EMEC 22

22nd European Meeting on
Environmental Chemistry

BOOK of ABSTRACTS

5 – 8 December, 2022,
Ljubljana, Slovenia

Univerza v Ljubljani
Zdravstvena fakulteta

Association of
Chemistry and the
Environment

ASSOCIATION OF
CHEMISTRY AND THE
ENVIRONMENT

University of Ljubljana
Faculty of Health Sciences

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Environmental Chemistry**

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Organised by:	University of Ljubljana (Faculty of Health Sciences), Association of Chemistry and the Environment
Edited by:	assist prof. dr. Mojca Bavcon Kralj, prof. dr. Polonca Trebše, dr. Franja Prosenc, Urška Šunta, dr. Lara Čižmek
Published by:	University of Ljubljana Press
For the publisher:	Gregor Majdič, rector of the University of Ljubljana
Issued by:	University of Ljubljana, Faculty of Health Sciences
For the issuer:	Andrej Starc, Dean of Faculty of Health Sciences, University of Ljubljana
Cover design:	Tina Jeler
Cover page photo:	©Luka Esenko, Ljubljana Tourism photo library (www.visitljubljana.com)
Printed by:	A-media marketing in oblikovanje d.o.o., Slovenia
Print run:	125

Ljubljana, 2022

First edition

Publication is free of charge.

First e-edition. Digital copy of the book is available on: https://e-knjige.ff.uni-lj.si
DOI: 10.55295/9789612970352

Katložni zapis o publikaciji (CIP) pripravili v Narodni in univerzitetni knjižnici v Ljubljani

Tiskana knjiga
COBISS.SI-ID 130826243
ISBN 978-961-297-034-5

E-knjiga
COBISS.SI-ID 130983427
ISBN 978-961-297-035-2 (PDF)

November 15th, 2022

Dear EMEC22 participants,

EMEC22 continues the tradition of annual meetings of the Association of Chemistry and the Environment, providing a forum for the exchange of ideas on recent advances in research and development in environmental chemistry and technology for people from research, academia, and industry at the same time. The session topics solid matrices, water, atmosphere, sustainable development and one health are all devoted to the environment and community.

Our annual meeting is always a warmly expected event. This year it is very special. Firstly, after the pandemic it is planned only as an on-site event. Secondly, an important role in the organisation was given to the group of enthusiastic early-stage researchers, who actively contributed to the foundation of the network, connecting prospective researchers among European countries at the beginning of their scientific pathway. With hopes and wishes that younger generations would keep the spirit of EMEC for the future.

This year, EMEC22 has caught its event number with the actual year, and it is held in a unique conference venue: the Grand Hotel Union. The hotel was the first modern hotel not only in Ljubljana but in the whole South-eastern Europe, built between 1903 and 1905 as a fine example of the Art Nouveau style, and situated a street away from the central Prešeren Square. In that time, it was considered as a grand achievement and even nowadays represents a milestone in history, art, and science.

Many things have changed since then. The population has grown five times and today, the 15th of November 2022, is a special date. Today the world's population has hit eight billion. We are wondering, what will remain strong and firm for the next more than a hundred years as a point of inspiration?

The tradition of searching the right way is not the easiest. Science is a passion of research, more than this, it is a life decision. Strength of struggling for the progress of environment by changing community. Art of beauty and art of cooperation, even from the opposite point of view.

This conference contains those points of inspiration. It brings together researchers working in the field of various topics related to environmental chemistry, sustainability, and resilience, whose duties are sharing experiences and competencies with younger generations.

Dear participants, we hope you will enjoy your stay in Ljubljana, and keep it in your heart as one of the most precious memories of EMEC meetings.

Inspire each other, be an artist of science, and enjoy EMEC22!

Mojca Bavcon Kralj
Chair of the *EMEC22* Organising committee

Organising Committee

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Nuno Ratola, *Portugal*

22nd EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY PROGRAMME

Monday, Dec 5th, 2022

10:00-16:00	Pre-conference Tour to Bled (optional)
16:00-18:00	Registration (Grand hotel Union)
18:00-21:00	Get together at Grand hotel Union

Tuesday, Dec 6th, 2022

07:30-08:30	Registrations		
08:30-09:00	Opening Ceremony		
09:00-09:45	**Plenary Lecture**	**Emerging Chemicals: A Journey from Source to Environment**	**Prof. Ester Heath**
09:45-10:00	Session: **Water**	HPLC-HRMS Determination in Water Environment of Anticancer Drugs Subjected to Heterogenous Photocatalysis Mediated by Semi-Conductor	Federica Dal Bello
10:00-10:15		Design and Manufacture of an in-situ Extraction Functionalized Device Using 3D Printing for the Determination of Sulfonamides from Water Samples by HPLC-DAD	Diego Barzallo
10:15-10:30		Enantiomeric Determination of Main Fluoroquinolone Antibiotics and Their Metabolites in Wastewater and Surface Water	Irene Aparicio Gomez
10:30-10:45		Formation and Decomposition of Thiocyanate in Natural Aquatic Systems	Alexey Kamyshny
10:45-10:55		Session Discussion	
10:55-11:25	Coffee break & Poster Session		
11:25-11:55	**Keynote Lecture**	**Adsorption process puzzle in novel water treatment for organics removal**	**Prof. Ivana Ivančev Tumbas**
11:55-12:10	Session: **Water**	Nutrient Removal and Recovery from Water Using Fuctionalised Biochars	Szabolcs Pap
12:10-12:25		Natural Abiotic Degradation of Phenol and Chlorophenol in Aquatic Environment	Aleksander Kravos
12:25-12:40		Ionic and Porous Materials for Efficient and Sustainable Water Purification Processes	Luis Branco
12:40-12:55		Development of a New Synthetic Chalcone as a Promising Non-Toxic Antifoulant for the Prevention of Marine Biofouling	Daniela Pereira
12:55-13:10		Session Discussion	
13:10-14:25	Lunch		
14:25-14:40	Session: **Water**	Water Pollution Threats in Important Bird and Biodiversity Areas	Maria Dulsat-Masvidal
14:40-14:55		Environmental Quality of the Hyporheic Zone of the Sava River Under Anthropogenic Influence	Marijana Erk
14:55-15:10		Photochemical Fate of Organic Micropollutants in the Sea Surface Microlayer	Carole Abdel Nour
15:10-15:25		Distribution and Remobilization of Organic Pollutants by Floods - the Case Study Rur River, Germany	Christina Alina Schwanen
15:25-15:40		Monitoring of the Occurrence and Patterns of Regulated Persistent Organic Pollutants and Emerging Flame Retardants in the Eastern French Mediterranean Coastline	Camille Rigal
15:40-15:55		Session Discussion	
15:55-16:25	Coffee break & Poster Session		
16:25-16:55	**Keynote Lecture**	**Public health advances in environmental monitoring and disinfection by nanotechnologies**	**Prof. Vincenzo Romano Spica**

16:55-17:10	Session: **One Health**	Innovative Data Visualisation Tool to Aid Addressing Pharmaceutical Pollution in the Scottish Water Environment	Lydia Niemi
17:10-17:25		Assessing Particle Toxicity of Two African Cities Using the Ascorbic Acid Assay	Eduardo José dos Santos Souza
17:25-17:40		Mass Flow Balance of Gadolinium-Based Contrast Agents in Workplaces with Magnetic Resonance Imaging Services	Frederika Mišíková
17:40-17:50		Session Discussion	
17:50-18:30	**Ljubljana by night**		
18:30-22:00	**Early-career workshop & social**		

Wednesday, Dec 7th, 2022			
07:30-08:30	Registrations		
08:30-09:15	**Plenary Lecture**	**Air pollution and health: New methods for characterisation of composition and biological effects of anthropogenic and biogenic emissions as well as ambient aerosols**	**Prof. Ralf Zimmermann**
09:15-09:30	Session: **Atmosphere**	Insights into Fenton-like reaction in the presence of oxalate complexes and implications for the atmospheric aqueous phase	Daniele Scheres Firak
09:30-09:45		Solving the mystery of the Chukotka stinky Gray whales	Albert T. Lebedev
09:45-10:00		Comparing Smoke and Aerosols from Classic and Electronic Cigarettes, and from "Heat-not-Burn" Devices	Borut Poljšak
10:00-10:15		Air Quality Mobile Monitoring Campaign in Novi Sad Urban Area in Winter and Summer 2022	Miloš Davidović
10:15-10:30		Session Discussion	
10:30-11:00	**Keynote Lecture**	**Nanoplastics in the environment**	**Dr. Dušan Materić**
11:00-11:30	**Coffee break & Poster Session**		
11:30-12:00	**Keynote Lecture**	**Studies on sampling and molecular characterization of bioaerosol viral and bacterial components in outdoor and indoor environments**	**Prof. Pierluigi Barbieri**
12:00-12:15	Session: **One Health**	Gasoline additives in groundwater in Paraguay - case study: Methyl t-butyl ether in the Patiño Aquifer	Juan F. Facetti
12:15-12:30		Assessing the Nature and the Impact of By-Products Issued from Industrial Chlorinated Discharges into the Sea	Jean Luc Boudenne
12:30-12:45		Impact of Polyhydroxybutyrate Microparticles on the Floating Freshwater Plant Duckweed *Lemna minor*	Petra Procházková
12:45-13:00		Session Discussion	
13:00-14:15	**Lunch**		
14:15-14:45	**Keynote Lecture**	**Promising bioactive compounds from marine macroalgae: from basic research to potential application**	**Dr. Sanja Babić**
14:45-15:00	Session: **One Health**	At-Source Hospital Wastewater Treatment To Eliminate Harmful Pharmaceuticals: A Novel Approach Using UV-LED Activated Photocatalytic Nanomaterials	Manuel Thomas Valdivia
15:00-15:15		Implications of Polystyrene Microplastics on the Gastric Digestion of Bovine Milk	Maria Krishna de Guzman
15:15-15:30		The Role of Secondary Metabolites from *Cannabis Sativa* L. in Health	Roman Štukelj
15:30-15:45		Session Discussion	
15:45-16:15	**Coffee break & Poster Session**		

16:15-16:45	**Keynote Lecture**	**What does the circular economy really mean in our daily lives?**	**Prof. Güray Salihoğlu**
16:45-17:00	Session: **Sustainability**	Urban Wastewater Treatment and Volatile Methylsiloxanes Removal with Microalgal Cultures	Eva Margarida Salgado
17:00-17:15		Faty Acid Profile of *Dunaliella tertiolecta* in Response to Different Selenium Concentrations	Maja Galić Perečinec
17:15-17:30		Plastic Waste Material as a Sustainable Source of Alternative Fuels and Valuable Chemicals	Ivana Jovančičević
17:30-17:45		Development of Ionic Liquid Based Hydrogels for Iron and Cooper Metallic Patinas on Stone Surfaces	Pablo Irizar
17:45-18:00		New Reactor Approach for Low-Temperature Catalytic Methane Decomposition	Vitor Pereira
18:00-18:15		Session Discussion	
18:15-19:30	Pre-Conference dinner time		
19:30-23:30	**Conference dinner**		

Thursday, Dec 8th, 2022

08:30-09:15	**Plenary Lecture**	**Soils, a sink for legacy and emerging pollutants. Impacts in natural areas**	**Prof. Silvia Lacorte**
09:15-09:30	Session: **Soil & Solid Matrices**	Geochemical and Ecotoxicity Properties of Therapeutic Peloid Muds from Serbia and Slovenia	Gorica Veselinović
09:30-09:45		Spatial and Temporal Distribution of Volatile Methylsiloxanes in Sand	Nuno Ratola
09:45-10:00		Salinity and Flooding Mobilize Mercury from Polluted Soils and Sediments	Elisa Pellegrini
10:00-10:15		Geochemical Characterization of Different Areas of the Portuguese Continental Shelf for Potential Aquaculture	Carla Mesquita Palma
10:15-10:30		Bergamot Pastazzo as Suitable Platform for Cd^{2+} Removal and Sensing in Multicomponent Aqueous Solutions	Anna Irto
10:30-10:45		Session Discussion	
10:45-11:15	**Coffee break**		
10:45-11:15	**ACE General Assembly**		
11:15-11:45	**Keynote Lecture**	**Photocatalysis for pollution remediation: treating air, water and hard surfaces**	**Dr. Andraž Šuligoj**
11:45-12:00	Session: **Water**	Photodegradation of Triclosan on the Kaolinite Surface: Aqueous Phase Photodegradation and Molecular Modelling of the Clay Surface Interactions	Mohamed Sarakha
12:00-12:15		Fenton and Fenton-like Processes for the Removal of Emerging and Recalcitrant Contaminants from Wastewater	Davide Vione
12:15-12:30		Reactivity and Photodegradation Mechanism of Metazachlor in Aqueous Phase: Determination of the Rate Constants and Identification of the Main Photoproducts	Gilles Mailhot
12:30-12:45		Bisphenols S, Poorly Determined Substitute of Bisphenol A - Comparison of Electrochemical and Chromatographic Detection in Water Media	Kristina Žagar Soderžnik
12:45-13:00		Photocatalytic Removal of Nine Pesticides by Graphitic Carbon Nitride Coated Recycled Glass Beads and Economical UV-A 365 nm LEDs	Indira de Menezes Castro
13:00-13:15		Synergistic Action of UV Irradiation and Hydroxyl Radicals: Removal of Emerging Contaminant from Water	Praveen Kumar
13:15-13:30		Session Discussion	
13:30-14:00	**Awards & Closing Ceremony**		
14:00-15:15	**Lunch**		
15:30-17:30	**Visit of Ljubljana & Ljubljana Castle**		

Session chairs

Tuesday, Dec 6th 2022		
Time	Session	Chairs
9:45-10:55	Water	Polonca Trebše and Nuno Ratola
11:55-13:10	Water	Mojca Bavcon Kralj and Manuel Thomas Valdivia
14:25-15:55	Water	Lara Čižmek and Albert T. Lebedev
16:55-17:50	One Health	Malgorzata Iwona Szynkowska-Jóźwik and Szabolcs Pap

Wednesday, Dec 7th 2022		
Time	Session	Chairs
9:15-10:30	Atmosphere	Lydia Niemi and Gilles Mailhot
12:00-13:00	One Health	Franja Prosenc and Marco Contin
14:45-15:45	One Health	Gordana Gajica and Jan Schwarzbauer
16:45-18:15	Sustainability	Ester Heath and Branimir Jovančićević

Thursday, Dec 8th 2022		
Time	Session	Chairs
9:15-10:45	Soil & Solid Matrices	Helena Prosen and Jean Luc Boudenne
11:45-13:30	Water	Urška Šunta and Stuart Gibb

Get together on Monday, December 5th, 2022, and Visit to Ljubljana & Ljubljana Castle on Thursday, December 8th, 2022 are held under the patronage of Ljubljana Tourism organisation.

Ljubljana
Turizem Ljubljana

POSTER SESSIONS

Tuesday, Dec 6th 2022			
Session Topic	Poster Title	Presenting Author	Board Number
Soil & Solid Matrices	Organic compounds in surface sediments of different estuaries and continental shelf areas of Portugal for potential aquaculture	Carla Palma	05
	Analytical Methodology for Monitoring Microplastics in Sewage Sludge from Wastewater Treatment Plants	Irene Aparicio	14
	Sustainable mining and acid mine water treatment	Aleksandar Jovanović	19
	Urban water quality through time in Paris, France: what can be learned from $CaCO_3$ deposits found in undergrounds structures	Edwige Pons Branchu	20
	The removal of thiophanate-methyl using novely synthesized catalysts CeO_2-P25 under simulated sunlight: Structural characterisation and photocatalytic activity	Aleksandar Jovanović	25
	The use of an algal micriobiotest to assess the toxicity of degradation products after herbicide photocatalysis	Dominika Josefová	28
	Thermodynamic Solution Properties of Trans-Aconitic acid and Its Sequestering Ability toward Cd^{2+}, Pb^{2+} and Mn^{2+} at different experimental conditions.	Anna Irto	31
Water	Occurrence, Distribution Pattern and Origin of Polycyclic Aromatic Hydrocarbons in the River Marina Sediments of the Kovin Dunavac (Kovin, Serbia)	Katarina Antić	07
	Ultrasound and mixing assisted sediment washing with selected reagents – a comparison study	Jernej Imperl	10
	The Assessment of Sources of Polycyclic Aromatic Hydrocarbons Pollution of the Vrbas River Sediments	Branimir Jovančićević	11
	Influence of Maturation Processes on *n*-Alkane Distribution in Peloids from Sečovlje Saltpans Nature Park Slovenia	Gordana Gajica	12
	Metal-Organic Framework Coated Portable 3D-printed Paddle Stirrer for Extraction of Chlorophenols, P-Nitrophenol and Bisphenol A in Biodigester and Wastewater Samples	María Alejandra Vargas Muñoz	17
	Residues of drugs of abuse: treatment efficiency, environmental occurrence and risk assessment	Ester Heath	18
	Chromatographic and spectrophotometric investigation of V(V) interaction with biologically important thiols	Lucija Knežević	23
	Development of Reliable Analytical Methods for the Monitoring of Emerging Pollutants' Removal by Advanced Oxidation Processes	Helena Prosen	24
	Potential of Correlograms to Detect and Characterise Autocorrelation in Water Monitoring Data	Konstantin Ilijević	32
	Sorption and Biosorption of Petroleum Pollutants from Water Samples Using Biochar, Hydrocarbon Degrading Microorganisms and Their Combination	Gordana Gajica	34
	Sorption of diesel from aqueous solution on biochar	Jelena Avdalović	35

Session Topic	Poster Title	Presenting Author	Board Number
Atmosphere	Trace elements levels in urban soil samples from central Poland	Malgorzata I. Szynkowska-Jóźwik	03
	Risk Assessment of Water Organic Micropollutants in Important Bird and Biodiversity Areas	Maria Dulsat-Masvidal	29
Sustainability	Determination of pollution status of urban forest Obrenovacki Zabran (Serbia) – Part B: microelement concentration in soil and sediments	Nevena Antić	02
	Monitoring of pesticides in soil from South Banat district in Serbia and Timis county in Romania	Milana Zaric	08
	Role of mineralogical composition and physico-chemical properties of sediment on badlands classification	Nevena Antić	13
	Presence of Microplastics in Natural and Drinking Waters by Py-GC-MS	M. Rosa Boleda	15
	Influence of Operating Parameters on the Efficiency of a Pilot-Scale Photocatalytic Reactor for Water Treatment	Qasim Jamil	16
	Seasonal distribution of trace metals in heavily industrialized Pula Bay, Croatia	Ozren Grozdanić	21
	Optimization of Materials on a Graphite Glass Composite Thick Film Working Electrode for Voltammetric Detection of Neonicotinoids	Maksimiljan Dekleva	26
	Monitoring of pesticides in water bodies from the agricultural region of South Banat district in Serbia	Nenad Zaric	27
	Propranolol Degradation Products after Non-thermal Plasma Treatment using Coaxial DBD Reactor	Sladjana Savić	30
	Synthesis of zinc oxide nanoparticles using a Japanese knotweed root extract	Miha Ravbar	33
One Health	Anions determination as an important property of soil in urban forests: case study Avala Mountain, Serbia	Emilija Vukićević	01
	Saturated Hydrocarbons Proxies as a Tool for Differentiation Between Anthropogenic and Natural Organic Matter Inputs to the Surface Soils of the Sava River Alluvium	Tatjana Šolević Knudsen	04
	Occurrence of semi-volatile organic compounds in sediments of the Nerbioi-ibaizabal estuary: spatial and geographical distribution and ecological risk assessment	Pablo Irizar	06
	Leaching of insecticides in soil amended with microalgal biomass: the effect of microplastics in the soil	Urška Šunta	09
	Accumulation of Macro- and Trace Elements in Amphipod *Synurella ambulans* from Hyporheic Zone of the Sava River, Croatia	Zuzana Redžović	22
	Engineered Bioremediation - Technology of Choice for Treatment of Aquifer Contaminated with Oil Pollutants	Srdjan Miletić	36

Wednesday, Dec 7th 2022

Session Topic	Poster Title	Presenting Author	Board Number
Soil	Influence and Contribution of Traffic on $PM_{2.5}$ Concentrations During Four Seasons in Novi Sad	Jelena Radonić	02
	Unregulated Landfills as Sources of PM Emissions	Maja Turk Sekulić	03
	Adaption of a Solid Phase Extraction Method for Copper (I) Determination in Marine Waters and Estuaries	Dora Crmaric	13
	Heavy Metals In The River Water And Sediment -An Impact To Human Health	Željko Jaćimović	18
	Heavy Metals In Edible Mushrooms -An Health Risk Assessment	Željko Jaćimović	19
	GC-MS analysis of liquid fractions obtained by off-line pyrolysis of reference synthetic and natural polymers	Dajana Savić	27
	Arthrospira platensis as a Highly Sustainable Ingredient for Eco-friendly Cosmetics	Ana Martić	34
Water	Road Dust Enrichment of Rare Earth Elements Collected in the Vicinity of the Coal Combustion Power Plant	Konstantin Ilijević	04
	Effects of COVID-19 Lockdown On Particulate Matter And Trace Elements Levels In The Ambient Air Of Urban And Rural Location In Extremadura (Spain)	Lorenzo Calvo Blázquez	05
	Evaluation of Extraction Procedures to Yield the Highest Pigment content, Antioxidant and Antityrosinase activity from Green Algae *Ulva lactuca*	Lara Čižmek	07
	Photostability and photoprotective effects of brown macroalgae *Halopteris scoparia* influenced by seasonal changes	Lara Čižmek	08
	Preparation of PET Particles By Cryomilling and Potential Environmental Impact of Microplastics	Petra Procházková	12
	Development of novel method for determination of disinfection agent N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine using HPLC-DAD	Lovro Tomazin	15
	Persistent Organic Pollutants in the European Eel from the Karstic River (Raša River, Croatia)	Karla Jagić	16
	Biohydrometallurgical Methods for Cobal and Nickel Recovery from Printed PC Motherboard	Jelena Avdalović	20
	Phytotoxicity of Endocrine Disrupters Nonylphenol and Bisphenol A in Pelargonium Zonale	Katarina Antić	25
	Determination of the products of bacterial lignin degradation: targeted and non-targeted screening	Helena Plešnik	26
	Comparison of off-line pyrolysis of commercial biopolymers and biomass samples	Jelena Isailović	28
	Physicochemical Characterization of Biomass Samples Used for Pyrolysis and Co-Pyrolysis for Pyrolytic Processes	Emilija Vukićević	29
Atmosphere	Characterization of Atmospheric Aerosols (PM_{10} and $PM_{2.5}$) in the Area of the Republic of Slovenia	Maja Ivanovski	01
	The use of ethanolic extracts of basil to improve the oxidative stability of cold-pressed sunflower oil	Mališa Antić	10
	Pyrolysis Characteristics of Sewage Sludge and Municipal Solid Waste Subjected to the Torrefaction Process	Maja Ivanovski	30

Session Topic	Poster Title	Presenting Author	Board Number
Sustainability	Evaluation of *Chlorella vulgaris* Potential as Nutraceutical and Sustainable Food Supplement	Marija Baković	06
	Determination of Hydrodynamic Radius of Extracellular Particles from Conditioned Media of Microalgae *Phaeodactylum Tricornutum* by Interferometric Light Microscopy	Anna Romolo	09
	Synthesis of Iodine monochloride Using a Chlorine Solution in Glacial acetic acid with Simultaneous Disinfectant Generation	Sladjana Savić	23
	Determination of PAHs in flying ashes from multi-cyclones and baghouse dust filters	Polonca Trebše	24
	Life Cycle Assessment of Nature-Based Solution for Wastewater Treatment	Maja Turk Sekulić	31
One Health	Acrylamide content in cookies based on spelt flour and beetroot powder	Vesna Antić	11
	Determination of Pollution Status of Urban Forest Obrenovački Zabran (Serbia) – Part A: Anion Concentrations in Soil and Sediments	Gorica Veselinović	14
	Comparative Analysis of Metal Accumulation in Liver and Muscle of Northern Pike from the Mrežnica River: Spatial and Tissue-Specific Differences	Tatjana Mijošek	17
	The role of Ni film structure on catalytic methane decomposition	Luís Alves	21
	Effect of Calcination Step in the Activity of Ir/M-SnO_2 Catalysts for PEM Technology	Luís Alves	22
	Environmental Bioremediation Is The Technology Of The Future In Sustainable Development	Srdjan Miletić	32
	Microalgal cultures for wastewater polishing: application of artificial neural networks for process modelling and control	Eva Salgado	33
	Potential of nature-inspired prenylated flavonoids as a sustainable alternative to commercial biocides against marine biofouling	Daniela Pereira	35

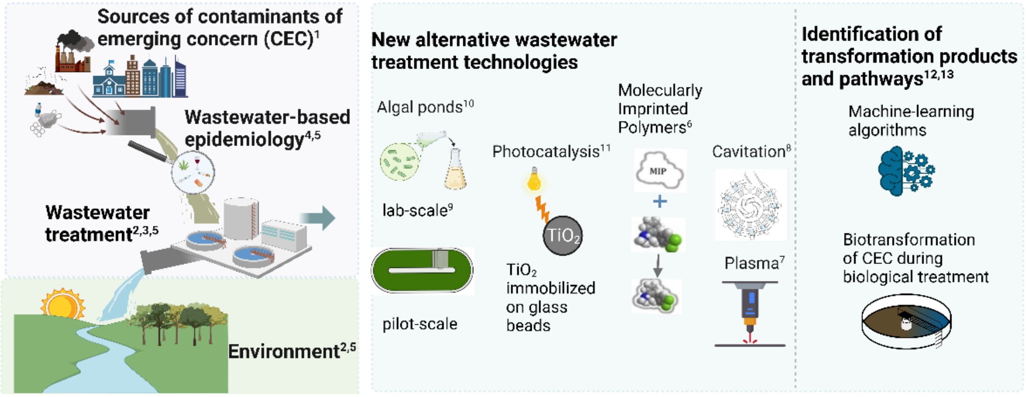
PLENARY LECTURES

Emerging Chemicals: A Journey from Source to Environment

Ester Heath[1,2,*]

(1) Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia, (2) International Postgraduate School Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia

[*]*ester.heath@ijs.si*



Evaluating sources, cycling and fate of emerging chemicals is vital since they have been detected at low levels in surface and groundwater, and there is growing concern that these chemicals can negatively impact ecosystem well-being. Emerging chemicals include pharmaceuticals, personal care products, and other potent endocrine disrupting compounds, including bisphenols. Accordingly, approaches for limiting their input into the environment and developing efficient and green technologies for removing them from wastewater are needed. This presentation will address possible sources [1] of these compounds in wastewater and research into conventional [2,3,5] and alternative treatment technologies [6,7,8,9,10,11]. Their removal efficiencies, degradation kinetics and general advantages and disadvantages will be compared to conventional biological treatment and concepts such as the formation of transformation products [12,13] will be discussed.

Acknowledgements

The study was performed with the financial assistance of the Slovenian Research Agency, namely Program Group P1-0143 and Projects N1- 0143, L7-1848, L1-9191, N1-0047, J1-8147, J2-8162, L1-7544, J1-6744 and L1-5457

References

[1] M. Česen, K. Lenarčič, V. Mislej., M. Levstek, A. Kovačič, B. Cimrmančič, N. Uranjek, T. Kosjek, D. J. Heath, M. Sollner Dolenc, E. Heath (2018) *Science of the Total Environment,* 616-617, 744-752.

[2] M. Česen, D. J. Heath, M. Krivec, J. Košmrlj, T. Kosjek, E. Heath (2018) *Environmental pollution,* 242, 143-154.

[3] A. Kovačič, M. Česen, M. Laimou-Geraniou, D. A. Lambropoulou, T. Kosjek, D. J. Heath, E. Heath (2019) *Environmental Research,* 179, 108738.

[4] T. Verovšek, I. Krizman-Matasic, D. J. Heath, E. Heath (2021) *Science of the Total Environment,* 799, 150013.

[5] T. Verovšek, A. Šuštarič, M. Laimou-Geraniou, I. Krizman-Matasic, H. Prosen, T. Eleršek, V. Kramarič Zidar, V. Mislej, B. Mišmaš, M. Stražar, M. Levstek, B. Cimrmančič, S. Lukšič, N. Uranjek, T. Kozlovič-Bobič, T. Kosjek, D. Kocman, D. Heath, E. Heath (2022) *Science of the Total Environment,* accepted for publication, Nov. 2022.

[6] T. Gornik, S. Shinde, Sudhirkumar, L. Lamovšek, M. Koblar, E. Heath, B. Sellergren, T. Kosjek (2021) *Polymers,* 13, 120.

[7] A. Kovačič, M. Modic, N. Hojnik, A. Vehar, T. Kosjek, D. J. Heath, J. L. Walsh, U. Cvelbar, E. Heath (2022) *Science of the Total Environment,* [in press].

[8] A. Kovačič, D. Škufca, M. Zupanc, J. Gostiša, B. Bizjan, N. Krištofelc, M. Sollner Dolenc, E. Heath (2020) *Science of the Total Environment,* 743, 140724.

[9] F. Prosenc, J. Piechocka, D. Škufca, E. Heath, T. Griessler Bulc, D. Istenič, G. Buttiglieri (2021) *Journal of hazardous materials,* 418, 126284.

[10] D. Škufca, A. Kovačič, T. Griessler Bulc, Tjaša, E. Heath (2021) *Chemosphere,* 271, 129786.

[11] B. Žener, L. Matoh, P. Rodič, D. Škufca, E. Heath, U. Lavrenčič Štangar. (2021) *Journal of environmental chemical engineering,* 9, 1-9.

[12] T. Gornik, A. Kovačič, E. Heath, J. Hollender, T. Kosjek (2021) *Water research,* 181, 115864.

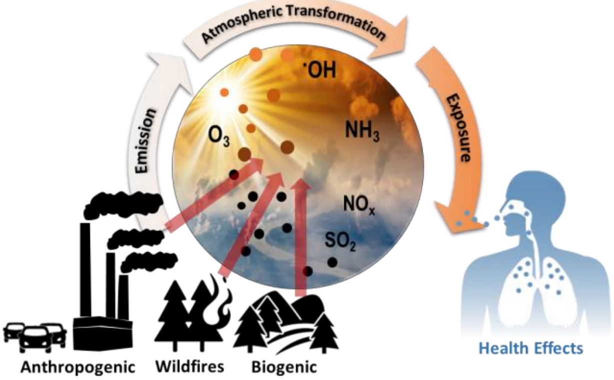
[13] A. Kovačič, C. Gys, M. R. Gulin, Martin Rafael, T. Gornik, T. Kosjek, D. J. Heath, A. Covaci, E. Heath (2021) *Journal of hazardous materials,* 404, 124079

Air Pollution and Health: New Methods for Characterisation of Chemical Composition, Biological Effects and Toxicological Impact of Ambient Air and Aerosol Emissions

R. Zimmermann[1,2], J: Passig[1,2], R. Irsig[3], H. Czech[1,2], P. Martens[1], J. Schade[1,6], S. Ehlert[3], T. Gröger[2], O.Sipulla[7], E. Zimmermann[1,2], J. Pantzke[1,2], S. Offer[1,2], Y. Rudich[4], M. Prado[4], A. Kiendler-Scharr[5], T. Hohaus[5], M. N. Delaval[2], S. Di Bucchianico[1,2], T. Adam[6] and other members of the aeroHEALTH consortium (www.aerohealth.eu)*

(1) University of Rostock, Analytical Chemistry and Department LL&M, Germany, (2) Helmholtz Centre Munich, CMA, Munich, Germany, (3) Photonion GmbH, Schwerin, Germany, (4) Weizmann Institute, Revohot, Israel, (5) Forschungszentrum Jülich, Jülich, Germany, (6) Universität der Bundeswehr-München, München, Germany, (7) University of Eastern Finland, Kuopio, Finland

[*]ralf.zimmermann@uni-rostock.de



Air pollution with inhalable particle matter (PM) is known to be one most severe environmental health-risks worldwide (WHO, 2001). The investigation of the adverse effect mechanisms of aerosols (i.e. suspended, airborne particles) is a complex, multidisciplinary task with many scientific and technological challenges. In order to better understand the causes of the health effects, new methods and technologies for a more comprehensive characterisation of the chemical composition and physical properties of aerosols (i.e. particles and gases) need to be developed. Furthermore, improved biological assessment approaches for the adverse/toxic effects of aerosols are needed. In this lecture new approaches for both, the chemical and the toxicological characterisation of aerosols are presented, discussed and demonstrated by application examples.

