerosols following emissions. PM can be broken down into size fractions, with the terms PM_{2.5} and PM₁₀ (referring to PM smaller than 2.5 and 10 microns respectively) generally used in monitoring. PM can also be defined by the pathway it enters the air, with primary PM being directly released to the atmosphere and secondary PM being formed in the atmosphere through chemical processing of precursor gases. In this regard the contribution of NH₃ to the PM_{2.5} fraction through secondary aerosol formation is under-researched in an Irish context.

NH₃ emission is a key challenge to agricultural expansion in Ireland. By the end of 2018, total cattle numbers were approx. 6.6 million, the number of pigs were approaching 1.6 million, and the number of poultry stands were around 11 million [1]. Ireland is committed to the EU National Emissions Ceilings Directive (2016/2284/EU), which sets emission reduction targets for air pollutants such as NO_x, non-methane volatile organic compounds (NMVOCs), sulphur dioxide, NH₃ and PM_{2.5}, contributing to poor air quality. Ireland has been exceeding NH₃ emissions ceilings since 2016 and is obliged to reduce NH₃ emissions by 1% per year compared to 2005 levels

until 2029 and 5% annually thereafter. Similarly, PM_{2.5} is to be reduced by 18% compared to 2005 levels until 2029 and 41% annually thereafter [2]. A reduction in NH₃ would also lead to reduction in ambient PM_{2.5} levels. The health and environmental concerns associated with PM means it is of the utmost importance to understand its formation, concentration, composition, and size regime in various environmental settings. This is the main motivation for the work presented here. IMAGE will determine the concentrations of both PM_{2.5} and NH₃ at various sites within Ireland. This will be undertaken via the combination of offline chemical and biological analysis of collected filter samples and real-time PM and bioaerosol concentration determination of the fine and coarse fraction of PM. This multi/interdisciplinary work, evaluating ambient environment will provide information of both primary emissions of PM and secondary formation from precursors such as NH₃. Determination of primary sources of PM_{2.5} will greatly aid in the deconvolution of the secondary fraction of PM_{2.5}.

Acknowledgements

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Airborne Microplastic Particle Concentrations and Inhalation Exposure

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Environmental pollution from microplastics (MP) in air is a matter of growing concern because of human health implications. Airborne MP can be directly and continuously inhaled. Especially high MP contributions can be found in indoor air due to the erosion and breakage of consumer, domestic and construction materials. Apart from this source of MP, during the COVID-19 pandemic, the use of face masks has been a worldwide primary protection measure to contain the spread of the virus. However, very little information is known about the relationship between the possible inhalation of MP from wearing masks.

According to our previous research where we found high MP concentrations in different indoor microenvironments [1], a pilot study was performed to evaluate the presence of MP accumulated in nostrils from face masks through the nasal lavages technique. Although different techniques could be used to estimate emissions from masks (e.g., breathing simulation experiments), a simple approach as nasal lavages proved to be a useful tool in this context [2]. Six different commercial face masks were evaluated in 18 participants during five working days (8h use/day).

In total, microplastics were found in 100% of the volunteers using Fourier Transform Infrared Spectroscopy (FTIR). The average number of microplastics found in the nostrils of each individual was 24.0 ± 17.0 MP/5 mL nasal solution. Eight different polymers were found in the samples. Polystyrene (PS) was the most frequent one (36.3%), followed by polyamide (PA) (23.0%), poly(ethylene – propylene) diene monomer

(EPDM) (16.9%), polyester (PES) (12.4%), polyethylene (PE) (5.5%), polyvinylidene fluoride (PVDF) (5.2%), polypropylene (1.2%), and polyvinyl chloride (PVC) (0.5%). PS was the only polymer detected in all the samples. The identification of EPDM, a copolymer used as a component of natural and synthetic rubber, probably indicates the contribution from the non-exhaust traffic-derived particles originated from tyre, brake, and road wear. PDFV was only present in participants who wore a specific facial mask. PVDF charged nanofiber filters have been developed to enhance capture efficiency in the masks because of the COVID-19 virus small size (60 nm). However, the relatively small amounts of PP found in the samples could indicate that masks are not a considerable source of MP.

Although there is not a clear correlation between wearing face masks during the investigation and the concentration of MP found in the participants, other sources of inhalable MP have been detected (e.g., textiles, non-exhaust emissions).

Acknowledgements

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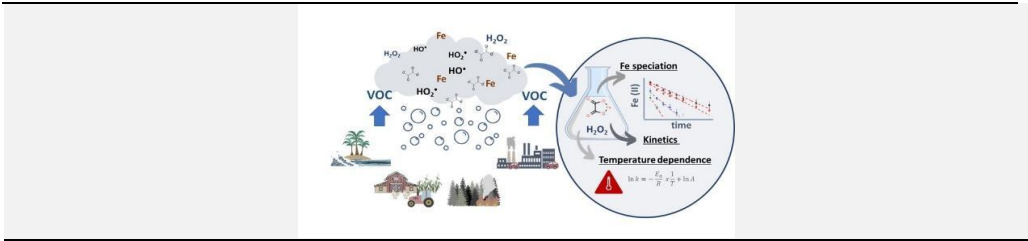
Temperature Dependency of Fenton and Fenton-like Reactions in the Presence of Oxalate – Implications to Atmospheric Particle Aqueous Phase Chemistry

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Due to the presence of Fe and peroxides, Fenton reactions have demonstrated importance in the hydroxyl radical budget in the aqueous particle phase [1]. The temperature dependence of Fenton rate constants has been investigated since 1934, when Haber and Weiss first proposed the mechanisms of hydroxyl radical formation [2].

The monitoring of the Fe conversion has been conventionally used to investigate rate constants of Fenton reactions, which have been determined to be dependent on the Fe speciation, and therefore, pH-independent in the pH range from 1 to 5 in the absence of Fe ligands [3]. Several observations of increased rate constants are reported in the presence of ligands [4,5], but Arrhenius plots have not been frequently derived. Herein, we have investigated the temperature dependence of the Fenton-like reaction in the presence of oxalic acid ($\text{FeC}_2\text{O}_4 + \text{H}_2\text{O}_2$), a ligand found in high concentrations in the aqueous particle phase. Figure 1 compares Arrhenius plots found in the literature [2,6] and the results obtained in this work. Estimated thermochemical parameters are shown in Table 1.

Differences in the slopes were minimal among the different studies, demonstrating the enthalpy values (ΔH^\ddagger) are well-established for Fenton reactions. Slight differences in the entropic term (ΔS^\ddagger) among the Fenton investigations result from the different methods applied. However, the enormous difference observed in the presence of FeC_2O_4 demonstrates that the coordination environment of Fe increases the entropic term for Fenton-like reactions, increasing the overall reaction rate constant.

Table 1. Thermochemical parameters for Fenton and Fenton-like reactions in the presence of FeC_2O_4 .

	Fe^{2+}	FeC_2O_4
E_a (kJ/mol)	38 ± 5	54 ± 10
A (1/M s)	$(4.4 \pm 0.6) 10^8$	$(8.4 \pm 1.2) 10^{12}$
ΔH^\ddagger (kJ/mol)	36 ± 5	52 ± 10
ΔS^\ddagger (J/K mol)	-87 ± 9	-6.0 ± 0.8

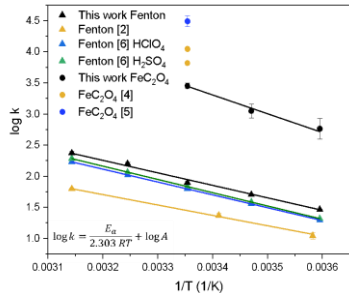


Figure 1. Linearized Arrhenius plots of Fenton and Fenton-like in comparison to literature values (equation shown in the graph).

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Levogluconan In Biomass Combustion Products

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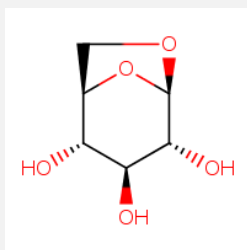
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Emissions from biomass combustion impact global climate and human health. Combustion of biomass is an important source of smoke aerosol and ashes, the composition of which includes water-soluble substances of inorganic and organic origin, including levoglucosan. Levoglucosan is considered a good chemical marker of biomass burning that leads to the creation of environmental pollution, especially because its presence can be proven in air, soils and water. The aim of this study was to measure the content of levoglucosan after different wood biomass combustion, by using a GC-MS method. Results showed a variation in the content of levoglucosan after combustion of different wood biomass used in Bosnian rural households. Furthermore, factors governing emissions from wood stoves (as the typical appliance used in residential heating) are evaluated.

Key words: levoglucosan, wood biomass, GC-MS method.

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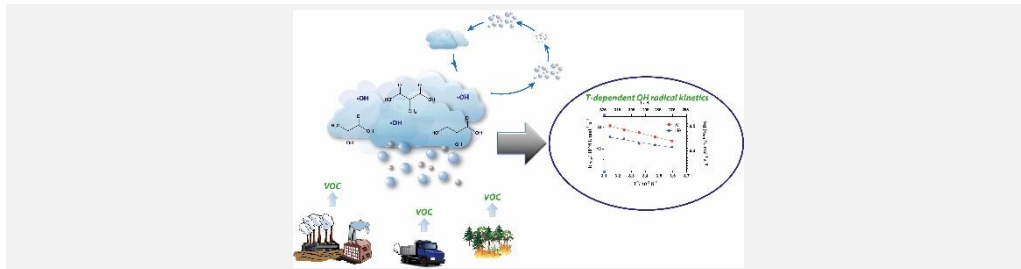
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T- and pH-dependent OH Radical Kinetics of Lactic Acid, Glyceric Acid and Methylmalonic Acid in the Aqueous Phase

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Carboxylic acids are a common class of compounds found in atmospheric aerosols and cloud droplets[1]. These originate from atmospheric decomposition and transformation of volatile and semi-volatile organic compounds (VOCs). Both anthropogenic or biogenic sources emit VOCs into the atmosphere [2]. VOC decomposition reactions are often initiated by gas-phase radical reactions where oxidation results in an increase in water solubility of oxidation products, such as carboxylic acids. In addition, the oxidation products also contribute to the formation of secondary aerosols (SOA) and to an increase in the hygroscopicity of the aerosols [3]. In this study, the kinetics of oxidation of several carboxylic acids in the aqueous phase (cloud droplets, fog, rain or hygroscopic particles) with the atmospherically important OH radical were investigated. The rate constants of the OH radicals were determined by applying the thiocyanate competition kinetics method with the laser flash photolysis-laser long path absorption (LFP-LLPA) technique as a function of temperature and pH [4].

The following carboxylic acids were studied: Lactic acid, glyceric acid, and methylmalonic acid. The Arrhenius equations are as follows (unit in L mol⁻¹ s⁻¹): Lactic acid: $k(T, HA) = (1.26 \pm 0.04) \times 10^{10} \times \exp[(-910 \pm 160 \text{ K})/T]$ and $k(T, A^-) = (1.26 \pm 0.02) \times 10^{10} \times \exp[(-800 \pm 80 \text{ K})/T]$, glyceric acid: $k(T, HA) = (5.95 \pm 0.17) \times 10^{10} \times \exp[(-1100 \pm 170 \text{ K})/T]$ and $k(T, A^-) = (3.58 \pm 0.06) \times 10^{11} \times \exp[(-1500 \pm 100 \text{ K})/T]$ and methylmalonic acid: $k(T, H_2A) = (5.49 \pm 0.97) \times 10^{10} \times \exp[(-1750 \pm 100 \text{ K})/T]$, $k(T, HA^-) = (1.37 \pm 0.02) \times 10^9 \times \exp[(-530 \pm 80 \text{ K})/T]$ and $k(T, A^{2-}) = (9.58 \pm 0.42)$

$\times 10^{10} \times \exp[(1500 \pm 270 \text{ K})/T]$. The general trend of the OH rate constant was obtained $k(A^{2-}) > k(HA^-) > k(H_2A)$.

The energy barriers of the OH radical reaction and thus the most probable position of H-atom abstraction were also calculated with density functional theory (DFT) simulations in GAUSSIAN using the M06-2X method and the 6-311++G(3df,2p) basis set. These simulations show that the protonation and deprotonation of the carboxylic acid group causes a significant change in the Gibbs energy barrier, which corresponds to the change in reactivity. The oxidation of organics by OH radicals acts as a sink process in the aqueous phase, and pH- and T-dependent rate constants of OH radical reactions allow a better description of the degradation of carboxylic acids. Furthermore, the kinetic experimental findings can be implemented in the chemical radical mechanisms (e.g. CAPRAM) to improve the predictive capabilities of the models and the impact on the oxidation capacity of the tropospheric aqueous phase.

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TOPIC 4

SUSTAINABLE DEVELOPMENT



The Urban Water Cycle and Its Modifications Through Time: Diachronic Approach Based on Strontium Isotopes Study of Perched Aquifer Waters and Calcareous Deposits in Paris, France

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Knowledge of the urban water cycle and its evolution through urban development is important to take into account from a sustainable development perspective.

This is the main objective of the Huniwers project, funded by the French National Research Agency (ANR). We have developed a combined study of present-day perched aquifer water (quality and quantity), and of past water quality by analyzing urban secondary calcareous deposits (USCDs) formed by past water.

In a previous study, we showed that sulfur pollution of water is due to the use of gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) from former quarries as backfill during urbanization process. We have also shown that in the north of Paris, near the Grand Aqueduc of Belleville, this sulfur pollution began in the mid-1800s when the area was urbanized. [1].

In the new phase of the project presented here, we tested the use of strontium isotopes to track urbanization and help provide chronological constraints for undated USCDs. To do this, we first worked on a chronologically well-constrained USCD and identified that the increase in sulfur is contemporaneous with a change in Sr isotopic composition.

The change in Sr isotopic composition is due to the contribution of Sr from gypsum (independently identified signature).