In order to assess the toxicological impact of aerosols, reliable biological in-vitro models are needed which allow a reproducible aerosol exposure and straight-forward biological effect analysis. In the last decade, air-liquid-interface (ALI) exposable biological lung models, consisting either of simple mono cell-type-cultures or more complex co-culture- or differentiated lung tissue models have been developed. New automated ALI exposure systems (Vitrocell GmbH) enable the direct exposure of lung cells grown on a semipermeable membrane to moisturized aerosols, e.g. from combustion sources or aerosol generators. After the exposure, cells are harvested and subjected to state-of-the-art toxicological and molecular biological analysis. As an example, a study elucidating the impact of atmospheric photochemical aging on aerosol particle-induced health effects is discussed (in framework of aeroHEALTH, www.aeroHEALTH.eu). The model experiments address differences in toxicological effects of Secondary Organic Aerosols (SOA), generated by photochemically aging of either a common biogenic (β-pinene) or anthropogenic (naphthalene) gaseous organic precursors. Different lung cell models (e.g. A549 lung epithelial cells or a co-culture model of A549 and EA.hy926-endothelial cells) were exposed for 4 h to different SOA concentrations (β-pinene-SOA or naphthalene) at the air-liquid interface (ALI). The aerosols were comprehensively physico-chemically characterized and cytotoxicity, intracellular oxidative stress, genotoxicity, inflammatory effects etc. were determined **[1]** followed by a RNAseq transcriptome analysis. At functional level, SOA_{NAP} augments e.g. secretion of malondialdehyde (lipid peroxidation) and IL-8. An activation of endothelial cells (co-culture) was confirmed by comet assay, suggesting secondary genotoxicity. Chemical characterization revealed distinct differences in the composition of the two SOA-types. Both SOA-types cause significant toxicological effects with greater adverse impact of SOA_{NAP} compared to $\text{SOA}_{\beta\text{PIN}}$. Aromatic precursors, such as naphthalene, form more oxidized and aromatic SOA of higher oxidation potential with higher toxicity compared to aliphatic precursors (e.g. β-pinene). Recently also fresh and photochemical aged gasoline car emissions (EURO 6 level) were tested, showing a significant toxification of the emissions by photochemical aging, highlighting the important influence of atmospheric chemistry for the adverse health-outcomes of air pollution and emissions.

In the second part or the lecture, a new concept for an improved aerosol characterisation approach is presented. The chemical composition of the particles is considered to be highly relevant for the PM-toxicity. In particular, the content of toxic compounds such as soot, polycyclic aromatic hydrocarbons (PAHs) or transition metals (e.g. Fe or Cu) is of concern. In conjunction with particle toxicological studies, usually a detailed analysis of the PM composition is performed by chemical analysis of PM-filter samples. This approach gives integral values on the pollutant concentrations (i.e. amount per cubic meter). However, any information on the mixing state of toxicants is missing. The mixing state, however, likely is crucial to assess health effects: the toxicants may either be equally distributed over many particles (internally mixed) or could be highly concentrated within a specific, small sub-population (externally mixed), inducing different effects upon particle in-lung deposition. In the latter case, the particles with a very high concentration of toxicants will induce stronger cellular effects at the deposition site due to local overwhelming of defense mechanisms (e.g. antioxidant capacity depletion) and due to DAMP signaling (i.e. if necrotic cell death is induced). Consequently, novel on-line analysis techniques, addressing the mixing state of health relevant PM-chemicals on a single-particle scale are required. A new approach for on-line single particle analysis bases on bipolar laser mass spectrometry (Photonion GmbH). The aerosol is directly sampled from the air. The organic coating of the size-classified aerosol particles (laser velocimetry) is desorbed by an IR-laser pulse. A few µs later, the relevant toxicants (transition metals, PAH and soot) are ionized by a novel combined laser ionization scheme and are detected in the mass spectrometer. The new Single Particle Mass Spectrometric (SPMS) method will be presented and explained **[2]**. It has been already applied e.g. for ambient aerosol analyses or combustion emission monitoring and is giving new insights into the mixing state of the air toxicants (PAH/metals/soot) and other compounds (e.g. nitrate, sulfate etc.).

Acknowledgements

Funding by the Helmholtz Association (HGF) for the aeroHEALTH Helmholtz International Lab and the German Science Foundation is gratefully acknowledged.

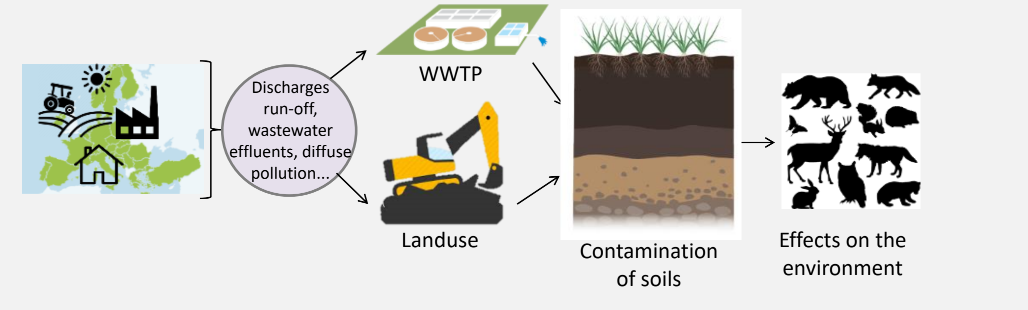
References

[1] S. Offer et al. (2022) *Environ. Health Perspect*,130, 2.
[2] J. Schade et al. (2019) *Anal. Chem.*, 91, 10282–10288

Soils, a Sink for Legacy and Emerging Pollutants. Impacts in Natural Areas

S. Lacorte[1,*], *M. Dulsat-Masvidal*[1], *R. Mateo*[2]

(1) Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain,
(2) Instituto de Investigación en Recursos Cinegéticos (IREC), CSIC-UCLM-JCCM, 13005 Ciudad Real, Spain.
[*]silvia.lacorte@idaea.csic.es



Nowadays soils are stressed by multiple anthropogenic factors associated with land use such as urban expansion, industrialization, road infrastructures, waste disposal and intensive agriculture. These activities may directly or indirectly cause the release of contaminants to the environment, which can thereafter be deposited or accumulated in soil [1]. Therefore, soils, especially those with high organic matter content, act as sinks and reservoirs of a myriad of contaminants such as flame retardants, plasticizers, pesticides or metals, among others [2]. Contamination of soils affects the quality and productivity of crops and poses groundwater resources at risk [3]. There is also evidence that contaminants present in soil can be transferred to the food chain, and affect wildlife and human health. As soils reflect both historical and recent pollution inputs, assessment of their contamination status is extremely relevant as soil pollution affects ecosystem structure and soil functions.

In this study, we have assessed the soil pollution levels in natural areas including National and Natural Parks. These areas have a high protection level and are of ecological interest as are intended to preserve biodiversity and wildlife. However, they may be impacted by contaminants due to the various activities performed within the boundaries of the Parks such as tourism, farming, animal rearing, timbering or indirectly by atmospheric deposition. We have undertaken a soil monitoring program to determine the presence of legacy contaminants such as PCBs, PAHs and organochlorine pesticides and also of plasticizers, flame retardants and metals. The most prevalent contaminants in soil were identified and their accumulative risk assessed according to Predicted No Effect Concentrations (PNEC), as a tool to evaluate their impact [4]. We have used Principal Component Analysis and Corine land use information to determine main pollution patterns, their geographical distribution and identification of pollution sources according to the activities carried out in each area. It has been observed that artificial land, mining, and pesticide use were the main activities affecting the quality of soils. Overall, this study highlights the importance of soil monitoring studies to evaluate the impact of contaminants in a matrix highly stressed by anthropogenic factors.

Acknowledgements

The Spanish Ministry of Science and Innovation is acknowledged for financial support [PID2019-105732GBC21] from CIN/AEI/10.13039/5011000 11033 and for the Severo Ochoa project Grant CEX2018-000794-S funded by MCIN/AEI/ 10.13039/501100011033 to IDAEA-CSIC as Centre of Excellence.

References

[1] C.S.S.Ferreira, S. Seifollahi-Aghmiuni, G. Destouni, N. Ghajarnia, Z. Kalantari (2022) *Science of the Total Environment*, 805, 150106.

[2] T.J. McGrath, A. S., Ball, B. O. Clarke (2017). *Environmental Pollution* 230, 741-757.

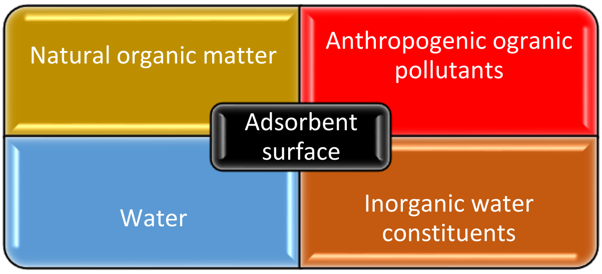
[3] P. Colomer-Vidal. L. Jiang, W. Mei, C. Luo, S. Lacorte, A. Rigol, G. Zhang (2022) *Journal Hazardous Materials* 421, 126768-127776.

[4] NORMAN ecotoxicology database, 2021. Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php.

KEYNOTE LECTURES

Adsorption Process Puzzle in Novel Water Treatment for Organics Removal

I. Ivančev-Tumbas[1,*], M. Bogunović[1]
(1) University of Novi Sad, Faculty of Sciences, Trg D. Obradovića 3, 21000 Novi Sad, Serbia
[*] ivana.ivancev-tumbas@dh.uns.ac.rs



Adsorption has been successfully used in water treatment for removal of colour, taste and odour compounds, fractions of natural organic matter and removal of some organic pollutants for almost one century. Surprisingly, after decades, the same topic still remains a puzzle. This is caused by the recently acquired knowledge about complexity and pollution of different water matrices and both natural and anthropogenic changes that are globally occurring. "Old" adsorption related topics for the most frequently used adsorbent, activated carbon, are on the research agenda again but enlightened from the new perspectives. Reopened questions relate to sorbent production, relevant characterisation, but also optimisation of its use which is found to be influenced by complex interactions in water matrices and the way they are treated (e.g. place of adsorption process in whole water treatment train, contact time of adsorbent and water, combination with other process materials, etc). Desorption of pollutants [1] and competition with natural organic matter [2] remain the challenge both in research and real water treatment. The reason is huge number of pollutants in aquatic environment that we are aware of since 1990-ties and versatile nature of the natural organic matter. Fragmented results need generalizations and require new modelling tools. Additionally, high relevance of bacteria and viruses removal from water nowadays brings application of relatively novel hybrid treatment into the focus of researchers. Combination of adsorption with various types of membrane filtration in different process configurations is effective both in removal of organic micropollutants and microorganisms. However, it also requires fine, research based tuning [3] related to the way of the carbon application (dosing suspension concentration, single or continuous dosing during filtration, hydraulic contact time).

The lecture will compile our recently published results related to organic micropollutants removal from water with focus on inspirational open issues in activated carbon adsorption and interactions with natural organic matter [e.g. 4, 5]. It will be shown how increase of surface oxygen content affected adsorption of selected organic compounds on carbonaceous graphite surface that is more homogenous than activated carbon. Furthermore, the methodology of comparison of various carbons for anthropogenic markers removal from water will be discussed based on lessons learned from recent work.

Acknowledgements

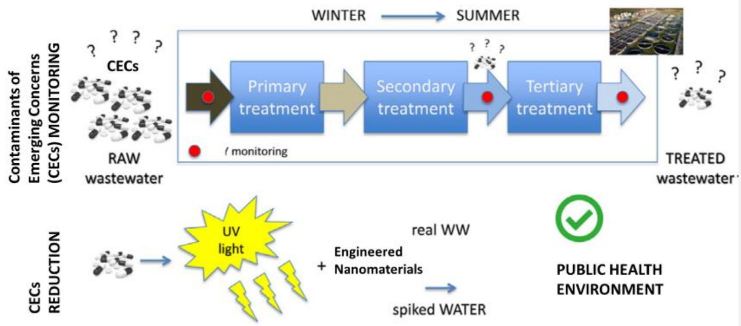
The authors acknowledge financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. *451-03-68/2022-14/200125)*.

References

[1] G. Aschermann, L. Neubert, F. Zietzschmann, M. Jekel (2019) *Water Research*, 161,161-170.
[2] R. Guillossou, J. Le Roux, R. Mailler, C. S. Pereira-Derome, G. Varrault, A. Bressy, E. Vulliet, C. Morlay, F. Nauleau, V. Rocher, J. Gasperi (2020) *Water Research*, 172, 115487.
[3] G. Hoffmann, Rathinam K., Martschin M., Ivančev-Tumbas I., Panglisch S. (2021) *Water*, 13, 3578.
[4] I. Ivancev-Tumbas, L. Landwehrkamp, R. Hobby, M. Vernillo, S. Panglisch (2020) *Adsorption Science and Technology*, 38 (7-8), 286-303.
[5] M. Bogunović, Marjanović T., Ivančev-Tumbas I. (2022) *International Journal of Environmental Research and Public Health*, 18, 8691.

Public Health Advances in Environmental Monitoring and Nano-Based Disinfection

V. Romano Spica[1,*], *G. Lofrano*[1]
(1) University of Rome “Foro Italico”, Piazza Lauro De Bosis 6, Rome, Italy
[*]*vincenzo.romanospica@uniroma4.it*



Nanotechnology is one of the fastest growing field in science, being considered the emblem of the twenty-first century innovation. In particular, the feverish development of engineered nanoscale materials (NMs) represents a technological revolution for the development of innovative materials and new productive sectors at the service of citizens [1].

The environmental monitoring is recently facing the presence of contaminants of emerging concern (CECs), including any chemical or microorganism discovered in water or into the environment that was not previously detected, or being present at very low levels.

Proper wastewater disinfection represents the base for the prevention of waterborne infections induced by pathogenic microorganism, which can outbreak and increase the disease burden, especially in developing countries, with subsequent social and economic impacts. Moreover, treated wastewater is also a reliable and attractive alternative source of water supply in developed countries (EU 2022/952 regulation). In this regard, disinfection is mandatory before wastewater discharge and reuse to kill/inactivate pathogens [2].

Contemporary conventional water disinfection technologies, including chlorination and ultra-violet radiation (UV), have been extensively discussed due to their various operational and environmental burdens, such as the formation of potentially hazardous disinfection by-products (DBPs), which are inevitably produced due to the reaction between disinfectants, halides, and organic matter, and high energy consumption.

Thus, the identification of alternative technologies is a necessary challenge for human health and ecosystem protection. A variety of treatment technologies have been reported in the literature to prevent the release of faecal indicator bacteria (FIB) (*i.e.*, *Escherichia coli* and enterococci) into the environment via effluent discharge/reuse, with varying levels of success. Among them, advanced oxidation processes (AOPs) have emerged as promising, innovative water treatment technologies. Photocatalysis has gained growing attention owing to its intelligent design and adjustable operational efficiency and costs. In the last decades, several engineered nanomaterials have been developed to overcome the drawbacks of the conventional materials and to maximize process behaviours in the removal of a wide range of CECs including several emerging pathogens as well [3].

Acknowledgements

This study was partially founded within Grant European Union MUR DM 1062 2021
code C0-G-14733-1 and MIUR-Fund-PON R&I 2014-2020 React-EU code DOT17C0959-2. The authors thank Forniture Tessili Cimmino srl and GeneS Start Up for supporting the research for innovation in the field in collaboration with the University of Rome “Foro Italico”

References

[1] G. Lofrano, G. Libralato, J. Brown (Editors) Nanotechnologies for environmental remediation. Springer, 2017, 6.

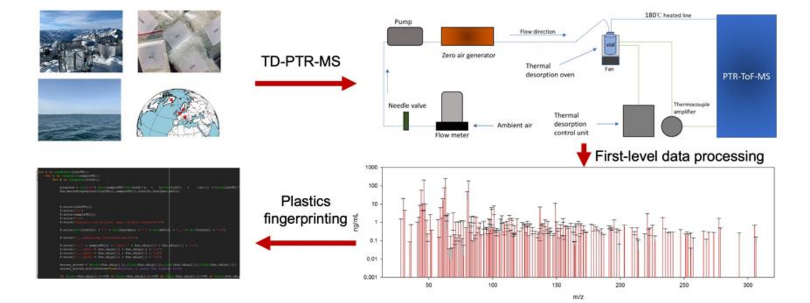
[2] J. Wang, K. Huang, Z. Wu, Y. Yu (2022) Ultrason. Sonochem., 82, 105905.

[3] G. Lofrano, F. Ubaldi, L. Albarano, M. Carotenuto, V. Vaiano, F. Valeriani, ... & V. Romano Spica (2022) Nanomaterials, 12(16), 2831.

Nanoplastics Measurements in the Environment: What Did We Learn So Far?

D. Materić[1,*]

(1) *Helmholtz Centre for Environmental Research (UFZ), Permoserstraße 15, 04318 Leipzig, Germany*
[*] *dusan.materic@ufz.de*



Plastic pollution has been recognised to be a global problem, as particles of various sizes have been detected in water, soil and air, from urban to remote areas. Plastics are one of the most commonly used materials, with an annual production of 368 million tonnes worldwide, of which 57.9 million tonnes (15.7 %) are produced in Europe [1]. When plastics are disposed, they fragment from larger to smaller particles, e.g. from macro- to microplastics (size <5 mm) to nanoplastics (particles <1 µm).

Nanoplastics have been suspected to be a significant environmental problem; however, until recently, no quantitative method was available to measure the nanoplastics in environmental samples. However, I have developed the first method capable of sensitive quantification of nanoplastics in the environmental samples [2] – closing the well-known methodological gap. The method works on the following principle: different plastics have different melting points and release different organic vapours (i.e. smells) when heated up. A gradual increase in the temperature combined with real-time, high-resolution, quantitative mass spectrometry (PTR-MS) allows us to selectively and sensitively measure both concentrations and types of nanoplastics. As the method is compatible with the analysis of air (e.g. aerosol filters) and liquid samples (e.g. surface water [3], snow/ice/rain [4–6], seawater [7]), it provides a suitable platform for a systematic analysis of environmental nanoplastics.

We successfully measured nanoplastics in Alps [4], rural surface water in Sweden and Siberia [3], and Greenland ice core and Antarctica sea ice [5]. In these first measurements that involved an international and multidisciplinary team, we applied a strict quality control protocol and found two striking facts: (a) the nanoplastic concentrations were very high - we measured high concentrations and deposition rates of nanoplastics (42 kg km^{-2} year^{-1}) in the remote sites [4], and they were similar to the mass reported for microplastics [6,7]; (b) the nanoplastics pollution problem is actually not new - we detected the nanoplastics in the Greenland ice record, dated back to 1960s [5]. Thus, our work suggests that nanoplastics are a much larger, more expansive and older environmental problem than anticipated.

Acknowledgements

I acknowledge the support from Dutch Research Council (NWO) grant numbers: OCENW.XS2.078 and OCENW.XS21.2.042.

References

[1] PlasticsEurope, Plastics - the Facts 2020, (2021). https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/.

[2] D. Materić, A. Kasper-Giebl, D. Kau, M. Anten, M. Greilinger, E. Ludewig, E. van Sebille, T. Röckmann, R. Holzinger, *Environ. Sci. Technol.* 54 (2020) 2353–2359. https://doi.org/10.1021/acs.est.9b07540.

[3] D. Materić, M. Peacock, J. Dean, M. Futter, T. Maximov, F. Moldan, T. Röckmann, R. Holzinger, *Environ. Res. Lett.* 17 (2022) 054036.

[4] D. Materić, E. Ludewig, D. Brunner, T. Röckmann, R. Holzinger, *Environmental Pollution*. (2021) 117697. https://doi.org/10.1016/j.envpol.2021.117697.

[5] D. Materić, H.A. Kjær, P. Vallelonga, J.-L. Tison, T. Röckmann, R. Holzinger, *Environmental Research*. 208 (2022) 112741.

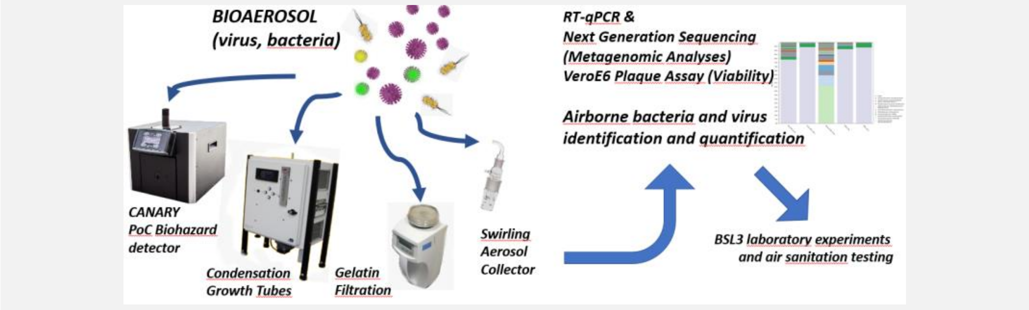
[6] S. Allen, D. Materić, D. Allen, A. MacDonald, R. Holzinger, G.L. Roux, V.R. Phoenix, *Journal of Hazardous Materials Advances*. 7 (2022) 100104.

[7] D. Materić, R. Holzinger, H. Niemann, *Science of The Total Environment*. 846 (2022) 157371.

Studies on Sampling and Molecular Characterization of Bioaerosol Viral and Bacterial Components in Outdoor and Indoor Environments

A.S.Gaetano[1], S.Semeraro[2], A.Pallavicini[3], L.Zupin[4], M.G.Perrone[5], F.Fontana[6], E.Greco[1,2], S.Licen[1,2], P.Barbieri[1,2]*

(1) DSCF University of Trieste, Via Giorgieri 1, Trieste, Italy, (2) Interuniversity Consortium INSTM, Via Via Giusti, 9, Firenze, Italy (3) DSV University of Trieste, Via Giorgieri 5, Trieste, Italy, (4) IRCCS Burlo Garofolo Via dell'Istria 65, Trieste, Italy (5) TCR-Tecora Srl, via delle Primule16,Cogliate (MB), Italy (6) ASUGI, Ospedale S.Polo Via Galvani1, Monfalcone (GO), Italy
**barbierp@units.it*



Societal issues as the COVID-19 pandemic and healthcare criticalities as the Anti-Microbial-Resistance emergency have risen attention to bioaerosols and the presence of pathogenic components in air. Despite this relevance, there is lack of standardized or well accepted procedures of instrumental approaches for characterizing bacterial and viral components of bioaerosols. Different sampling tools and molecular analysis protocols for microorganisms both from outdoor and indoor environments have been proposed, but little information on comparative assessments has been published. We started an intercomparison exercise for sampling approaches, considering Condensation Growth Tubes (Aerosol Devices-Biospot BSS310 ViVAS sampler), swirling aerosol collector (SKC-BioSampler), gelatin impactors and filters (Sartorius-MD8 Airport). Sampling approaches keeping microbial integrity allowing sound recovery and viability/infectivity assessment are addressed. Aiming at qualitative and quantitative microbial detection of bacteria and viruses in (intrinsically diluted) air samples [1] an approach has been developed and deployed using rt-PCR metagenomic analyses for bacteria on 16S gene [2] and targeted detection of SARS-CoV-2, also testing Cellular Analysis and Notification of Antigen Risks and Yields (CANARY) detection [3] after high volume sampling by Smiths Detection BioFlash.

Samplings sessions have been completed in May and July 2022 in close proximity of the aeration tanks of untreated effluents from the Waste Water Treatment Plant of the city of Trieste. Same air volume (1,440 m^3) collected with different samplers and media produce different results in terms of amount of DNA sequences defining Operational Taxonomic Units (OTU). First results shows that low flow Condensation Growth Tubes sampler with DNA/RNA shield produces higher OTU amount and microbial diversity information as compared to Swirling Aerosol Collector and portable gelatin filtration sampler. No on-site/in field SARS-CoV-2 detection has been revealed by CANARY assay.

A consequent study from a poorly aerated (CO_2 monitored) isolation room of a COVID-19 weakly symptomatic individual is presented, reporting evidences by ViVAS, BioFlash, swab samples and residual infectivity testing in a BSL3 laboratory by CPE plaque test on VERO E6. No infectivity/cytopathic effect has been detected by cellular models, but good correlation between viral RNA sampled by low and high volume samplings.

Experimental settings and protocols for assessing samplers, PPE for SARS-CoV-2 aerosols in a BSL3 laboratory [4] have been designed and realised; the settings will be applied to the study of interactions between biotic and abiotic aerosol components.

Acknowledgements

ACEGAS-APS-AMGA utility company and Società Italiana di Medicina Ambientale are kindly acknowledged for the support to the research.

References

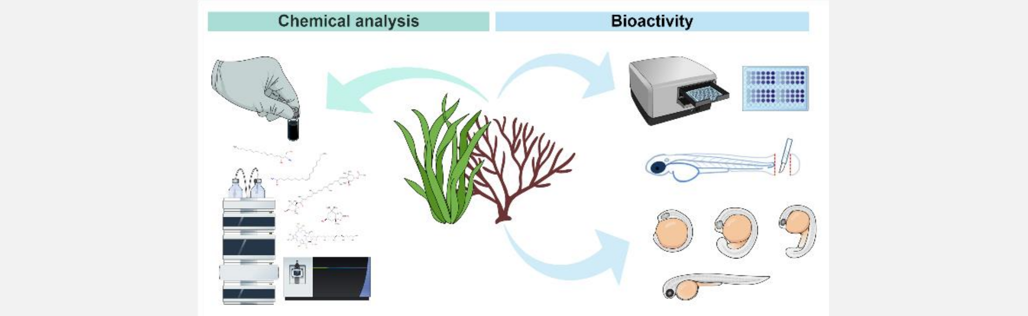
[1] H. Mbareche, E. Brisebois, M. Veillette, C. Duchaine (2017) *Science of the Total Environment*, 599, 2095-2104.
[2] A. Giglio, M.L. Vommaro, F. Gionechetti, A. Pallavicini (2021) *J. Applied Entomology*, 145, 986-1000.
[3] T.H. Rider. M.S. Petrovick, F.E. Narqi, J.D. Harper, et al. (2003) *Science*, 301, 213-215.
[4] L. Zupin, S. Licen, M. Milani et al. (2021) *Int. J. Environmental Research Public Health*, 18, 11172-86.

Promising Bioactive Compounds from Marine Macroalgae: from Basic Research to Potential Application

S. Babić[1,2,*]

(1) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (2) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

[*]*babic@irb.hr*



Marine macroalgae (seaweeds) represent a novel and sustainable reserve of highly diverse molecules already recognized by the pharmaceutical, cosmetic, and food industries. In order to survive in a very competitive and harsh environment, seaweeds had to develop defence strategies, resulting in an extraordinary chemical and bio-diversity of secondary metabolites that vary considerably even between the same species [1]. The Adriatic Sea, characterized by high salinity, seasonal oscillations of temperature, relatively low depth, and increased UV radiation impact [2], yielded numerous endemic species and caused intraspecific variations that are, despite the immense scientific effort, not being thoroughly investigated. The Scientific Centre of Excellence (BioProCro) and project Bioprospecting of the Adriatic Sea thus represent the first attempt to access the resources of Croatian marine ecosystems comprehensively and speed up and simplify the processes of discovering novel natural compounds and determine their beneficial activities. Bioassays play a central role in such projects and their selection and application have to focus on assessing specific endpoints for bioactivity identification. Since certain bioactivities can be increased/decreased/annulled upon metabolism processes, bioassays using zebrafish *Danio rerio* embryos and larvae appear ideal for this purpose since they combine the organism-level approach with the advantages of the *in vitro* format [3]. The oral presentation will focus on bioactivities of methanolic and dichloromethane fractions of brown and green macroalgae *Fucus virsoides, Ericaria crinita, Ericaria amentacea, Cystoseira compressa Codium adhaerens*, and *Dasycladus vermicularis* obtained within the BioProCro. The results suggest that mentioned algae might be a potent source of natural molecules with antioxidant, anti-inflammatory, regenerative and osteogenic activities, such as pigments, terpenes, and porphyrin-based compounds.

Acknowledgements

This study was supported by the Scientific Centre of Excellence for Marine Bioprospecting (BioProCro), a project co-financed by the Croatian Government and the European Union through the European Regional Development Fund—the Competitiveness and Cohesion Operational Programme (KK.01.1.1.01).

References

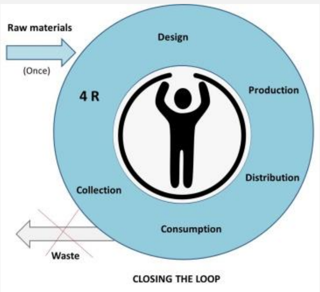
[1] A.M. Cikoš, S. Jokić, D. Šubarić, I. Jerković (2018) *Marine Drugs*, 16(10), 348.

[2] B. Grbec, F. Matić, G. Beg Paklar, M. Morović, R. Popović, I. Vilibić (2018) *Pure and Applied Geophysics*, 175, 4031–4046.

[3] C. Di Paolo, T.B. Seiler, S. Keiter, M. Hu, M. Muz, M., W. Brack, H. Hollert (2015) *Environmental Sciences Europe*, 27(1), 1-11.

What Does the Circular Economy Really Mean in our Daily Lives?

G. Salihoglu[1,*]
(1) Bursa Uludag University, Environmental Engineering Department, Bursa, Türkiye
[*] *gurays@uludag.edu.tr*



Circular economy model replaces the "end-of-life" concept, the "waste" concept, in other words [1]. It is defined as a restorative industrial system by intention and design, which eliminates the use of toxic substances, encourages renewable energy use, and recovery [1]. Superior design of materials, products, systems, and business models is the key [2].

The circular economy concept is viewed as an operationalization for business to implement sustainable development concept [3]. The waste management hierarchy, or 4R (reduce, reuse, recycle, and recover) framework of the European Union (EU) Waste Framework Directive is generally regarded as the core principle of circular economy [4]. The 4R framework may be regarded as one way of operationalization of circular economy concept. However, the fact that "most recycling is actually down cycling since the quality gets deteriorated over time" should be noted with the 4R framework [5]. Circular economy necessitates a systemic shift (Kirchherr et al., 2017). Kirchherr et al. [6] made a cloud analysis of the circular economy definitions and identified the term "economic" as one of the most prominent terms. They concluded that this result may infer economic prosperity as a key aim of circular economy [6].

Although circular economy describes an economic system that is based on business models, a significant portion of the system operates at micro level including products and consumers. Therefore, circular economy has different reflections in our daily lives. In most of the times consumers are at the point that the loop can be closed. However, it is not always up to the consumers to close the loops. The possibility of closing the loop is mostly determined at the design stage of the products or services. In a circular economy, waste does not exist, and products and raw materials are (designed to be) reused as long and intensive as possible over and over again. Waste is the new raw material. In this paper the possibility and reality of closing the circular economy loops for certain products will be discussed. Electronic wastes, organic wastes, several industrial wastes, packaging and plastic wastes etc. will be examined in circular economy approach. Sustainable product initiative and digital product passport concepts will be explored.

References

[1] EMF, Ellen MacArthur Foundation (2012) Towards the Circular Economy: Economic and Business Rationale for an Accelerated Transition.

[2] Geissdoerfer, M., Savaget, P., Bocken, N.M.P., Hultink, E.J. (2017) *Journal of Cleaner Production*, 143, 757–768.

[3] Ghisellini, P., Cialani, C., Ulgiati, S. (2016) *Journal of Cleaner Production*, 114, 11–32.

[4] Zhu, Q., Geng, Y., Lai, K. (2010) *Journal of Environmental Management*, 91 (6), 1324–1331.

[5] Braungart, M., McDonough, W. (2002) Cradle to Cradle: Remaking the Way We Make Things. North Point Press, New York, United States.

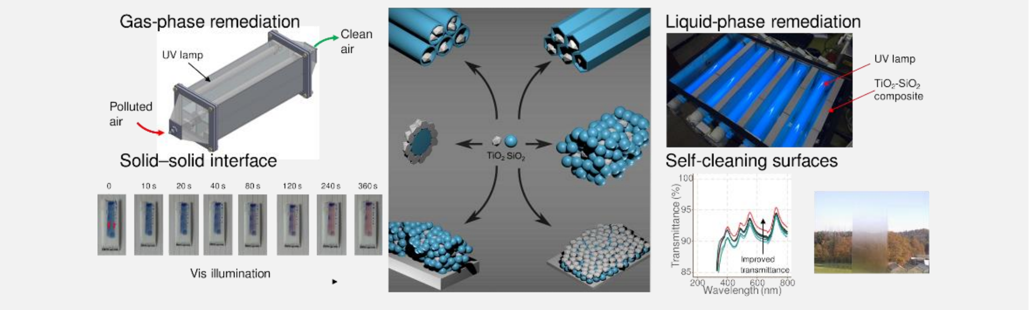
[6] Kirchherr, J., Reike, D., Hekkert, M. (2017) *Resources, Conservation & Recycling*, 127, 221–232.