We discuss this Sr isotopic signature in present-day water at several sampling points in the aquifer

and discuss its variation as a function of recharge and the possible impact of gypsum dissolution.

Secondly, we use Sr isotopic composition in USCDs of unknown age (USCDs whose detrital content is too high to be dated by the uranium-thorium method) to chronologically calibrate them according to the urbanization stage.

This correlation-dated USCD can then be used to discuss temporal variations in heavy metals and rare earths contents.

Acknowledgements

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Sustainable Food Protein and Water Purification Processes using Ionic and Porous Material Systems

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Sustainable development Goals from Agenda 2030 (SDG2030) are relevant for the future of modern societies [1]. In this context, sustainable FOOD and WATER RESOURCES are very important goals according the associated climate and continuous growth of the world population.

Nowadays, the possibility to find protein valorisation processes to be incorporate as ingredients for alternative food products is a great challenge. Ionic Liquids as organic salts with low melting points possessing peculiar physical and chemical properties and significant interest for extraction and separation applications [2]. In addition, DES as innovative materials prepared by suitable combination of hydrogen bond donors (HBD) and acceptors (HBA) have been reported for several applications [3]. Water resources are the main vehicle for the environmental dispersion of chemical pollutants [4]. Consequently, the discovery of efficient and sustainable processes for purification of the contaminants from water is highly required. Different strategies for removal of pollutants from water streams have been described including liquid-liquid extraction and adsorption processes. Hydrophobic Ionic Liquids (ILs) or deep eutectic solvents (DES) are tested for this kind of approach. Additionally, porous materials such as activated carbon, zeolites, Metal Organic frameworks (MOFs) and Covalent Organic frameworks (COFs) are considered suitable adsorbents for water purification systems.

Herein, we presented two development sustainable approaches:

1) **PROTEIN FOOD (Goals 1&2):** The extraction, separation and purification of food protein from *Tenebrio molitor* (larvae) can be performed using biocompatible ionic liquids and deep eutectic solvents as alternative solvents.

2) **WATER (Goal 6):** Hydrophobic ILs and DES for liquid-liquid extractions [5] and COFs as porous materials for adsorption of contaminants from water streams [6]. Several organic and metal contaminants based on antibiotics, pesticides, plastic additives and heavy or critical metals have been selected. The optimized analytical methodology involved the quantification of contaminants in water phase by UPLC-DAD, UPLC-MS/MS and ICP-AES.

Acknowledgements

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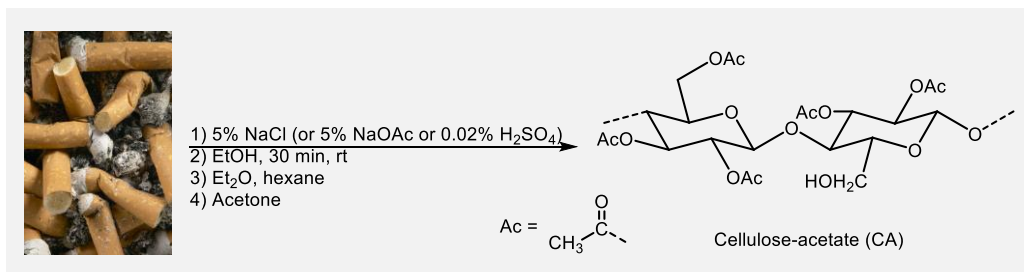
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Removal of Heavy Metals from Cigarette Butts in Different Ways and Their Recycling

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Smoking is one of the biggest problems of today, and the waste that is created on that occasion (butts) are one of the most common types of frequent and used toxic waste all around the world. Smoking is a major risk factor for human health (diseases of the cardiovascular system, high blood pressure and carcinogenic diseases). It has been reported that about 130 chemicals of organic and inorganic origin 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. Some of such substances are: benzopyrene, arsenic, acetone, toluene, formaldehyde, phenol, nicotine, benzene, cadmium etc. Some of these substances are natural ingredients of tobacco and some are formed during its combustion. The main ingredient of butts (95%) is cellulose acetate (CA). 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. The aim of our work is to recycle cellulose acetate from tobacco waste as well as the release of this polymer from heavy metals. In that way, we would remove hazardous waste from the environment.

In this regard, a measured mass of 20 cigarettes is treated with aqueous solutions of one of the following chemicals: 5% sodium chloride, 5% sodium acetate or 0.02% sulfuric acid, at room temperature for half an hour. The separated

aqueous extracts are collected, the largest part of the water is evaporated in a water bath, and the content of heavy metals is analyzed in the rest. 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. As far as the content of heavy metals in the water extracts is concerned, it is very comparable in all three cases, so we conclude that most of the heavy metals can be removed by using any of the mentioned water solutions.

Acknowledgements

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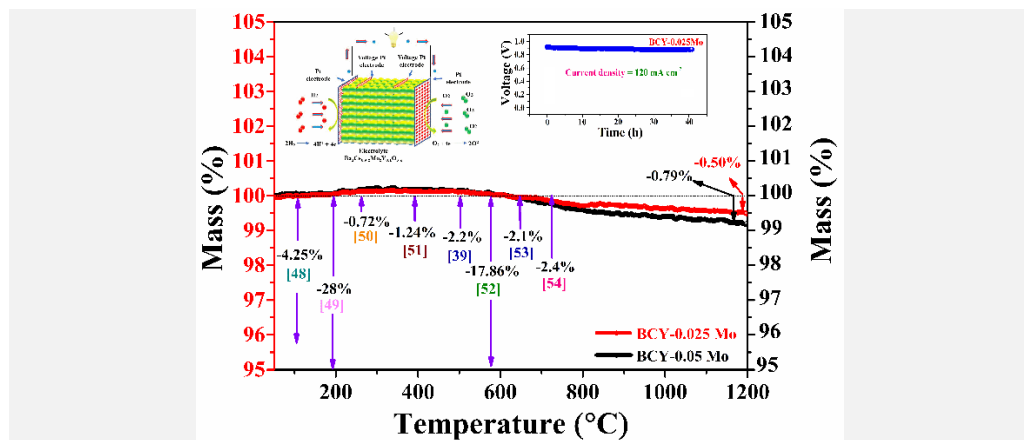
Effect of Mo-doping on Proton-Conducting $\text{Ba}_1\text{Ce}_{0.9-x}\text{Mo}_x\text{Y}_{0.1}\text{O}_{3-\delta}$ Electrolyte at Intermediate Temperature SOFCs

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Introduction

Perovskites have been attracting much attention because of their many potential applications as electrolytes in solid oxide fuel cells (SOFC). Among them the $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCY) have been investigated extensively due to its good stability and high protonic conductivity. However, the sintering temperature of BCY is above 1600 °C to achieve the required densification. High sintering temperature leads to evaporation of barium and the subsequent segregation of doped elements. So, in order to overcome this issue, we doped Mo- to BCY and reduce the sintering temperature of the electrolyte without compromising its performance [1-4].

Abstract

Researchers' interest in proton-conducting reversible solid oxide cells (RSOCs) is growing due to their distinct benefits. In the present work, single-phase $\text{BaCe}_{0.9-x}\text{Mo}_x\text{Y}_{0.1}\text{O}_{3-\delta}$ ($x = 0, 0.025, 0.05, 0.1, 0.2$) electrolyte is prepared via sol-gel method and sintered at 1400 °C for 10 h. Optimal density, structure, composition, electrochemical performance, and thermal stability are confirmed via SEM, XRD, EDS, XPS, FTIR, EIS, and TGA/DSC. The conductivity of the grain interior

and boundaries between 127–727 °C is reported for the first time in SOFC studies. The $\text{BaCe}_{0.875}\text{Mo}_{0.025}\text{Y}_{0.1}\text{O}_{3-\delta}$ sample shows a grain interior conductivity of $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at 707 °C with grain interior activation energy of 0.75 eV (127–727 °C), and a grain boundary activation energy of 0.85 eV (380–727 °C), 0.43 eV (167–357 °C) in air atmosphere, respectively. $\text{BaCe}_{0.875}\text{Mo}_{0.025}\text{Y}_{0.1}\text{O}_{3-\delta}$ showed extreme stability for 300 h, and thus can be considered suitable for an efficient protonic conductor at intermediate temperatures.

Acknowledgements

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Volatile Methylsiloxanes (VMSs) Profiles in Wastewater Originated from Different Sources

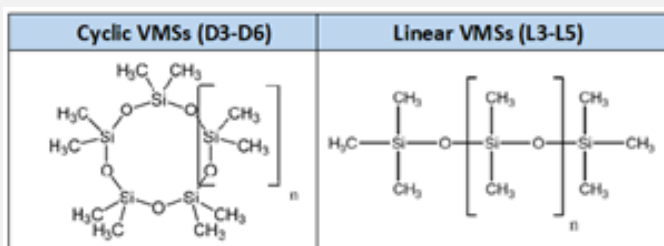
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Volatile methylsiloxanes (VMSs) are synthetic organosilicon compounds. Based on the structure, VMSs can be divided into two major groups, linear (lVMSs) and cyclic (cVMSs) [1]. Due to their interesting properties (e.g., low surface tension, high thermal stability, low water solubility), they are widely used in the manufacture of innumerable types of products such as cosmetics, medical devices and electronics [2].

This work focused on the analysis of 7 VMSs (L3-L5 and D3-D6) in wastewater collected from four different sources that were forwarded to a WWTP in Portugal. Most literature revolved around the analysis of influent and/or final effluent of the WWTPs, rather than contrasting the different wastewater sources that reach at the WWTP entrance, to identify the main routes of contamination. Not only did the stipulated approach allow the evaluation of similitude of VMSs levels, relatively to wastewaters from other countries, but also fathom possible sources of contamination. A long monitoring period was selected, to include the four seasons. Several consecutive days were contemplated, to try to pin down trends in the concentrations. Finally, a risk assessment was conducted. Considering the combination of the 4 Entrances in a single input and considering a direct discharge without any treatment, 4 samples (14%) exhibited high risk, mainly due to the presence of D5, while the other

24 samples (86%) demonstrated medium risk. Thus, in cases with direct discharge without any treatment, a risk to the environment may occur.

Acknowledgements

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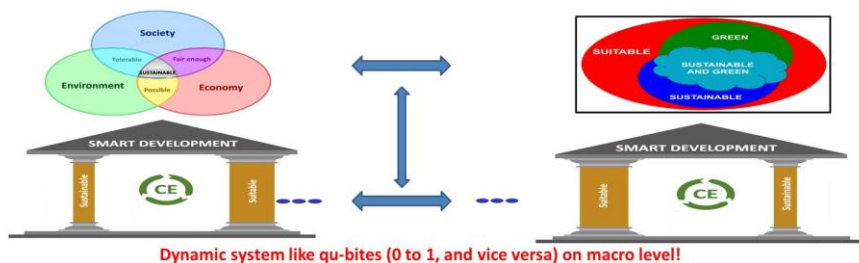
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From Sustainable, Through Suitable to Smart Development

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Sustainable development forms the foundational block, emphasizing the importance of minimizing environmental impacts, conserving resources, and safeguarding ecosystem integrity. Environmental chemistry plays a pivotal role in this stage, providing the analytical tools and methodologies needed to assess environmental contamination, understand chemical processes in natural systems, and devise eco-friendly materials and practices. Green chemistry principles underpin this approach, reducing the environmental footprint through the design of less hazardous chemicals and cleaner production processes [1].

The transition through suitable development represents the next step in this evolution. It acknowledges the need for practical solutions that can be seamlessly integrated into modern society. Environmental chemistry continues to contribute by developing convenient and efficient technologies for pollution control, waste management, and sustainable energy sources. It explores catalytic and adsorption processes, nanomaterials, and emerging technologies such as bioremediation [2].

Ultimately, the journey culminates in smart development. Smart development leverages technology and big data to optimize resource management, enhance monitoring and remediation strategies, and develop predictive models for environmental changes. Advanced analytical techniques, such as different instrumental methods and, e.g. environmental sensors, allow for real-time data acquisition, creating a more connected and responsive approach to environmental issues [3].

In conclusion, smart development is a holistic approach encompassing the evolution of all impacts, not only environmental chemistry's, which contribute to real development. It underscores the importance of minimizing environmental impact, adapting to the needs in future of environment, society and economy. Environmental chemistry, with its green analytical and innovative capabilities, remains at the forefront of this transformation, including circular economy, providing the necessary tools and insights for a cleaner, greener world.

Our concept of smart development as a dynamic system that includes risk assessment and management gives hope for a happier future, especially to the most vulnerable groups. Considering the crisis in which sustainable development and the 2030 agenda have evidently fallen, it is to be expected that this approach is one of the possibilities for further progress. It is inevitable that AI will contribute to the acceleration of smart development [4].

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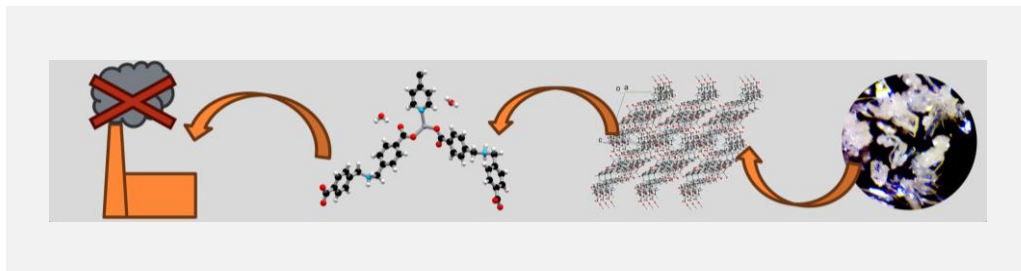
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Synthesis and Structure of New Polymeric Zn(II) Complex with Bis(4-carboxybenzyl)ammonium chloride and trans-1,2-bis(4-pyridyl)ethene as Building Blocks of Potential Network Materials

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One of the most significant challenges of today is achieving energy efficiency in the purification and storage of carbon dioxide, with the aim of its long-term storage and later use as a starting material or fuel [1]. The results of our previous research have shown that suitable adsorbents for carbon dioxide could be three-periodic coordination polymers, but also those of lower periodicity [2, 3].