Photocatalysis for Pollution Remediation: Treating Air, Water, and Hard Surfaces

A. Šuligoj[1,2,*], *N. Novak Tušar*[2,3], *U. Lavrenčič Štangar*[1,3]

(1) Faculty of Chemistry and Chemical Technology, Večna pot 113, Ljubljana, Slovenia, (2) National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia, (3) University of Nova Gorica, Vipavska 11c, Ajdovščina, Slovenia

[*]Andraz.Suligoj@fkkt.uni-lj.si



Solar photocatalysis, a part of broader term advanced oxidation processes (AOP) under which other technologies such as Fenton, ozonation and photocatalysis in general are present, is one of the most applied technologies of its filed. The commercial aspects of solar photocatalysis go back to mid-1990s in Japan and spread later also to north America and Europe [1]. As such, it is one of the most interesting fields, probably due to its environmentally friendly nature and the fact that it promises to employ solar irradiation as its energy source – a source which is bountiful in many parts of the Earth.

Although solar photocatalysis is the holy grail of the majority of efforts of researchers, some applications are void of interest in solar spectral response. These include closed HVAC systems and underground reactor set-ups, when applied. Nevertheless, improving the quantum yield of any material is a common theme amongst the published literature on photocatalysis in the last half century.

Of the many applicable semiconductor materials for photocatalysis, titanium dioxide (TiO_2) is by far the most researched. Efforts for increasing the applicability of TiO_2 and other semiconductors in industrial scale have led to studies of mixed TiO_2–M_XO_X oxides [2], where M stands for metal, usually Si, W, Cu, Fe, etc., doping, and introduction of co-catalyst [3], to name a few approaches. However, the effects of such modifications can be seen on the macroscopic, i.e., structural level as well as on the electronic level. It is therefore critical to understand both aspects of such modifications to exploit the full potential of such systems.

Herein the efforts and effects of several modification methods to improve the photocatalytic activity of TiO_2 and ZnO will be presented. The changes are discussed on the electronic and on the structural level, as well as on the aspect to which such modifications affect the photocatalytic performance in gas-, solid-, and liquid-solid interface. Real-life applications of these materials will also be presented for liquid-solid and self-cleaning applications.

Acknowledgements

The acknowledgements should be written here. Thank you for spending your time in reading the instructions. Feel free to contact us for any further information (emec22@zf.uni-lj.si).

References

[1] A. Fujishima, A. K. Honda (1972) *Nature*, 238, 37–38.
[2] A. Šuligoj, U. L. Štangar, A. Ristić, M. Mazaj, D. Verhovšek, N. N. Tušar (2016) *Applied Catalysis B Environmental*, 184, 119–131.
[3] A. Šuligoj, I. Arčon, M. Mazaj, G. Dražić, D. Arčon, P. Cool, U. L. Štangar, N. N. Tušar (2018) *Journal of Material Chemistry A*, 6, 9882–9892.

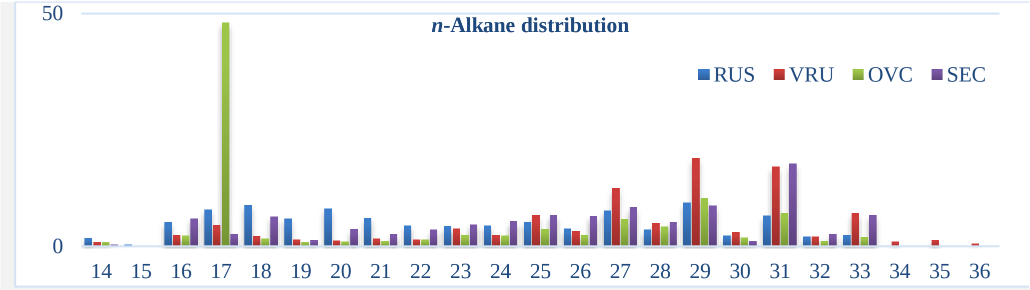
SESSION 1: Soil & Solid Matrices

Geochemical and Ecotoxicity Properties of Therapeutic Peloid Muds from Serbia and Slovenia

A. Šajnović[1], *S. Stojadinović*[1], *G. Gajica*[1,*], *G. Veselinović*[1], *N. Glavaš*[2], *P. Trebše*[3], *F. Prosenc*[3], *I. Gevinç*[3,4], *B. Jovančićević*[5]

(1) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia, (2) SOLINE Pridelava soli d.o.o., Seča 115, Portorož, Slovenia, (3) University of Ljubljana, Faculty of Health Sciences, Zdravstvena pot 5, 1000, Ljubljana, Slovenia, (4) Bursa Uludag University, Faculty of Engineering, Environmental Engineering Department, 16059, Bursa, Turkey, (5) University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia

[*] *gordana.gajica@ihtm.bg.ac.rs*



The samples assessed in this study were therapeutic peloid muds from Slovenian (Sečovlje (SEC)) and Serbian spas (Rusanda (RUS), Vrujci (VRU), and Ovča (OVC)). Sampling was simply done directly from the spa areas. Each collected sample was kept separately in glass jars in a refrigerator until further analysis.

Organic and inorganic geochemical analyses have been used for estimation of the origin and maturity of organic matter, depositional environment characteristics and assessment of the pollution status. Additionally, the toxicity potential measured by the inhibition of luminescence of *Vibrio fischeri*, as well as the content of large microplastics (1 – 5 mm) were determined.

Obtained results indicate predominantly terrestrial organic matter with certain contributions of algae and/or bacteria in samples VRU, RUS and SEC in precursor biomass. The presence of bacteria and other microorganisms in peloids has the potential to "boost" their therapeutic value. The pronounced dominance of n-C_{17} among saturated hydrocarbons was noted in sample OVC and amounts to approximately 50 % of their overall distribution. This indicates the recent input of microalgae or cyanobacteria in precursors biomass, which can have great potential and influence on cosmetic properties of peloids [1]. Besides this, all peloid samples contain other classes of organic compounds which are useful and purposeful (for example, fatty acid methyl esters, fatty acid ethyl esters, and steranes). Thus, the lower homologues of fatty acid methyl esters ($< C_{20}$) which are characteristic of investigated samples indicate aquatic organisms, algae, and bacteria as precursors [2]. A significant contribution of algae in OVC and RUS samples is confirmed by the abundance of regular C_{27} sterane and short chain C_{21} and C_{22} steranes.

In comparison with reference values [3], elevated concentrations were found for microelements: As, Bi, Li and Se, at all investigated sites, while Cr and Ni were elevated in VRU and SEC. The enrichment factor and geoaccumulation index show that the highest enrichment was by Se. However, it is considered that Se has no significant toxicological features and a limit value for cosmetic products has not been proposed. Some of the peloids can cause toxic effects due to As content and Cr and Ni, the elements considered as partly toxic.

The highest content of microplastics and the highest toxicity were observed for the OVC sample with the luminescent inhibition of almost 100 %. SEC and VRU exhibited comparable luminescence inhibition of 16 and 21 %, respectively.

Acknowledgements

This research is a part of the bilateral project 2021–2023 between the Republic of Serbia and Slovenia ''Geochemical approach in characterisation of therapeutical peloid mud from Serbian and Slovenian spas''.

References

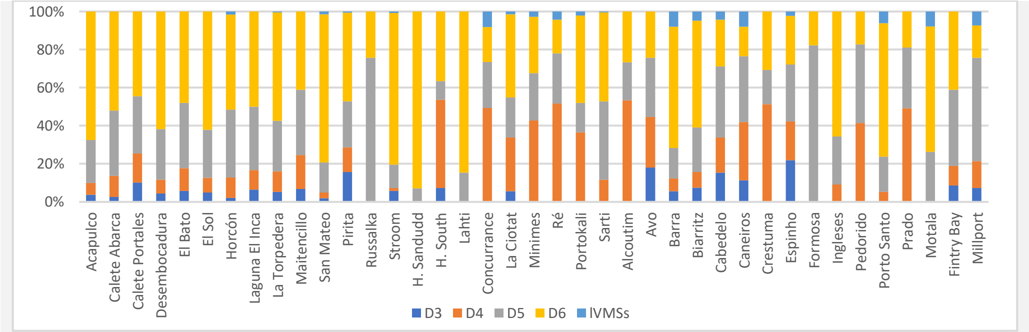
[1] M.L. Mourelle, C.P. Gómez, J.L. Legido (2021) *Marine drugs*, 19, 666-682.
[2] *The Biomarker Guide, Biomarkers and Isotopes in the Environment and Human History.* K.E. Peters, C. Walters, J.M. Moldowan, University Press, Cambridge, 2005.
[3] S.R. Taylor, S.M. McLennan (1995) *Reviews of Geophysics*, 33, 241-265.

Spatial and Temporal Distribution of Volatile Methylsiloxanes in Sand

S. Ferreira[1,2], D. Capela[1], H. Sá[1], C. Espregueira[1], F. Sánchez-Soberón[1], I. Bragança[1], J. Castro-Jiménez[3], P. Jiménez-Guerrero[4], F. Cereceda-Balic[5], X. Fadic[5], V. Homem[1,2], N. Ratola[1,2,]*

(1) LEPABE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; (2) ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; (3) IFREMER, Rue de l'Ile d'Yeu, BP 21105, 44311, Nantes, Cedex 3, France; (4) GMAR, Department of Physics, University of Murcia, Campus de Espinardo, 30100 Murcia, Spain; (5) CETAM and Department of Chemistry, Universidad Técnica Federico Santa María, Valparaíso, Chile

[*]nrneto@fe.up.pt



Given their unique physicochemical properties, volatile methylsiloxanes (VMSs) are used in numerous applications, particularly intensive in personal care products (PCPs), which increases the presence of these compounds in the environment, namely in coastal areas [1]. To have an idea of the presence of VMSs in these areas, sand can be used as an indicator [2].

This work aimed perform a wide screening to analyze the presence of seven VMSs, four cyclic (D3-D6) and three linear (L3-L5), in beach sand samples from 10 countries in Europe and South America and assess some temporal trends that may be linked to such presence (using examples from Portugal, Spain and France).

The use of the QuEChERS extraction technique followed by GC-MS analysis was successful for the analysis of VMSs in sands.

VMSs were detected in all samples with concentrations ranging from n.d. to 33 ± 7 ng/g_{dw} (D4) and predominance of the cyclic congeners. The total levels of VMSs varied between 0.33 ± 0.07 ng/g_{dw} in a beach in Estonia and 115 ± 9 in a beach from the Canary Islands, Spain. In spatial terms, the VMSs levels were higher in the Canary Islands (Spain) and lower in the north European countries (Estonia, Finland, Sweden, and UK), likely reflecting a lower use of PCPs and other sources of VMSs.

Considering the temporal trends, higher concentrations were observed in the summer months, corresponding to a greater presence of tourists. Moreover, an intra-day study in a crowded beach revealed that VMS levels tend to follow the beach attendance.

Acknowledgements

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy), funded by national funds through FCT/MCTES (PIDDAC); (ii) Project "HealthyWaters", Ref. NORTE-01-0145-FEDER-000069, co-financed by Programa Operacional Regional do Norte (NORTE 2020), through Portugal 2020 and FEDER; (iii) ANID-FOVI210064 and CETAM-UTFSM; (iv) V. Homem thanks national funds through FCT, under the Scientific Employment Stimulus - Individual Call - CEECIND/00676/2017.

References

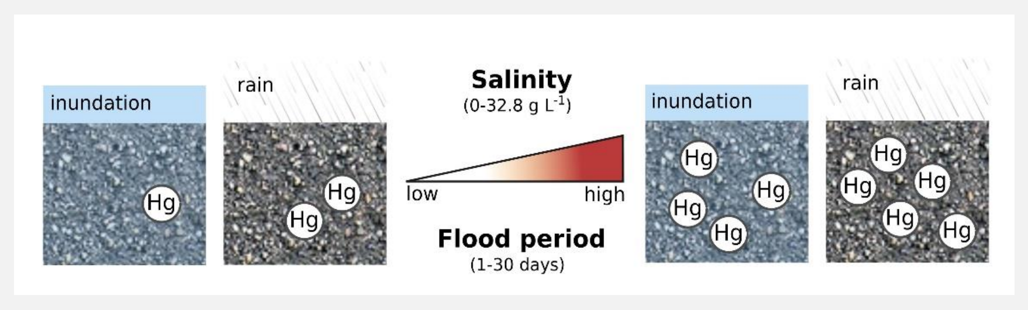
[1] F. Rocha, V. Homem, J. Castro-Jiménez, N. Ratola, (2019). *Science of the Total Environment*, 650, 2364-2373.
[2] D. Capela, M. Vila, M. Llompart, T. Dagnac, C. García-Jares, A. Alves, V. Homem (2019) *Marine Pollution Bulletin*, 140, 9-16.

Salinity and Flooding Mobilize Mercury from Polluted Soils and Sediments

S. Tomat[1], *E. Pellegrini*[1], *M. Horvat*[2], *B. Piani, M. De Nobili*[1] *M. Contin*[1,*]

(1) Department of Agricultural, Food, Environmental and Animal Sciences, University of Udine, Udine, Italy, (2) Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

**marco.contin@uniud.it*



Mercury (Hg) contamination of soils is a concerning issue worldwide because of its toxicity and risk for human health. Source of contamination, chemical form and environmental conditions affect its mobility and bioavailability [1]. As a consequence of climate change, contaminated coastal soils, in particular, could potentially become hotspots of Hg re-mobilisation, because of flooding and salinization caused by the expected increase of the sea level [2].

The aim of the present work was to assess changes in Hg solubility in soils and sediments, contaminated by different sources, after exposure to increasing salinity and flooding.

A soil contaminated with cinnabar-Hg from mining activity and a sediment heavily contaminated with elemental Hg from a chlor-alkali plant were collected in North-East Italy. Mercury speciation was performed either by Thermal Desorption (TD) from 25 to 800 °C [3], or by a Sequential Extraction Procedure (SEP) to quantify operationally defined binding forms (soluble, exchangeable, bound to Mn or Fe oxides, bound to organic matter, non-cinnabar). Thermal desorption showed the presence of two main forms of Hg: organic bound Hg (peak at low T) and HgS (peak at high T). The HgS peak prevailed in the mine-contaminated soil, whereas the organic-bound-Hg peak prevailed in the chlor-alkali contaminated sediment. This difference was confirmed by the SEP speciation. A laboratory simulation of salinity and flooding effects on Hg mobilization was carried out in columns filled with 20 g of soil/sediment and 25 mL of solutions from 0 to 32.8 g L^{-1}salt. Soils were kept submerged for 1, 7 and 30 days after the flooding treatment, then saline waters were let to drain by gravity and a rain event was simulated using freshwater. The leached solutions were collected separately and the Hg solubilised was measured by ICP-MS spectrometry.

Hg mobility increased with increasing salinity and flooding time. The effect of salt concentration was more pronounced after longer flooding periods. After 1 day of inundation, the amount of solubilised Hg was very low and did not respond clearly to salinity. On the contrary, after 7 days, Hg levels in the most concentrated solution (32.8 g L^{-1}) reached 0.9 and 9.3 μg L^{-1} in the solutions leached from the soil and the sediment, respectively. The mobility of the contaminant increased substantially after 30 days, and was about 22 times larger in the soil (19.8 μg L^{-1}) and 10 times larger in the sediment (89.8 μg L^{-1}).

Our results point out to a potential risk of Hg re-mobilization from contaminated coastal soils and sediments as consequence of global sea level rise.

Acknowledgements

Regione FVG - Servizio disciplina gestione rifiuti e siti inquinati for financial support.

References

[1] Li, H., Zheng, D., Zhang, X., Niu, Z., Ma, H., Zhang, S., Wu, C. (2020) *Bulletin of Environmental Contamination and Toxicology*, 104(6), 778-785

[2] Mahzar, S., Pellegrini, E., Contin, M., Bravo, C., De Nobili, M. (2022) *Frontiers in Environmental Science,* 10, 909415.

[3] Han, F.X., Su, Y., Monts, D.L., Waggoner, C.a., Plodinec, M.J. (2006) *Science of the Total Environment,* 368, 753–768.

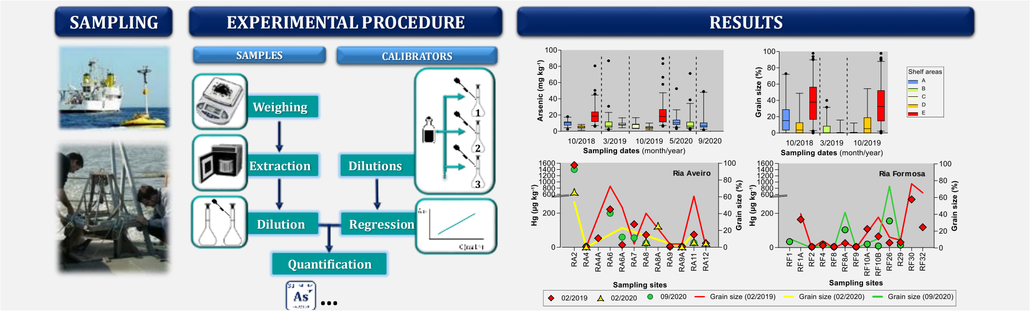
[4] Sedlar, M., Pavlin, M., Popovič, A., Horvat, M. (2014) *Open Chemistry,* 13 (1), 404–419.

Geochemical Characterization of Different Areas of the Portuguese Continental Shelf for Potential Aquaculture

C. Palma[1,], C. Gonçalves[1], C. Rocha[1], C. Borges[1], P. Santos[1], R. Silva[1]*

(1) Instituto Hidrográfico, Rua das Trinas, 49, 1249-093 Lisboa, Portugal

[*]carla.palma@hidrografico.pt



The Strategic Plan for Portuguese Aquaculture (2014-2020) [1] aims to contribute to the development of sustainable aquaculture in environmental and biodiversity terms. It is essential that the different aquaculture areas have an initial characterisation in terms of oceanographic, physico-chemical, geochemical and biological conditions of the Portuguese coastal zone and the AQUIMAR project has emerged with the objective of carrying out this initial characterisation.

This work presents metals concentrations, grain size and organic carbon in sediments of five shelf areas (A to E) and of four Portuguese inland waters (Ria de Aveiro, Ria Formosa, Mira River and Mondego river) (Fig 1). The results of metals concentrations are expressed with uncertainty as a function of the composition heterogeneity of the studied area and the analytical uncertainty.

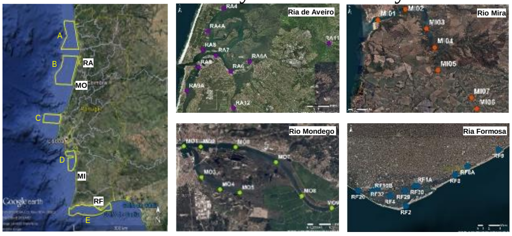


Fig. 1 – Map of the five oceanic (A to B) and the four estuarine study areas: A - Viana do Castelo to Porto; B - Aveiro to Figueira da Foz; C - Peniche; D - Setúbal to Sines; E - Tavira to Sagres, RA – Ria de Aveiro; MO – Rio Mondego; MI – Rio Mira and RF – Ria Formosa.

Sediment samples were collected in different sampling campaigns and the sampling points were the same. From the oceanic areas 465 samples were collected using a Smith-McIntyre grab sampler and from the estuarine areas 86 samples were collected with a Petit Ponar Grab sampler. The samples were freeze-dried, homogenised and reduced to a fine power in a mortar and pestle. Two different acid digestion were performed to estimate the total or acid-extractable mass fraction of metals. The elements were quantified in the sample solution by flame atomic absorption spectrometry using a calibration curve obtained from external calibration.

The results obtained show that sediments with a higher percentage of fines have higher concentrations of the metals analysed. There was no textural and metal content differences between the campaigns carried out in the same locations. Comparing with the criteria defined in the OSPAR guide documents, there are some estuarine stations most exposed to anthropogenic action and that should be evaluated in the context of being future aquaculture sites [1, 3].

Acknowledgements

This work was supported by the Operational Program Mar2020 through project “AQUIMAR-Caracterização geral de áreas aquícolas para estabelecimento de culturas marinhas” (MAR2020 n° MAR-02.01.01-FEAMP-0107).

References

[1] PEAP (2015). Plano Estratégico para a Aquicultura Portuguesa 2014-2020. Governo de Portugal, 96 pp.

[2] OSPAR (2008). 2007/2008 CEMP Assessment - Trends and concentrations of selected hazardous substances in the marine environment. *OSPAR Commission*, 378/2008, 7-16.

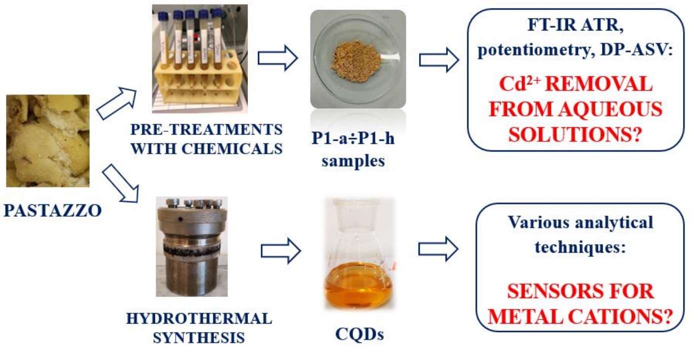
[3] OSPAR (2014). Levels and trends in marine contaminants and their biological effects - CEMP Assessment Report 2013. *OSPAR Commission*, 631/2014, 20-21.

ORAL
(#1)

Bergamot Pastazzo as Suitable Platform for Cd^{2+} Removal and Sensing in Multicomponent Aqueous Solutions

A. Irto[*], *G. Lando, C. De Stefano, P. Cardiano*

CHIBIOFARAM Department, University of Messina, V.le F. Stagno d'Alcontres, 31 – 98166 Messina (Italy)
**airto@unime.it*



In the last years, citrus waste was used as suitable platform for the design and development of multifunctional nanomaterials (MNMs), able to efficiently and selectively interact with organic (pesticides, dyes, drugs, POPs) and inorganic (metals, anions) contaminants in natural fluids, employing sorption mechanisms [1, 2].

This contribution is focused on the preliminary results obtained using new biobased materials for Cd^{2+} sequestration from multicomponent solutions simulating the experimental conditions of natural fluids (study scheme in figure).

A sample of bergamot pastazzo (peels, pulp, seeds) from the *Femminello* and *Fantastico* cultivars, representative of the November 2021-January 2022 harvest season variability, was provided by the *Capua 1880* company (Reggio Calabria, Italy). The supplied waste was mechanically ground and divided in two aliquots.

A first fraction (P1, raw pastazzo) was dried at t = 60°C for 72 hours and pre-treated with various chemicals, such as NaOH, HNO_3, H_2O_2, H_2O, 2-propanol at different temperatures, to check for a possible enhancement of the pastazzo metal sorption capacity [3-5]. A second aliquot (P2) was lyophilized, thermally pre-treated in an autoclave at t = 180°C for 6 hours and purified in dialysis bags, to obtain carbon quantum dots (CQDs) [6].

P1 and P2 fractions were characterized by FT-IR ATR spectroscopy to evaluate surface functional groups. Potentiometric experiments were carried out at $t = 25°C$, $I = 0.10$ mol L^{-1} in $NaNO_{3(aq)}$ to investigate their acid-base properties and complexing ability towards Cd^{2+}. The P1 pre-treated samples sorption capacity was studied by performing kinetics and batch experiments, in which the metal concentration in solution was determined by DP-ASV. The experimental data were analysed by various isotherm models [7]. The mentioned analytical technique is currently employed to investigate the metal desorption from pastazzo, to check for the material stability and reusability after Cd^{2+} recovery.

The investigations on CQDs behaviour in aqueous solutions and the assessment of their metal sorption capacity, for possible applications as sensors for metal cations, are still ongoing by means of various analytical techniques.

References

[1] N. Mahato, K. Sharma, M. Sinha E. R. Baral, R. Koteswararao, A. Dhyani, M. H. Cho, S., Cho (2020) *J. Adv. Res.*, 23. 61–82.
[2] T. Chatzimitakos, A. Kasouni, L. Sygellou, A. Avgeropoulos, A. Troganis, C. Stalikas, Talanta, 175 (2017) 305–312.
[3] U. Suryavanshi, S.R. Shukla (2010) *Ind. Eng. Chem.* Res. 49, 11682–11688.
[4] S. Schiewer, S.B. Patil (2008) *Bioresour. Technol.*, 99. 1896–1903.
[5] M. Russo, A. Arigò, M.L. Calabrò, S. Farnetti, L. Mondello, P. Dugo (2016) *J. Funct. Foods*, 20, 10–19.
[6] Z. Wang, Y. Xie, Z. Lei, Y. Lu, G. Wei, S. Liu, C. Xu, Z. Zhang, X. Wang, L. Rao, J. Chen (2019) *Anal. Chem.*, 91, 15, 9690-9697.
[7] S. Schiewer, S. B. Pati (2008) *J. Hazard. Mat*., 157, 8–17.

Anions Determination as an Important Property of Soil in Urban Forests: Case Study Avala Mountain, Serbia

T. Tosti[1,*]*, S. Štrbac*[2]*, S. Blagojević*[3] *N. Antić*[2]*, V. Rončević*[4]*, E. Vukićević*[1]*, M. Kašanin-Grubin*[2]

(1) Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia (2) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia; (3) Institute of General and Physical Chemistry Studentski trg 12-16, Belgrade, (4) Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, Serbia

**tosti@chem.bg.ac.rs*

Figure 1: Soil sampling site on Avala mountain

Climate-Smart Forestry in mountain regions is an approach that can help to emphasize influence of climate changes on the forest ecosystems, as well as the ecosystems services. Due to those changes the environment becomes more hostile and many of the animals and plants are brought into jeopardy of distinguishing. Directly and indirectly climate changes affect the growth and productivity of forests through changes in soil properties, plants activity. The effects of climate change on soils are expected mainly through alteration in soil properties and increasing amount of inorganic and organic carbon levels [1]. These changes influence complex forest ecosystems changing organic and nitrogen cycles, nutrient and water retention, filter functions and erosion control.

In this study, the most abundant anions of the forest soils of the mountain Avala were investigated due to their specific roles in forests ecosystems. Carbonate and sulphate play important role in soil structure, water holding capacity and soil density, phosphate and organic carbon can be regarded as markers of decomposition of various trees part especially leaves. The mobility of phosphate is mostly affected by adsorption and usability, whereas mobility of nitrate is regulated almost solely by biological processes. The chloride is relatively uninvolved in either biological or inorganic chemical reactions.

The framework of this study is to develop adequate database of forest ecosystems, and investigated how they are affected by changes in environment. For that purpose, 9 soil samples profiles from depth 0-10 cm, 10-20 cm, >20 cm were collected from Avala mountain forests (Fig. 1). Dionex ICS 3000 was used for anion analysis. Concentrations of sulphate and nitrate anions are increasing with depth of the soils, and phosphate, carbonate and organic carbon exhibits the highest concentration near the surface. Such behaviour could be explained by the anion leaching and decomposing of trees. Climate change leads to leaching of basic anions which leaves the soils more compact and this can be even more severe in soils containing high concentrations of sulphates [2]. The database of the major anion concentrations can be used for building appropriate model for assessing and predicting the effects of the climate changes on forest ecosystems. The outcomes of this study will be used to prevent and protect further deterioration of the forests of the Avala mountain regions.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Grant No. 451-03-9/ 2022-14/200026; 451-03-9/2022-14/ 2001684 and 451-03-68/2022-14/20005) for financial support.

References

[1] N. Pareek (2017) *MOJ Eco Environ Science*, 3, 136-139.

[2] Z. Rengel, in Part of the Soil Biology book series (SOILBIOL, volume 29). Springer, 2011, 69-85.

Determination of Pollution Status of Urban Forest Obrenovacki Zabran (Serbia) – Part B: Microelement Concentration in Soil and Sediments

M. Kašanin-Grubin[1,], T. Tosti[2], S. Stojadinović[1], N. Antić[1], N. Mijatović[3], N. Živanović[4], S. Štrbac[1]*

(1) Institute of Chemistry, Technology, and Metallurgy, University of Belgrade, Njegoseva 12, Belgrade, Serbia, (2) Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, Belgrade, Serbia, (3) Institute for testing of materials, Bulevar vojvode Mišića 43, Belgrade, Serbia (4) Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, Belgrade, Serbia

[*]milica.kasanin@ihtm.bg.ac.rs

Figure 1. Map of the Obrenovac Zabran, Serbia

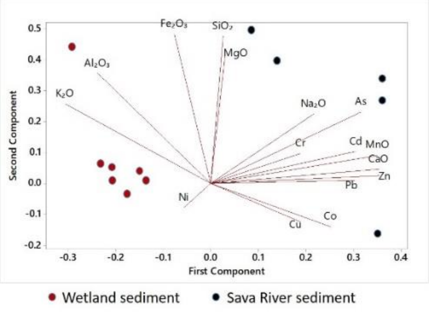


Figure 2. Multivariate analysis of the microelement content in Obrenovac Zabran sediments

Floodplains and river-marginal wetlands are vital landscapes to human society because they provide ecosystem services such as climate regulation, nutrient cycling, retention of flood waters, infiltration and stabilization of groundwater levels, and recreational activities. When pollutants reach the environment, the effects on the ecosystems and their services will depend on a range of factors, such as persistence, mobility and the bioavailability of pollutants in the ecosystem. Previous studies indicate that chromium, cadmium, copper, lead, and zinc widely exist in sediments impacted by industrial sources **[1]**. These heavy metals pose a potential threat to the ecosystems and human health due to their toxicity, persistence and bioaccumulation **[2]**. Therefore, understanding of the fate and risk of heavy metals in sediments is of crucial importance. Assessment of the pollution status of the urban wetland area includes determination of the content of potentially harmful microelements in river sediments.

The aim of this research is to assess pollution status and origin of heavy metals in soils and sediments of the Obrenovacki Zabran (OZ), Serbia. The OZ forest and wetland is exposed to the urbanization pressure and pollutants transported by the Sava and Kolubara Rivers (Fig. 1). The OZ covers 47.77 ha, of which 41.82 ha is under forest vegetation and in the central part of the park there is a wetland with groundwater discharge from the Kolubara River. In this study content of microelements was assessed in 5 Sava riverbank and in 7 forest/wetland soils. Concentrations of minor elements were determined using the Inductively Coupled Plasma (ICP). All solutions were prepared using analytical grade reagents and deionized water with resistivity 18.2 MΩcm−1 obtained from a Milli-Q system.

The concentration of microelements for both locations is decreasing in the following order: Zn>Cr>Ni>Pb>Cu>As>Co>Cd. However, there is difference in concentrations between the two locations. The Sava River sediments have higher contents of microelements Pb, Cd, Zn, Cu, Co, Cr indicating larger anthropogenic pressure (Fig. 2). Wetland sediments, which are recharged by the Kolubara River do not have significant microelement content. Furthermore, similar contents of Ni in both areas, as well as multivariate analyses results indicate that this element has geogenic origin.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No: 451-03-68/2022-14/200026).

References

[1] Sundaray SK, Nayak BB, Lin S, Bhatta D (2011) *Indian Journal of Hazardous Material*, 186,1837–1846.
[2] Luo XS, Yu S, Zhu YG, Li XD (2012) *Science of the Total Environment*, 421,17–30.

Trace Elements Levels in Urban Soil Samples from Central Poland

M.I. Szynkowska-Jóźwik, D. Kryszczak, I. Gabrych, A. Pawlaczyk, E. Maćkiewicz, P. Wysocki, M. Gajek, J.Albińska*

(1) Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology, Żeromskiego 114, 90-543 Lodz
**malgorzata.szynkowska@p.lodz.pl*

Soil is recognised as the foundation of an ecosystem functioning in urban green spaces and provides key ecosystem services for a liveable city. Soils can also play a vital role in the quality of the urban environment and the health of its residents. Urban soils seem to be highly specific since they are treated as a mixture of natural soil-forming factors and anthropogenic activities [1]. Soils within the urban territories include among others: (i) soils consisting of a mixture of materials of different origins, with inorganic or organic compositions, and from agricultural or forest areas, which are largely transformed by human intervention, (ii) soils in parks and green gardens that offer different compositions, uses, and management of agricultural land; and (iii) soils or mixtures resulting from various construction or metallurgical activities within cities [1,2]. City soils and street dusts accumulate various contaminants like toxic elements from a variety of anthropogenic sources [1-3]. These human activities involve transport sources (e.g. motor exhausts, brake pads, tire wear), commercial and industrial emissions (energy production, metallurgical industry, chemical plant, fuel combustion, incinerators, etc.), domestic activities (waste disposal, wastewater), and agricultural operations (fertilizers, pesticides). Emission of harmful substances, including toxic elements has become a worldwide environmental concern in urban areas since the industrialization and urbanization have been developed rapidly [3]. Undoubtedly, direct characterization of soils in reference to toxic elements contamination can be potentially used as an effective scientific tool to diagnose the sources of contamination. Therefore, the verified indicators for soil quality assessment seems to be required in order to fully understand the spatial heterogeneity of soils collected from urban areas [1-3].