Among them, zinc-based complexes offer numerous advantages and could expand their applications significantly. Zinc is an essential trace metal, and because of its low toxicity, its coordination polymers are promising candidates for use in biological systems [4]. Furthermore, the environmentally friendly properties of these compounds, along with their cost-effectiveness, make them suitable for treating polluted water [5].

Considering all the above mentioned, the synthesis and structural characterization of new zinc-based coordination polymers is of high interest.

The colorless block-shaped single crystals of the newly synthesized polymeric zinc complex were obtained in the reaction of zinc-nitrate, trans-1,2-bis(4-pyridyl)ethene, and bis(4-carboxybenzyl)ammonium chloride in the mixture of DMF and H₂O (2:1). The reactants underwent sonication for 1 minute and were then heated in Screw Neck Vial at 100 °C for one day.

The asymmetric unit comprises one zinc ion, two dicarboxylate ligands, one half of a dipyridyl co-ligand, and two water molecules. In this structure, the zinc ion is situated in a distorted tetrahedral environment, with three dicarboxylate ligands, two

of which serve as bridging ligands, coordinating in an exo-bidentate manner, and one as a monodentate ligand. The fourth coordination site is occupied by the co-ligand, which also coordinates in an exo-bidentate manner.

Selected crystallographic data and refinement details: C₃₈H₃₃N₃O₈Zn·1.333(H₂O), *P* $\bar{1}$, *a* = 9.6712(3) Å, *b* = 12.7926(5) Å, *c* = 14.7934(6) Å, α = 107.440(1)°, β = 96.137(1)°, γ = 93.012(1)°, *V* = 1729.18 (11) Å³, *Z* = 2, *R* = 6.8 %, for 478 parameters and 7905 independent reflections.

Acknowledgements

The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200125).

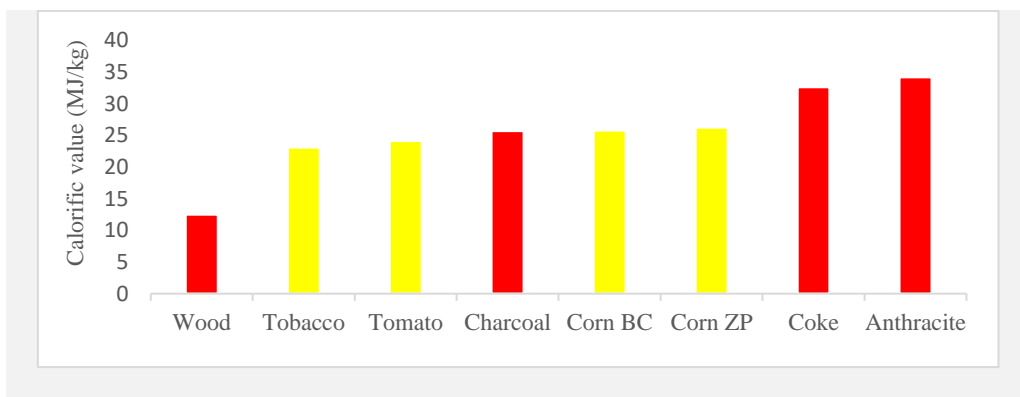
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Potential of Biochar as Fuel Obtained by Pyrolysis of Agricultural Waste

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Tomato, corn, and tobacco are some of the most grown and used plants in Serbia. The stalks remain after harvesting crops and do not have further use; thus, this waste is usually burned on the field. One possible reduction of waste is using it for pyrolysis processes. Pyrolysis products are solid residue (biochar), liquid fraction (bio-oil), and gaseous compounds. This study aimed to analyze solid residues obtained by pyrolysis of different agricultural residues and compare their fuel characteristics with widely used solid fuels such as wood, coal, coke, and charcoal [1].

In this research, pyrolysis took place at 400 °C and at a nitrogen flow of 70 ml/min in Carbolite, UK furnace, model MTF 10/15/130. Analyses performed on biochar were determination of ash content (ASTM D2584, ASTM D5630), calorific value (IKA C400, SRPS CEN/TS 16023:2014), ICP-OES analysis (Spectroblue TI; methods EPA M 200.7, sample preparation EPA M 3052/ISO 2598-1).

The calorific value is one of the most important fuel characteristics. The calorific value of biochars from tomato, tobacco, corn ZP6263, and corn BC398 is 24.12 MJ/kg, 23.09 MJ/kg, 26.24 MJ/kg,

and 25.78 MJ/kg, respectively. Regarding solid fuels, the calorific value of wood is 12.5 MJ/kg; for different types of coal, it can be from 13 MJ/kg to 36 MJ/kg; for coke, 32.6 MJ/kg and for charcoal, it is 25.7 MJ/kg [2]. It is obvious that the calorific values of biochar are close to the value of charcoal. The ash content of biochar is from 12 to 20 %, which aligns with the ash content of solid fuels. ICP-OES analysis of biochars showed the absence of heavy metals and high concentrations of Ca, K, Na, and Mg, which remain in ash.

Results obtained in this research lead to the conclusion that biochar produced by pyrolysis of tomato, tobacco, and corn stalks shows good potential for use as a solid fuel.

Acknowledgements

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Green Synthesis of Silver Nanoparticles and Its Potential Antitumor Effect on HCT-116 Human Colon Cancer Cell Line

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Silver nanoparticles (AgNP) have a wide range of applications due to their unique properties. Some common uses include catalysis, electronics, drug delivery, cancer therapy, antimicrobial agents, and food packing [1]. Due to the increasing demand and wider application of AgNP, many new methods for their synthesis are being developed. The synthesis of AgNP using plant extracts is a sustainable and environmentally friendly method that avoids the use of hazardous chemicals [2].

In this work, the aqueous extract of the aerial part of *Salvia verticillata* L. was used for green synthesis of silver nanoparticles as a potential antitumor agent to colon cancer cell lines (HCT-116). *S. verticillata* is mostly used in traditional medicine as an expectorant and to treat wounds. The synthesis of silver nanoparticles using *S. verticillata* extracts (SVAgNP) was performed from silver-nitrate under low temperature, using water as a solvent, and without the addition of any synthetic chemicals. Different instrumental techniques were used for SVAgNP characterization, and its determined average size was from 40 to 70 nm. Based on the results obtained by the MTT test, the highest applied concentration of SVAgNP (100 $\mu\text{g/mL}$) had a low influence on the viability of healthy lung fibroblast cells (MRC-5), while the treatment of HCT-116 cell lines with the same concentration of SVAgNP led to the significant reduction in cell viability (36.18% viability of cells after 72 h) [3]. The influence of SVAgNP on the migration capacity of HCT-116 cells was also monitored. Silver nanoparticles showed a significant antimigratory potential of HCT-116 cells, reducing their migratory ability after 24 h approximately 35%

compared to the untreated control cells. The influence of synthesized SVAgNP on matrix metalloproteinase 9 (MMP-9) concentration of HCT-116 cells was examined by ELISA test. Also, the quantitative PCR (qPCR) method was used for the determination of MMP-9 gene expression. Metalloproteinases, a group of extracellular enzymes, have a role in carcinogenesis, cancer invasion, and metastasis. The treatment of HCT-116 cells with SVAgNP in the concentration of 44.62 $\mu\text{g/mL}$ (IC_{50} in the MTT test) significantly reduced MMP-9 amount. Also, SVAgNP in the same concentration decreased the level of MMP-9 gene expression compared with the untreated cells by 45% after 24 h. The results suggest that AgNP synthesized according to the principles of green chemistry using *S. verticillata* extract possess different antitumor mechanisms on the HCT-116 human colon cancer cell line and have potential for further research as anticancer therapeutic.

Acknowledgements

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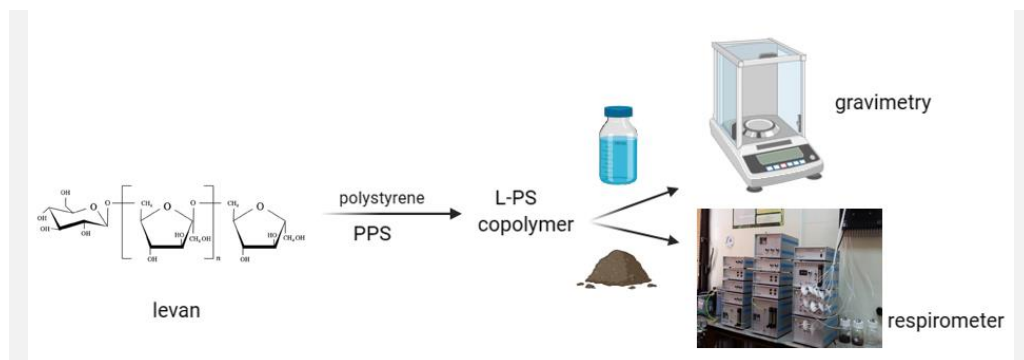
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Investigation of Biodegradability of Levan-Polystyrene Graft Copolymers in Liquid and Solid Medium

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One of the widely used plastic material is polystyrene (PS) due to its low cost, heat resistance and fitting to variety of applications, however it causes environmental concerns [1]. Graft copolymerization combines properties of the polymers involved obtaining specific and improved polymer materials [2].

Levan is a fructose-based polysaccharide that can be produced by various microorganisms, especially strains of *Bacillus*, *Geobacillus*, *Lactobacillus* and *Zymomonas* species. It is a biodegradable, non-toxic and highly biocompatible compound, and therefore suitable for development of novel materials [3].

In the present study graft copolymer with microbial levan and polystyrene was synthesized and its biodegradable potential in liquid and soil medium was investigated.

Levan was isolated using *Bacillus licheniformis* strain. Synthesis of copolymer was performed in nitrogen atmosphere by the free radical reaction using potassium persulfate (PPS) as initiator [4]. Biodegradation in liquid medium was performed in citrate buffer (pH 3.5) at 37 °C for 28 days and monitored by weight loss of copolymer. Soil burial test lasted 30 days with continuously measuring of

CO₂ production using Micro-Oxymax respirometer (Columbus Instruments, Ohio).

After 28 days in liquid medium 94 % of total mass of levan-polystyrene copolymer was lost. Cumulative production of CO₂ after respirometric measurements were higher in both levan and copolymer samples (696 and 626 mL, respectively) compared to control (156 mL) and polystyrene (146 mL).

Results of aerobic biodegradation in both liquid and solid medium shows that obtained graft copolymer of levan and polystyrene has biodegradation potential. However, additional tests for biodegradation are needed such as six-month soil burial test.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Contract numbers: 451-03-47/2023-01/200026, 451-03-47/2023-14/200168 and 451-03-47/2023-01/200288) for financial support.

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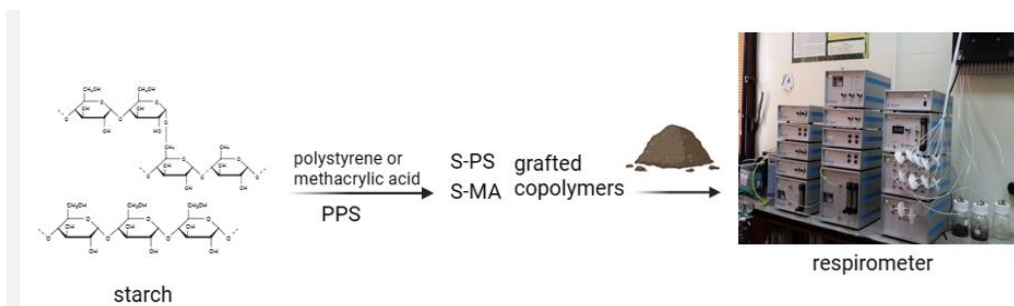
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Starch Copolymers with Enhanced Biodegradability

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Starch is a natural polymer that can be found in various cereal grains and it is mainly composed from two glucose polymer unit (amylose and amylopectin). Plasticized starch is biodegradable, but its applications are limited due to water solubility or leaching of the plasticizers. To overcome this, starch can be improved by physical, chemical, or enzymatic modifications [1]. Graft copolymerization of starch allows the construction of specific polymer architectures and at the same time can induce beneficial effects such as hydrophilicity, biocompatibility and biodegradability to materials. A more sustainable alternative to traditional, petroleum-based plastic materials is already developed and includes products such as biodegradable flatware, dishes, and thin films [2].

In the present study graft copolymers combining starch with polystyrene (S-PS) or methacrylic acid (S-MA) were synthesized and its biodegradable potential was investigated.

Syntheses of copolymers were performed by the free radical reaction using potassium persulfate (PPS) as initiator [3,4]. Biodegradation potential in soil aerobic conditions of the obtained copolymer was investigated using Micro-Oxymax respirometer (Columbus Instruments, Ohio). O₂

consumption and CO₂ production of samples mixed with soil were measured over 31 days.

Cumulative consumptions of O₂ after respirometric measurements were higher in both copolymer samples (S-PS – 689 mL, S-MA – 765 mL) compared to control (224 mL) and polystyrene (232 mL). Similar results were observed for the production of CO₂ (678 and 757 mL for S-PS and S-MA, respectively) and for control (199 mL) and polystyrene (202 mL).

Results after 31 days for soil aerobic biodegradation shows that obtained copolymers with starch have biodegradation potential and they are promising materials for developing more environmentally friendly products.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Contract numbers: 451-03-47/2023-01/200026, 451-03-47/2023-14/200168 and 451-03-47/2023-01/200288) for financial support.

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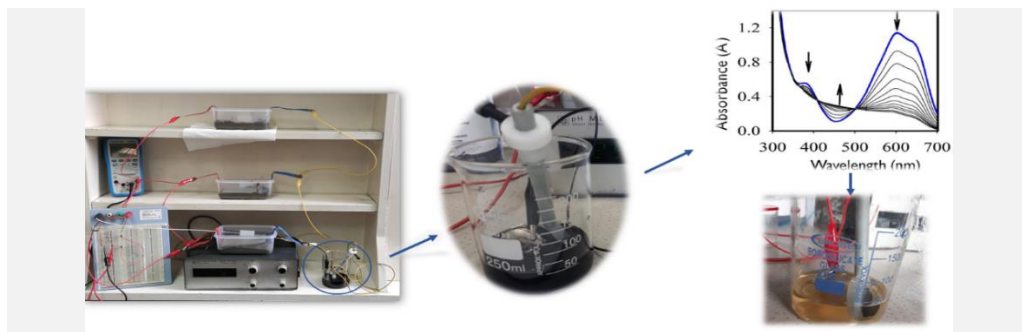
Decolorization of Azo Dye Through the Utilization of Microbial Fuel Cells Connected in Parallel Configuration

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Microbial fuel cells (MFCs) are a promising technology that has the potential to solve environmental problems while simultaneously generating electricity. Thanks to the direct use of energy from the substrate and its conversion into electricity, as well as the controlled production of activated sludge, the multiplicity of independent applications highly qualifies MFC for the use of wastewater treatment [1]. Wastewater from various industries is an ideal source of organic substrate that can potentially be used in MFC systems. In this way beside degrading organic pollutants, generated energy can be obtained as added value and used for various purposes.

The textile industry, as one of the largest industrial chains, produces the most wastewater, among which dyes are the main pollutants in the environment. Different types of dyes, such as azo, direct, reactive, and dispersed contain organic molecules that are very difficult to decompose and their negative impact on the environment is huge. Azo dyes contain aromatic rings with at least one -N=N-, which is responsible for the origin colour of the dye. The release of water containing azo dyes with this structure harms photosynthesis, oxygen solubility, and is highly toxic to living organisms [2]. This study aims to exploit the potential of MFC to produce current, which will be enough for the electrochemical decolourization of organic wastewater containing the azo dye Reactive black 5.

The construction of 3 parallel-connected MFCs was carried out with the river sediment, previously described [3]. The electro-Fenton decolorization process was carry out with the use of two electrodes, Fe (15% Fe and 12.56 cm²) as the working electrode and Pt as the counter electrode (area 3 cm²). Electrodes were immersed in 100 mL of dye solution. The dye solution, Reactive black 5 (≥50%, Sigma-Aldrich) was prepared with 0.1 M Na₂SO₄ (Merck, Germany) as a supporting electrolyte. H₂O₂ was added to the solution at a final concentration of 1 mM.

The results presented in this study show that three parallel-connected MFCs formed from river sediment were able to produce a current density of 273 mA/m³, which, in combination with small quantities of H₂O₂, successfully degrades 25 mg/L RB5 dye in just 6 h, with a decolorization efficacy of over 90%. Decolorization were confirmed visually and using UV spectroscopy.

Acknowledgements

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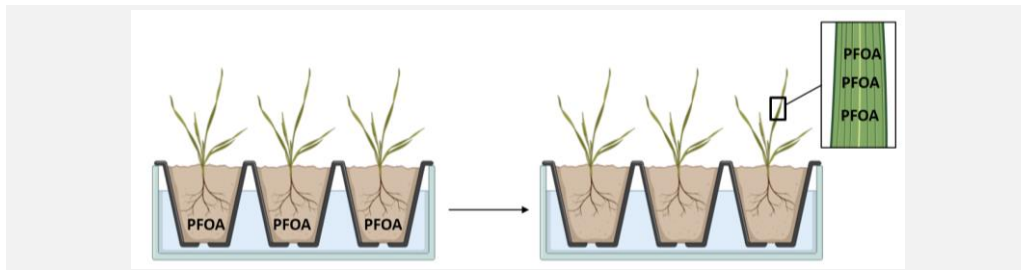
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Exploring the Potential of Plants for the Degradation of Perfluorooctanoic Acid

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Poly- and perfluoroalkyl substances (PFASs) are synthetic chemicals, which are introduced to the environment through anthropogenic activities. Remediation of PFAS contaminated soil and aqueous media is challenging, which is attributed to the chemical and thermal stability of PFAS and the complexity of PFAS mixtures [1].

Plants absorb water and nutrients through their roots to maintain their continuous healthy growth. Phytoremediation is a method that uses the ability of plants to remove and stabilize contaminants from the environment. Applicable to a wide range of atmospheric, aquatic, and geosphere compartments, it is an *in situ*, ecosystem-friendly, and socially acceptable remediation technology [2]. The greatest advantage of phytoremediation is that it costs only about 10 % of the total cost of conventional strategies [3]. In addition, it stabilizes bare soil and protects it from erosion, thus minimizing secondary pollution, such as the spread of contaminated dust and soil by wind and water. It also prevents landscape damage by retaining moisture in the soil and maintains a healthy ecosystem by increasing microbial activity and diversity [4]. Furthermore, through their root systems, plants can absorb low concentrations of chemicals from a variety of sources, making them suitable for remediation of even low concentrations of pollutants. These advantages make phytoremediation an attractive alternative to the physical and chemical methods currently used for remediation.

The aim of this study was to investigate the plant growth in the presence of high concentrations of PFOA using the germination test, and further investigate their potential to degrade PFOA in soil. The accumulation of PFOA in plants was monitored using target LC/MS/MS analysis.

This study showed positive results in the germination test for all tested plants and PFOA concentrations (up to 10 ppm) and no differences were observed compared to the control samples. Wheat (*T. aestivum*) showed the fastest growth on all tested concentrations and was selected for further tests. Target analysis of PFOA showed a significant decrease of PFOA from soil and accumulation in plants, however further research is needed to clarify the mechanism of uptake and translocation.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, #6684, *Phytoremediation for in situ treatment of agricultural soil and surface waters polluted with per- and polyfluoroalkyl substances – research on PFOS and PFOA as model compounds* – PhytoPFAS.

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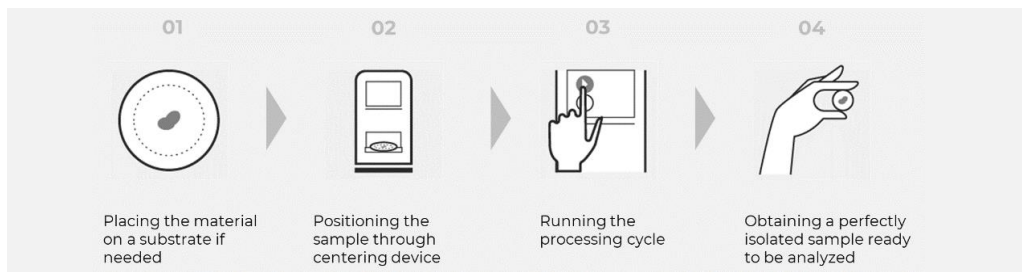
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A Green Sample Preparation Procedure for Elemental Analysis of Environmental Samples by X-ray Fluorescence Analysis with Smart Store®

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Sample preparation is a critical step in chemical analysis that can significantly impact the accuracy and reliability of the results. Elemental analysis of solid samples is usually performed by digestion procedures posing several challenges and problems, such as loss of sample, contamination, and use of toxic chemicals, resulting in an environmentally unfriendly procedure that can pose also the operator in danger.

An alternative sample preparation procedure with respect to the conventional ones is represented by the Smart Store®, which permits a direct measurement of the sample by X-ray fluorescence (XRF) based techniques. This procedure is based on 4 simple steps: firstly, the sample is placed on a substrate, if needed. Then the sample is inserted in the device and, by running the processing cycle, it is plasticized and cut in a disc of 30 mm diameter. The obtained sample can be measured several times, also with different instruments, or simply stored for records or future analyses. This preparation procedure presents several advantages: it is fast, non-destructive and allows to obtain a sample free of contaminations that can be preserved over time. This represents a green sample preparation approach [1] because it avoids the use of chemical reagents such as acids and consequently minimizes waste generation. The sample can be analysed with XRF based instruments, which allow to obtain qualitative and quantitative information about the elemental composition of the sample.

The Smart Store sample preparation procedure was successfully tested in several fields of

applications and few case studies are presented. It was employed for particulate matter (PM) filters, which are usually analysed after solubilization. Some calibration sample that can be employed as reference materials for PM filters were created and prepared with the Smart Store. After XRF analysis calibration lines were built, allowing for elemental quantification [2]. This method for direct analysis of PM filters was proposed to ISO community under the name ISO 23971 "Analysis of Air PM Filters by XRF under Grazing Incidence". The Smart Store device was also used to prepare leaves, which represent bio-monitors in the context of air quality monitoring. PM deposits on the surface of tree leaves and their direct analysis allows metal detection [3]. The same preparation procedure was applied to indoor and outdoor dust, useful for assessing household exposure to heavy metals.

By enabling direct analysis of the sample without the need for extensive preparation steps, Smart Store streamlines the process and reduces the risk of sample loss, contamination, and the use of toxic chemicals. This not only enhances the safety of operators and the environment but also saves time in obtaining analysis results, resulting very useful for screening and quality control purposes.

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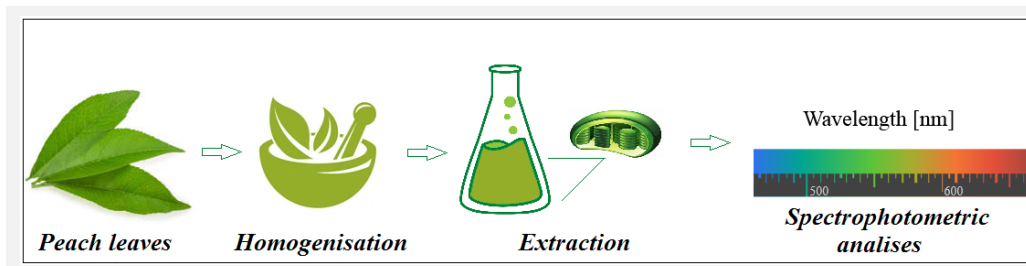
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Influence Of Insecticides On The Photosynthetic Pigments Content In Peach Leaves

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Insecticides have been widely used in the field of agriculture in order to increase yields and achieve better results. But, on the other hand, their inappropriate and excessive use can lead to certain adverse effects on the treated plants.

During 2020, the impact of eight insecticides (cyantraniliprole, chlorantraniliprole, spinetoram, indoxacarb, deltamethrin, piriproxfen, chlorpyrifos and acetamiprid) on the content of chlorophyll and carotenoid in the peach leaves was assessed. These insecticides are widely used for the control of peach moth (*Grapholita molesta* Busck), in peach orchards.

The insecticides were applied at a concentration/amount of 0.06%, 0.02%, 0.3 kg/ha, 0.33 L/ha, 0.05%, 0.1%, 0.25% and 0.025%, respectively. The experiment was set up in three replications for each insecticide as well as for the untreated control, according to Holm and Von Wettstai [1, 2] in peach orchards (variety „Royal gem”) at the locality of Mala Remeta (Serbia). Foliar treatments were carried out by a back sprayer, with a water consumption of 1000 l/ha, according to EPPO standards [3, 4, 5]. At the time of treatment, the peaches were in the BBCH 75 phenophase. Leaves were sampled after 3 and 7 days of the treatment, followed by laboratory analyses (determination of chlorophyll (a), (b), carotenoids and total chlorophyll a + b).

The results showed that 3 and 7 days after the insecticide application, chlorophyll (a + b) content was reduced in all treatments (from 7.3% to 43.7%) compared with the untreated control. The content

of carotenoids, after 3 days decreased by 2.0-17.6%, except in the leaves treated with cyantraniliprole. After 7 days, the content of carotenoids decreased in variants treated with piriproxfen, deltamethrin, indoxacarb and acetamiprid from 3.23% to 30.65%, while other treatments exhibited an increase up to 41.9%. The analyzed pigments in peach leaves showed a different biochemical reaction depending on the applied insecticides. Applied insecticides caused significant changes in the leaf pigment content, but it is assumed that these short-thermed changes will not significantly affect the plant growth and quality of the peach.

Acknowledgements

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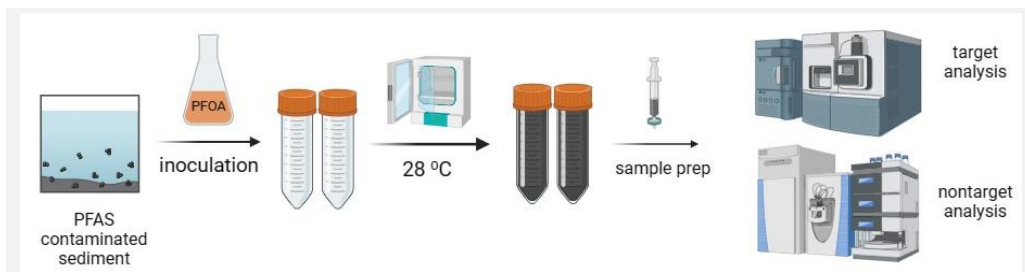
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Investigation of the Capacity of the Isolated Sulfate-Reducing Bacteria to Degrade PFOA

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PFAS, or per- and polyfluoroalkyl substances, are a group of synthetic, highly stable compounds known as "forever chemicals" due to their resistance to decay. The most studied PFAS in the environment, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been identified in water, soil, food, and even human blood. Existing physical and chemical PFAS remediation methods are often costly and impractical for in situ cleanup [1]. Therefore, there's an urgent demand for novel approaches, particularly in addressing PFOA contamination, with bioremediation emerging as the most promising solution. While there are indications that PFAS biotransformation can occur successfully under anaerobic conditions, and a connection between PFAS metabolism and the sulfur cycle in the environment has been suggested [2], the interactions between sulfate-reducing bacteria (SRB) and PFOA remain largely unexplored.

The aim of this study was to isolate and select SRB from PFAS-contaminated sediment and assess their potential for PFOA biodegradation. The levels of PFOA were monitored using target LC/MS/MS analysis, whereas the metabolites generated during this process were analysed using non-target LC/MS/MS analysis.