The aim of this study was to quantify and assess the variability of various elements in urban soils using a systematic sampling strategy and a common methodology. In this work at least 70 sampling points within the city of Lodz and its region near the high traffic roads, located in the central Poland were studied. Soil samples preparation prior quantitative analysis by ICP-OES and AAS techniques included drying of soil materials, sieving and grinding in a porcelain mortar. Weighed samples (approx.0.3 g) were treated with a mixture of 4.5 ml HNO_3 (Baker) and 1.5 ml HCl (Merck). After the sample decomposition in a closed microwave energy system UltraWave (Milestone) samples were transferred into 50 mL flasks. All the samples were filtered using vacuum pump system. The levels of selected elements (such as Ca, Mg, Fe, Zn, Ni, Mn, Cu, P, S, Pb, Cd, etc.) were quantitatively determined using spectroscopic techniques. The obtained results were compared with the values given in the literature and indicated in national and international standards. The distribution of data was tested with the Shapiro–Wilk's test ($p < 0.05$). Due the fact that hypothesis regarding normal distribution of the data was not fulfilled, the non-parametric statistics was employed. As a consequence, the non-parametric Kruskal–Wallis test was applied to determine the differences among studied groups of sampled. The degree of correlation between the levels of analysed elements was assessed with Spearman correlation matrix. Moreover, the PCA analysis was employed in order to identify parameters responsible for sample grouping and to reduce the number of variables. The applied multivariate analysis turned out to be helpful in identification of the relationships among levels of studied elements and allowed the observation of clusters formation based on specific parameters e.g. depending on the distance from the high traffic roads or the type of soil.

Acknowledgments

Agreement No.67 / OPP / 2022 on cooperation in the creation of a database and monitoring the level of heavy metals and platinum group metals in soils located in the vicinity of the main roads of the Łódź Voivodeship.

References

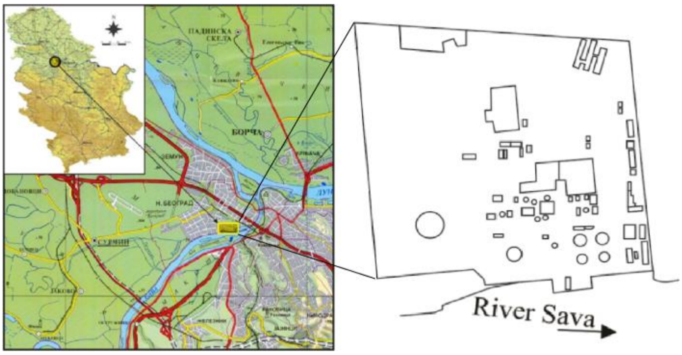
[1] R. O'Riordan, J. Davies, C. Stevens, J.N Quinton, C. Boyko (2021) *Geoderma*, 395, 1-12.
[2] S. Modabberi, M. Tashakor, N. Sharifi Soltani (2018) *Environ Monit Assess*, 190:715, 1-18.
[3] Q. Mao, G. Huang, A. Buyantuev, J. Wu, S. Luo, K. Ma (2014) *Ecol Process* 3, 23, 1-19.

Saturated Hydrocarbons Proxies as a Tool for Differentiation Between Anthropogenic and Natural Organic Matter Inputs to the Surface Soils of the Sava River Alluvium

T. Šolević Knudsen[1,*], *M. Ilić*[1], *G. Dević*[1], *S. Bulatović*[1], *N. Marić*[2], *J. Avdalović*[1], *J. Milić*[1]

(1) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia, (2) University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11030 Belgrade, Serbia

[*]*tsolevic@chem.bg.ac.rs*



The largest heating plant in Belgrade (the capital of Serbia), is located in the residential area New Belgrade, close to the Sava River (Figure 1). Due to the potential risk of contamination, this site has been a subject of a detailed environmental monitoring for several years. The aim of our present study was to investigate the source of the organic matter input to the surface soils of the Sava River Alluvium at this location.

The surface soil samples were collected at 20 micro locations from this locality. From these samples the organic matter was extracted with dichloromethane using a Soxhlet apparatus. Saturated hydrocarbons were isolated from the extracts using a column chromatography. For that purpose, silica gel and aluminium oxide were used as adsorbents. Saturated hydrocarbons were eluted by hexane and analysed by gas chromatography - mass spectrometry. *n*-Alkanes were identified using mass ion *m*/*z* 71, hopanes using mass ion *m*/*z* 191 and steranes using mass ion *m*/*z* 217.

Saturated hydrocarbons proxies used in this research were: short to long hydrocarbon chains ratio, average weighted carbon chain lengths for long *n*-alkanes (for $C_{24–33}$ range) [1], the terrestrial-to-aquatic ratio [2], the carbon preference index for the entire alkane range [3] the P*aq* proxy [4] and the unresolved complex mixture [5].

Distribution of hopanes and steranes in the samples was analysed to confirm the presence of petroleum-derived residues.

The results indicated that the organic matter in the samples analysed was contributed from the multiple natural allochthonous and autochthonous organic matter sources such as: aquatic macrophytes, algal, bacterial and terrestrial plant sources, and bacterial reworking. Furthermore, presence of the petroleum-sourced hydrocarbons was confirmed as well indicating a contribution of the anthropogenic sources of hydrocarbons to the organic matter of the investigated samples.

All these results point to the complex processes of migration and mixing of the organic matter in the surface soils at the investigated location.

Considering the fact that the presence of the oil pollutants was confirmed in the samples analysed, further research is needed to reveal the environmental pollutions status of the environment at this locality.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant No: 451-03-68/2021-14/200026) for financial support.

References

[1] M. Kumar, T. Boski, F.J. González-Vila, N.T. Jiménez-Morillo, J.A. González-Pérez (2020) *Estuarine, Coastal and Shelf Science*, 197, 104076.

[2] R.A. Bourbonniere, P.A. Meyers (1996*) Limnology and Oceanography*, 41, 352–359.

[3] E.E. Bray, E.D. Evans (1961) *Geochimica et Cosmochimica Acta*, 22, 2–15.

[4] K.J. Ficken, B. Li, D.L. Swain, G. Eglinton (2000) *Organic Geochemistry*, 31, 745–749.

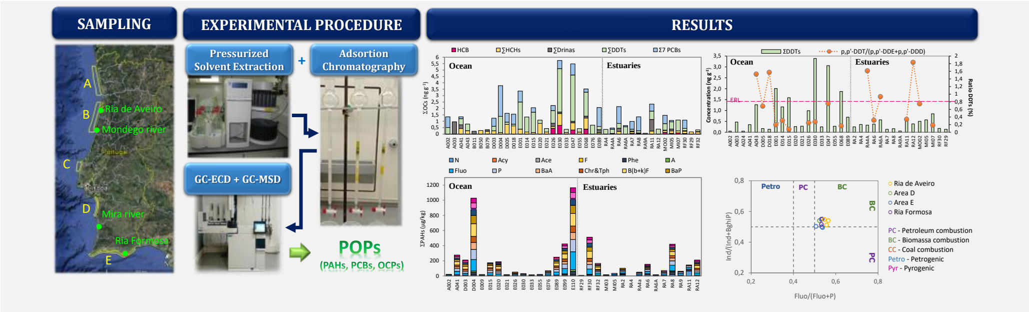
[5] M.A. Gough, S.J. Rowland (1990) *Nature*, 344, 648–650.

POSTER
(#1)

Organic Compounds in Surface Sediments of Different Estuaries and Continental Shelf Areas of Portugal for Potential Aquaculture

C. Palma[1,*], *C. Rocha*[1], *P. Santos*[1], *C. Borges*[1], *C. Gonçalves*[1], *R. Silva*[1]

(1) Instituto Hidrográfico, Rua das Trinas, 49, 1249-093 Lisboa, Portugal
[*]*carla.palma@hidrografico.pt*



The Strategic Plan for Portuguese Aquaculture (2014-2020) [1] aims to contribute to the development of sustainable aquaculture in environmental and biodiversity terms. The AQUIMAR project has emerged with the objective of carrying out the initial characterisation of the Portuguese coastal zone in terms of oceanographic, physico-chemical, geochemical and biological conditions.

This work presents the distribution of persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), grain size, total organic carbon and organic matter in sediments of five shelf areas (A to E) and of four Portuguese inland waters: Ria de Aveiro, Ria Formosa, Mira river and Mondego river. The results of POPs are compared with sediment quality guidelines (SQGs) to understand the biological risks [2, 3]. The main origin of some POPs was also assessed [2, 4].

Sediment samples were collected in different sampling campaigns. Thirty-three samples were collected on the oceanic areas using a Smith-McIntyre grab sampler and on the estuarine areas 24 samples were collected with a Petit Ponar grab sampler. The samples were freeze-dried, homogenised and reduced to a fine power in a mortar and pestle. The PAHs and the PCBs and OCPs were analysed by gas chromatography coupled to a mass spectrometry and to a electron capture detector, respectively, after extraction by pressurized liquid extraction and purification of the extracts by adsorption chromatography using silica gel and aluminium oxide.

The results obtained show that the main origin of PAHs is pyrogenic related to fuel and biomass combustion but perylene is mostly biogenic. The hexa-PCBs (PCB153 and PCB138), the organochlorine pesticides DDTs and the PAHs fluoranthene, pyrene and benzo(b+k)fluoranthenes are predominant in the samples of this study. The seven indicator PCBs congeners and the PAHs were relatively low when compared with sediment SQGs, namely the Effects Range Low (ERL).

Acknowledgements

This work was supported by the Operational Program Mar2020 through project "AQUIMAR- Caracterização geral de áreas aquícolas para estabelecimento de culturas marinhas" (MAR2020 n° MAR-02.01.01-FEAMP-0107).

References

[1] PEAP (2015). Plano Estratégico para a Aquicultura Portuguesa 2014-2020. Governo de Portugal, 96 pp.

[2] N.V. Hidayati, L. Asia, I. Khabouchi (2021) *Chemosphere*, 263, 128372.

[3] G. Hu, X. Luo, J. Dai, J. Guo, S. Chen, C. Hong, B. Mai, M. Xu (2010) Organochlorine compounds and polycyclic aromatic hydrocarbons in surface sediment from Baiyangdian Lake, North Chine: concentrations, sources profiles and potential risk.

[4] E. Stogiannidis, R. Laane (2015). Source Characterization of Polycyclic Aromatic Hydrocarbons by Using Their Molecular Indices: An Overview of Possibilities. (D. M. Whitacre, Ed.) *Reviews of environmental contamination and toxicology*, 234, 49-133.

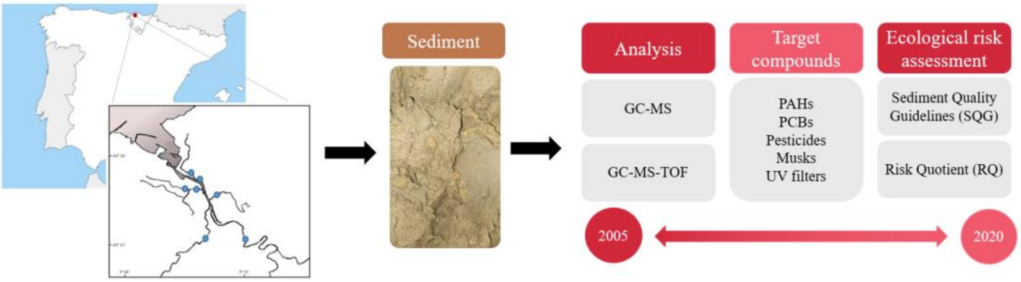
POSTER
(#1)

Occurrence of Semi-Volatile Organic Compounds in Sediments of the Nerbioi-ibaizabal Estuary: Spatial and Geographical Distribution and Ecological Risk Assessment

*U. Uribe[1, *], P. Irizar[1], D. Bilbao[1, 2], L. Mijangos[1, 2], A. de Diego[1, 2]*

(1) Depart. of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.K. 48080 Bilbao, Spain., (2) Research Centre for Experimental Marine Biology & Biotechnology (PIE), University of the Basque Country (UPV/EHU), P.K. 48620 Plentzia, Spain

[*] *uxue.uribe@ehu.eus*



Sediments constitute a tool to evaluate the quality of aquatic systems, giving an idea of the degree of contamination accumulated over time at a given point, and the potential of the sediment as a source of future contamination [1]. In this sense, the present study investigates the presence and toxicity of 56 relevant semi-volatile organic compounds, belonging to PAHs, PCBs, pesticides, musks and UV filters families, in sediments collected from 2005-2013 and 2020. The distribution of the contaminants was investigated in the intertidal area (7 stations) of the Nerbioi Ibaizabal estuary, in which a wastewater treatment plant is located. In addition to the targeted analysis carried out by gas chromatography coupled to a quadrupole mass spectrometer (GC-MS), a suspect analysis was also performed using a GC-MS- TOF with an in-house library of 239 compounds [2].

Up to 49 analytes were found in the sediments. The concentrations measured ranged from few ng/g d.w. up to 62949 ng/g d.w. for ΣPAHs, 2503 ng/g d.w. for ΣPCBs, 817 ng/g d.w. for ΣHCH, 695 ng/g d.w. for Σmusks and 166 ng/g d.w. for ΣUV filters. Organochlorine pesticides, and specifically lindane, were detected in all sampling campaigns, suggesting that these compounds, even if they have been banned, are still being used for agricultural purposes and/or that they leach from illegal landfill sites. The concentrations of PAHs and PCBs showed a decreasing trend from 2009 to 2011, and after 2009, respectively.

In addition to the targeted analysis, 6 additional compounds (2 phthalates, a pesticide, two food additives and an organophosphate flame retardant) were identified by suspect analysis: Dicyclohexyl phthalate, bis(2-ethylhexyl) terephthalate, 2,6-diisopropylnaphthalene, thymol, bornyl acetate and tris(1- chloro-2-propyl) phosphate.

Regarding the ecological risk assessment, the concentrations of PAHs, PCBs and lindane in sediments were compared with Sediments Quality Guidelines (SQG). For PAHs the concentrations found were, in general, below the ERM values, while for PCBs and lindane were well above the ERM and PEL values, respectively. Finally, Risk Quotient (RQ) were also computed to estimate the possible threat posed by the non-regulated targeted compounds. The highest RQ values (»1) were obtained for lindane, celestolide and tonalide.

Acknowledgements

This work has been financially supported by the Spanish Government through the research project "PLASTeMER" (Ref. PID2020-118685RB-I00) and by the Basque Government through the project "IBeA, Consolidated Research Group 2019–2021" (Ref. IT1213-19). P. Irizar gratefully acknowledges his pre-doctoral grant from the MINECO (PRE-2018-085888), and U. Uribe is grateful to the University of the Basque Country (UPV/EHU) for her pre-doctoral fellowship.

References

[1] O. Solaun, M.J. Belzunce, J. Franco, V. Valencia y Á. Borja (2009) *Revista de Investigación Marina*. 10-47.
[2] V. Castro, J. B. Quintana, J. López-Vázquez, N. Carro, J. Cobas, D. Bilbao, R. Cela, R. Rodil (2022) *Analytical and Bioanalytical Chemistry*, 414(21), 6327–6340.

POSTER
(#1)

Occurrence, Distribution Pattern and Origin of Polycyclic Aromatic Hydrocarbons in the River Marina Sediments of the Kovin Dunavac (Kovin, Serbia)

K. Antić[1,], I. Kojić[2], T. Šolević Knudsen[1]*

(1) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia, (2) University of Belgrade, Innovation Center of the Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia
[*] *katarina.antic@ihtm.bg.ac.rs*

Kovin is a small city in Serbia, located on the banks of the Danube River, 50 km east from Belgrade. The Danube passes through the municipality of Kovin in a length of 46 kilometres, creating beautiful meanders, river islands and backwaters. An arm of the Danube, Dunavac is a 1800 m long natural shelter for smaller river crafts. This marina has a capacity to accommodate 100 smaller nautical vehicles. Considering the fact that many boats in this marina are using diesel engines, pollution of this small water body with petroleum pollutants is a real threat.

The aim of this study was analysis of the occurrence, abundance, distribution and origin of polycyclic aromatic hydrocarbons (PAHs) in sediments of the Kovin Dunavac.

A composite sediment sample from the Kovin Dunavac was extracted in a Soxhlet apparatus with dichloromethane as a solvent. The extract was cleaned up and fractionated using column chromatography. In the fraction of aromatic hydrocarbons, PAHs were analysed by gas chromatography – mass spectrometry (GC-MS) in a selected ion monitoring (SIM) mode. The ions monitored were: $m/z = 128$ (naphthalene), $m/z = 152$ (acenaphthylene), $m/z = 154$ (acenaphthene), $m/z = 166$ (fluorene), $m/z = 178$ (phenanthrene and anthracene), $m/z = 202$ (fluoranthene and pyrene), $m/z = 228$ (benzo[a]anthracene and chrysene), $m/z = 234$ (retene), $m/z = 252$ (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[e]pyrene and benzo[a]pyrene), $m/z = 192$ (methylphenanthrenes and methyl anthracene); and $m/z = 184$ (dibenzotiophene).

The PAHs were quantified against four perdeuterated PAHs as internal standards, and their concentrations were expressed in mg kg^{-1} of a dry sediment. Using these quantified values, numerous PAHs diagnostic ratios were calculated.

The results showed that the total PAHs were present in a concentration of 2.6 mg $kg^{-}1$ of a dry sediment. Although this concentration was higher than the threshold value for sediments, this result, however, did not indicate a significant pollution of the investigated sediment with PAHs [1].

The PAH profile of the investigated soil sample was dominated by 3-, and 4-ring PAHs. Additionally, parent compounds were more abundant that their alkylated homologues.

Numerous PAHs diagnostic ratio revealed that these compounds in the sample investigated originated from multiple sources. According to these results, it was concluded that the dominant pollution sources of the sediment in the Kovin Dunavac were petrogenic (diesel vehicular source) and pyrogenic (grass, wood, and coal combustion).

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant No: 451-03-68/2022-14/200026 and 451-03-68/2022-14/200168) for financial support.

References

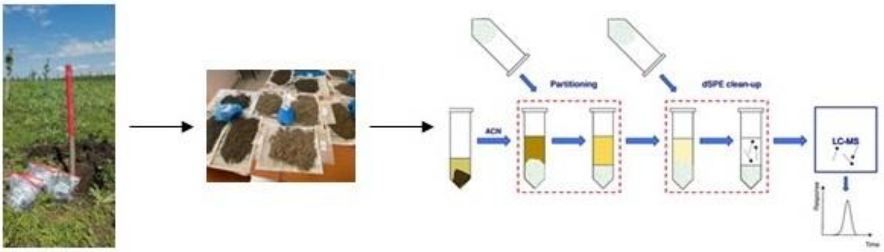
[1] RS Official Gazette (2010). The regulation on the program for the systematic monitoring of soil quality, soil degradation risk assessment indicators and methodology for the development of remediation programs (No. 88/2010) (in Serbian).

Monitoring of Pesticides in Soil from South Banat District in Serbia and Timis County in Romania

M. Zaric[1,2,*], F. Crista[3], I. Radulov[3], I. Hotea[3], N. Zaric[4]

(1) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoseva 12, Belgrade, Serbia, (2) Centre of Excellence in Environmental Chemistry and Engineering – ICTM, University of Belgrade, Belgrade, Serbia (3) University of Life Sciences "King Michael I" from Timişoara, Calea Aradului 119, Timişoara, Romania, (4) University of Belgrade – Faculty of Biology, Studentski trg 12, Belgrade, Serbia

milana.zaric@ihtm.bg.ac.rs



Growing population has led to larger demand for global food production. In turn this has led to the development of novel agricultural techniques to improve yield. In addition, new compounds were developed to protect corps from pests. These compounds are known as pesticides. They are widely used in agriculture to protect crops and to improve their yield. However, in addition to their positive effects they can also negatively reflect on the environment as well as on animal and human health. This is the reason why they should be closely monitored in the environment.

In this work we have monitored pesticides in soil samples collected in the agricultural areas of South Banat district in Serbia and Timis county in Romania. Both of those regains have very fertile soil and are well known for food production.

Soil samples were gathered four times per year, once for each season. In each country samples were taken from 50 locations, adding up to 100 locations in total. The samples were taken from the topsoil level, 20 – 40 cm depth and 40 – 60 cm depth. The samples were prepared using a QuEChERS approach. In shorth 10 g of homogenized soil sample was added to a 50 mL tubes. 10 mL of water was added to increase the sample moisture. Afterword 10 mL of acetonitrile as added as an extraction solvent and the sample was shaken for 1 minute. Following this, 4 g Anhydrous $MgSO_4$, 1 g Trisodium Citrate, 0,5 g Disodium Citrate and 1 g NaCl were added to the tube and it was shaken as quick as possible. The samples were centrifuged for 5 minutes at 5000 rpm. Then, a clean-up dispersive solid phase extraction step was carried out by adding 10 mL of the supernatant to a 15-mL centrifuge tube that contained 150 mg PSA + 150 mg C18 + 900 mg $MgSO_4$. The samples were again shaken and centrifuged for 5 minutes at 5000 rpm. An aliquot of 1 mL was transferred to an amber HPLC vial and evaporated to dryness. Before the analysis it was reconstituted with 1 mL of methanol.

The analysis was performed on a TSQ Quantis™ Triple Quadrupole Mass Spectrometer. Quantification was obtained by comparing it to a standard six-point calibration curve. We have screened all the samples for 250 most commonly used pesticides.

Most of the 250 pesticides were not detected in our soil samples. Around 20 pesticides were detected in almost each soil sample. They were divided amongst different groups, including herbicides, insecticides and fungicides. The most detected in soil samples were insecticides. It could be that they are the most frequently used pesticides and this is the reason for their most dominant presence.

Acknowledgements

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

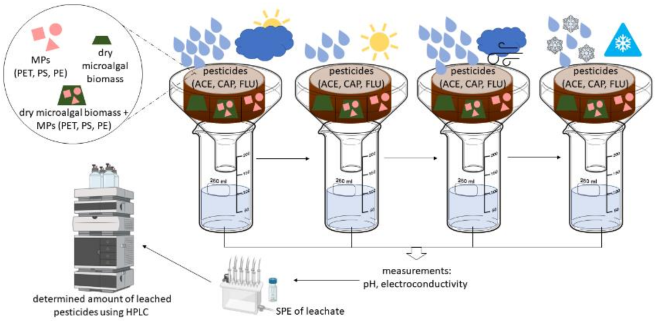
POSTER
(#1)

Leaching of Insecticides in Soil Amended with Microalgal biomass: the Effect of Microplastics in the Soil

U. Šunta[1,*], *G. Veselinović*[2], *T. Griessler Bulc*[1,3], *M. Bavcon Kralj*[1]

(1) Faculty of Health Sciences, University of Ljubljana, Zdravstvena pot 5, Ljubljana, Slovenia, (2) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, (3) Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jamova cesta 2, Ljubljana, Slovenia

urska.sunta@zf.uni-lj.si



Fertilizers as well as plant protection products (PPPs) play an important role in agriculture, as they ensure the production of a sufficient amount of quality food. The sources of crucial nutrients in fertilisers, nitrogen and phosphorus, are finite. Closing of the nutrient loops is thus needed to preserve them in the environment. A way to recycle nutrients is to use the microalgal biomass produced in the process of wastewater treatment with microalgae. Microalgae as soil amendment were found to have beneficial effects on soil properties, plant growth, and fruit production [1]. Higher crop yields are also ensured with the application of PPPs. However, their residues can end up on the soil, where sorption to other particles, transport to the deeper soil layers till groundwater reservoirs, and accumulation in the soil can occur [2]. Another widespread pollutant originating mainly from mulching, application of fertiliser, and wind deposition in the soil are microplastics (MPs). Their presence affects the physicochemical properties of soil, the sorption of pollutants, and alters plant growth through changes in the soil microbiota [3].

Understanding the complex interaction between soil, microalgae, pesticides, and MPs is crucial for the future of the soil system. This study focused on the leaching of three model pesticides (acetamiprid (ACE), chlorantraniliprole (CAP) and flubendiamide (FLU)) from soil amended with microalgal biomass in the presence of MPs, exposed to the simulation of precipitation and temperature conditions within a year - four seasons. After each simulated season, leachates were collected, the volume of the leachate, pH and electroconductivity were measured, and the amount of each leached pesticide was determined by HPLC.

The results showed that in the simulated year, ACE leached the most (454.0 ± 137.4 μg), followed by FLU (162.6 ± 30.5 μg) and CAP (123.1 ± 9.7 μg). The highest degree of leaching for all three pesticides occurred in the second cycle, i.e., in summer conditions. The leaching of pesticides from soil was more influenced by the presence of MPs than the amendment of microalgal biomass.

Since the leaching of pesticides heavily depends on the yearly precipitations, further leaching studies of pesticides from the soil, where complex interactions are involved with longer exposure time in a real environment would be of interest.

Acknowledgements

The authors would like to thank dr. Rok Mihelič from Biotechnical Faculty, University of Ljubljana, for contributing the microalgal biomass and acknowledge the support of the Slovenian Research Agency (ARRS) - research core funding P3-0388, the postgraduate research funding programme (1000-22-0510), project ALGreen (J2-4427) and the CEEPUS Network SI-0905-08-2122.

References

[1] J.F. Lorentz, M.L. Calijuri, P.P. Assemany, W. Sousa Alves, O. Gomes Pereira (2020) *Journal of Cleaner Production*, 276, 124130.

[2] D. Pietrzak, J. Kania, E. Kmiecik, G. Malina, K. Wator (2020) *Chemosphere*, 255, 126981.

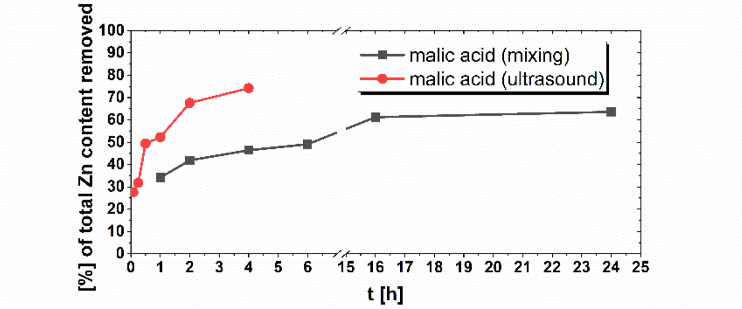
[3] S. Yadaw, E. Gupta, A. Patel, S. Srivastava, V.K. Mishra, P.C. Singh, P.K. Srivastava, S.K. Barik (2022) *Reviews in Environmental Science and Bio/Technology*, 21, 771-798.

Ultrasound and Mixing Assisted Sediment Washing with Selected Reagents – a Comparison Study

J. Imperl[1,*], *M. Kolar*[1], *A. Robba*[1], *M. Božič*[2], *B. Gregorc*[2]

(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia, (2) Dravske elektrarne Maribor, d. o. o., Obrežna ulica 170, SI-2000, Maribor, Slovenia

[*]*Jernej.Imperl@fkkt.uni-lj.si*



Accretion of sediments poses a problem in river management, especially in accumulation lakes, and therefore justifies the removal of sediment from the riverbed or lakebed. Disposal and reuse of dredged sediment is hindered if the sediment is contaminated by high levels of heavy metals. Sediment washing is one of the possible techniques for removal of heavy metals from polluted sediments and/or soils [1].

Our research focused on two samples of sediment (old and newly dredged) from Lake Ptuj, an accumulation lake on the Drava River [2]. This sediment contains elevated levels of zinc (Zn), lead (Pb), and cadmium (Cd). Total metal contents of these metals were determined by leaching the sediment with a boiling solution of nitric(V) acid (1+1) and were found to be ~1100 ppm for Zn, ~400 ppm for Pb, and ~8 ppm for Cd. Three reagents were used for the sediment washing procedure – EDTA, citric and malic acid – all under already optimized conditions. Mixing with an orbital shaker and an ultrasound bath at different lengths of time were used for assisting the sediment washing [3,4]. A two-time sequential washing of the sediment was also tested at the established optimum washing time with both mixing and ultrasound. Concentrations of the heavy metals in the leachate were determined using ICP-OES.

Under both conditions (mixing and ultrasound) all reagents were able to extract large amounts of Zn, Pb, and Cd with around 60 % Zn, 40 % of Pb, and 70 % of Cd removed as a percentage of total heavy metal content. Sediment washing using the ultrasound bath proved to be more time efficient than mixing. The extraction efficiency which was achieved in 6 h for mixing with the orbital shaker was at approximately same value or sometimes higher using the ultrasound bath for only 1 h (from figure: removal of Zn with malic acid washing with mixing for 6 h – 49 % – and with ultrasound for 1 h – 52 %). While extractions with citric and malic acid were more efficient at higher washing times, extractions with EDTA were found to be almost independent of the washing time for mixing and ultrasound.

In both cases (mixing and ultrasound), with all three reagents (EDTA, citric and malic acid), and for all three heavy metals (Zn, Pb, and Cd) two-time sequential extractions were more efficient – the second washing was able to remove extra amounts of the heavy metals. For example, two-time sequential washing with citric acid using mixing was able to remove 5 percent points (pp) more of Zn, 15 pp more of Pb, and 20 pp more of Cd.

Acknowledgements

The authors acknowledge the support of the Slovenian Research Agency (ARRS); project grant L7-2629: ″Evaluation and remediation of sediments for further use in the building sector (READY4USE)″.

References

[1] L. Di Palma, R. Mecozzi (2007) *Journal of Hazardous Materials*, 147, 768-775

[2] V. Ducman, K. F. Bizjak, B. Likar, M. Kolar, A. Robba, J. Imperl, M. Božič, B. Gregorc (2022) *Materials*, 15, 4303-4321

[3] J. Choi, D. Lee, Y. Son (2021) *Ultrasonics Sonochemistry*, 74, 105574

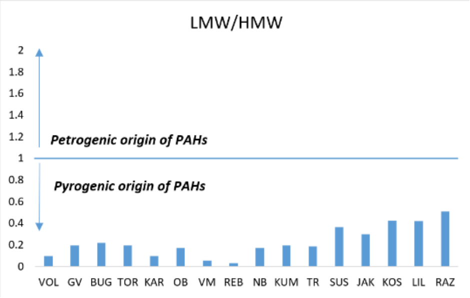
[4] S. Chen, X. Fei, C. Zhang, Y. Chen, Q. Ge (2021) *Journal of Soils and Sediments*, 21, 3825-3833

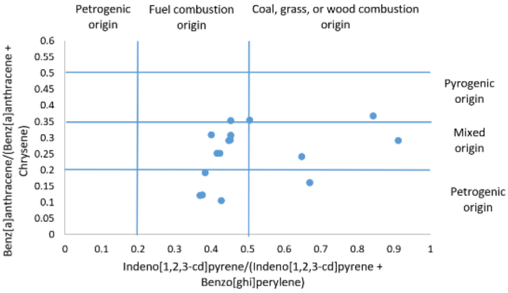
The Assessment of Sources of Polycyclic Aromatic Hydrocarbons Pollution of the Vrbas River Sediments

S. Pržulj[1], G. Veselinović[2,], S. Stojadinović[2], M. Kašanin-Grubin[2], S. Štrbac[2], M. Balaban[1], B. Jovančićević[3]*

(1) University of Banja Luka, Faculty of Natural Sciences and Mathematics, Mladena Stojanovića 2, Banja Luka, Bosnia and Herzegovina, (2) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia (3) Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia

[*]gorica.veselinovic@ihtm.bg.ac.rs





PAHs are a group of ubiquitous persistent organic pollutants that cause sever global environmental concerns for ecosystems and human health due to their potential toxicity and carcinogenicity. PAHs are a group of organic pollutants strongly related to anthropogenic activities such as settlement, transport, and industrial development. Due to their lipophilicity and persistence, PAHs are readily adsorbed in the particulate matter once they enter the urban river system and are finally deposited in the sediment. [1]

The aim of this work was to evaluate the distribution of PAHs in the sediments of Vrbas River, to assess their occurrence and to establish the origin (pyrogenic/petrogenic) of pollution sources.This study focussed on investigation on the state of pollution and identification of potential sources of contamination of river sediments by polycyclic aromatic hydrocarbons along entire course of the Vrbas River (Bosnia and Herzegovina).

Nineteen sampling points were selected covering the entire course of the Vrbas River (Bosnia and Herzegovina). The samples were extracted in a Soxhlet apparatus and fractionated using column chromatography. In the fraction of aromatic hydrocarbons, PAHs were analysed by gas chromatography - mass spectrometry (GC-MS) in a selected ion monitoring (SIM) mode. The ions monitored were: m/z = 128 (naphthalene), m/z = 152 (acenaphthylene), m/z = 154 (acenaphthene), m/z = 166 (fluorene), m/z = 178 (phenanthrene andanthracene), m/z = 202 (fluoranthene and pyrene), m/z = 228 (benzo[a]anthracene and chrysene), m/z = 252 (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[e]pyrene and benzo[a]pyrene), m/z = 276 (indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene), and m/z = 278 (dibenzo[a,h]anthracene) [2]. Thereafter numerous PAH diagnostic ratios were calculated and analysed.

High molecular weight polycyclic aromatic hydrocarbons (4, 5 or 6 rings) are more prevalent in the observed samples. The analysis of different PAH diagnostic ratios indicate the pyrogenic PAHs origin. In most samples, according to calculated parameters, these are combustion products of coal, grass, and wood, while in some samples these parameters implicate the fuel combustion origin of PAHs. No regularity was observed in the distribution of PAHs in the samples, indicating the existence of multiple sources of these compounds in the investigated area. Thus, the conclusion is that this area was exposed to both point and diffuse sources of PAH contaminants.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No: 451-03-68/2022-14/200026)

References

[1] X.L. Zhang, S. Tao, W.X. Liu, Y. Yang, Q. Zuo, S.Z. Liu (2005) *Environmental science & technology*, 39(23), 9109-9114.

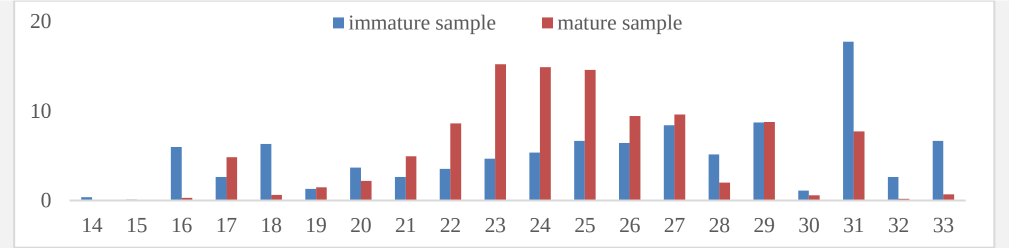
[2] S. Stojadinović, A. Šajnović, M. Kašanin-Grubin, G. Gajica, G. Veselinović, S. Štrbac, B. Jovančićević (2022) *Journal of Soils and Sediments*, 22(2), 640-655.

Influence of Maturation Processes on *n*-Alkane Distribution in Peloids from Sečovlje Saltpans Nature Park Slovenia

A. Šajnović[1], G. Veselinović[1,], G. Gajica[1], S. Stojadinović[1], N. Glavaš[2], P. Trebše[3], F. Prosenc[3], B. Jovančićević[4]*

(1) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia, (2) SOLINE Pridelava soli d.o.o., Seča 115, Portorož, Slovenia, (3) University of Ljubljana, Faculty of Health Sciences, Zdravstvena pot 5, 1000, Ljubljana, Slovenia, (4) University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia

[*] gorica.veselinovic@ihtm.bg.ac.rs



Slovenia has 15 certified natural health resorts located in untouched natural environments that practice the centuries-old tradition of thermal treatments. Sečovlje Saltpans Nature Park is one of the most attractive natural and cultural heritage sites of Slovenia located at the Adriatic Sea. Salt is recovered from the sea water by solar evaporation. Beside salt, thermal mud and brine are important products usually used for therapeutic purposes. The physical, chemical, microbiological and sedimentological properties of the thermal mud have been relatively well documented [1]. Organic geochemical analysis in Sečovlje peloid has not been performed so far.

The maturation of peloids is based on complex processes involving biochemical processes related to the growth of microorganisms and microalgae, depending on the habitats in the open-air tanks where the clay is left to mature. It is precisely during this maturation process that the different biological action compounds, partly responsible for the therapeutic actions, are formed [2].

In Sečovlje Saltpans Nature Park healing mud maturate in the natural sedimentary environment where it occurs. The aim of this work was to determine the influence of peloid maturation on the *n*-alkane distribution. For this purpose, the sample before and after maturation was examined.

Azeotrope mixture of methanol and dichloromethane was used for the Soxhlet extraction. Elemental sulphur was removed by adding copper to the mixture. Only the saturated fraction was isolated from soluble organic matter using column chromatography (adsorbents: SiO_2 and Al_2O_3, eluent: *n*-pentane). Subsequently, saturated fraction was analysed on an Agilent 7890A GC gas chromatograph coupled to the Agilent 5975C mass selective detector. Mass fragmentograms of the saturated fraction used for the interpretation of biomarkers were *m/z* 71 for *n*-alkanes and isoprenoids. *n*-Alkanes of immature sample are characterized by bimodal distribution with prevalence of odd long chain homologues with maximum at n-C_{31}. Among short chain *n*-alkanes domination of n-C_{16} and n-C_{18} is noticeable. Even carbon number predominance of short chain *n*-alkanes is mainly from bacteria [3]. It means that organic matter in addition to terrestrial plants is composed of aquatic organisms such as bacteria [3], deposited under reduction condition (phytane > pristane). Presence of bacteria and other microorganisms in peloids has the potential to enhance their therapeutic value. It is obvious that the distribution of *n*-alkanes changed during of peloid maturity. Mature sample have a common unimodal distribution where middle chain *n*-alkanes (n-C_{23} to n-C_{25}) dominated and probably have mixing sources.

Acknowledgements

This research is a part of the bilateral project 2021–2023 between the Republic of Serbia and Slovenia ‘‘Geochemical approach in characterisation of therapeutical peloid mud from Serbian and Slovenian spas’’.

References

[1] N. Kovač, N. Glavaš, T. Ramšak, M. Dolonec, N. Rogan Šmuc (2018) *Science of The Total Environment*, 664, 350-359.

[2] M.L. Mourelle, C.P. Gómez, J.L. Legido (2021) *Marine drugs*, 19, 666-682.

[3] The Biomarker Guide, Biomarkers and Isotopes in the Environment and Human History. K.E. Peters, C. Walters, J.M. Moldowan, University Press, Cambridge, 2005.

POSTER
(#1)

Role of Mineralogical Composition and Physico-chemical Properties of Sediment on Badlands Classification

N. Antić[1,*], *M. Stefanović*[2] ,*S. Štrbac*[1] ,*S. Stojadinović*[1],*T. Tosti*[3], *M. Kašanin-Grubin*[1], *B. Jovančićević*[3]

(1) Institute of Chemistry, Technology, and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia, (2) Innovation Center of the Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia, (3) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia

[*]*nevena.antic@ihtm.bg.ac.rs*

Figure 1. Badland areas from which samples were collected.

Badlands, areas exposed to wide range of geomorphological processes and sparse or absent in vegetation, thanks to differences in soil and rock characteristic can be formed in different climate conditions [1].

Beside common morphological properties, these kind of terrains fall under a wide range of geomorphic activities and dynamic behaviors.

Diversity of factors, led by lithology, weathering and erosion processes, play a significant role in formation of badland terrains. That diversity implies the complexity of the interactions and processes that are a part of badlands origin and evolution.

It was observed that in terrains with different lithologies may have different erosion rates and general processes, depending on the lithology. But not only that, even areas with same lithology may behave differently depending on the conditions that occur in the environment.

For these reasons mineralogical and physico-chemical characterizations attracted researchers' attention with the aim to link material properties, weathering and erosion processes and form current "site signatures". Link between sodium adsorption ration and electrical conductivity (SAR/EC) or pH (SAR/pH) are some of already established site signatures that define dispersivity of badland materials.

Knowing that, physico-chemical and mineralogical analysis were conducted on~ 40 unweathered badland sediments samples taken from different areas (Fig. 1) with the aim to determine critical properties of material for development of badlands and to make additional classification of dispersive materials.

Wide database formed of data such as: mineralogical composition, grain size, pH, electrical conductivity, ions concentrations, the content of organic carbon (C_{org}) was formed. Results processing and a large number of statistical analysis showed that classification of sediments dispersivity based on its mineralogical compositions is mainly influenced by C_{org}.

Materials susceptibility to erosion processes is where C_{org} generally has an important role, while higher C_{org} have important role in improvement of materials resistance to dispersion.

In conclusion, this results processing suggested that a current importance of C_{org} obvious and that it could lead to forming a new site signature that would contain some of analyzed parameters combined with measured C_{org} values and would classify them based on their dispersity.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No: 451–03-68/2022–14/200026, 451–03–68/2022–14/200169).

References

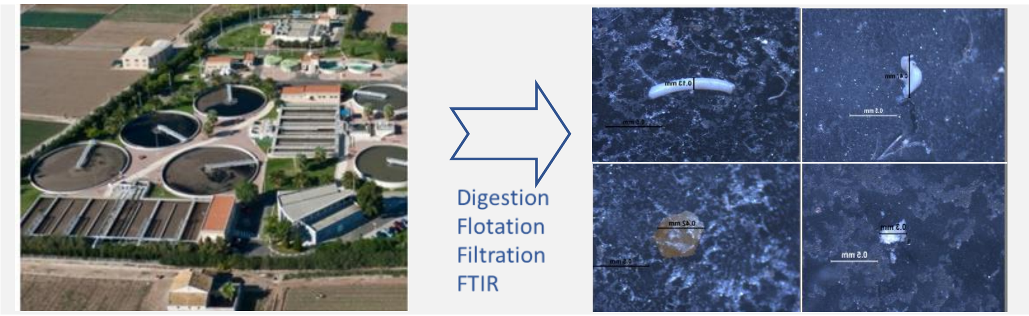
[1] Bryan, R.B., Yair, A., 1982. *Badland Geomorphology and Piping*. Geo Books, Norwich, England

POSTER
(#1)

Analytical Methodology for Monitoring Microplastics in Sewage Sludge from Wastewater Treatment Plants

J. Martín, M. Arenas, J.L. Santos, I. Aparicio, E. Alonso*

Escuela Politécnica Superior, Department of Analytical Chemistry, Universidad de Sevilla, Spain
*anquimed@us.es



There is an increasing concern, not only by the scientific community but also by international organisms, about the presence of microplastics in many environmental and biological matrices. Microplastics are widely accepted as plastics fragments up to 5 mm in diameter. Microplastics themselves, are considered an environmental threat due to their persistence, ubiquity, toxicity potential but they can also act as vectors of organic and inorganic pollutants due to their high sorption capacity [1,2].

Wastewater treatment plants (WWTPs) have been identified as an important pathway for the release of microplastics into the environment, through discharges of effluent wastewater or treated sludge disposals as soil fertilizer [3,4]. In addition, it has been reported that more than 90% of microplastic removed from wastewater in WWTPs are entrapped in sludge [5]. Therefore, analytical strategies are needed to obtain information about the presence, behaviour and removal of microplastics alongside sewage sludge stabilisation treatments.

In this work, an analytical strategy for microplastic monitoring alongside sewage sludge treatment is proposed. To achieve this aim, sewage sludge samples were taken from different sludge stabilisation stages in a WWTPs that mainly treats urban wastewater. Sludge samples were collected in glass flasks with metallic caps in 24-hour sampling cycles. Flasks were previously washed and conditioned for sample conservation.

Sample treatment was carried out by digestion with potassium hydroxide, extraction by flotation with a sodium chloride solution and filtration of the supernatant. Microparticles retained in the filter were collected for further analysis and identification by microscopy and Fourier-transform infrared spectroscopy (FTIR).

Four types of plastic materials were identified (polyethylene, polypropylene, polystyrene and polycarbonate). Their particle size was in the range from 0.24 to 3.40 mm. The average concentrations of microplastics in primary and secondary sludge were 7.5 and 10.7 particles/L, respectively. The average concentration in digested sludge was 79.5 particles/L. The proposed method revealed to be efficient for routine analysis of microplastics in sewage sludge.

Acknowledgements

The authors acknowledge financial support from Consejería de Economía, Conocimiento, Empresas y Universidad, Junta de Andalucía (Proyect I+D+i PAIDI Andalucía No. P20_00556).

References

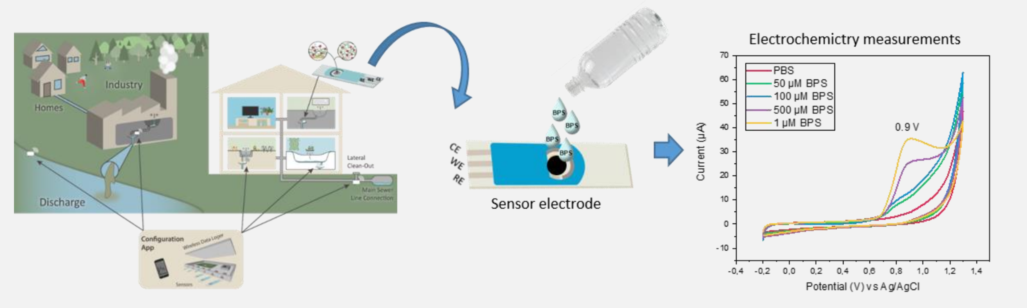
[1] L.H.M.L.M. Santos, S. Rodríguez-Mozaz, D. Barceló (2021) *Case Studies in Chemical and Environmental Engineering*, 3, 100079.
[2] J. Martín, J.L. Santos, I. Aparicio, E. Alonso (2022) *Trends in Environmental Analytical Chemistry*, 35, e00170.
[3] D. Harley-Hyang, F.A. Memon, N. Jones, T. Galloway (2022) *Science of the Total Environment*, 823-153765.
[4] X. Li, L. Chen, Q. Mei, B. Dong, X. Dai, G. Ding, E.Y. Zeng (2018) *Water Research*, 142, 75-85.
[5] A.S. Reddy, A.T. Nair (2022) *Environmental Technology and Innovation*, 28, 102815.

SESSION 2: Water

Bisphenols S, Poorly Determined Substitute of Bisphenol A - Comparison of Electrochemical and Chromatographic Detection in Water Media

K. Žagar Soderžnik[1,*] , *Š. Črešnovar*[2], *A. Korenta*[1], *Š. Trafela*[1], *P. Trebše*[2], *M. Bavcon Kralj*[2]

(1) Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia, (2) Faculty of Health Sciences, University of Ljubljana, Zdravstvena pot 5, 1000 Ljubljana, Slovenia
[*]kristina.zagar@ijs.si



Persistent mobile chemicals - PMCs are the result of the development of modern organic chemistry, which has been flourishing since the middle of the 20th century and it has been found nowadays in tens of thousands of everyday products. Although modern chemicals have been around for many years its negative effects on human and animal health are only beginning to be understood [1,2]. On the top of the priority list of PMCs are bisphenols. Bisphenol S (BPS) is one of the most common phenols in the environment. In plastics, it is used as a substitute for bisphenol A (BPA), which is known hormone disruptor. Although BPS threats the human health in the same way, it is still allowed and poorly regulated [2].

In fact, there is a need for urgent development of selective electrochemical sensors for on-site detection supported by powerful chromatographic techniques. Within this study, the development of receptor element for detection of three bisphenols, namely BPS, BPA and bisphenol F (BPF) is presented. To guide sensor development and its effectiveness, conventional chromatographic analysis (high performance liquid chromatography with diode array detection - HPLC DAD detector) with proper sample preparation (solid phase extraction – SPE) was applied.

The electrochemical detection of bisphenols is possible due to irreversible oxidation of phenol group [3] leading to different oxidation peaks for each bisphenol (BPS at 0,7-1,0 V) [4]. The chemical or electrochemical processing of receptor elements was evolved on commercial screen-printed electrodes (SPE), with carbon as a working electrode, platinum as counter electrode and silver as reference electrode. The receptor element working electrode was modified using a material that provides a large surface area (carbon black or SWCNT's) that exhibits efficient redox characteristics for a given analyte at low potential. Characterized and fully understood receptor elements were integrated into proof of concept system and exposed to target analytes in water. For detection of bisphenols in water solutions electrochemical measurements, e.g. cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) were applied. CA was used to calculate the calibration curve to obtain the sensitivity and limit of detection (LOD) for certain experimental conditions. Finally, the sensor was tested for selectivity. Selective detection of BPS, BPA and BPF was observed by using DPV on the same SPE working electrode with a solution containing all three isomers.

In the future, the sensors could be strategically placed in every household to disambiguate impacts from possible sources coming from everyday products.

Acknowledgements

The authors acknowledge the project (Sense PMC, ID J2-3051) and the research core funding No. P3-0388 (Mechanisms of Health Maintenance) both financially supported by the Slovenian Research Agency.

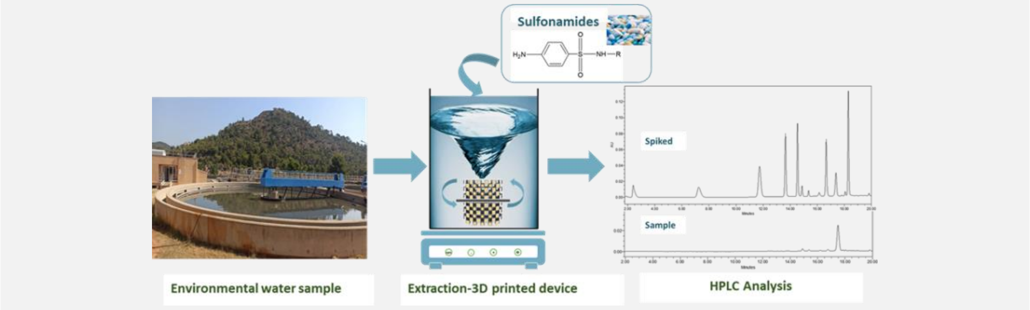
References

[1] D. Zahn, I.J. Neuwald, T.P. Knepper (2020). *Analytical and Bioanalytical Chemistry*, 412, 4763 – 4784.
[2] H. Rüdel, …, T. Reemtsma (2020). *Enviromental Sciences Europe 32(5).*
[3] Y. Zhang, …, L. Jianke (2021) *Food Chemistry*, 346, 128895.
[4] Y.-H. Pang, …, Y. Wang (2020) *Environmental Pollution*, 263.

Design and Manufacture of an In-situ Extraction Functionalized Device Using 3D Printing for the Determination of Sulfonamides from Water Samples by HPLC-DAD

D. Barzallo[1,*], E. Palacio[1], L. Ferrer[1]

(1) Environmental Analytical Chemistry Group, University of Balearic Islands, Cra. Valldemossa 7.5 km, Spain
[*]dbarzallo@uib.es



Sulfonamides (SAs) are pharmaceutical products widely used in human and veterinary medicine to systematically treat infectious diseases, which are poorly absorbed by the human body and thus are released into the environment as parent compounds or metabolites via urine or feces [1]. For this reason, they are considered as emerging chemical substances or "pseudo-persistent" pollutants due to their continuous entry into the ecosystem and their low biodegradability, which can cause the development antibiotic resistant bacteria, causing a negative impact on human health [2]. Wastewater treatment plants (WWTPs) are the main source of SAs release into the environment since they are not completely eliminated during their treatment [3]

A 3D printed device coated with Oasis MCX resin was developed allowing both the on-site and laboratory extraction and pre-concentration of sulfonamides (SAs) and subsequent determination by HPLC with diode array detection (DAD). The device has been designed and printed by stereolithographic 3D printing and functionalized with a SPE resin by stick and cure immobilization technique. Images of 3D printed coated devices obtained by scanning electron microscopy (SEM) allowed its characterization. Various parameters that affect the extraction efficiency (eluent, eluent volume, extraction and elution times) were studied and under optimal conditions, seven sulfonamides (Sulfanilamide, SAM; Sulfadiazine, SDZ; Sulfamerazine, SMR; Sulfamethazine, SMZ; Sulfamethoxypyridazine, SMP; Sulfamethoxazole, SMX; and Sulfadimethoxine, SDX) have been satisfactorily quantified after the 3D coated-device extraction. Detection limits of 6, 6, 0.9, 0.9, 0.8, 0.7, and 0.6 µg L^{-1} were achieved for SAM, SDZ, SMR, SMZ, SMP, SMX, and SDX, respectively.

In all cases, a good linearity was observed up to 1000 µg L^{-1} with R^2 between 0.9987-0.9998. The interday precision expressed as relative standard deviation (n=3) varied between 2.2 and 5.5 % RSD, showing the good precision of the proposed methodology. Finally, the developed method was successfully used for the simultaneous analysis of seven SAs in samples of tap water and wastewater. Therefore, the 3D printed device is an efficient, miniaturized and simple alternative for monitoring emerging contaminants derived from Pharmaceutical and Personal Care Products such as SAs in environmental water samples.

Acknowledgements

The authors acknowledge financial support from project PID2019-107604RB-I00 funded by MCIN/AEI/ 10.13039/501100011033. Diego Barzallo acknowledges the support from the Spanish Ministry of Science, Innovation and Universities (MCIU) for the pre-doctoral research fellowship (FPU20/06399). The authors thanks to Calvia2000 WWTP for the provision of wastewater samples.

References

[1] M. Seifrtová, L. Nováková, C. Lino, A. Pena, P. Solich (2009) *Anal. Chim. Acta*, 649, 158–179.
[2] G. Prasannamedha, P.S. Kumar (2020) *J. Clean. Prod.*, 250, 119553.
[3] K.G. Karthikeyan, M.T. Meyer, (2006) *Sci. Total Environ.*, 361, 196–207.

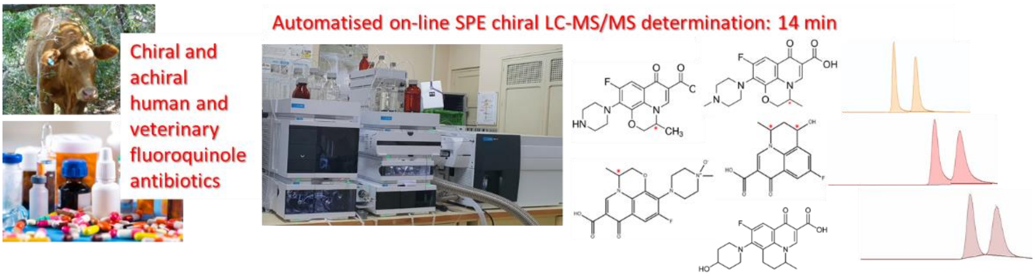
ORAL
(#2)

Enantiomeric Determination of Main Fluoroquinolone Antibiotics and Their Metabolites in Wastewater and Surface Water

C. Mejías, J.L. Santos, J. Martín, I. Aparicio, E. Alonso*

Escuela Politécnica Superior, Department of Analytical Chemistry, Universidad de Sevilla, Spain

**anquimed@us.es*



There is an increasing concern about the overuse and misuse of antibiotics because such practices are resulting in a rising antibiotic resistance that is threatening the treatment of common infection diseases.

Fluoroquinolones are antibiotics of significant environmental concern as they are used not only in human medicine but also in veterinary medicine and not only as therapeutic agents but also to promote livestock growth and in aquaculture. They have been included in the list of critically important antimicrobials by the World Health Organization [1] and one of them, ciprofloxacin (CIP), in the watch list of substances for Union-wide monitoring in the field of water policy [2].

Some fluoroquinolones and their metabolites are chiral compounds. Chirality has a great impact on the environment because, although physical and chemical processes affect in the same way to both enantiomers, they can act differently with other chiral molecules (such as proteins: receptors or enzymes), which can result in different biological and toxicological behaviours [3] and pharmacokinetic and pharmacodynamic responses. Nevertheless, in spite that enantioselective analytical methods are required for a proper environmental risk assessment they have been scarcely reported [4].

In this work, a green analytical method has been developed and validated for the first time automatised enantioselective determination of environmental significant fluoroquinolones and their metabolites in wastewater and surface water samples. Target fluoroquinolones were selected by their extended use in human (ciprofloxacin and ofloxacin) or veterinary (flumequine) medicine.

The analytical method was based on on-line solid-phase extraction-chiral liquid chromatography-tandem mass spectrometry (LC-MS/MS). Analysis, including sample extraction and chiral LC-MS/MS determination was carried out in just 14 min.

The method was validated for its application to surface water and effluent and influent wastewater samples. Accuracy values were in the range from 61.4 to 122 % in wastewater and from 73.4 to 119 % in surface water. Precision, expressed as relative standard deviation, was lower than 13.6 % for all the compounds in all matrices. Method quantification limits were in the range from 0.2 to 50 ng L^{-1} for all compounds in wastewater and surface water.

Method application to wastewater and surface water samples revealed the enantioselective transformation of (*S*)-OFL into (*R*)-OFL in surface water and the prevalence of OH-FLU D2 metabolite with respect to OH-FLU D1 in influent wastewater.

Acknowledgements

This work was supported by the Ministerio de Ciencia e Innovación-Agencia Estatal de Investigación (grant number: PID2020-117641RB-I00 by MCIN/AEI/10.13039/501100011033) and by the Junta de Andalucía, Consejería de Economía y Conocimiento (grant reference: US-1254283). C. Mejías acknowledges the University of Seville for her predoctoral grant (VI PPIT-US 2021 II.2A).

References

[1] *Critically Important Antimicrobials for Human Medicine* (2018) World Health Organization, Antimicrobial Resistance Division, 6th edition.

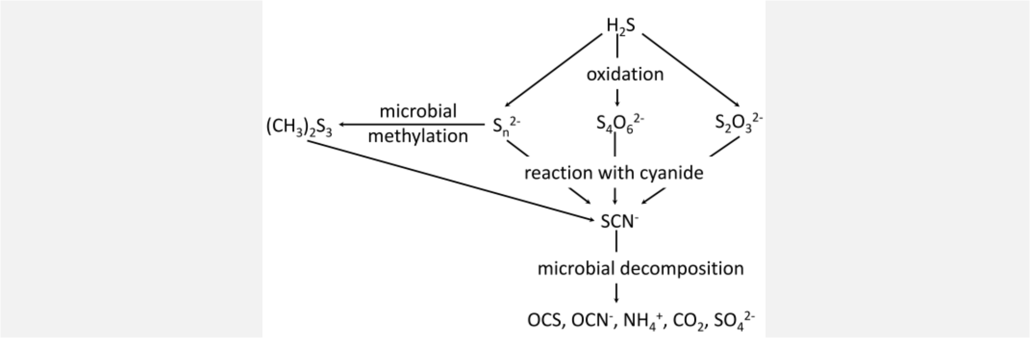
[2] European Commission Decision 2020/1161/EU (2020) *Official Journal of the European Union* 57, 32–35.

[3] C. Mejías, M. Arenas, J. Martín, J.L. Santos, I. Aparicio, E. Alonso (2022) *Reviews of Environmental Contamination and Toxicology*, 260, 3.

[4] M. Arenas, J. Martín, J.L. Santos, I. Aparicio, E. Alonso (2021) *TrAC - Trends in Analytical Chemistry* 143, 116370.

Formation and Decomposition of Thiocyanate in Natural Aquatic Systems

A. Kamyshny[1,*], *I. Kurashova*[1]
(1) Ben-Gurion University of the Negev, P.O.B. 653, Beer-Sheva, 84105 Israel
[*]*alexey93@gmail.com*



Thiocyanate (SCN^-) is formed in various natural and industrial processes. It is found in waste waters from coal and oil processing, steel and gold manufacturing, petrochemical industry and pesticide production. Thiocyanate is toxic to aquatic species. Natural sources of thiocyanate include plants, biological and abiotic decomposition of organic matter, and in vivo detoxification of cyanide. Several species of bacteria, algae, fungi, plants, and animals are physiologically capable of detoxifying cyanide, and in most cases one of the end products of detoxification is thiocyanate. Another important mechanism of thiocyanate formation in natural aquatic systems is the reaction between hydrogen cyanide and sulfide oxidation intermediates, which contain sulfur-sulfur bonds.

We have studied the rates of thiocyanate formation by reactions of free and iron-complexed cyanide with thiosulfate ($S_2O_3^{2-}$) [1], tetrathionate ($S_4O_6^{2-}$) [2] and dimethyltrisulfane ($(CH_3)_2S_3$) [3] and compared them with the rates of the reaction between cyanide and polysulfides (S_n^{2-}) [4]. In another study we have assessed the stability of thiocyanate in the natural aquatic systems, including waters and sediments of marine and limnic systems under oxic, anoxic, iron-rich, manganese-rich and sulfide-rich conditions [5].

Results of our research suggest that reactivity of iron-complexed cyanide toward sulfur species is very low and do not contribute to thiocyanate formation in the natural aquatic systems. Reactivity of sulfur species toward free cyanide decreases in the order: polysulfide ≥ tetrathionate > dimethyltrisulfane > thiosulfate. Cyanide anion is more reactive toward sulfur species than hydrogen cyanide.

Although thiocyanate is chemically stable in aqueous solutions under environmental conditions, its biological decomposition is relatively fast and may be described by Michaelis-Menten kinetic model. Half-life of thiocyanate in 1 µM - 1 mM range may vary from 1 day to tens of years. The dependences of thiocyanate decomposition rates on conditions were evaluated. It was found that these rates are higher in the presence of oxygen than in its absence. In the sediments, the rates are higher or equal to the rates in water column. In the anoxic systems, the rates are higher in the presence of hydrogen sulfide than in the presence of dissolved iron and manganese. Lag times before the decrease in thiocyanate concentrations starts were varies between <1 day in oxic marine sediment to 79 days in anoxic seawater.

Acknowledgements

This research was funded by Marie Curie Actions CIG PCIG10-GA-2011-303740 (ThioCyAnOx) Grant. We are grateful to Itay Halevy, Tamir Buchshtav, Ido Ben Laish, Valeria Boyko, Werner Eckert, Asaph Rivlin, Valeria Boyko and Hanni Leibowitz for help with sampling, samples analyses and data processing.

References

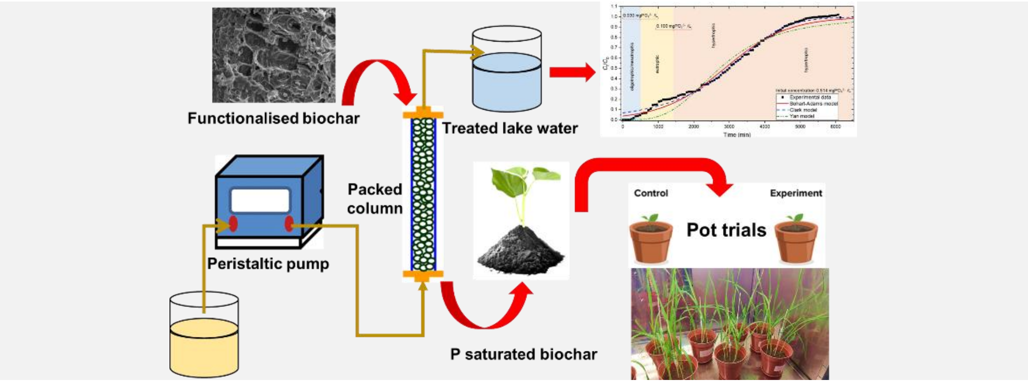
[1] I. Kurashova, A. Kamyshny (2019) *Aquatic Geochemistry*, 25, 219-236.
[2] I. Kurashova, A. Kamyshny (2021) *Aquatic Geochemistry*, 27, 63-77.
[3] I. Kurashova, A. Kamyshny (2021) *Environmental Chemistry*, 18, 81-90.
[4] R. G. Luthy, S. G. Bruce Jr. (1979) *Environmental Science & Technology*, 13, 1481-1487.
[5] I. Kurashova, I. Halevy, A. Kamyshny (2018) *Environmental Science & Technology*, 52, 1234-1243.

Nutrient Removal and Recovery from Water Using Functionalised Biochars

<u>S. Pap</u>[1,], Q. Zhao[1,2], P. Gaffney[1], C. Kirk[3], S.W. Gibb[1], M.A. Taggart[1]*

(1) Environmental Research Institute, UHI North Highland, Thurso, Scotland, KW14 7JD, UK; (2) School of Civil & Architecture Engineering, Xi'an Technological University, Xi'an, Shaan Xi, 710021, China; (3) School of Chemistry, University of Edinburgh, David Brewster Rd, Edinburgh EH9 3FJ, UK

[*]szabolcs.pap@uhi.ac.uk



This work looked to explore biochar's potential to mitigate against pollution by testing its capacity to capture excess nutrients [1]. We propose that waste wood converted to biochar may be transformed into a value-added water treatment material and fertiliser product [2].

We determined the best biochar production method using a Response Surface Methodology approach [3]. Raw biochar was then functionalised with Ce/La/Zr metal hydr(oxides). All biochars were characterised using SEM-EDX, BET, FTIR, XRD and XPS techniques. Removal efficiency /adsorption capacity of nutrients (PO_4^{3-}, NO_3^- and NH_4^+) was optimised through a series of batch studies to explore the kinetic/thermodynamic behaviour and equilibrium phase of the biochar/nutrient system in an aquatic environment. The performance of the two best biochars (La-OB and CeLa-OB) were evaluated in dynamic regimes with synthetic PO_4^{3-} solutions and hypereutrophic lake water (~0.5 mg P/L). The feasibility of using biochar in a 'real life' scenario was studied with reusability/desorption trials using multiple cycles. Toxicity in a soil environment was also considered using seed germination and pot trials. Recommendations for future applications through scale-up and cost calculations were also considered.

Results suggested that raw biochar only weakly adsorbed nutrients, which was especially true for the anionic forms of PO_4^{3-} and NO_3^- due to electrostatic repulsion elicited by the negatively charged biochar surface. Chemical functionalisation significantly increased adsorption capacity for all nutrients (especially for PO_4^{3-}, with >1000-fold improvement). Instrumental characterisation showed that adsorption mechanisms were dominated by metal-phosphate precipitation reactions, and inner-sphere complexation onto metal ligands. The maximum adsorption capacity for the biochars studied was 78 mg P/g in column filtration trials. The biochars showed a high efficiency in treating hypereutrophic lake water, low toxicity in seed germination and had a positive effect on plant yield during pot trials.