The result of this study is a bacterial consortium tolerant to high PFOA levels (up to 500 ppm), that could have a potential to degrade PFOA, indicated by a notable reduction in PFOA concentration after 21 days of incubation. Non-target analysis didn't reveal any fluorinated metabolites, however some variations were present in the short-chain fatty acid composition that could indicate the differences in microbial metabolism in the presence and absence of PFOA. To clarify the mechanism and specific metabolic changes, further research is needed.

Acknowledgements

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Biological effectiveness of newly synthesized [CuL(H₂O)] on fungy *Colletotrichum acutatum*

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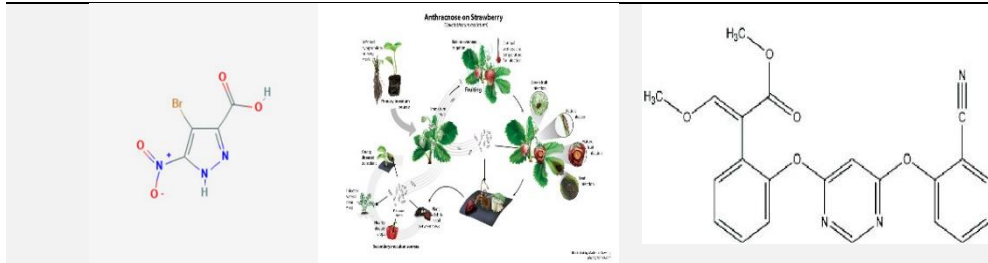
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Complexes of metals with pyrazole and their derivatives occupy a special place in the scientific research field, which is discussed in a large number of scientific papers^[1]. Bearing in mind the practical application of pyrazole derivatives as active substances in fungicides^[2] this work initiates activities to determine the inhibitory effect of newly synthesized [CuL(H₂O)] on the development of the mycelium of the fungus *Colletotrichum acutatum* (it cause of disease strawberry anthracnose). In some cases, strawberry anthracnose caused serious damage, with up to 80% of the yield.

A representative selection of metal salts such as Cu(II)acetate and the pyrazole ligand 4-bromo-3-nitro-1Hpyrazole-5-carboxylic acid (L-C₄H₂N₃BrO₄)^[3] was made for the synthesis of potential fungicide active substances. We note that the transition metal Cu is most often used in the production of fungicides to control the aforementioned disease, while the selected pyrazole ligand was not used in synthetic and biological tests. At the same time, the newly synthesized [CuL(H₂O)] complex was characterized by the following techniques: CHNS, IR and XRPD.

The biological effectiveness of the newly synthesized Cu complex is reflected in the assessment of the reduction in the diameter of the mycelium of the fungus *Colletotrichum acutatum* (in a set of four measurements) after treatment with the newly synthesized complex compared to the fungicide Azokostrobin, which has a wider effective use in the protection of fruit trees in

Montenegro. The diameters of the mycelia of *Colletotrichum acutatum* as parameters of the inhibitory effect of prepared samples of the newly synthesized complex in the range of concentrations (C₁=10.3·10⁻⁴; C₂=5.1·10⁻⁴, C₃=2.5·10⁻⁴, C₄=1.2·10⁻⁴, C₅=0.6·10⁻⁴) were processed by analysis of variance, and the testing of means was performed using the LSD test.

The analysis of the obtained results revealed statistically significant concentration values of the newly synthesized complex (four initial concentrations), which caused a decrease in the diameter of the mycelium of the subject fungy by more than 0.250 cm compared to the mean values of the diameter of the mycelium of the control sample. The obtained results represent a good basis for further research on the biological efficiency of the newly synthesized complex towards other plant pathogenic fungi.

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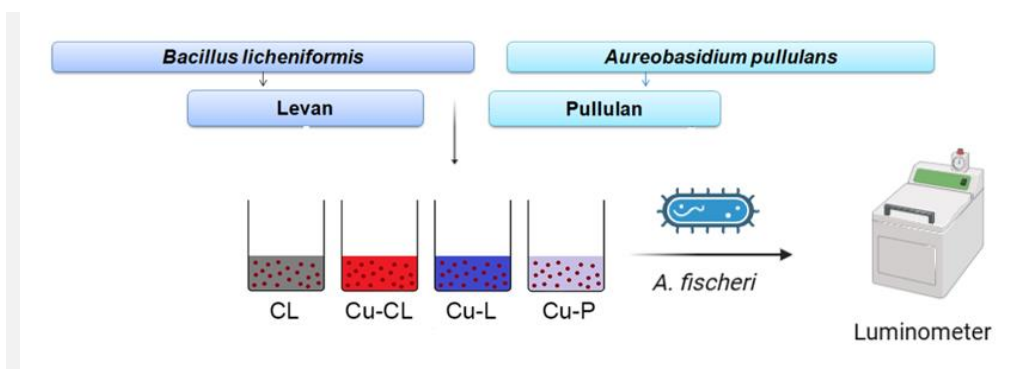
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Reducing Adverse Effects of Copper on *Alivibrio fischeri* Using Microbial Levan and Pullulan

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The range of extracellular polysaccharides (EPS) produced by microorganisms is extensive. EPS are responsible for biofilm formation, surface adhesion and cell to cell communication and are protective barrier and nutrition source. EPS are extensively studied due to their suitable chemical properties for many applications [1]. Use of EPS for reduction of heavy metal ions from environment is considered as environmentally gentle method, and therefore preferred over other techniques [2]. Levan is a polysaccharide produced by various bacteria and it is composed of fructose monomer units. Pullulan is a fungal EPS composed of maltotriose repeating units [3].

Aim of this study was to determine effects of levan and pullulan on bioluminescence of *A. fischeri* after acute Cu^{2+} exposure.

Levan and pullulan were isolated after fermentation of *Bacillus licheniformis* NS032 and *Aureobasidium pullulans* CH-1. The inhibitory effect on the light emission of *A. fischeri* was examined according to the ISO 11348 standard, using BioFix® Lumi-10 (Macherey-Nagel GmbH & Co. KG, Duren, Germany). The toxicity of Cu^{2+} was investigated in the presence of levan and pullulan, with starting concentrations of Cu^{2+} and polysaccharides 25 mg/L and 100 mg/L,

respectively. All tests were done in triplicate and EC_{10} values were determined.

Results show that in the presence of both EPS, EC_{10} increased after 15 min and 30 min of exposure, compared to samples with only Cu^{2+} . Interestingly, EC_{10} after 30 min for the Cu^{2+} solution with levan was threefold higher in comparison to the Cu^{2+} solution with pullulan.

The bioluminescence test indicated a decrease of Cu^{2+} toxicity in the presence of both investigated microbial polysaccharides. This indicate that levan and pullulan could be used as a resource in mitigating the adverse effects of heavy metals in contaminated environments.

Acknowledgements

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Behaviour of Herbicide Prosulfuron in Agricultural Soil

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To achieve sustainable soil management and the production of quality food, the crucial is the implementation of measures to preserve soil quality and limit contamination. Knowledge of the fate and behavior of pesticides is of great importance because these compounds can significantly influence soil and water quality.

This study gives insight into the behavior of the sulphonilurea herbicide prosulfuron in soil. Prosulfuron is a herbicide used for the control of a wide range of broad-leaved weeds in maize. Sulfonylureas are highly effective in very low concentrations; however, the low application rate does not guarantee low environmental risks. Their residues could be present in soil and through the leaching process, could reach groundwater. The persistence of these residual herbicides and their metabolites can affect sensitive plant species during crop rotations, causing phytotoxicity [1].

For the evaluation of the dissipation dynamic of prosulfuron after its application, a field experiment was set up at the locality Palić (Serbia), at soil type chernozem. Plant protection product (750 prosulfuron a.s. g/kg, WG) was applied at the recommended rate of 20 g/ha. Soil sampling was performed in the layer of 0-30 cm, immediately after application and weekly, till harvest. Prior to the analysis, samples were milled and sieved. For the extraction of prosulfuron, a modified QuEChERS-based method, followed by the HPLC-DAD analysis, was used. The validated

method completely fulfilled SANTE/2020/12830 the criteria [2].

The highest residue levels in soil taken 1 h after the application, was 1.23 mg/kg, while after seven days it was 1.09 mg/kg. At harvest time of maize prosulfuron was below the LOD of 0.01 mg/kg.

The results showed that the dissipation of prosulfuron at the applied dose followed the first-order kinetics with a half-life of 2.93 days.

Based on the results of prosulfuron residues in chernozem soil, the application of this herbicide could be considered ecotoxicologically safe for the most sensitive terrestrial non-target organism and does not cause phytotoxicity, since the final concentration was far below 0.05 mg/kg [2].

Acknowledgements

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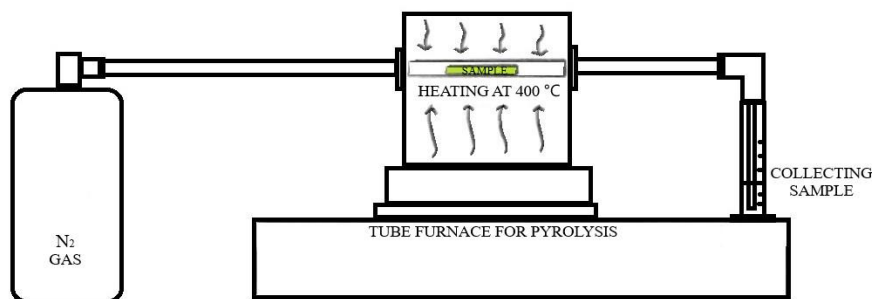
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Physicochemical Characteristics of Biofuel Obtained by Pyrolysis of Corn Waste

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Due to the increased consumption of fossil fuels and the ecological consequences of their use, modern society faces significant challenges [1-2]. Accordingly, the emphasis is placed on the development of alternative energy sources while at the same time mitigating the harmful consequences for the environment, such as, for example, disposal of waste biomass [3].

Therefore, one of the important research directions is using biomass as a renewable energy source, focusing on waste biomass from corn [4]. In this paper, the waste biomass of two types of corn was characterized and subjected to the pyrolysis process in a tube furnace at 400 °C. The results of the thermogravimetric analysis of the biomass, carried out in a nitrogen atmosphere, helped choose the pyrolysis temperature. A detailed physicochemical characterization of the obtained liquid fraction (biofuel) was performed, and the values were compared with literature data. The calorific values of biofuel were above 22 MJ/kg which is typical for bio-oil [5], indicating the excellent potential of corn waste biomass as an energy source. The functional groups of the biofuel obtained from both types of corn were characterized by FTIR spectroscopy. At the same

time, the most abundant fractions of compounds were identified using GC-MS analysis.

With appropriate further changes in the composition of the waste, by adding materials with a higher carbon and hydrogen content, the biomass of corn waste, due to its wide availability, can represent a significant source of energy with at the same time a better regulation of disposal and storage of agricultural plant waste.

Acknowledgements

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TOPIC 5

ONE HEALTH



Nicotine Release in Saliva - Effect of Time, pH, Alcohol and Sugar Content on Nicotine Release from Pouches Available on Slovene Market

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Tobacco free nicotine pouches, first introduced in Sweden, are a relatively new product on the market, made as a less hazardous product for cigarette consumers. Instead of tobacco leaves, they consist of nicotine-containing powder and other ingredients such as water, salts, natural aromatic oils and others, that will boost the effect and flavor, and make it last longer. [1]

This research aimed to investigate the extraction efficiency of nicotine from pouches of different brands. The effects of alcohol and sugars present in saliva at different pHs and consumption time were investigated as well, trying to simulate the conditions related to everyday lifestyle. We optimised a HPLC-DAD method for nicotine determination and its quantification. We used reversed phase chromatography (RP)-HPLC, with C18 columns and a mixture of sodium hydrogen carbonate and acetonitrile (ACN) as a mobile phase (85:15, v/v). Flow rate was 1.2 mL/min, injection volume 20 μ L and stop time 15 min. [2]

Different brands of nicotine pouches were used: *White fox*, *Siberia*, *Velo* and *Thunder*. We used three types of White fox pouches: *The original* (blue) and *Double-mint* (green), both with 12 mg of nicotine per pouch (0.75 grams), and *Full-charge* red) with 16 mg of nicotine per pouch (1 gram). *Siberia* pouches were *Regular* with 16.4 mg of nicotine per pouch and *Slim* with 10.66 mg of nicotine per pouch.

White fox and *Siberia*, showed the best nicotine extraction rate, so we continued our experiments on them. With all pouches nicotine extraction rate showed positive linear dependence with time. The

efficiency of extraction was measured at different intervals, up to two hours, without getting a plateau, with the maximum extraction of 25%. Nicotine extraction lowers with the increasing volume of saliva.

The obtained results have shown that the increasing ethanol concentration in saliva (from 5-40% EtOH) leads to a higher extraction rate, coming up to 85% with some pouches.

In the case of sugar addition, the results were variable. Experiments with *White fox* pouches have shown that extraction of nicotine decreases with a higher concentration (5%, 10% and 15%) of sugar. On contrary, *Siberia* pouches do not exhibit that correlation, potentially because of the difference in pouch material or ingredients in them. We observed, the sacks are less tight and nicotine could be distributed unevenly.

When it comes to pH, we used pH range that usually vary in saliva (from 5 to 8), and the results have shown no significant differences.

Acknowledgements

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Environmental Pollution, Human Health Risk and Bioaccessibility Assessment of Potentially Toxic Elements from Agricultural Soils and Grapes

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In agricultural environments, frequent agrochemical applications and activities from surrounding pollution sources (such as highway roads, metal foundries, industrial activities, waste disposal etc.) directly lead to increase pollutant concentrations in soil and grapevine. We performed several experiments in agricultural areas in Serbia [1,2,3], mostly in the vineyards.