Future work will include pilot-scale studies to observe nutrient recovery at larger scale.

Acknowledgements

We gratefully acknowledge financial support from: the RSPB Forsinard Flows National Nature Reserve; the University of the Highlands and Islands WaterHub Challenge Fund; the Natural Science Foundation of Education Department of Shaanxi Province (Grant No: 18JK0375); The Royal Society of Chemistry 'RSC Research Fund' (Grant R20-7810) and SAGES Small Grants Scheme (10th SSGS).

References

[1] *Integrated and Hybrid Process Technology for Water and Wastewater Treatment*. S. Pap, B. Bremner, M. Turk Sekulic, M.A. Taggart, Amsterdam, Elsevier, 2021.

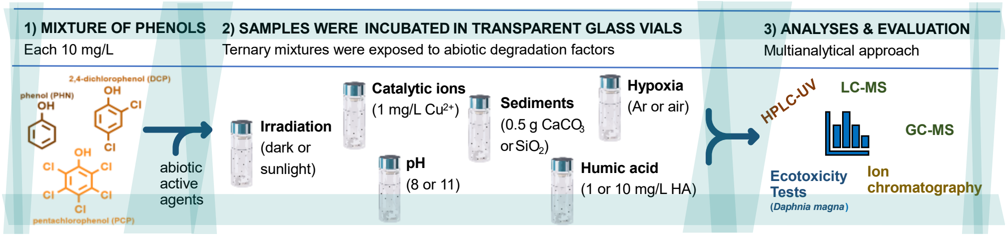
[2] S. Pap, C. Kirk, B. Bremner, M. Turk Sekulic, L. Shearer, S.W. Gibb, M.A. Taggart, *Water research*, 173 (2020) 115573.

[3] S. Pap, P.P. Gaffney, Q. Zhao, D. Klein, Y. Li, C. Kirk, M.A. Taggart, *Industrial Crops and Products*, 185, (2022) 115165.

Natural Abiotic Degradation of Phenol and Chlorophenols in Aquatic Environment

A. Kravos[*], *G. Kalčikova, H. Prosen*

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, Ljubljana, Slovenia
[*]*aleksander.kravos@fkkt.uni-lj.si*



The presence of phenol and chlorophenols in the environment is reportedly still significant even after decades of their limited use, because of their high stability. In natural waters, e.g., rivers, wetlands, ocean bed, phenols experience natural degradation processes led by biotic and abiotic factors [1]. Despite being well-researched as hazardous pollutants [2], their chemical fate, persistency, and interactions in natural waters have not yet been fully addressed [3].

Tracking such complex natural phenomena as biotic and abiotic degradation of persistent pollutants is a real challenge. However, it can be studied by laboratory simulations. As so, this study assesses environmental behaviour of three representative industrial pollutants (phenol, 2,4-dichlorophenol, and pentachlorophenol) in model aquatic matrices. Due to their high toxicity and resistance to biodegradation, herein, focus was placed only on abiotic factors that are significantly understudied. The chemical stability of phenols was investigated by simulating natural conditions in incubated lab-scale test mixtures.

We evaluated the effect of visible light irradiation, alkalinity, carbonate- and silicate-based sediments, humic substances, copper (II) ions, and hypoxic conditions on degradation of the three mentioned phenolic compounds. Multianalytical approach allowed collection of data on (i) phenols' stability, (ii) their dechlorination, (iii) chemical transformations, and (iv) detoxification. Accordingly, liquid, anion-exchange, and gas chromatography were applied. The use of mass spectrometry in the form of GC-MS and LC-MS allowed for simultaneous identification of the transformation by-products. Ecotoxicity tests were included in the study through testing of acute inhibition tests on water fleas *Daphnia magna*.

Degradation processes turned out to be dynamic, complex, and progressive. Dechlorination of chlorophenols was highly preferential. Processes were accelerated by alkaline pH, aerobic conditions, and presence of abiotic active agents, especially humic acid. An array of photoinduced chemical transformations proceeded, that induced formation of less toxic mixtures of transformation by-products. Altogether revealed chemical lability of the studied phenols in semi-real natural waters without any biological factors present.

In conclusion, this study contributes to broadening of the knowledge of the environmental self-cleaning capabilities triggered by abiotic processes. By knowing phenols' chemical fate in simulated aquatic environment, their persistency, interactions, and long-term influence on ecosystems could be better understood in the future.

Acknowledgements

The study was funded by Slovenian Research Agency through programmes P1-0153 and P2-0191.

References

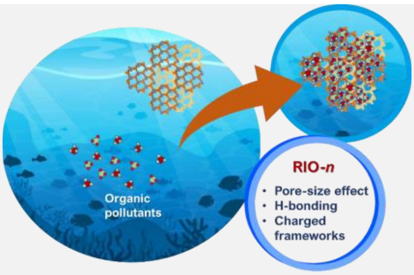
[1] M. Czaplicka (2004) *Science of the Total Environment*, 322, 21-39.
[2] A. Karci (2014) *Chemosphere*, 99, 1-18.
[3] M. Foszpańczyk, E. Drozdek, M. Gmurek, S. Ledakowicz (2018) *Environmental Science and Pollution Research*, 24, 34968-34975.

Ionic and Porous Materials for Efficient and Sustainable Water Purification Processes

L. C. Branco[1]*, *K. Zalewska*[1], *S. Freitas*[1,2], *L. Rodrigues*[2], *I. Matos*[1], *M. Bernardo*[1], *M. J. Nunes*[1], *P. Mothé- Esteves*[2]

(1) LAQV-REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal, (2) Instituto de Química, Universidade Federal do Rio de Janeiro, Brazil

**l.branco@fct.unl.pt*



Water resources are the main vehicle for the environmental dispersion of chemical pollutants [1]. Consequently, the discovery efficient processes to promote the purification of the contaminants from water is highly required. The presence of these contaminants in the environment may cause risks to ecosystems and to human since they are designed to have a specific action on the human body and to act in very low concentrations. It is very relevant the possibility to combine an efficient extraction methodology with high-precision analytical methods for a correct identification and quantification of water samples containing pollutants, particularly pharmaceutical drugs, such as antibiotics, which are permanently released into the environment [2]. The combination of porous materials, ionic liquids (ILs) and deep eutectic solvents (DES) have been developed for efficient removal of micropollutants from water streams. ILs as organic salts with low-melting points possessing peculiar physical and chemical properties and significant interest for extraction and separation applications [3]. In addition, DES as innovative materials prepared by suitable combination of hydrogen bond donors (HBD) and acceptors (HBA) have been reported for several applications [4]. Herein, we presented different purification processes using hydrophobic ILs and DES for liquid-liquid extractions [5-7] as well as porous materials for adsorption systems. As proof of concept, several organic and metal contaminants based on antibiotics (amoxicillin, ampicillin, oxytetracycline, ciprofloxacine, enrofloxacine and chloramphenicol), pesticides, plastic additives (bisphenol A) 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.

In addition, Porous materials based on activated charcoal and covalent organic frameworks (COFs) as efficient adsorbents have been developed and tested for water purification processes. The most promissory porous materials and ionic systems will be tested for effective removal of contaminants from river water samples.

Acknowledgements

The Associate Laboratory for Green Chemistry LAQV which is funded by national funds from FCT/MEC (UIDB/50006/2020) and co-financed by the ERDF under the PT2020 Partnership agreement (POCI-01-0145-FEDER – 007265) are acknowledged for financial support. MAR2020 (MAR-02.01.01-FEAMP-0042; INOVA4AQUA project) and Solchemar company. The authors also thanks the FCT-CAPES collaborative project, INOVA4AQUA project (MAR2020 (MAR-02.01.01-FEAMP-0042) and Solchemar company.

References

[1] P. Kehrein, M. van Loosdrecht, P. Osseweijer, M. Garfí, J. Dewulf, J. Posada (2020) *Environ. Sci.: Water Res. Technol.* 6, 877.

[2] M. Patel, R. Kumar, K. Kishor, T. Mlsna, C. U Pittman Jr, D. Mohan (2019) *Chem Rev* 119, 3510.

[3] Sónia P. M. Ventura, Francisca A. Silva, Maria V. Quental, Dibyendu Mondal, Mara G. Freire, João A. P. Coutinho (2017) *Chem. Rev.* 117, 6984.

[4] C. Florindo, L. C. Branco, I. M. Marrucho (2019) *ChemSusChem* 12, 1549.

[5] C. Florindo, F. Lima, L. C. Branco, I. M. Marrucho (2019) *ACS Sustainable Chem. Eng.* 7, 14739.

[6] C. Florindo, N. V. Monteiro, B. D. Ribeiro, L. C. Branco, I. M. Marrucho (2020) *J. Mol. Liq.* 297, 111841.

[7] M. J. Nunes, V. Paz, C. M. Cordas, J. P. Noronha, L. C. Branco (2022) *Anal. Methods*, 14, 935.

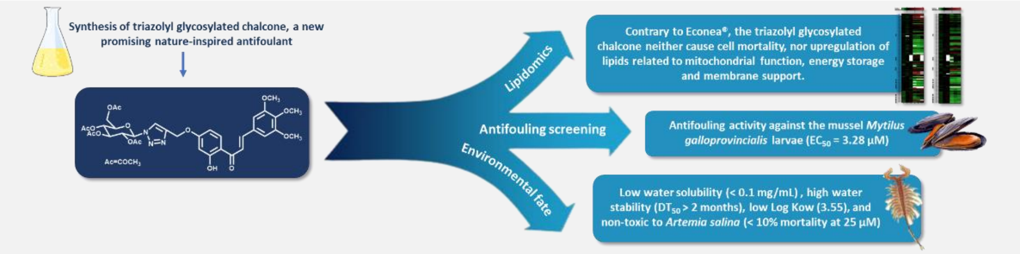
ORAL
(#2)

Development of a New Synthetic Chalcone as a Promising Non-Toxic Antifoulant for the Prevention of Marine Biofouling

D. Pereira[1,2,*], *C. Vilas Boas*[1,2], *L. Running*[3], *C. Gonçalves*[2], *V. Vasconcelos*[2,4], *M. Pinto*[1,2], *G. E. Atilla-Gokcumen*[3], *D.S. Aga*[3], *J.R. Almeida*[2], *M. Correia-da-Silva*[1,2], *H. Cidade*[1,2]

(1) Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313, Porto, Portugal, (2) CIIMAR – Interdisciplinary Centre of Marine and Environmental Research , University of Porto, Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n 4450-208 Matosinhos, Portugal, (3) Chemistry Department, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA (4) Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4069-007 Porto, Portugal

[*] *up200904461@edu.ff.up.pt*



Synthesis of triazolyl glycosylated chalcone, a new promising nature-inspired antifoulant

Contrary to Econea®, the triazolyl glycosylated chalcone neither cause cell mortality, nor upregulation of lipids related to mitochondrial function, energy storage and membrane support.

Antifouling activity against the mussel *Mytilus galloprovincialis* larvae (EC_{50} = 3.28 μM)

Low water solubility (< 0.1 mg/mL) , high water stability (DT_{50} > 2 months), low Log Kow (3.55), and non-toxic to *Artemia salina* (< 10% mortality at 25 μM)

Marine biofouling remains a huge challenge for maritime industries, causing massive material and economic losses. Due to the settlement and transportation of marine microorganisms through different parts of the world, this occurrence also has ecological implications, causing modifications of biodiversity. To prevent this phenomenon, antifouling (AF) coatings with tributyltin (TBT) were widely used by maritime industries for decades. However, due to TBT toxicity for the marine environment, antifouling coatings based on this biocide were banned. New alternatives to AF coating were based on copper compounds with the incorporation of biocide boosters but, even being less harmful to the environment than organotin biocides, these biocides have showed to be a threat to the marine environment [1]. Based on the potential of nature and nature-inspired synthetic flavonoids [2,3], as well as the triazole ring, for the prevention of marine biofouling, our research group developed a new triazolyl glycosylated chalcone hybrid which showed promising anti-settlement activity against Mytilus galloprovincialis, as well as antimicrofouling activity against microalgae Navicula sp. This compound also showed to be non-toxic against the non-target marine microorganism Artemia salina, with less of 10% mortality at 25 μM, while the commercial biocide Econea® showed 100% mortality at the same concentration. Moreover, by comparing the toxicity of the commercial biocide Econea® and the new promising chalcone on retinal human cells by lipidomic approaches, it was found that, contrary to the new chalcone, Econea® caused cell mortality at the lowest concentration tested, increasing some lipids related to mitochondrial function, energy storage, and membrane support. Through environmental fate studies, it was found that the obtained chalcone is low water soluble, stable in seawater after 2 months, low bioaccumulation potential (Log Kow = 3.55), which can be useful for incorporation in antifouling coatings as a promising agent.

Acknowledgements

This research was supported by national funds through FCT (Foundation for Science and Technology) within the scope of UIDB/04423/2020, UIDP/04423/2020, and under the projects PTDC/CTA-AMB/0853/2021 by FCT through national funds. D.P. and C.V.-B. acknowledge FCT for their Ph.D. scholarships (grant numbers SFRH/BD/147207/2019 and SFRH/BD/136147/2018, respectively).

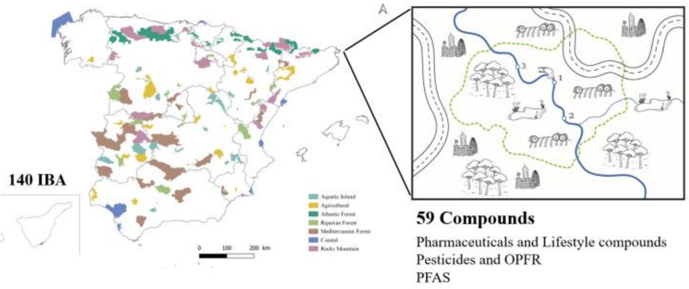
References

[1] C. Parisi, J. Sandonnini, M.R. Coppola, A. Madonna, F.K. Abdel-Gawad, E.M. Sivieri, G. Guerriero (2022) *Journal of Marine Science and Engineering*, 10, 792.
[2] J.R. Almeida, J. Moreira, D. Pereira, S. Pereira, J. Antunes, A. Palmeira, V. Vasconcelos, M. Pinto, M. Correia-da-Silva, H. Cidade (2018) *Science of The Total Environment*, 643, 98-106.
[3] D. Pereira, C. Gonçalves, B.T. Martins, A. Palmeira, V. Vasconcelos, M. Pinto, J.R. Almeida, M. Correia-da-Silva, H. Cidade (2021) *Marine Drugs*, 19, 5.
[4] C. Vilas-Boas, L. Running, D. Pereira, H. Cidade, M. Correia-da-Silva, G.E. Atilla-Gokcumen, D.S. Aga (2022) *Molecules*, 27, 5247.

Water pollution threats in Important Bird and Biodiversity Areas

M. Dulsat-Masvidal[1,*], C. Ciudad[2], O. Infante[2], R. Mateo[3], S. Lacorte[1]

(1) IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain, (2) SEO/BirdLife, Melquiades Biencinto, 34, 28053 Madrid, Spain, (3) IREC- CSIC-UCLM-JCCM, 13005 Ciudad Real, Spain
*mariadulsat@gmail.com



It has long been recognized that surface waters are a common endpoint for organic micropollutants (OMP) released from anthropogenic activities, including wastewater treatment plants (WWTP) discharges, urban runoff, and agricultural practices. In recent years, several studies have shown how emerging contaminants, such as pharmaceuticals, polar pesticides, organophosphate esters (OPEs), perfluoroalkyl substances (PFAS), and other chemicals, occur in rivers and estuaries with urban pressures. However, there is still scarce information about the presence and distribution of OMP in natural areas and their potential risk that those chemicals can represent for biodiversity conservation, especially regarding the assessment of complex chemical mixtures which raise concern from a toxicological point of view **[1]**. Therefore, water pollution is an important risk factor for the management of key biodiversity areas. In this study, we established a monitoring scheme to determine the presence and distribution of widely used pharmaceuticals, pesticides, organophosphate esters (OPEs) and perfluoroalkyl substances (PFAS) in water bodies from Important Bird and Biodiversity Areas (IBAs) from Spain. The monitoring scheme included georeferenced sampling of rocky mountain, Atlantic Forest, riparian forest, Mediterranean forest, agricultural, inland aquatic and coastal aquatic IBAs, with the aim to evaluate the impact of widely used chemicals on these aquatic resources. Water samples were extracted using a generic solid-phase extraction protocol and analysed by three analytical methods based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

Organic micropollutants have been found to be widespread in natural freshwater ecosystems key for biodiversity conservation. Lifestyle compounds, pharmaceuticals, and OPEs were the most ubiquitous chemical families. Pesticides and PFAS showed detection frequencies below 25%. Agricultural land use has been identified as the most important source of OMP to surface waters. WWTP discharges have been identified as important sources of pharmaceuticals, lifestyle compounds, and PFAS in surface waters, and the influence of artificial areas has been identified to contribute to the release of lifestyle compounds and PFAS. This is the first study to quantify water pollution as a threat to the IBAs. Our results demonstrate the importance of considering land use and pollution sources inside and outside the boundaries of IBAs, as the results indicate a strong influence of land use around surface waters to explain the distribution of pollutants.

Acknowledgements

The Spanish Ministry of Science and Innovation is acknowledged for financial support [PID2019-105732GBC21] from CIN/AEI/10.13039/501100011033 and for the Severo Ochoa project Grant CEX2018-000794-S funded by MCIN/AEI/ 10.13039/501100011033 to IDAEA-CSIC as Centre of Excellence.

References

[1] Altenburger, R., Backhaus, T., Boedeker, W., Faust, M., Scholze, M., (2013). *Environ. Toxicol. Chem.* 32, 1685–1687.

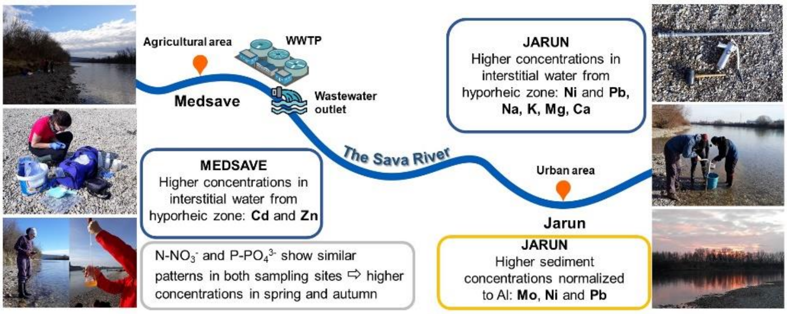
ORAL
(#2)

Environmental Quality of the Hyporheic Zone of the Sava River Under Anthropogenic Influence

M. Erk[1,], Z. Redžović[1], S. Gottstein[2], M. Sertić Perić[2], M. Cindrić[1]*

(1) Ruđer Bošković Institute, Bijenička c. 54, Zagreb, Croatia, (2) University of Zagreb, Faculty of Science, Department of Biology, Rooseveltov trg 6, Zagreb, Croatia

[*]erk@irb.hr



The hyporheic zone (HZ) belongs to the groundwater connected ecosystems and as a key component of fluvial ecosystems, it plays a crucial role in ecohydrology, biogeochemical cycling, nutrient turnover, retention and biotransformation of trace organic compounds, remineralisation of organic matter, retention of fine particulate matter and pollutant attenuation [1, 2].

The aim of this study was to assess anthropogenic impact on the environmental quality of the HZ of the Sava River by measuring basic physico-chemical parameters, nutrients, organic carbon and metal contaminants in the interstitial water and sediment at two gravel bar locations (Medsave and Jarun) during four seasons (winter 2018, spring, summer and autumn 2019). Medsave is located 3 km upstream from the wastewater discharge of the town of Zaprešić as a point source of contamination, and Jarun 13 km downstream from it.

Physico-chemical parameters, including concentrations of nutrients and organic carbon were affected by wastewater discharge, but also by hydrometeorological conditions, such as water level and river discharge. In summer and autumn, at both sampling sites lower average water level (-249 cm) and discharge (122 m^3/s) were recorded, compared to spring and winter (-214 cm; 179 m^3/s). Nitrates were higher in spring and autumn at both sampling sites, which can be linked to higher atmospheric precipitation and leaching from agricultural lands. At the Jarun site, phosphate levels in interstitial water in the spring, summer, and autumn indicated less than good water quality status according to the water quality standards for the respective river type HR-R_5b [3]. The observed increased concentrations of dissolved organic carbon in water and total organic carbon in sediment at Medsave may be related to the intensive use of agricultural fertilizers. The concentrations of macro elements (Na, K, Mg and Ca) in interstitial water from the HZ were higher at the Jarun sampling site than at Medsave. Their enrichment in the HZ compared to the surface water was observed at Jarun. In the interstitial water from the HZ, the concentrations of common environmental contaminants Ni and Pb were higher at the Jarun sampling site, while Cd and Zn were higher at Medsave. Higher concentrations of Ni and Pb were observed in interstitial water than in river water. Sediment concentrations of Mo, Ni and Pb normalized to Al showed slightly higher values at Jarun. However, the concentrations of ecotoxic elements were below the environmental quality standards set for surface freshwaters [3].

In conclusion, the environmental quality of the HZ of the Sava River was slightly affected by anthropogenic influences, although it was not yet severely disturbed. Therefore, monitoring of basic parameters and contaminant concentrations in the HZ is recommended.

Acknowledgements

This research was supported by ERDF Qua/Qua Protein project, grant no. KK.01.1.1.07.0023 and the Croatian Science Foundation AQUAMAPMET project no. IP-2014-09-4255. We thank to Mr. Ivica Barač for his great help in the field work and Dr.Sc. Zrinka Dragun for ICP-MS analyses.

References

[1] F. Boano, J.W. Harvey, A. Marion, A.I. Packman, R. Revelli, L. Ridolfi, A. Wörman (2014) *Reviews of Geophysics*, 52, 603–679.

[2] B.M. Mueller, H. Schulz, J. Lewandowski (2022) *Encyclopedia of Inland Waters*, 2, 301–311.

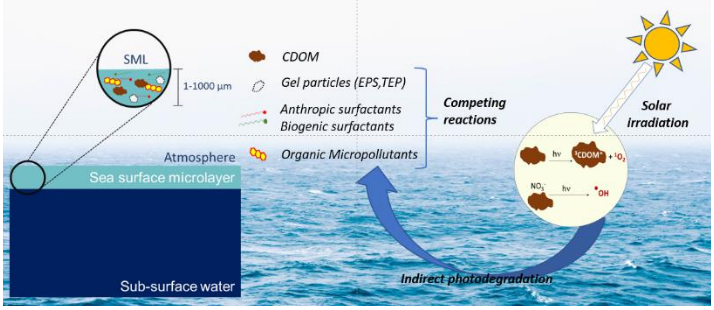
[3] Government of the Republic of Croatia (2019) *Official Gazette*, No. 96, Zagreb.

ORAL
(#2)

Photochemical Fate of Organic Micropollutants in the Sea Surface Microlayer

C. Abdel Nour[1,*], S. Rossignol[1], P. Wong-Wah-Chung[1]

(1) Aix-Marseille Université, CNRS, LCE, Europôle de l'Arbois, BP 80, 13545 Aix-en-Provence, FRANCE
*carole.abdel-nour@univ-amu.fr



The photochemical processes in the environmental aquatic compartments have been intensively studied during the last few decades because of the occurrence of many organic pollutants in these water bodies. The sea surface microlayer (SML), that includes the air-water interface as well as the few hundreds of micrometers below, is a very particular photoreactor due to both significant enrichment in organic material, mainly biogenic one notably deriving from marine biota (polysaccharides, biogenic amphiphilic compounds …), and its constant interaction with the atmosphere [1,2]. The SML is also known to accumulate numerous organic contaminants but is for now almost ignored when talking about their reactive fate in marine waters.

In this work, we characterize the photochemical fate of two marine organic micropollutants, carbamazepine and phenanthrene in the SML: The main objective being the study of the effect of the SML's enrichment in organic matter on the photodegradation kinetics of these two organic micropollutants against $HO^{\cdot}$ radical attack. The approach consisted in simplifying the complexity of the SML matrix using model surfactants to test the effect of the polarity of micropollutants on their trapping in surfactants micelles, and beyond their protection against radical attack [3].

To achieve this, an irradiation system equipped with a 300 W Xenon lamp allows the accelerated and controlled irradiation of a photochemical reactor in which the conditions encountered in SML are recreated, using commercially available surfactant proxies: sodium dodecyl sulfate (SDS) and rhamnolipids (RL) at concentrations below and after their critical micelle concentrations (CMC).

The main results show the ability of the SML proxies to slow down the photoinduced degradation of model pollutants via competing reactions or quenching of reactive species. In a more detailed approach, the apparent kinetic rate constants of $HO^{\cdot}$ radicals and model pollutants were determined using the relative kinetic method at different surfactant concentration, before and after their CMC. When concentrations higher than the CMC are added, $k_{app(pollutant,HO^{\cdot})}$ significantly decreases; which indicates that, depending on the polarity of the pollutant, it is less accessible for $HO^{\cdot}$ radical attack when it's protected in the micelles of surfactants [3].

In the SML, the photochemical fate of organic micropollutants is therefore influenced by their trapping in micelles or in monolayers of surfactants at the sea-atmosphere interface; This can lead to potentially increase their lifetime compared to those known in diluted bulk waters and contribute to their accumulation in the natural environment.

Acknowledgements

Funding of this work was provided by the Agence Nationale de la Recherche ANR through the project PhotoSeaSMiL.

References

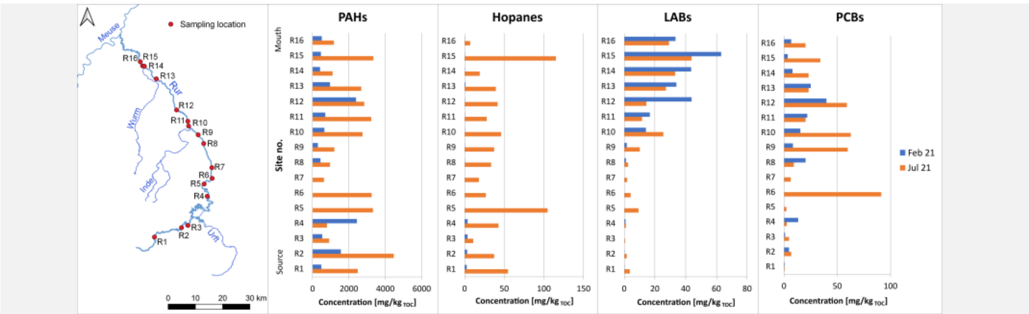
[1] O. Wurl *et al.* (2017) *Elementa: Science of the Anthropocene*, 5, 31.
[2] A. Engel *et al.* (2017) *Front. Mar. Sci.*, 4, 165.
[3] B. Samiey *et al.* (2014) *Journal of Chemistry*, 2014, 1–14.

ORAL
(#2)

Distribution and Remobilization of Organic Pollutants by Floods – the Case Study Rur River, Germany

C.A. Schwanen[1,*], J. Müller[1], J. Schwarzbauer[1]

(1) Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstrasse 4-20, 52056 Aachen, Germany
[*]christina.schwanen@emr.rwth-aachen.de



Extreme precipitation and subsequent runoff can cause severe flooding with damages to natural habitats like floodplains, as well as infrastructure, including populated, agricultural, or industrial areas [1]. In connection with extreme flood events, the release and input of a variety of organic pollutants into river systems occurs. This also includes the remobilization and displacement of old burdens, e.g., from the industrial or mining sector.

In general, the Rur catchment area covers various land uses such as urban settlement, numerous industrial applications (especially from the paper industry), agriculture, and historical underground mining as well as current lignite mining [2]. Nevertheless, there are also several natural river sections and floodplains throughout the Rur's course, which have been sampled immediately after two different flood events in February and July 2021.

The main objectives were to determine pollutant concentrations, distribution, and accumulation in comparison between flood events of different dimensions and dynamics. Furthermore, possible remobilization processes and emission sources were identified. In addition, the relevance of floodplains for sediment and pollutant retention was evaluated.

GC-MS based non target screenings revealed the presence of different organic substances such as polycyclic aromatic hydrocarbons (PAHs), hopanes, polychlorinated biphenyls (PCBs), linear alkylbenzenes (LABs) and different industrial compounds (e.g., di-*iso*-propylnaphthalenes). They are indicative of petrogenic, urban (wastewater), industrial, or mining pollution (current and historical).

An acute enrichment of organic pollutants was detected mainly for the extreme flood event in July (concentrations up to mg/g_{TOC}). This points to additional emission sources in summer compared to the smaller flood event in February. Generally, the substantially higher discharges in July led to more severe flooding and associated damage to the Rur river itself and its tributaries. Accordingly, these tributaries then also had a much greater influence on the input and hence concentrations of organic pollutants at the Rur.

Furthermore, the dispersion and concentrations of LABs are remarkable. Unlike for most of the other organic pollutants, the LAB contamination was similar in both events and thus independent of the flood dynamics. Since LABs are an anthropogenic indicator of pollution from wastewater, special attention should be given to their introduction during flood events of any dimension.

Overall, specific distribution patterns were identified in this study, e.g., for LABs or regarding the influence of tributaries or other structural features such as dams or renaturalized areas. These findings and the knowledge about the behavior and fate of specific organic pollutants during and after (extreme) flood events are of great importance for the assessment of short- and long-term environmental risks and hazards.

Acknowledgements

Special thanks to the RWTH Scholarships for Doctoral Students.

References

[1] S. Crawford., M Brinkmann., et al. (2022) *Journal of Hazardous Materials*, 421, 126691.
[2] C. Schwanen, J. Schwarzbauer (2022) *Water, Air, & Soil Pollution*, 233, 33.

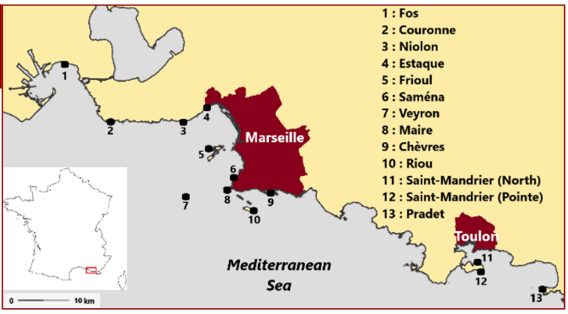
ORAL
(#2)

Monitoring of the Occurrence and Patterns of Regulated Persistent Organic Pollutants and Emerging Flame Retardants in the Eastern French Mediterranean Coastline

C. Rigal[1,], N. Sarkis[2], V. Fauvelle[3], L. Asia[1], P. Doumenq[1], P. Mirleau[2], L. Malleret[1]*
(1) Laboratoire Chimie Environnement, Aix Marseille Univ, CNRS, Europole de l'Arbois, Aix-en-Provence, France, (2) IMBE – Aix Marseille Univ, Avignon Université, CNRS, IRD, Marseille, France, (3) MIO – Aix Marseille Univ, CNRS, IRD, Marseille, France
[*]camille.rigal@univ-amu.fr

13 coastal stations
Suspended matter and Sediments

Regulated pollutants	Emerging flame retardants
16 HAPs *7 PCBs* *8 PBDEs* *Short-chain chlorinated paraffins*	*23 new brominated flame retardants* *16 organo-phosphate esters* *Medium-chain chlorinated paraffins*



Global pollution represents a threat to environmental and human health. Aquatic ecosystems are burdened by emission and discharge of xenobiotic contaminants, especially in densely populated and industrialized areas, such as Marseille, the second biggest city in France which houses harbour, industrial, recreational and domestic activities along the coastline. On the one hand, the international regulatory frameworks of the 2000s aim at limiting pollutants release to preserve natural resources. Several contaminants have thus been classified as persistent organic pollutants by the Stockholm Convention (2001) and candidates are regularly reviewed. Forty-five compounds or group of molecules were listed as priority substances according to the European Water Framework Directive [1]. Some of them, hardly degradable, will remain in the environment many years after their bans or limitations. They are of major concern since they are bioaccumulative and present toxic activities, such as endocrine disruptive or genotoxic/carcinogenic effects [2]. On the other hand, the ban on the use of some substances led to the synthesis and production of an ever-increasing number of emerging chemicals that cannot be regulated for now because of their unknown environmental impacts and fate, such as brominated, chlorinated and organophosphate plasticizers and flame retardants [3].