The experiments were conducted to assess environmental implications, the worst-case scenario of workers' and consumers' health risks and the bioaccessibility of PTE in the human gastrointestinal tract (GIT). Performing the *in vitro* unified bioaccessibility method (UBM), the bioaccessible concentrations in human GIT were determined.

The concentrations of potentially toxic elements (PTEs) were investigated in soil, soil extracts, grapevine, and gastrointestinal extracts of soil and grape samples. The element concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). Control of the element chemical analyses was done by analyzing analytical blanks and certified reference materials.

Environmental risk assessments pointed out the most polluted locations between investigated vineyards. The Biological accumulation concentration (BAC) showed the highest bioaccumulation of Zn and Cu from the soil easily available fraction to the grapevine (BAC >1).

Human health risk assessment (worst-case scenario) showed some risk for workers in the vineyards but there were also risks and moderate risks for consumers of some grape varieties. It was identified that Cr and Ni concentrations in the soil and grapes mostly contributed to environmental implications and increasing the human health risk. The highest contribution to increasing the risk for workers had pseudo-total concentrations of Ni, then Cr, Co and Mn from the soil, and for consumers Ni, Cr, Mo and B concentrations from grapes. However, these elements from soil and grapes were negligibly bioaccessible in human GIT assessed by the *in vitro* UBM bioaccessibility test,

especially Cr and Ni whose bioaccessible fractions were not detectable in the investigated soils. In investigated vineyard soils Co bioaccessible fraction ranged from 3 to 36%, for Mn from 0.1 to 20% compared to pseudo-total concentrations. Bioaccessible B fraction from grapes represents 0.4 to 8,3% of total B concentration in the grapes. Copper, which can be easily accumulated in the grapevine, was bioaccessible in human GIT only 0.1 to 11% compared to the total Cu in grapes.

Also, Cr and Ni were highly bonded in residual soil fraction and they were not mobile, while Co and Mn were bonded in reducible soil fraction. Easily available were Mo and B from the soil, but they were negligibly bioaccessible to human.

The worst-case scenario risk assessment can be used as a precautionary measure. Finally, PTEs in samples from vineyards accompanied by environmental and human health risks with bioaccessibility assessments may improve vineyard production and management. This type of research in agricultural ambients could be beneficial to obtain safe food production.

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Wild Mushrooms From Eastern Bosnia And Heavy Metals Accumulation

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Heavy metals: zinc, copper, cobalt, iron, cadmium, arsenic, nickel, selenium and chromium were determined in selected wild mushrooms (true morels, chanterelle, black trumpet) from Eastern Bosnia. The mushroom samples which traditionally used as food and medicine, were collected from Jahorina and Sjemeč mountains. The assessment of the carcinogenic risk and noncarcinogenic risk which was measured by target hazard quotient (THQ) and hazard index (HI) was also done to estimate an impact to human health. Obtained results for the heavy metals were compared according to the WHO/FAO standard. The study showed a potential health risks of wild mushroom consumption caused by accumulation of determined heavy metals. It is necessary to continue investigation on chemical composition of wild mushrooms from Eastern Bosnia.

Key words: heavy metals, wild mushrooms, toxicity, health impact.

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New Neurotensin Analogue: Effects on Prosocial Behaviour in Experimental Model of Parkinson's Disease

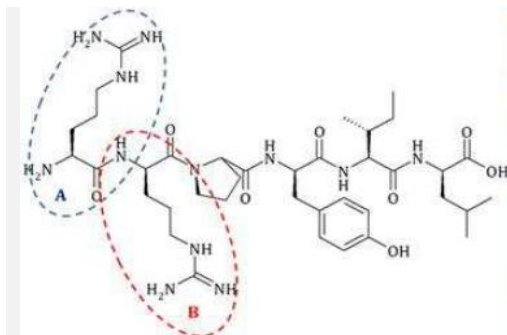
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Code	A	B	Rt (min)	Yield, %	ESI-MS [M+H ⁺]
NT	Arg	Arg	16.38	45	818
NT1	Lys	Cav	16.00	40	837
NT2	Cav	Lys	16.15	38	837
NT3	Cav	Cav	17.85	47	912
NT4	Arg	Cav	16.85	41	865
NT5	Cav	Arg	16.78	44	865

Parkinson's disease (PD) is one of the most common neurodegenerative disorders associated with motor symptoms and loss of dopaminergic neurons. However, there is a growing evidence that the non-motor symptoms precede the motor ones and also play a pivotal role in PD pathology. The brain dopaminergic system is significantly involved in the regulation of motor activity in one hand, and regulation of motivation in another. Therefore, the neurodegeneration of the dopaminergic limbic system is often associated with symptoms such as apathy and impairment of prosociality. The neurotensin system was found to be closely associated with dopamine, therefore it is often a therapeutic target in dopaminergic related pathology.

New NT-analogue (with code NT2) was synthesized through standard solid-phase method. Peptide chain was assembled on a Wang resin (0.1 mmol scale) with Fmoc/Boc strategy. Coupling of each amino acid was performed in the presence of 3 mol excess of Fmoc-amino acid, 3 mol excess of HOBt, 3 mol excess of DIC and 5 mol excess of DIPEA. The cleavage step from the resin and the final deprotection of all remained protecting groups was done in standard cocktail containing TFA, TIPS, thioanisole and water.

The scope of the present study was to evaluate some effects of new neurotensin hexapeptide analogue NT2 on some aspects of the social and prosocial behaviour of rats with experimental

model of Parkinson's disease.

Male Wistar rats were used in our experiments. PD model was induced with injection of the neurotoxin 6-hydroxydopamine (6-OHDA, 12 µg in 2 µl saline) directly into striatum, and the rodents were treated with a new neurotensin analogue in an effective dose (5 mg/kg, i.p.) for 5 consecutive days after 6-OHDA injection. NT2 effects were evaluated via behavioural tests for motor activity and prosocial behaviours two and three weeks after surgery. Student's *t*-test was used at *P* < 0.05 to process the acquired data.

PD model was verified by rearing test on the 2nd and 3rd week after the operation and was compared to sham-operated animals. There was a significant performance decrease in the social and prosocial interactions in both PD groups. However, in NT2 treated animals the negative impact was reduced (both on the 2nd and 3rd week) as compared to PD rats. NT is a multiple route effector: immune-modulator and neuromodulator. Probably its analogue NT2, facilitates the reduction of the necrosis and apoptosis in the 6-OHDA trauma area, and modulates some of the transmitters systems related to the studied behaviours.

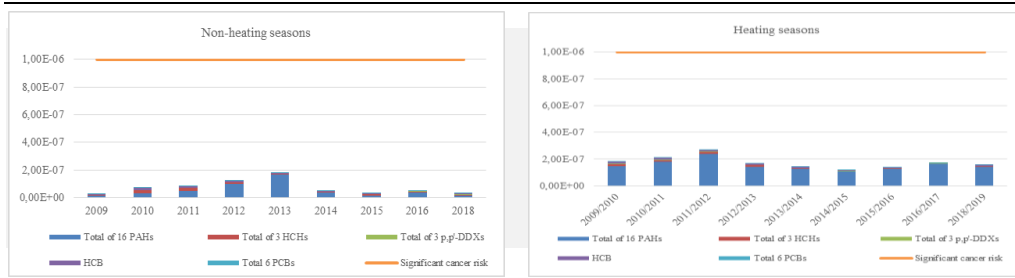
In conclusion, NT2 improves some of the non-motor symptoms related to prosociality in an animal model of PD. This preventive effect might be related to modulation by NT2 of the brain dopaminergic and neuroimmune systems.

Are the Residents of AP Vojvodina, Serbia, Exposed to Persistent Organic Pollutants and Polycyclic Aromatic Hydrocarbons Through Inhalation?

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Inhaling contaminated air is a significant route of human exposure to persistent organic pollutants (POPs) and the main pathway of exposure to polycyclic aromatic hydrocarbons (PAHs). POPs are toxic to the human population and other living organisms and show mutagenic, teratogenic, and carcinogenic effects [1]. At the same time, out of all PAHs, benzo(a)pyren (BaP) is proven carcinogenic according to the IARC. POPs have been extensively used in various products, including pesticides and industrial chemicals (like PCBs). They also can be released unintentionally into the environment (dioxins and furans). PAHs are emitted primarily into the air by different sources - traffic, heating and power plants that are powered by coal, oil derivatives, gas, and wood, accidental events of uncontrolled solid waste combustion, industrial processes like coal production, cement manufacturing and oil and natural gas refining. Among the mentioned sources of PAH emission, heating plants are seasonally dependent, while traffic, power plants, and other stationary sources are less influenced by seasonal temperature changes [2].

The paper presents the assessment of the ambient air quality at the background measuring site on Fruška Gora Mountain, Serbia, and the cancer risk during heating and non-heating seasons from 2009-2019, using US EPA methodology [3,4]. According to the US EPA approach, the exposure is considered significant, if the result of the risk factor is higher than $1 \cdot 10^{-6}$ (1 occurrence over one million people). The air quality and human exposure were evaluated regarding PCBs, HCHs,

DDXs, HCB, and 16 EPA PAHs, using a passive air sampling technique. The calculated total cancer risk values for all investigated POPs/PAHs cannot be treated as significant for the human population during both seasons (during non-heating seasons risk was within the range $2.54 \cdot 10^{-8} - 1.80 \cdot 10^{-7}$, while during the heating seasons risk ranged from $1.18 - 2.71 \cdot 10^{-7}$). The highest risk was obtained for PAHs. Obtained health risks may have been underestimated since the particulate phase of the substances hasn't been considered, as well as because inhalation was the only route of exposure reflected within the research.

Acknowledgments

This work has been supported by the RECETOX Research Infrastructure (the project of the Ministry of Education of the Czech Republic LM2023069) and by the Ministry of Science, Technological Development and Innovation through project no. 451-03-47/2023-01/200156 "Innovative scientific and artistic research from the FTS (activity) domain".

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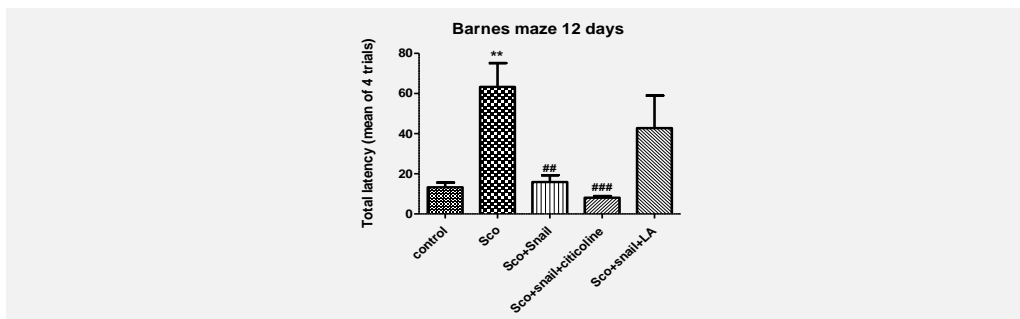
Synergic Action of Citicoline and Standardized Snail Extract in Alzheimer's Dementia

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Alzheimer's disease is a complex neurodegenerative disorder with multifactorial etiology, unsatisfactory treatment and necessity for broad-spectrum active substances for cure. Citicoline (cit) increases the synthesis of acetylcholine and restores the content of phospholipids in the brain. On the other hand, mucus from snail *Helix aspersa* is a mixture of bioactive molecules with antimicrobial, anti-inflammatory, antioxidant and anti-apoptotic effects. The aim of this study was to determine the effects of the combination standardized snail extract (SE) plus citicoline in scopolamine (Sco)-induced Alzheimer's type dementia in rats. SE obtained from garden snail *Helix aspersa* was analyzed by sodium dodecyl sulphate polyacrylamide gel electrophoresis. Molecular masses of protein in mucus fraction >20 kDa was measured by an AutoflexTMIII, High-Performance MALDI-TOF. Animals were divided into the following groups: 1) Controls; 2) Sco; 3) Sco+SE; 4) Sco+SE+cit; 5) Sco+SE+Lipoic acid (LA). The rats received during 40 consecutive days orally the substances: cit (100mg/kg); SE (0.5ml/100g); SE+cit (0.5ml/100g and 100mg/kg), SE+LA (0.5ml/100g and 0.4 ml/100 g), while the controls received water (0.5ml/100g). The animals were treated for another 11 days with the tested substances with a simultaneous injection of Sco (2 mg/kg) or saline for the control group. Basic parameters of learning and memory were

evaluated. After that cortex and hippocampus were separated and markers of oxidative stress were examined. Additionally, in cortex and hippocampus the acetylcholinesterase activity, acetylcholine and monoamines (dopamine, noradrenaline and serotonin) content, levels of main oxidative stress markers, expression of brain-derived neurotrophic factor (BDNF) and cAMP response element-binding protein (CREB) were determined.

The results showed that the administered SE+cit combination increased the scopolamine-reduced glutathione levels in the cortex to the values of the controls. These changes were accompanied with a decrease in the Sco-enhanced enzyme activities of superoxide dismutase and catalase in both brain structures, and for glutathione peroxidase, beneficial effects of SE+cit were found only in the cortex. In hippocampus SE+cit improved significantly spatial learning and memory of dement rats and also increased CREB levels.

In conclusion, the combination of standardized snail extract plus citicoline effectively reduced oxidative stress and improved memory in Sco-induced damage of rat brain, so it could be of interest for further studies in Alzheimer's dementia.

Acknowledgements: This work was supported by Grant D01-217/30.11.2018 „BioActiveMed“ and partially by the National Research Program "Young scientists and postdoctoral fellows", BAS.

Antioxidant Potential of Myrtenal and Its Adamantane Conjugates in Dementia Rat Model

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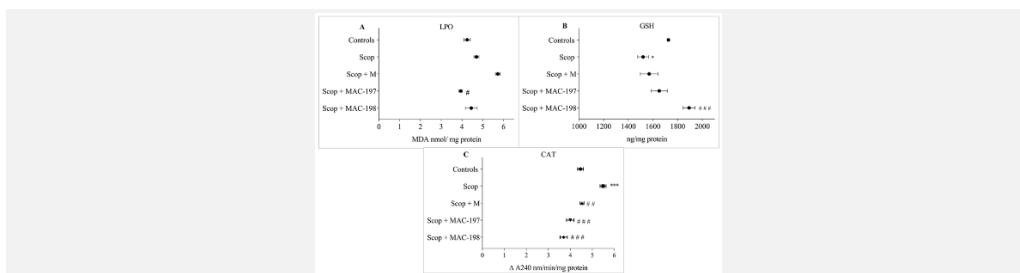
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Alzheimer's disease (AD) is the most common form of dementia worldwide, characterized by multi-factor ethiopathology. There is a growing attention on natural substances with a complex mechanism of action, including antioxidant, for its prevention and/or treatment. **Aim** of the study was to evaluate the antioxidant potential of myrtenal (M) and two M-adamantane conjugates (MACs) as a component of their neuroprotective mechanisms on rats with experimental model of dementia.

Methods: In phase I of the experiment, dementia was induced by scopolamine (Sc) application in rats in a verified dose modification to reproduce the non-linear progression of neurological damage – 0.1 mg/kg for 8 consecutive days and a final dose of 20.0 mg/kg on day 9. The animals were simultaneously treated with M (40 mg/kg) and an antioxidant referent Lipoic/Thioctic acid (30 mg/kg). In phase II of this study Sc (1 mg/kg) was applied i.p. in rats for 11 days, simultaneously with MAC-197 and MAC-198 (1 mg/kg) or M (40 mg/kg) as a referent, respectively. Brain oxidative status was determined by the following parameters: lipid peroxidation product levels (LPO), total glutathione content (GSH) and catalase (CAT), superoxide dismutase (SOD), glutathione peroxidase (GPx) activity.

Results: The referent Lipoic acid (LA) increased tGSH content in the brain (11 %; $P < 0.05$) and restored changed by the Sc SOD activity to the control level with a 20.5 % decrease. M showed better potential by reducing LPO product levels (by 19%; $P < 0.05$) and increasing the tGSH content (by 14.8%) as compared to the Sc group. It restored SOD activity (increased by Sc) by 24.5 % ($P < 0.05$) to levels observed in Controls. In the second phase, the main manifestation of M's specific antioxidant properties was the restoration of the elevated by scopolamine CAT activity to close to the control level (by 17.5 %, $P < 0.01$) vs Scop group. MACs significantly affected the parameters for oxidative status – MAC-197 decreased LPO products level by 16.1 % ($P < 0.05$) and MAC-198 increased GSH content by 24.6 % ($P < 0.001$) compared to Sc. Both substances decreased the elevated by Sc application CAT activity – by 27.2 % for MAC-197 and by 32.6 % for MAC-198 ($P < 0.001$).

Conclusion: For the first time the antioxidant potential of Myrtenal in rodents with an experimental model of dementia was established. MAC-197 and MAC-198 showed stronger than the natural M effects, which makes the substances promising candidates for Alzheimer's disease treatment.

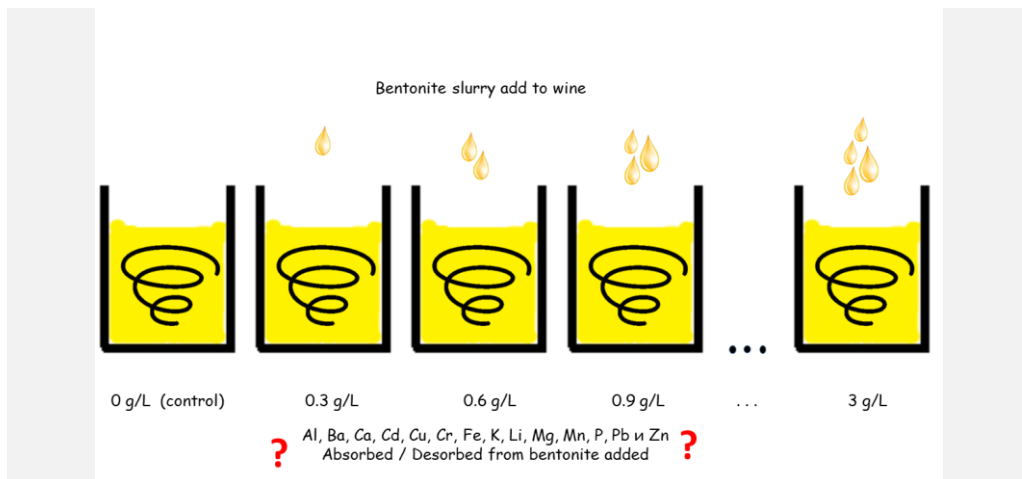
Investigation on Some Elements Content in White Wine After its Treatment With Different Dose Bentonite

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Winemaking has a thousand-year history. For the human it is important to consume wine with good quality as from organoleptic point of view, as well from the human's health point of view.

The step of colloidal stabilization is absolutely necessary during the white and rose wine making process. Nowadays bentonite usage in this step has no analogue in industrial scale.

Bentonites are natural product – mineral from the clay family. It has a layered structure including hydroxyl groups on the surface of the individual layer which determines a negative charge of bentonite particles. As a natural product bentonite could contain some ions in its structure which could be exchanged. Bentonite has strong swelling ability which determines a great sorption capacity. The above mentioned give bentonites' an important role in oenology for colloidal stabilization of wines.

Bentonite dosage is important to establish as from economic point of view, as well regarding to wine's organoleptic quality and chemical

compounds content. The aim of the present study is to investigate how the concentration of selected chemical elements changes as a result of applied increasing doses of bentonite. A number of 10 parallel white wine samples (Chardonnay, 2021 vintage year) were treated with previously selected bentonite in acceding dosage from 0,3 to 3 g/L bentonite. After acid mineralization the content of some important elements was determined. The elements Al, Ba, Cd, Cu, Cr, Fe, Mg, Mn, P, Pb and Zn were measured by ICP-OES, whether FAAS was used for determination of Ca, K, Li.

Acknowledgements

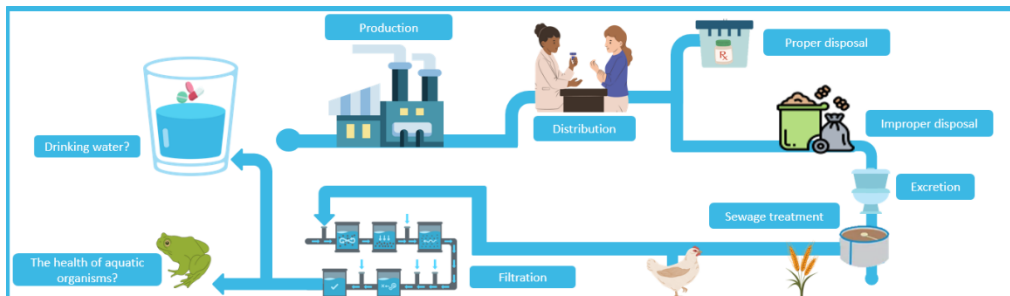
The authors are grateful for the financial support from the Sofia University "St. Kliment Ohridski" Scientific Research Fund via contract 80-10-148 / 2022. Research equipment of the Distributed Research Infrastructure INFRAMAT, part of the Bulgarian National Roadmap for Research Infrastructures, supported by the Bulgarian Ministry of Education and Science, has been used in this investigation.

Ecopharmacovigilance - Necessary Discipline for a Greener Future

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Pharmacovigilance is the science and activities relating to the detection, assessment, understanding and prevention of adverse effects or any other medicine/vaccine related problem.

On the other hand, ecopharmacovigilance can be defined as science and activities concerning detection, assessment, understanding, and prevention of adverse effects or other problems related to the presence of pharmaceuticals in the environment, which affect human and animal species [1].

Daily increase in medicines consumption, improper disposal of leftover medicines, characteristics of medicines in terms of elimination from the body and hydrosolubility of metabolites are dominating cause of environmental contamination with medicines.

There are numerous examples of cases where it has been shown that medicines have reached the living environment in different ways. However, there is no adequate measurement of the impact and scope of this problem on public health and the environment.

Although, effect of very low doses of medicines found in nature is not clear, special populations like pregnant women, geriatric population, persons with renal or hepatic insufficiencies and children may remain at a greater risk to such exposure because in these categories the pharmacokinetics gets altered and even minor doses may also prove to be toxic [2].

Similarly, some drugs in these micro doses may also show synergistic actions. Furthermore, type B adverse reactions may occur at these doses [3].

Major problems in this area are poor regulation in most countries, including Montenegro, and lack of knowledge of the impact of the improper disposal of medicines on the environment.

Good practice in reducing the risk of environmental contamination by medicines is Environmental Risk Assessment (ERA) for pharmaceutical products for human and veterinary use. This assessment has become mandatory before seeking marketing authorisation of drugs in European Union (EU).

However, it should be kept in mind that the results of ERA are affected by different factors like dose of the drug used, characteristics of drug, metabolism of drug, biodegradation, measured environmental concentration, and ecotoxicity. Apart from that, it is difficult to predict the chronic hazard potential of a drug in subacute concentrations only on the basis of acute toxicity studies [4,5].

The situation would be improved by introducing regulations in the field of pharmaceutical waste management, and by educating both the professional and the general public about ecopharmacovigilance as discipline which wants to spread awareness about the impact of medicines on the environment.

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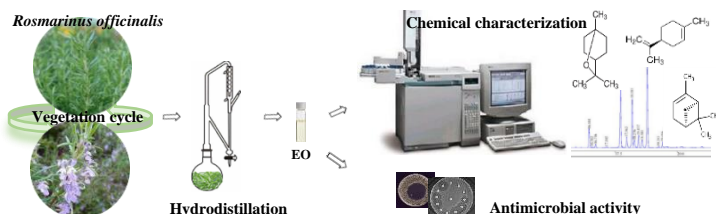
Effect of Vegetation Cycle on the Chemical Composition and Antimicrobial Activity of *Rosmarinus officinalis* Essential Oil

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Rosemary (*Rosmarinus officinalis* L., Lamiaceae) is an aromatic plant native to the Mediterranean area. The rosemary essential oil, characterized by unique aromatic characteristics, is used in perfumery and as a component of disinfectants and insecticides [1].

Essential oils are used in food industry as biopreservatives to increase the quality of food and to prolong the shelf life of foods, by reducing or eliminating pathogenic bacteria and products.

Monitoring the phytochemical content and their quality in phenological growth stages can display the pattern of these compounds accumulation. The determination of the optimal phenological stage for harvesting the plant can be helpful in obtaining the highest amount of biological compounds in extracts for pharmaceutical or food industries [2].

The changes of abiotic environmental factors at plant growth period affect secondary metabolism pathways, which may result in differences in the pharmacological and therapeutic properties of the harvested plant at different phenological stages [3].

In this study fresh leaves of *R. officinalis*, collected before flowering and during flowering stage (May and June), from the central part of Montenegro (Nikšić), were extracted by hydrodistillation in a Clevenger-type apparatus for 2 h.

Chemical composition of the obtained essential oil was determined by gas chromatography-mass spectrometry (GC/MS).

Diffusion technique was applied to test sensitivity of certain Gram-positive and Gram-

negative bacteria to rosemary essential oil in comparison to some standard antibiotics.

A total of 26 constituents were identified in the rosemary essential oil obtained from herb before flowering and after flowering stage with major components: α -pinene (17,27% and 20,59%), 1.8 cineol (16,67% and 14,70%), camphor (11,79% and 8,97%) and borneol (7,22% and 5,65%), respectively.

The gained results revealed that vegetation stage effects the chemical composition and antimicrobial activity of *R. officinalis* essential oil.

Acknowledgements

The authors gratefully acknowledge the financial support through EUREKA project E! "Active substances from supercritical plant extracts for high value added products".

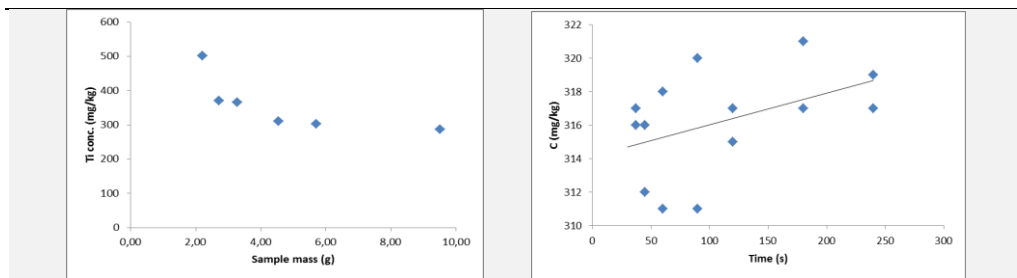
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Relevant Parameters for Standardless Determination of TiO₂ in Food Samples by Portable X-ray Fluorescence Spectroscopy (PXRF)

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TiO₂ particles have numerous relations to PFAS. They are considered as catalyst for PFAS degradation [1] [2], potent absorbers [3] and for many other interactions involved with PFAS.

TiO₂ is also known as a food additive (E171) used as food colorant and colour enhancer in many food products. Based on the latest EU regulation TiO₂ is not allowed to be used in any type of food.

Methods for easy and rapid standardless quantification of TiO₂ are obviously needed for scientific research but also for better food control. Portable X-ray fluorescence spectroscopy (PXRF) is one non-destructive analytical technique able to measure concentrations of analysed elements regardless of the type of compound that contains them.

We have proved that PXRF can be successfully used for quantification of TiO₂ in food by analysing different cream fillings which contain TiO₂ particles, but it remained unexplored which factors and to what extent affect accuracy of TiO₂ measurements.

Samples were placed at holder whose diameter was 32 mm. The first factor which was investigated was the mass of the sample. It was determined that after a threshold is reached further increase of the sample mass will have predictable and minor influence to the result.