The aim of this study was to assess the impact induced by regulations and replacement with new chemicals on the quality state of the Mediterranean coastline. Sediments, acting as a sink for long-term pollution, and suspended matter, revealing more recent and localized inputs, were sampled. The thirteen coastal sampling stations included the industrial/port area of Fos, the Blue Coast, Marseille harbour and creeks. Samples were screened for regulated substances, i.e., 16 Poly Aromatic Hydrocarbons, 7 Poly Chloro Biphenyls, 8 Poly Bromo Diphenyl Ethers and Short-Chain Chlorinated Paraffins, and emerging contaminants, i.e., 23 new Brominated Flame Retardants, Medium-Chain Chlorinated Paraffins and 16 Organo-Phosphate Esters. Patterns and levels of contamination were compared between the 13 stations. Univariate and multivariate analyses were applied to identify correlations between geographical situation and contamination patterns. Levels and patterns of pollution were also compared with biological metrics determined in P. oceanica meadows and epiphytic assemblages. To our knowledge, this is the first screening of these emerging flame retardants on the French Mediterranean coast.

Acknowledgements

This work received support from the French government under the France 2030 investment plan, as part of the Initiative d'Excellence d'Aix-Marseille Université - A*MIDEX (AMX-19-IET-012). It was also funded by the LabEx DRIIHM, French Programme "Investissements d'Avenir" (ANR-11-LABX-0010) which is managed by the French ANR, under the Human-Environment Observatory "Mediterranean coast" and Rhône river (OHM Littoral Méditerranéen and Vallée du Rhône).

References

[1] Directive 2013/39/EU. JOUE n°L 226 du 24 août 2013.
[2] M. Iqbal, J. H. Syed, A. Katsoyiannis, …, K. C. Jones (2017) *Environmental Research*, 152, 26-42.
[3] Å. Bergman, A. Rydén, R.J. Law, …, I. Van der Veen (2012) *Environment International*, 49, 57-82.

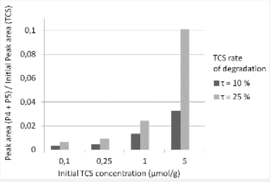
ORAL
(#2)

Photodegradation of Triclosan on the Kaolinite Surface: Aqueous Phase Photodegradation and Molecular Modelling of the Clay Surface Interactions

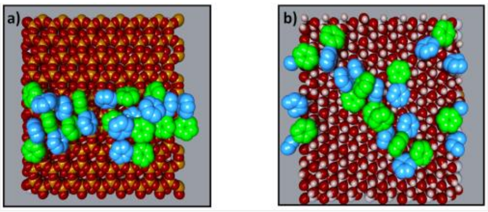
*C. Le Fur, F. Goujon, P. Wong Wah Chung, P. Malfreyt, M. Sarakha**

(1) Institut de Chimie de Clermont-Ferrand, Université Clermont Auvergne, UMR CNRS 6296, 24 avenue Blaise Pascal, 63178 Aubière Cedex, France

**mohamed.sarakha@uca.fr*



Evolution of the ratio (Peak area of dimers / Initial peak area of TCS) with the initial concentration of TCS for fixed degradation rates of TCS.



Snapshots of typical equilibrated configurations of a 12 TCS molecules deposited on the siloxane-like surface (a) and the gibbsite-like surface (b) of kaolinite.

Chemicals such as pesticides can be introduced into the environment as a result of their application for plant protection. Thus, the contamination of groundwater, rivers, soils, and also atmosphere is an inevitable effect of their application. The negative ecological consequences related to these contaminants are often assigned to their residence time and bioavailability. Owing to these environmental effects, there is an increase of the research activities toward the methods which could help in the study of the fate and also the elimination of such substrates. In recent years, various methods for water or air purification as well as soil decontamination have been developed including chemical, electrochemical, or photochemical processes. In several cases, sunlight degradation may represent one of the main destructive pathways for pesticides. Since several kinds of these contaminants present absorption spectra with a non-negligible overlap with that of solar light, an inexhaustible source, the photochemical process becomes of great interest. Thus, they can easily undergo photochemical transformation upon exposure to the solar light by direct absorption. This also leads to the formation of various by-products that can be more harmful than the parent compound. In the case where the contaminants do not absorb solar light, they may still undergo phototransformation through indirect reactions.

These processes photochemical processes may occur in aqueous solutions, in the atmosphere and at the surface of soils. The latter medium can be considered as an ultimate reservoir for pesticides whether they are applied directly or received indirectly from spray drift and residues of treated sites. Since soil support is a highly heterogeneous and unmixed medium compared with solution, it is obvious that several photophysical and/or photochemical processes as well as spectroscopic features will then be affected.

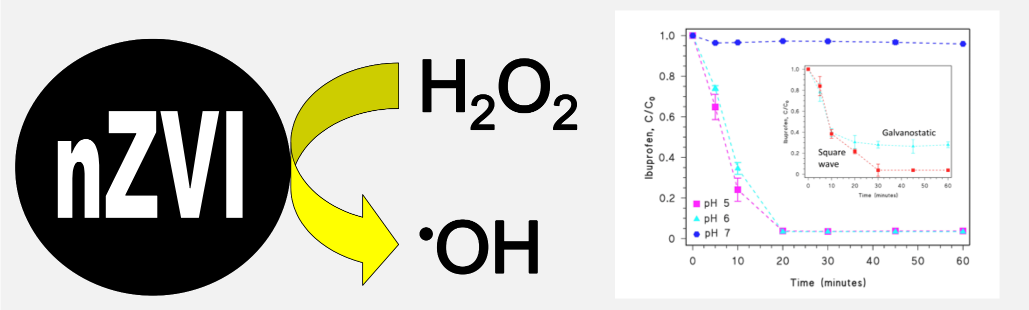
In the present work, the photodegradation of triclosan was investigated at the surface of kaolinite surface. The quantum yield was evaluated and the photoproducts identified showing that the photodegradation is completely different from that obtained in aqueous solution. The formation of dioxin derivatives, in particular, was shown to occur with a higher quantum efficiency when compared to aqueous solution. This suggests that TCS has an interaction with the clay that modifies its photoreactivity. Moreover, it has also been shown that at concentration >1 µmol/L, an increase in the TCS concentration in the kaolinite plate significantly decreases the photodegradation rate constant and promotes the formation of dimer-type photoproducts. This suggests that the distribution of Triclosan is clearly not homogeneous at the clay surface, and the formation of aggregates is more likely occurring. In order to get a better insight into this specific interaction, a molecular dynamic modelling of TCS adsorption on the surface of kaolinite was carried out. This clearly shows that, at equilibrium, TCS binds to kaolinite surface by hydrogen bonds involving the phenol function of TCS to the hydroxyl groups of the kaolinite surface. Such behaviour confers a particular conformation to the adsorbed TCS that is different from that obtained in water, and which may partly explain the difference in the photochemical reactivity. In addition, several TCS molecules appear to interact with each other through π-stacking phenomenon while retaining this hydrogen bond with the kaolinite surface. This leads to clusters formation on the clay surface.

ORAL
(#2)

Fenton and Fenton-like Processes for the Removal of Emerging and Recalcitrant Contaminants from Wastewater

D. Vione, M. Minella, F. Sordello*

Department of Chemistry, University of Torino, Via Pietro Giuria 5, 10125 Torino, Italy
**davide.vione@unito.it*



The classic Fenton process involves reaction between Fe^{2+} and H_2O_2, to yield the hydroxyl radical, $^{\bullet}OH$. The reaction is actually thought to produce other oxidising species alongside $^{\bullet}OH$, such as ferryl (FeO^{2+}), which is a less powerful oxidant than the hydroxyl radical, and is preferentially formed at ~neutral pH, or in the presence of organic ligands [1]:

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^{\bullet}OH$$
$$\text{(or)} \rightarrow FeO^{2+} + H_2O$$

Several alternatives to classic Fenton have been proposed over time, which entail replacement of one or both of the Fenton reagents. Fe(II) salts can be replaced by Fe-organic complexes, such as the Collin's reagent, or with Fe-containing solids, such as magnetite, titanomagnetites, or metallic Fe. In particular, nanometric zero-valent iron (nZVI) has shown excellent stability and Fenton performance, also at pH 5-6 where classic Fenton usually under-performs, compared to its optimum pH value (3-3.5) [1]. Alternatives to H_2O_2 have also been investigated, including for instance persulfate, sulfite, and metabisulfite. In these cases, different reactive species are produced (*e.g.*, $SO_4^{\bullet-}$ instead of $^{\bullet}OH$), which are more selective, although usually less reactive than the hydroxyl radical [2].

In the framework of nZVI-Fenton (nZVI + H_2O_2), we have shown that both reagents can produce and scavenge $^{\bullet}OH$. Therefore, an excess of either nZVI or H_2O_2 is detrimental to water treatment. Effective pollutant elimination may thus require addition of nZVI and/or H_2O_2 in multiple aliquots during the reaction, to avoid the occurrence of excessive loading/concentration values at any time point, which would produce unwanted scavenging of reactive species. For instance, effective nZVI-Fenton elimination of pharmaceuticals (*e.g.*, ibuprofen [3]), including antibiotics (cefazolin, imipenem, and vancomycin [4]) from urban wastewater at pH 5-6 requires multiple additions of both ZVI and H_2O_2.

In the case of H_2O_2, we have found that an interesting alternative to multiple additions is continuous electrochemical generation upon reduction of O_2 in air, bubbled in the electrochemical reactor. The optimal H_2O_2/nZVI ratio is obtained by regulating cathodic potential, as well as its form (galvanostatic *vs.* square-wave).

Interestingly, in addition to removing pollutants, nZVI-Fenton is also able to inactivate pathogenic bacteria that typically occur in urban wastewater, by a combination of acidic pH, occurrence of H_2O_2, and of traces of dissolved iron.

Acknowledgements

DV acknowledges financial support from Compagnia di San Paolo (project ABATEPHARM).

References

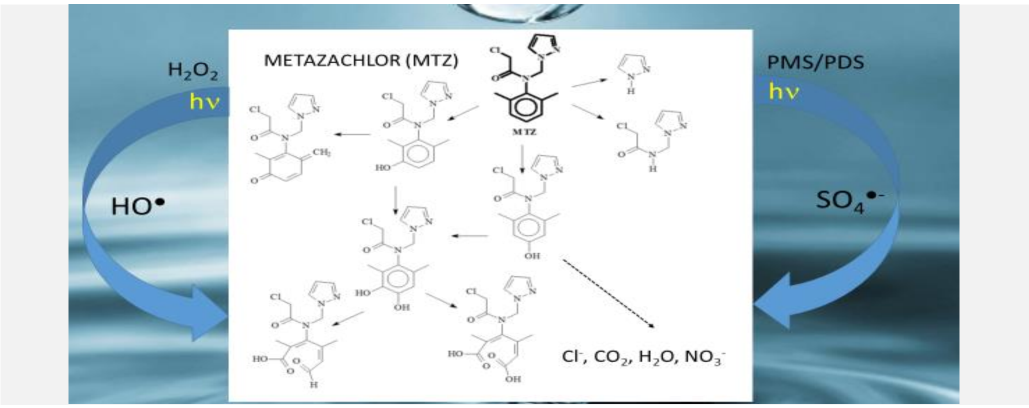
[1] M.H. Zhang, H. Dong, L. Zhao, D.X. Wang, D. Meng D (2019) *Science of the Total Environment*, 670, 110-121.
[2] E. Domingues, M.J. Silva, T. Vaz, J. Gomes, R.C. Martins (2022) *Science of the Total Environment*, 832, 155029.
[3] F. Furia, M. Minella, F. Gosetti, F. Turci, R. Sabatino, A. Di Cesare, G. Corno, D. Vione (2021) *Chemosphere*, 283, 131170.
[4] M. Minella, S. Bertinetti, K. Hanna, C. Minero, D. Vione (2019) *Environmental Research*, 179, 108750.

Reactivity and Photodegradation Mechanism of Metazachlor in Aqueous Phase: Determination of the Rate Constants and Identification of the Main Photoproducts

M. Mailhot[1], M. Sarakha[1], M. Brigante[1], F. Louis[2], G. Mailhot[1,]*

(1) Institut de Chimie de Clermont-Ferrand, Université Clermont Auvergne, UMR CNRS 6296, 24 avenue Blaise Pascal, 63178 Aubière Cedex, France, (2) Univ. Lille, CNRS, UMR 8522, Physico-Chimie des Processus de Combustion et de l'Atmosphère – PC2A, F-59000 Lille, France

[*] gilles.mailhot@uca.fr



With the growth of the agri-food industry, the use of pesticides has become increasingly important in agricultural practices in recent decades. As a result, pesticide pollution of surface and groundwater is now a global environmental issue. Metazachlor (MTZ), belonging to the group of organochlorine pesticides, is a common pre-emergence herbicide based on chloroacetamide. It is frequently used to control grasses and certain weeds in oilseed rape, soybeans, potatoes and other crops.

MTZ is one of the pollutants whose concentrations exceeded the quality limit more than 10 times in 2014 and 2015 in water intended for human consumption in France and other countries [1]. In general, pesticides and their residues can leach from the surface of soils or plants and end up in surface water. They can also migrate from agricultural soils to deeper soils or to groundwater, where they can remain for a long time because of their non-degradable properties. Therefore, these chemical compounds will be able to cause various serious problems, even at very low doses. Due to its properties and thus its toxicity, metazachlor, like many other pesticides, belongs to the large group of endocrine disruptors. Even though many of these compounds pass through wastewater treatment plants, which are not really designed to remove these contaminants, they will not be degraded and therefore many of them reach surface waters unchanged.

To address this issue, many groups around the world are working on advanced oxidation processes [2]. These processes are based on the generation of oxidising radicals, mainly hydroxyl radicals and sulphate radicals. These radicals demonstrated a real efficiency for the degradation of micro-pollutants [3].

In this work we focused our efforts on the determination of the rate constants of these radicals on MTZ. The constants with hydroxyl and sulphate radicals have determined for the first time. But our work was also especially focused on MTZ degradation and the identification of the by-products to establish a reaction scheme during its transformation in different kind of AOPs. This part is important to control the toxicity of the solution during the processes.

Acknowledgements

This work was supported by the "Federation des Recherches en Environnement" through the CPER "Environnement" founded by the "Région Auvergne," the French Government and FEDER from European community.

References

[1] P. Karier, G. Kraus, I. Kolber (2017) *Environmental Sciences Europe,* 29:25, 1-8.

[2] C. Dong, W. Fang, Q. Yi, J. Zhang (2022) *Chemosphere,* 308, 136205.

[3] D. Kanakaraju, B. D. Glass, M. Oelgemöller (2018) *Journal of Environmental Management*, 219, 189-207.

[4] X. Wang, W. Dong, M. Brigante, G. Mailhot (2019) *Applied Catalysis B: Environmental,* 245, 271-278.

HPLC-HRMS Determination in Water Environment of Anticancer Drugs Subjected to Heterogenous Photocatalysis Mediated by Semi-Conductor

F. Dal Bello[1,], P. Calza[2], C. Medana[1]*

(1) University of Turin, Dep. of Molecular Biotechnology and Health Sciences, Via P. Giuria 5, Turin, Italy (2) University of Turin, Dep. of Chemistry, Via P. Giuria 5, Turin, Italy

**federica.dalbello@unito.it*

Anticancer drugs are considered pseudo-persistent pollutants for the water environmental compartments due to their continuous emission in water bodies (lakes, rivers and reservoirs). Many sources contribute to the bioaccumulation of the drugs, from human activities to hospital waste, and a profound investigation of their residues and of their transformation products (TPs) fate is mandatory now more than even.

Here we present a HPLC-HRMS method developed to identify, characterized and semi-quantify the TPs of three anticancer drugs subjected to heterogenous photocatalysis mediated by titanium dioxide. The considered drugs were cyclophosphamide (CYC), an alkylating agent, 5-fluorouracil (5FU), an antimetabolites and nucleoside analogous, and oxaliplatin (OXA) an organometallic complex.

Heterogenous photocatalysis mediated by TiO_2 is frequently employed to simulate oxidation, or others chemical transformations, of a molecule [1,2]. After photodegradation and oxidative/reductive processes [3], more polar molecules were formed, and HPLC-(HR)MS analysis is the most suitable technique to detect them.

The irradiation experiments were performed using a Philips (Monza, Italy) TLK/05 lamp (40 W/m^2) with maximum emission at 340 nm at different time points (0-5-15-30-60-240 minutes for CYC and OXA, and 0-1-3-5-7-10-15 minutes for 5FU). HPLC separation of the antineoplastic drugs and of the TPs was achieved using a Phenomenex Sinergy RP-18 150×2 mm, 4 µm. Two chromatogram gradient ramps were developed: the first using 0.05% aqueous formic acid and methanol for positive ESI ionization mode and the other using ammonium acetate 0.1 mM and methanol for negative ESI ionization mode. A high resolution mass analyser LTQ orbitrap was used with a resolution of 30k in a full mass range between 50 and 700 *m/z*. Tandem MS events of antineoplastic drugs and TPs were acquired in CID activation type with different collision energy depending on the molecules, with a resolution of 30K.

With the developed HPLC-HRMS method we recognized and tentatively assigned the structures of 7 TPs for CYC, 5 TPs for 5FU and 1 TPs for OXA.

Finally, the developed analytical method was successfully applied to real environmental water samples coming from nine sampling sited of Po River. The water samples were pre-treated with a Solid Phase Extraction procedure to concentrate the amount of the analytes and then analysed. We found the presence of CYC in four site points at level of ppb.

References

[1] O. Porcar-Santos, A. Cruz-Alcalde, N. López-Vinent, D. Zanganas, C. Sans (2020) *Science of the Total Environment*, 736, 139605

[2] F. Dal Bello, E. Mecarelli, R. Aigotti, E. Davoli, P. Calza, C. Medana (2022) *Journal of Environmental Management*, 308, 114573.

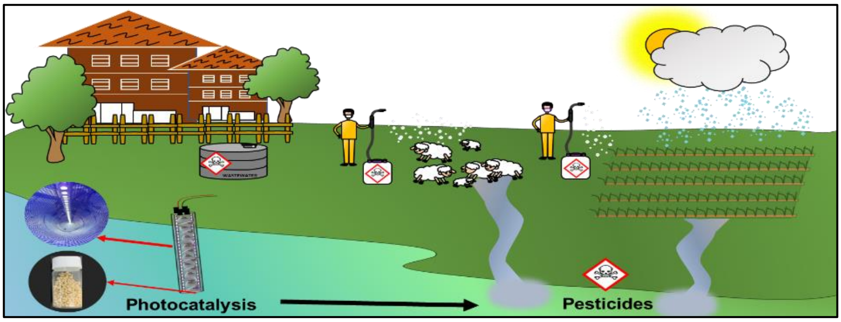
[3] M. Zhu, L. Ma, D. Zhang, K. Ray, W. Zhao, W.G. Humphreys, G. Skiles, M. Sanders, H. Zhang (2006) *Drug metabolism and disposition: the biological fate of chemicals*, 34(10), 1722–1733.

ORAL
(#2)

Photocatalytic Removal of Nine Pesticides by Graphitic Carbon Nitride Coated Recycled Glass Beads and Economical UV-A 365 nm LEDs

I. Menezes[1,*], *C.J. Pestana*[1], *B. Petrie*[1], *C. Edwards*[1], *L.A. Lawton*[1]

(1) Robert Gordon University, Garthdee Road, AB10 7GJ, Aberdeen, United Kingdom
[*]*i.de-menezes-castro@rgu.ac.uk*



Although pesticide use is necessary to increase food production and to promote agricultural efficiency, it has led to contamination of the environment due to stability, mobility and long-term effects of pesticides on other organisms [1,2]. Conventional water treatment can be ineffective for the removal of dissolved pesticides [3], therefore, it is necessary to evaluate complementary technologies that can be applied *in-situ* to remove these contaminants prior to the treatment plant or before discharge into the environment. Photocatalysis is an advanced oxidation process that can be used for the removal of pesticides, however, the removal of the powdered catalyst following the treatment and the high costs associated with the implementation of high energy-UV illumination represent challenges for *in-situ* application of photocatalysis [4,5].

In the current study, porous recycled glass beads were used as an immobilization matrix for coating with graphitic carbon nitride (g-C_3N_4) or titanium dioxide (TiO_2). The catalysts were activated using visible light or UV-A 365 nm in the format of economical light emitting diodes (LEDs). The treatment efficiency of the systems was tested for the photocatalytic removal of microcystin-LR (MC-LR), which is a cyanotoxin that was used as a model compound. The most efficient system tested was g-C_3N_4 coated beads illuminated by UV-A LEDs (100% degradation over 60 minutes), followed by g-C_3N_4/TiO_2 co-coated beads illuminated by UV-A LEDs (93% degradation over 180 minutes), TiO_2 coated beads illuminated by UV-A LEDs (87% degradation over 180 minutes) and g-C_3N_4 coated beads illuminated by visible light LEDs with main peak at 420 nm (no degradation over 180 minutes).

UV-A 365 nm LEDs and g-C_3N_4 coated beads were tested on the photocatalytic removal of nine individual pesticides (5 mg L^{-1} in artificial fresh water; acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam, diuron, atrazine, dimethoate and 2,4-dichlorophenoxyacetic acid). Pesticide concentration was determined by high-performance liquid chromatography coupled to photo diode array detector (HPLC-PDA). Most pesticides were completely removed within 24 hours of treatment (e.g., diuron with rate constant k=0.0041 min^{-1} and 2,4-dichlorophenoxyacetic acid k=0.0053 min^{-1}), however, other pesticides presented slower degradation rate (e.g., acetamiprid with rate constant k=0.0004 min^{-1}). Photocatalysis based on g-C_3N_4 coated beads illuminated by UV-A 365 nm LED irradiation was demonstrated to be a potential approach in the removal of pesticides from aquatic environments.

Acknowledgements

The authors would like to thank the Scottish Government's Hydro Nation Scholar Programme (I. Menezes) for funding this research.

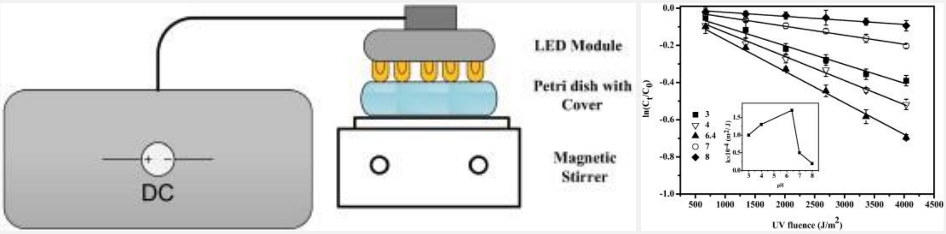
References

[1] F.P. de Albuquerque, J.L. de Oliveira, V. Mischini-Carlos, L.F. Fraceto (2020) *Science of The Total Environment*, 700, 134868.
[2] M. Nasiri, H. Ahmadzadeh, A. Amiri (2020), *TrAC - Trends in Analytical Chemistry*, 123, 115772.
[3] R.M. de Souza, D. Seibert, H.B. Quesada, F.J. Bassetti, M.R. Fagundes-Klen, R. Bergamasco (2020) *Process Safety and Environmental Protection*, 135, 22-37.
[4] C.J. Pestana, C. Edwards, R. Prabhu, P.K.J. Robertson, L.A. Lawton (2015) *Journal of Hazardous Materials*, 300, 347-353.
[5] S. Chae, T. Noeiaghaei, Y. Oh, I.S. Kim, J. Park (2019) *Water Research*, 149, 42-431.

ORAL
(#2)

Synergistic Action of UV Irradiation and Hydroxyl Radicals: Removal of Emerging Contaminant from Water

P. Kumar[1,*], *S. Verma*[2], *U. Lavrenčič Štangar*[1]
(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia
(2) School of Energy & Environment, Thapar Institute of Engineering & Technology, Patiala-147004, Punjab, India
**Praveen.Kumar@fkkt.uni-lj.si*



Cyanobacteria or blue-green algae are the prokaryotic photoautrophic organisms. 40 of the 150 genera of cyanobacteria produce toxic secondary metabolites. These toxic groups of secondary metabolites are known as cyanotoxins. Cyanotoxins can be divided into three groups based on their chemical structure: cyclic peptides (hepatotoxins), Lipopolysaccharides (LPS), and alkaloids (neurotoxins). The different types of neurotoxins produced by cyanobacteria are: Homoanatoxin-a, Anatoxin-a, Saxitoxins and Anatoxin-a(s) **[1,2]**.

Anatoxin-a is a bicyclic secondary amine 2-acetyl-9-azabycyclo[4,2,1]non-2-ene and synthesized by several strains of cyanobacteria, i.e., Cylindrospermum, Aphanizomenon, Anabaena flos-aquae, Planktothrix, Microcystis and Oscillatoria. The toxicity of anatoxin-a is described by the LD50 value, which is 200-250 µg/kg. Anatoxin-a exerts its toxicity to living organisms by binding to acetylcholine receptors without being degraded by acetylcholine sterase or any other enzyme. As a result, anatoxin-a is able to overstimulate muscles, leading to death when respiratory muscles are affected **[3]**.

In the present study, the UV-C LED/H_2O_2 and UV-C LED photolysis treatment processes were investigated for the degradation of anatoxin-a. The initial anatoxin-a concentration in the aqueous solution was maintained at 1µM. During treatment with UV-C alone, 50% degradation of anatoxin-a was achieved at a UV fluence of 4032 J/m^2. The optimal reaction conditions were: Initial pH = 6.4, λ = 260 nm, temperature = 24 °C, and distance from the water surface = 5 mm. The degradation of anatoxin-a followed first-order pseudokinetics. The degradation of anatoxin-a was reduced to 28% in the presence of carbonate ions (50 mg/L), and at higher concentrations of carbonate ions, the degradation was completely inhibited. The concentration of anatoxin-a was significantly lowered in the presence of dissolved organic matter (DOC), showing the photosensitizing effect of humic acid on the direct photolysis of anatoxin-a. It was also observed that the UV-C/H_2O_2 process increased the oxidation rate of anatoxin-a by 4.5 times compared to direct photolysis by UV-C LED, resulting in 97% degradation of anatoxin-a. In the lake water, anatoxin-a was 96% removed by photolysis with UV-C radiation alone and 79% by the UV-C/H_2O_2 process. The results showed a decrease in acute toxicity of the treated samples, both after UV-C LED photolysis and after the UV-C/H_2O_2 process.

Acknowledgements

This work was supported by Slovenian Research Agency through the Research Programme (P1–0134) "Chemistry for Sustainable Development" and the Ministry of Education, Science and Sport, Slovenia (European Regional Development grant C3330–19-952015) and research project N2–0188.

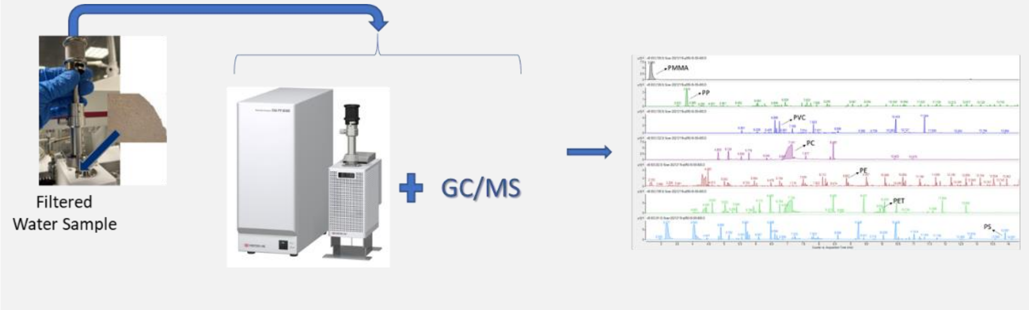
References

[1] S. Verma, S. Nakamura, M. Sillanpää (2016) *Chemical Engineering Journal*,284, 122-129.
[2] S. Verma, M. Sillanpää (2015) *Chemical Engineering Journal*,274, 274-281.
[3] B. Lévesque, M.C. Gervais, P. Chevalier, D. Gauvin, E. Anassour-Laouan-Sidi, S. Gingras, N. Fortin, G. Brisson, C. Greer, D. Bird (2014) *Science Total Environmental* 466, 397-403

Presence of Microplastics in Natural and Drinking Waters by Py-GC-MS

M. R. Boleda[1, *], J. Dalmau-Soler[1], S. Lacorte[2]

(1) Aigües de Barcelona, Empresa Metropolitana de Gestió del Cicle Integral de l'Aigua. C/General Batet 1-7, Barcelona, Spain, (2) Institute of Environmental Assessment and Water Research (IDAEA), Spanish Research Council (CSIC), C/Jordi Girona 18-26, Barcelona, Spain
[*]mboledav@aiguesdebarcelona.cat



The consumption of plastics in Europe was 57.9 million tonnes in 2019 and has increased progressively over the years. Today, the contamination derived from plastic represents a global threat and a matter of political, social and health concern. Many studies have shown that microplastics are widely distributed in the environment. Since most surface waters may be used as drinking water, the possible presence of microplastics in drinking water despite the treatments applied in Drinking Water Treatment Plants (DWTPs), is a matter of concern [1,3].

However, the lack of standardized analytical methods leads to a discrepancy of the results between different studies.

In the field of water policy, microplastics will be included in the watch list of the future European drinking water directive 2020/2184 [2] once a harmonised methodology has been adopted.

Thermoanalytical methods as pyrolysis-gas chromatography coupled to mass spectrometry (Py-GC-MS) provides the identification and the mass quantification (in terms of µg) about the concentration of the microplastics.

The objective of the present study is to develop a fast, quantitative, and validated routine analytical method based in Py-GC-MS, to determine the microplastics concentration in water samples.

The developed analytical methodology was applied to determine the concentrations and the distribution of microplastics along the Llobregat river basin (which serves as source of drinking water in the Barcelona area (Catalonia, NE-Spain)), and throughout the drinking water supply network of Barcelona urban area, that provide drinking water to 3.000.000 inhabitants.

Acknowledgements

Joan Dalmau-Soler acknowledges the support of Industrial Doctorates Plan of the University and Research Secretary of the Economy and Knowledge Department of the Generalitat de Catalunya. Authors also are grateful to the colleagues from the Organic Chemistry department for their help and support.

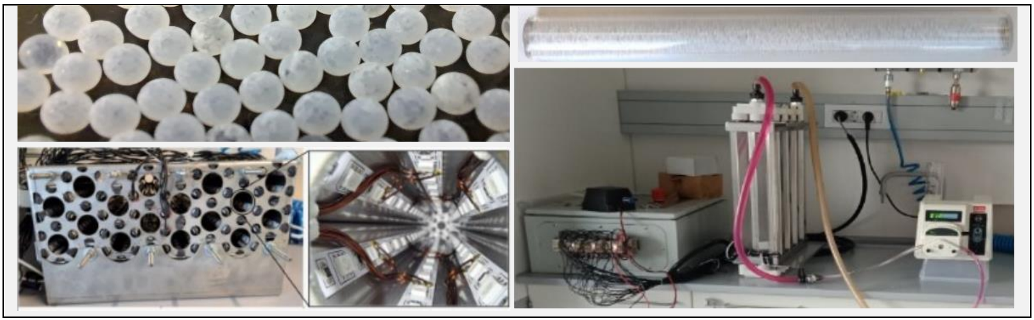
References

[1] J. Dalmau-Soler, R. Ballesteros-Cano, M. R. Boleda, M. Paraira, N. Ferrer, S. Lacorte (2021) *Environmental Science and Pollution Research*, 28, 59462–59472.
[2] Directive 2020/2184/EU; *Official Journal of the European Union*. L435/1, 23.12.2020.
[3] J. Dalmau-Soler, R. Ballesteros-Cano, N. Ferrer, M. R. Boleda, S. Lacorte. (2022) *Water and Environment Journal*, 36, 292-298.

Influence of Operating Parameters on the Efficiency of a Pilot-Scale Photocatalytic Reactor for Water Treatment

Q. Jamil[1,], L. Matoh[1], U. Lavrenčič Štangar[1]*

(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia
**qasim.jamil@fkkt.uni-lj.si*



Heterogeneous photocatalysis has been coined as a green water treatment method [1] because it is able to completely mineralize the contaminants of emerging concerns with no toxic residues. The requirement of additional filtration processes limits the use of conventional photocatalytic reactors in large-scale applications. These processes can be avoided by the immobilization of the photocatalyst on a suitable support material [2].

In the present work, a flow-through photoreactor with an immobilized photocatalyst was developed and evaluated. The effects of operating parameters such as light intensity, flow rate and contaminants have also been investigated. Commercially available Degussa P-25 titanium dioxide (TiO_2) was deposited onto glass beads by solvent deposition method, packed into columns connected in series and surrounded by LED lamps. The deposited photocatalytic material was characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and specific surface area (BET).