On the other side, it was determined that measurement duration does not affect value of the measurement, but it will affect precision (especially for the shorter measurement periods).

The last set of experiments was related to investigation of the measurement precision. It was determined that moving of the sample does not significantly affect precision, but it does produce certain trends which indicates that if this factors remains unattended it may increase systematic error.

Better understanding of factors which affect accuracy and precision of TiO₂ measurements performed by PXRF is expected to be beneficial for better design of experiments which investigate relations between PFAS and nanoparticles created from inorganic materials not limited exclusively to TiO₂.

Acknowledgements

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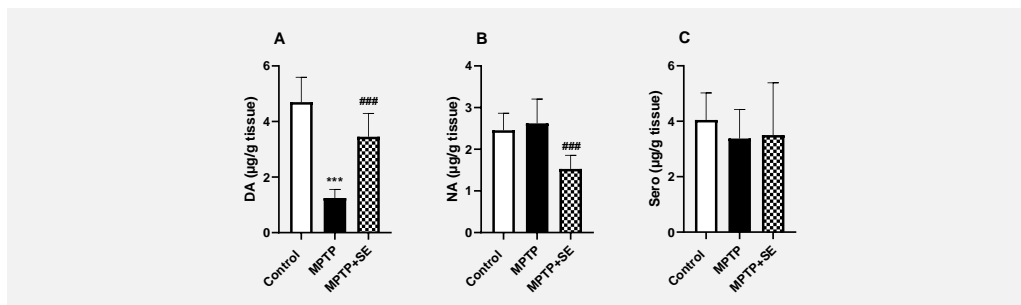
Induced by Toxin 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine Parkinson's Disease Model and the Effect of *Helix Aspersa* Extract In Vivo

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No strategies are currently known that can stop brain cell damage in Parkinson's disease (PD). Since snail extract (SE) possesses antioxidant, anti-inflammatory and anti-apoptotic properties, we investigated its effects in the 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (MPTP) mouse model of PD. The mucus was collected from snails of the species *Helix aspersa*, grown in Bulgarian eco-farms using patented technology. Male C57BL/6 mice aged 8 weeks were used to induce an experimental model of PD in vivo obtained by intraperitoneal injection of MPTP (30 mg/kg) for 5 consecutive days. The MPTP+SE group of mice was treated with standardized snail extract (0.1 ml/10 g b.w) by gavage for 12 consecutive days. All animals were tested for motor coordination and memory performance on days 16th and 17th. At the end of the experiment, the two brain structures mainly related to memory (prefrontal cortex and hippocampus) were isolated for biochemical and histological analyses. After 12 days of SE treatment (7 days before and 5 days concurrent with MPTP), we observed improvement in motor and memory performance in Parkinsonian animals. SE protects dopaminergic neurons, which we found both biochemically and also by histological studies. Twelve days after the first MPTP treatment, the reduction in brain dopamine content

was 73% as compared to the control group. Repeated administration of SE increased the brain level of dopamine by 176% and decreased that of norepinephrine by 42% as compared to the Parkinsonian group. We also observed significant anti-inflammatory effect of snail extract in Parkinsonian animals. In conclusion, our results provide insight into the protective effects of *Helix aspersa* extract in an experimental model of Parkinson's disease in vivo.

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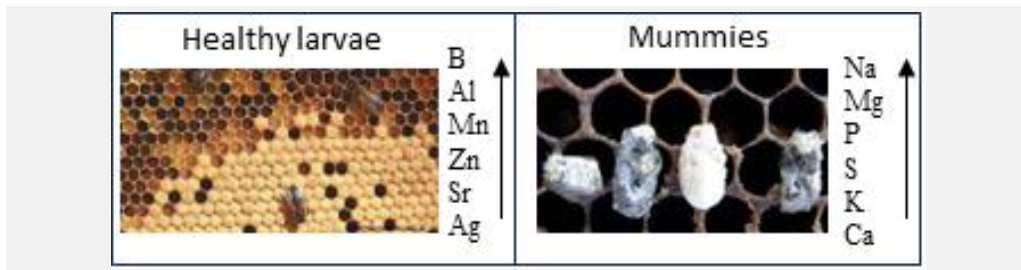
This work was supported by the Bulgarian Ministry of Education and Science (Grant D01-217/30.11.2018 and agreements D01-323/18.12.2019, D01-358/17.12.2020 and D01-278/03.12.2021) under the National Research Programme "Innovative Low-Toxic Bioactive Systems for Precision Medicine (BioActiveMed)" approved by DCM # 658 / 14.09.2018.

Micronutrient effect on the onset of chalkbrood disease in honey bees

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Chalkbrood is a fungal disease of honey bee brood caused by *Ascosphaera apis*. Although it is usually not lethal for the colony, it can hinder its development by reducing its population. Inherited genetic traits, such as hygienic behavior, play a role in onset of chalkbrood disease. Temperature and humidity are also factors that contribute to commencement of this disease. Adequate nutrition supports the development of healthy honey bee colonies, but until now there has been no direct link between poor nutrition and chalkbrood disease in honey bees.

The aim of this study is to determine whether there are any elemental composition differences between mummies and larvae in healthy honey bee colonies and in ones showing symptoms of chalkbrood disease.

Honey bee larvae and chalkbrood mummies were collected from two apiaries in Vršac, Serbia. Urban showing no symptoms of the disease and rural showing occasional chalkbrood symptoms. For each sample we have sampled three hives. The collected samples were pooled, leaving us with one pooled sample of: (1) healthy larvae from urban apiary, (2) healthy larvae from rural hives that do not show symptoms of chalkbrood disease, (3) healthy larvae from rural hives that show symptoms of chalkbrood disease and (4) mummies from rural colonies with chalkbrood disease.

The samples were freeze-dried before analyses. Afterwards dry samples were homogenized.

Around 100 mg of sample was digested with 5 mL mL conc. HNO₃ using an ultraCLAVE IV microwave digestion system. All element concentrations were determined using inductively coupled plasma mass spectrometry – ICPMS (Agilent ICPMS 7700x).

We here demonstrate that the elemental composition of chalkbrood mummies and healthy larvae from infected hives differ from that of larvae in healthy hives. Chalkbrood mummies have the highest concentration of macro elements such as Na, Mg, P, S, K, Ca and at the same time lowest concentration of B, As, Sr, Ag, Cd, Sb, Ba, and Pb. Larvae from the infected hives contain less Pb, Ba, Cs, Sb, Cd, Sr, As, Zn, Cu, Ni, Co, Mn, Cr, V and Al in contrast to healthy larvae from a healthy apiary. This is the first study to demonstrate these differences, suggesting that either larvae try to compensate food quality with quantity or that the parasite is trying to manipulate the host to consume more food.

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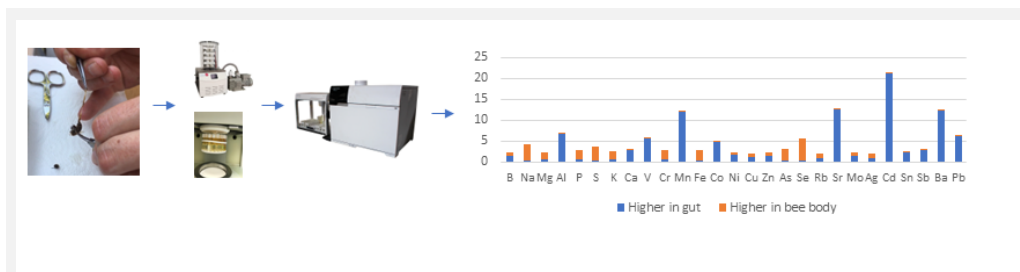
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Honey bee metal accumulation: midgut vs bee tissue

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Honey bee body composition of macromolecules is well studied but elemental composition is less investigated. Insects including honey bees have different needs for minerals, metals and metalloids. Some of them, for example Na, K, Ca, P, Fe, Zn, Mn, Cu, have known metabolic functions and are therefore considered essential. Their exact roles and amounts needed in insects and especially honey bees are not known in detail. Others, including Al, Ba, Cd, As, Pb, Sr, have no known functions in bees and are considered non-essential.

Elemental concentrations were usually measured in homogenized samples of honey bees. In these studies, honey bees were used as biomonitors of metal pollution in the environment. We have recently for the first determined elemental composition of individual bees [1].

This has raised a question of where are the elements in honey bees accumulated. The aim of this study was to determine whether elements detected in honey bees are found in their midgut, or are they accumulated in the honey bee tissue.

Honey bees were dissected, separating the gut from the rest of the body. The midgut and the honey bee body were analyzed separately.

Samples of midgut and honey bee bodies were first freeze dried. Each sample was digested with 2 mL conc. HNO₃ and 3 mL ultrapure H₂O using an ultraCLAVE IV microwave digestion system. All element concentrations were determined using inductively coupled plasma mass spectrometry – ICPMS (Agilent ICPMS 7700x).

We have calculated the results in total element amount per bee. The average mass of the midgut was 8.67 mg, while the average mass of the rest of the honey bee was 39.33 mg. This implies that the

midgut is only 18% of the total mass of one honey bee.

It was observed that the total amount of Na, Mg, P, S, K, Cr, Fe and Ag was higher in the honey bee body. This would be expected for all elements as the mass of the body is 5 times higher than that if the midgut. However, this is not the case.

Midgut has accumulated higher amounts of B, Al, Ca, V, Mn, Co, Ni, Cu, Zn, Sr, Mo, Cd, Sn, Sb, Ba and Pb. This means that honey bees are accumulating essential elements and that they are avoiding the non-essential and potentially toxic ones.

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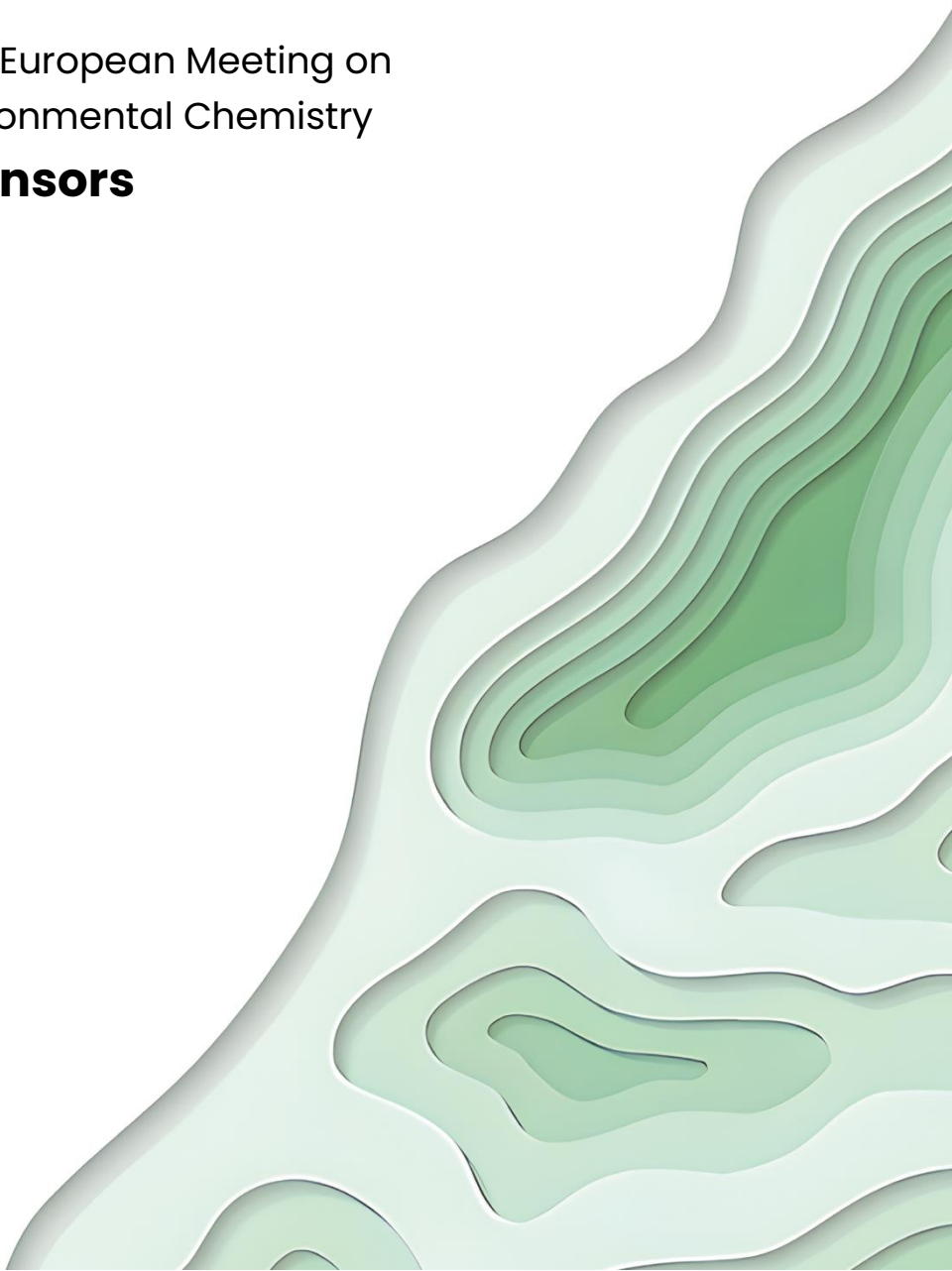
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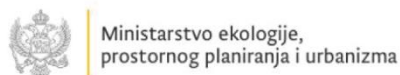


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An abstract graphic on the left side of the page, resembling a topographic map or a cross-section of a mountain range. It features several concentric, wavy lines in various shades of green, from light mint to a darker forest green, creating a sense of depth and contour. The graphic is positioned on the left side of the page, with the text to its right.

**“The trees are our lungs,
the rivers our circulation,
the air our breath,
and the earth our body.”**

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