The effect of the operating parameters was evaluated by observing the degradation of the Plasmocorinth B dye solution using the UV-Vis spectrophotometer and selected pharmaceuticals such as ibuprofen, diclofenac and sulfamethoxazole using high performance liquid chromatography (HPLC) in deionized and real wastewater treatment plant effluent at different flow rates under the illumination of varying light intensities. Total organic carbon (TOC) was measured in the resulting solutions to determine the rate of mineralization. It was found that the light intensity straightforwardly and the flow rate inversely affected the degradation of the parent compound. At lower flow rates, 87 to 97 % overall degradation of the contaminants in one flow was observed and reducing the light intensity by half resulted in a 10-15 % decrease in overall degradation. On the contrary, the TOC concentration decreases up to a certain light intensity and tends to increase afterwards. This study presents the photoreactor with immobilized catalyst as a potential solution for large-scale (waste)water treatment.

Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0134 and project L7-1848).

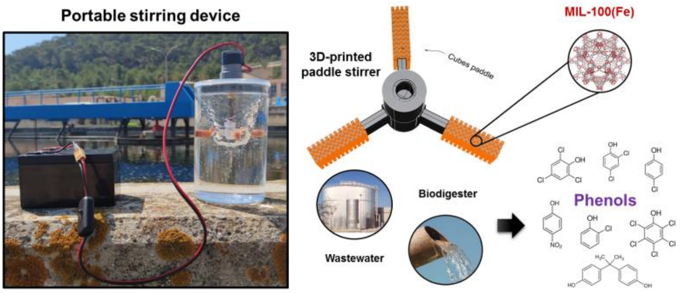
References

[1] D. Wang, M.A. Mueses, J.A.C. Márquez, F. Machuca-Martínez, I. Grčić, R. P.M Moreira, G. Li Puma. (2021) *Water Research*, 202, 117421.
[2] B. Žener, L. Matoh, P. Rodič, D. Škufca, E. Heath, U. Lavrenčič Štangar. (2021) *Journal of Environmental Chemical Engineering,* 9, 106814.

Metal-Organic Framework Coated Portable 3D-printed Paddle Stirrer for Extraction of Chlorophenols, P-Nitrophenol and Bisphenol A in Biodigester and Wastewater Samples

*M.A. Vargas-Muñoz**, *C. Palomino, G. Turnes, E. Palacio*

University of the Balearic Islands, Cra. Valldemossa km 7.5, Palma de Mallorca, Spain
**maavargasmu@gmail.com*



Phenols are a group of hazardous organic pollutants widely distributed in the environment. Phenols come from domestic, industrial, and agricultural activities, and include pharmaceuticals, dyes, pesticides, plastics and refinery products. These compounds are highly persistent and cumulative in the environment and represent a carcinogenic risk to humans [1, 2]. Therefore, most of them are classified as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) and European Union [3].

On the other hand, bisphenol A (BPA) is an emerging pollutant and a well-known endocrine disruptor, coming from production of plastics.

In this work, we propose a portable, simple and low-cost paddle stirrer for solid-phase extraction of phenols from wastewater samples.

The device consists of a small 3D-printed paddle stirrer attached to a small electric motor assembled on the lid of a jar (sample reservoir) and powered by a portable battery. The paddles of the stirrer were coated with metal-organic framework MIL-100(Fe), to be used as adsorbent for the simultaneous extraction and preconcentration of phenols. This sampler can be applied for *in-situ* extraction of the analytes, avoiding the transport of samples to the laboratory and allowing more accurate and precise results [4]. Only the extractive phases are taken for ultrasonic desorption before analysis by HPLC-DAD.

An exhaustive study of the effect of the stirring and extraction parameters was carried out. Under optimum conditions, the detection limits were in the range from 0.3 to 1.7 μg L^{-1} and, the precision as relative standard deviation obtained intraday and interday ranges between 1.2 and 5.1 %, and 4.5 and 6.8 %, respectively. The accuracy, evaluated using spiked samples of wastewater effluent and biodigester supernatant, provided relative recoveries in the range of 91.5 - 108.5 %.

The device is capable of extracting both, low and high concentrations of phenols (87.7 – 100 %), and therefore also has potential for the removal of organic contaminants for wastewater remediation. On a large scale, the device could also have a positive performance for water purification.

Acknowledgements

The authors acknowledge financial support from project PID2019-107604RB-I00 funded by MCIN/AEI/ 10.13039/501100011033. M.A.V-M. acknowledges the support from the Spanish Ministry of Science, Innovation and Universities (MCIU) for the pre-doctoral research fellowship (FPU19/06082).

References

[1] K.A. Mohamad Said, A.F. Ismail, Z. Abdul Karim, M.S. Abdullah, A. Hafeez (2021) *Process Safety and Environmental Protection*, 151, 257–289.

[2] N. Panigrahy, A. Priyadarshini, M.M. Sahoo, A.K. Verma, A. Daverey, N.K. Sahoo (2022) *Environ Technol Innov.*, 27.

[3] *European Commission*, Directive 2013/39/EU priority substances in the field of water policy, 2013.

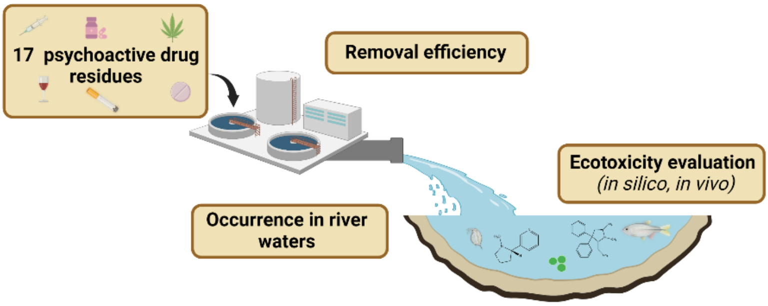
[4] J. Pawliszyn (2006) *TrAC - Trends in Analytical Chemistry*, 25, 633–634.

Residues of Drugs of Abuse: Treatment Efficiency, Environmental Occurrence and Risk Assessment

T. Verovšek[1,2], A. Šuštarič[3], M. Laimou-Geraniou[1,2], I. Krizman-Matasic[4], H. Prosen[3], T. Eleršek[5], V. Kramarič Zidar[6], V. Mislej[6], B. Mišmaš[6], M. Stražar[7], M. Levstek[7], B. Cimrmančič[8], S. Lukšič[8], N. Uranjek[9], T. Kozlovič-Bobič[10], T. Kosjek[1,2], D. Kocman[1], D. Heath[1], E. Heath[1,2,]*

(1) Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, (2) International Postgraduate School Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia, (3) Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia, (4) Rudjer Boskovic Institute, Bijenicka c. 54, 10000 Zagreb, Croatia, (5) National Institute of biology, Večna pot 111, 1000 Ljubljana, Slovenia, (6) JP Vodovod Kanalizacija Snaga, d.o.o., Vodovodna cesta 90, 1000 Ljubljana, Slovenia, (7) JP Central Wastewater Treatment Plant Domžale-Kamnik, d.o.o., Študljanska 91, 1230 Domžale, Slovenia, (8) Komunala Novo mesto, d.o.o., Podbevškova ulica 12, 8000 Novo mesto, Slovenia, (9) Komunalno podjetje Velenje, d.o.o., Koroška cesta 37/b, 3320 Velenje, Slovenia, (10) Marjetica Koper, d.o.o.-s.r.l., Ulica 15. maja 4, 6000 Koper, Slovenia

[*] *ester.heath@ijs.si*



Monitoring removal during wastewater treatment and occurrence in the aquatic environment is essential to understand the risk that drug residues pose to aquatic organisms. In this study, the presence of 17 psychoactive drug residues in wastewater and receiving waters from six Slovene wastewater treatment plants (WWTPs) differing in size and configuration are reported. Seasonal variations in removal efficiencies (REs) are also explored together with an evaluation of their ecotoxicity *in silico* (Ecological Structure-Activity Relationships software, ECOSAR) and *in vivo* (algal growth inhibition test).

Water samples were collected during spring, summer and winter. The analytes of interest (n=17) included licit drugs (tobacco and alcohol), medications of abuse (codeine, methadone, morphine and ketamine), and illicit drugs (cannabis, cocaine, amphetamine, methamphetamine, ecstasy and heroin). The method used was based on solid-phase extraction (SPE), supported liquid extraction (SLE) and liquid-liquid extraction with analysis using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

Most residues were efficiently removed during wastewater treatment (>90%), while methadone residues were removed to a lower extent (<30%). The REs were comparable between treatment technologies, except for the moving biofilm bed reactor, whose efficiency in removing nicotine and cocaine residues was poorer. Accordingly, higher levels of those residues were also detected in the receiving river. Although variations in REs and levels of drug residues in rivers were also observed, no general pattern was observed.

Regarding ecotoxicity, no significant inhibition of algal growth *(Chlamydomonas reinhardtii)* was observed for the tested compounds spiked individually or in a mixture at 1 mg/L during the exposure period (72h and 240 h), although effects were predicted using ECOSAR. Moreover, an environmental risk assessment revealed that nicotine, methadone residues, morphine, and 3,4-methylenedioxymethamphetamine (MDMA) at determined levels in receiving rivers pose a risk to aquatic plants and animals.

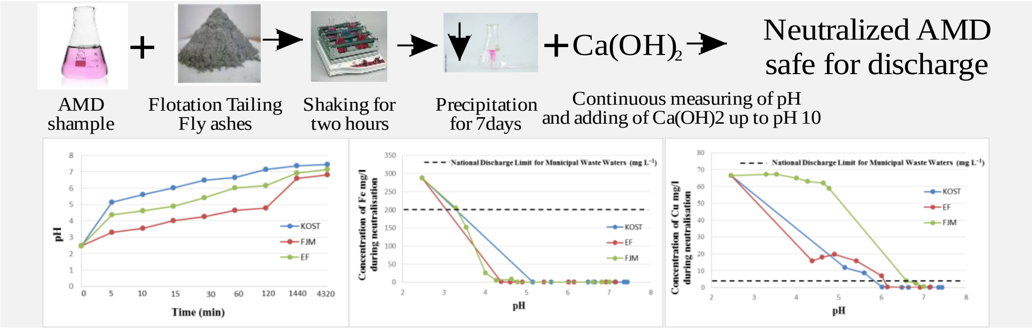
Acknowledgements

This work was supported by the Slovenian Research Agency (ARRS Program groups P1-0143, P1-0153 and P1-0245, and Projects L1-9191 and N1-0143).

Sustainable Mining and Acid Mine Water Treatment

N. Petronijević[1], G. Jovanović[1], M. Sokić[1], A. Jovanović[1,], D. Radovanović[2], Ž. Kamberović[3], S. Stanković[4]*

(1) Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franš d' Eperea street 86, Belgrade, Serbia, (2) Innovation Centre of the Faculty of Technology and Metallurgy Ltd., Belgrade 11000, Serbia, (3) Faculty of Technology and Metallurgy, University of Belgrade, Belgrade 11000, Serbia, (4) Federal Institute for Geosciences and Natural Resouces, Hannover, Germany
**a.jovanovic@itnms.ac.rs*



The mining sector, nowadays, faces rising challenges to find suitable practice that are sustainable for already disposed waste streams (AMD, flotation tailings and fly ash) [1]. There is a growing tendency globally to use waste from various industries to neutralize AMD, which has both economic and environmental benefits. In attempt to connect mining waste with concept of sustainable development in the Republic of Serbia, several experiments were taken into consideration: neutralisation of AMD from Bor's mine with a) flotation tailings from copper mine Majdanpek (FJM) b) fly ash (FA) from thermal power Nikola Tesla (EF) and Kostolac (KOST). All three samples of alternative product are voluminous, hazardous waste products, difficult and expensive for safe deposition, causes environmental pollution (by spontaneous leaching of useful components, which causes additional investment in the rehabilitation of that or reversibly lost compounds that pollutes the environment, or its dispersion by wind in surrounding streams and groundwater resources of drinking water, air or soil and also degradation by soil erosion) and can affects human health's if are not regularly discharged. But its benefits are that there are free of charge alkaline wastes, suitable to neutralize the AMD by altering pH, which leads to precipitation of valuable metal which can be reused, such as Fe or Cu. The chemical and mineralogical composition of the initial samples of FJM and FA was evaluated two standard leaching tests: TCLP and EN 12457-4, as well as *Acid Neutralization Capacity* test. These base materials were shown to have a large capacity to neutralize acid, making them a highly effective alternative material for neutralizing acid mine drainage and eliminating metals, even better than results of neutralisation with NaOH, as conventional reagent. According to the findings the FJM and FA neutralization experiments precipitated more than 99 % of Al, Fe, and Cu, 90 % of Pb, and 92 % of Zn. Leaching of these metals from FJM and FA raises Cd and Mn concentrations. Additional treatment was undertaken using hydrated lime to boost the pH to 10 and so offer circumstances for its removal, in order to reduce the concentration of Mn below the authorized limits by Serbian legislation. At the end, as a result of utilizing alternative materials such as FJM and two FA purified water, safe for release into the environment was obtained. In this way, resources are preserved for the future generation, and the treatment of already disposed amounts of waste reduces the contamination of the environment, the emission of toxic metals and the formation of acidic mine waters.

Acknowledgements

This investigation was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No. 451-03-68/2022-14/200023, 451-03-9/2022-14/200214 and 451-03-9/2022-14/200135).

References

[1] P. Kivikyto-Reponen et al., "Added value from responsible use of raw materials," VTT Research Highlights 13, ISBN 978- 951-38-8498-7, 2016

POSTER
(#2)

Urban Water Quality Through Time in Paris, France: What can be Learned from $CaCO_3$ Deposits Found in Undergrounds Structures

E. Pons-Branchu[1], P. Branchu[2], E. Dumont [2,] M. Fernandez[1, 3], A. Guillerme[3], L. Bordier[1], A. Dapoigny[1], E. Douville[1], G. Monvoisin[4], A. Noret[4], JL. Michelot[4], L. Lestel[5]*

(1) Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris Saclay, Gif-sur-Yvette, France (2) CEREMA : TEAM - 12 Rue Teisserenc de Bort, 78197 TRAPPES-en-Yvelines Cedex, AND 58 rue Roger Salengros, 94120 Fontenay sous-bois, France (3) Laboratoire histoire des technosciences en société, EA3716, Conservatoire national des arts et métiers, 2 rue Conté 75003 Paris, France (4) UMR 8148 GEOPS CNRS-Université Paris Saclay, rue du Belvédère 91405 Orsay, France (5) UMR 7619 METIS Sorbonne Université -Faculté des sciences, 4 place Jussieu 75252, Paris, France
[*]*edwige.pons-branchu@lsce.ipsl.fr*

The Saint Martin fountain - Section of $CaCO_3$ deposits studied, from North of Paris (left) and south of Paris (right).

The European Water directive 2000/60/EC, 23 October 2000 is focused on the protection of water bodies and the need to restore them to achieve good status. In urban zones, however, pre-urban state is very difficult to be defined for the surficial groundwater. We developed a methodology to build diachronic views of chemical state of the water that infiltrate the soils by studying $CaCO_3$ layers deposited from these waters. The studied speleothems like deposits were found on historical aqueducts, former quarries or undergrounds in Paris and neighbourhoods (France).
The first challenge was to build robust chronologies of these deposits. We used in some cases, uranium-thorium or ^{14}C chronology and/or laminae counting.

Some characteristics of past water quality was reconstructed using trace elements associated with isotopic analysis (lead and strontium), and in some cases carbon isotopes.

In this study, we underline that land use transformation is the most prominent factor affecting water quality, not only by the presence or absence of industries, but also by the use of some material for constructions or embankments (see [1], for the example of sulfur in water due to the use of gypsum).

In this study, we will present the example of past reconstructions build for the north of the town urbanized since the middle of the 19th century, and the comparison with data obtained for the water from the south of the town, less urbanized.

Acknowledgements

The authors acknowledge Agence Nationale de la Recherche (ANR 18 CE22 0009) and the Mairie de Paris / Eau de Paris for funding and site access. The author are very grateful to ASNEP (Association Source du Nord, Etude Protection) and their members. We are grateful to the Panoply analytical platform.

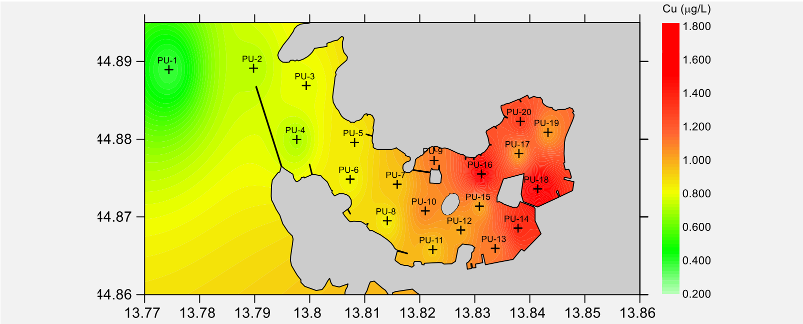
References

[1] E. Pons-Branchu, M. Roy-Barman, L. Jean-Soro, A. Guillerme, P. Branchu, M. Fernandez, E. Dumont, E. Douville, J.L. Michelot, M.A. Phillips (2017) *Science of the Total Environment,* 579, 124–132.

Seasonal Distribution of Trace Metals in Heavily Industrialized Pula Bay, Croatia

O. Grozdanić[1,], A.-M. Cindrić[2], I. Finderle[1], D. Omanović[2]*

(1) Teaching Public Health Institute of Istrian Region, Nazorova 23, 52100 Pula, Croatia, (2) Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
**ozren.grozdanic@gmail.com*



Spatial distribution of dissolved Cu in below-surface layer in July 2021

Pula Bay, Istria, Croatia is a zone that has been under strong anthropogenic influence for a long period of time. This part of Istrian coast is at the service of industry (shipyards, aluminous cement factory, quarry), harbour transhipment, nautical marinas and defence, and until 2015 it was also the final point of the Pula city's wastewater drainage system.

The subject of this research is seasonal distribution of trace metals in seawater of the Pula Bay. Research primarily focuses on ecotoxic metals (Zn, Cd, Pb, Cu, Ni and Co). Of particular interest were the studies of polluted zones in the port area, for which a significantly higher level of concentration was expected compared to the reference area of the coastal sea.

Four sampling campaigns were carried out in the Pula Bay during 2021 and 2022, corresponding to the four seasons: summer, autumn, winter and spring. Samples were taken from two depths: below the surface (0.5 m) and at the bottom of water column (variable depth). Total metal concentrations and dissolved metal concentrations (after filtration using 0,22 µm pore filters) were determined using electroanalytical techniques: differential pulse anodic stripping voltammetry for Zn, Cd, Pb and Cu [1] and differential pulse adsorptive cathodic stripping voltammetry for Ni and Co [2]. Samples for dissolved organic carbon (DOC) were also taken for gaining more information on metal fractionation. Vertical profiles of the main physic-chemical parameters were taken using the EXO2 CTD probe (YSI, Xylem). High-temperature catalytic oxidation (HTCO) was used for DOC.

General increase in both dissolved and total metal concentrations can be observed for all trace metals entering the bay from the open sea. This is applicable both for the below-surface and above-sediment (bottom seawater layer) samples. The increase of dissolved Cd, Ni and Co concentrations in below-surface samples was small for 3 sampling campaigns (factor up to 1.5), except for November 2021 campaign, for which factor of increase was up to 2.5 (Cd). For other metals, the dissolved concentration increased significantly, up to a factor of 11 (Zn), 17 (Pb) and 5 (Cu). Similar factors were found also in bottom seawater samples. Differences between the two depths are clearly seen in the case of Pb (concentrations increase with depth) and Cu (concentrations decrease with depth) in all sampling seasons. Seasonal variations can also be observed: maximum average concentration of total Pb for both depths in autumn 2021 (0.525 µg/L) and the lowest in winter 2022 (0.130 µg/L) can serve as an example. Repetitive high results of Zn concentrations in the vicinity of Uljanik shipyard and the former wastewater drainage area indicate the sources of pollution.

DOC measurements show increment in the same manner as metals with higher value on locations closer to the open sea during autumn 2021 and winter 2022.

This data set represents the first insight into the status and sources of pollution in Pula Bay as well as a set of input data for metal speciation and fractionation.

References

[1] D. Omanović, Ž. Kwokal, A. Goodwin, A. Lawrence, C. E. Banks, R. G. Compton, Š. Komorsky-Lovrić (2006) *Journal of Iranian Chemical Society*, 3, 128-139.

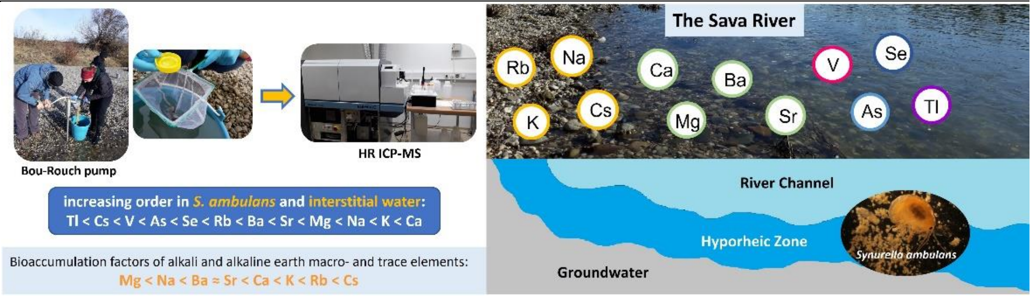
[2] M. Vega, C. M. G. van den Berg (1997) *Analytical Chemistry*, 69, 874-881

Accumulation of Macro- and Trace Elements in Amphipod *Synurella ambulans* from Hyporheic Zone of the Sava River, Croatia

Z. Redžović[1,*], M. Erk[1], S. Gottstein[2], M. Cindrić[1]

(1) Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia, (2) Faculty of Science, Rooseveltov trg 6, Zagreb, Croatia

**zuzana.redzovic@irb.hr*



The hyporheic zone (HZ) belongs to the local and regional interstitial groundwater ecosystems and to the most threatened aquatic environments. Bioaccumulation monitoring allows us to gain insight into the bioavailability of the pollutants in the environment and their biomagnification in the food chain. The aim of this research was to evaluate the accumulation of macro- and trace elements in stygophilous amphipod *Synurella ambulans* which inhabits HZ of the Sava River in Croatia. Concentrations of 12 elements (As, Ba, Cs, Rb, Se, Sr, Tl, V, Ca, K, Mg, and Na) in interstitial water and in amphipods were measured by high resolution inductively coupled plasma mass spectrometry. The study was conducted in the middle section of the Sava River at two study sites: 1) Medsave – located about 3 km upstream from the wastewater outlet of the city of Zaprešić and 2) Jarun – located about 13 km downstream from this wastewater outlet and within the Zagreb City area, during the 4 seasons: winter 2018, spring, summer, and autumn 2019.

At both sampling sites the increasing order of metals in *S. ambulans* was as follows: Tl < Cs < V < As < Se < Rb < Ba < Sr < Mg < Na < K < Ca. In interstitial water, metals at both sampling sites had similar increasing order as in *S. ambulans* and the concentration ranges were the following: $< 0.1\ \mu g\ L^{-1}$ (Cs, Tl), $< 1\ \mu g\ L^{-1}$ (As, Se, V), $1 - 5\ \mu g\ L^{-1}$ (Rb), $> 10\ \mu g\ L^{-1}$ (Ba) and $> 100\ \mu g\ L^{-1}$ (Sr). In general, higher metal accumulation was observed for Rb, Se, Tl, K, and Na in *S. ambulans* specimens from the Medsave site and for As, Ba, Cs, V, Ca, and Mg from the Jarun site in all studied seasons. Comparison between chemically similar alkali and alkaline earth macro- and trace elements in *S. ambulans* showed that bioaccumulation factors (BAFs) increase in the following order: Mg < Na < Ba ≈ Sr < Ca < K < Rb < Cs. In this case, the tendency to accumulate in *S. ambulans* increased with the relative atomic mass of the element. BAFs were generally higher at Medsave, with average values ranging from 165 to 19,534 L kg^{-1}, and Cs with the highest BAF. It is considered that Cs is concentrated by crustaceans probably because of its chemical similarity to K, and it may derive from the radioactive wastes in fresh water [1,2]. Cesium has the potential to biomagnify with increasing trophic levels in aquatic food webs [3]. Also, it has been shown that Cs had an impact on the neuromuscular system by increasing the amplitude of excitatory postsynaptic potentials [4].

Biomonitoring of HZ is crucial for protection and conservation of these generally little-considered groundwater connected ecosystems. These are the first results on concentrations of presented elements in *S. ambulans* and as such are essential for assessing point source of water pollution and global evaluation of groundwater ecological quality.

Acknowledgements

The financial support of the European Regional Development Fund for the Qua/Qua Protein project (KK.01.1.1.07.0023) and of Croatian Science Foundation for the AQUAMAPMET project (IP-2014-09-4255) are acknowledged. We are grateful to Mr. Ivica Barač for his great help in the field work and Dr.Sc. Zrinka Dragun for ICP-MS analyses.

References

[1] G. Bryan, E. Ward (1962) *Journal of the Marine Biological Association of the United Kingdom*, 42, 199-241.
[2] G. Bryan (1963) *Journal of the Marine Biological Association of the United Kingdom*, 43, 519-539.
[3] K. Pan, W.-X. Wang (2016) *Chemosphere,* 163, 499-507.
[4] H. L. Atwood, F. Lang (1973) *Journal of General Physiology*, 61, 747-66.

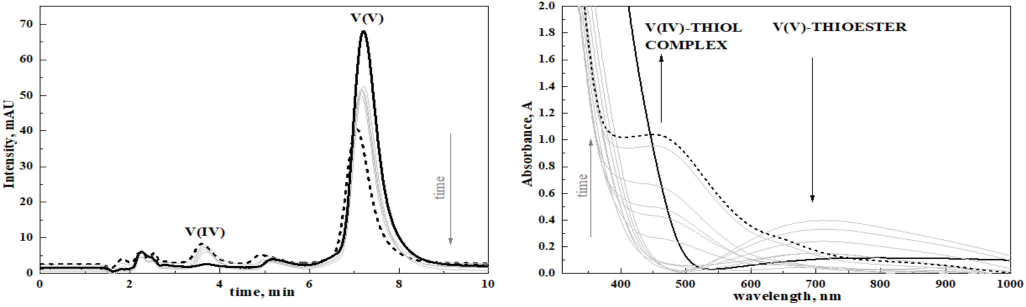
POSTER
(#2)

Chromatographic and Spectrophotometric Investigation of V(V) Interaction with Biologically Important Thiols

L. Knežević[1,*], *E. Bura-Nakić*[1]

(1) Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia
[*] *lknezev@irb.hr*

V(V)+L-Cysteine



Vanadium(V) interaction with sulphur containing ligands is still a matter of great relevance in better understanding of V chemical behaviour in environmental and biological mediums [1]. Sulphur containing ligands are found in active enzyme sites and depletion of thiol compounds due to the complexation with V(V) can lead to damage of cell membranes [2]. On the other hand, complexation mechanism of V(V) with thiol compounds that can possibly lead to its reduction to V(IV), can be important mechanism of V(V) decreased toxicity in biological or environmental mediums [3].

The reduction of vanadate(V) in the presence of different thiol ligands (L-Cysteine, thiol- acetic acid and ethanethiol) has been studied using chromatographic method for the determination of V(V) and V(IV) species in aqueous model solutions. Kinetic chromatographic measurements were carried out using anion-exchange column with UV-Vis detection. Prior to stated measurements, EDTA was added in each sample with the goal of terminating further reduction of V(V) and allowing V redox speciation based on the ligand exchange reaction. Additionally, absorbance studies of sample solutions without addition of EDTA was conducted to identify formation of intermediate species over reaction course. Observed strong pH dependence of the reduction rates further underlines the complexity of such reactions due to the rich V(V) aquatic chemistry and changes in the ionic forms of studied thiol compounds. The V(V) reduction is observed to proceed in following steps: i) formation of the intermediate V(V)-thioester species ii) reduction of V(V) and formation of V(IV)-thiol complexes. Obtained results strongly suggest that the reaction of vanadate (+V)-thioester formation is proton catalysed.

Acknowledgements

Research within this work was fully funded by the Croatian Science Foundation, project IP-2018-01-7813, “REDOX”.

References

[1] H. Nekola, D. Wang, C. Gruning, J. Ga1tjens, A. Behrens, D. Rehder (2002) *Inorganic Chemistry*, 41, 2379-2384.
[2] X. Shi, X. Sun, N.S. Dalal (1990) *FEBS Letters*, 271, 185-188.
[3] J. P. Gustafsson (2019) *Applied Geochemistry*, 102, 1-25.

Development of Reliable Analytical Methods for the Monitoring of Emerging Pollutants' Removal by Advanced Oxidation Processes

J. Račić[1], B. N. Malinović[2], A. Žgajnar Gotvajn[1], J. Derco[3], H. Prosen[1,]*

(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, Ljubljana, Slovenia, (2) Faculty of Technology, University of Banja Luka, Stepe Stepanovića 73, 78000 Banja Luka, Bosnia and Herzegovina, (3) Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

**helena.prosen@fkkt.uni-lj.si*

One of the biggest problems we face today is water pollution. Water is being constantly polluted through the discharge of industrial wastewater into the surface waters and thus spreading hazardous chemicals. Even though some of these pollutants are undergoing various regulations and are closely monitored in the environment, by the year 2019 there were over 1036 chemicals that were classified as emerging pollutants (EP). These are pollutants that are not yet monitored and thus their ecotoxicological effects as well as their behavior and fate in the environment are often not well understood [1]. For this reason, new selective and sensitive analytical methods need to be developed for their monitoring as well as new methods for their removal from wastewaters to prevent their occurrence in environmental compartments.

The aim of our work was to develop new reliable analytical methods for the determination of two important groups of EPs in wastewaters, surface waters and underground waters: benzotriazoles and alkylphenols. Polar benzotriazoles are water-soluble EPs that are known to exhibit chronic toxicity for some aquatic organisms [2]. Alkylphenols are frequently encountered residues of nonionic surfactants and are confirmed as endocrine disruptors in humans and animals. They are also acutely toxic for some aquatic organisms [3]. Ozonation and electrooxidation as examples of effective advanced oxidation processes were selected to treat model wastewater containing selected above-mentioned pollutants. Electrooxidation experiments were performed by using different anode materials and various electrolytes. Ozonation was accomplished at different ozone doses in bubble column batch reactor. The efficiency of these processes was monitored by newly developed analytical methods. HPLC-DAD method was used to follow benzotriazoles degradation and electrooxidation by-products were determined by LC-MS. To monitor alkylphenols' degradation by ozonation, both HPLC-DAD method and a more selective and sensitive GC-MS method was developed. Analytical methods' development and parameters, as well as results of degradation experiments are presented.

Acknowledgements

This work was supported by research Grants P1-0153 and P2-0191 (Slovenian Research Agency, Slovenia). Photo: courtesy of dr. Matej Čehovin.

References

[1] I. Haddaoui, J. Mateo-Sagasta (2021) *Environmental Science and Pollution Research*, 28, 68090–68110.X.

[2] J. S. Cornell, D. Pillard, M. T. Hernandez (2000) *Environmental Toxicology and Chemistry*, 19(6), 1465 - 1472.

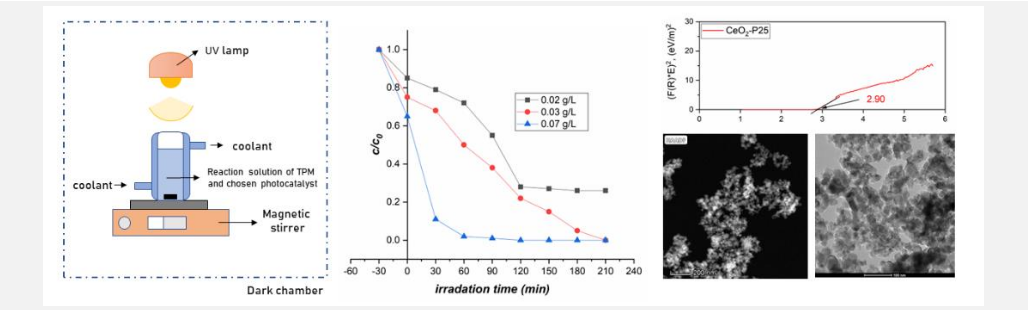
[3] G. Crini. C. Cosentino, C. Bradu, M. Fourmentin, G. Torri, O. Ruzimuradov, I. A. Alaton, M. C. Tomei, J. Derco, M. Barhoumi, H. Prosen, B. N. Malinović, M. Vrabeľ, M. M. Huq, J. Soltan, E. Lichtfouse, N. Morin-Crini (2022) *Environmental Chemistry Letters*, 20, 2597 – 2628.

The Removal of Thiophanate-Methyl Using Novely Synthesized Catalysts CeO_2-P25 Under Simulated Sunlight: Structural Characterisation and Photocatalytic Activity

A. Jovanović[1, *], M. Stevanović[2], M. Bugarčić[1], M. Sokić[1], A. Tomašević[2], A. Marinković[3]

(1) Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franš d' Eperea street 86, Belgrade, Serbia, (2) Institute of Pesticides and Environmental Protection, Banatska 31b, Belgrade, Serbia, (3) Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

**a.jovanovic@itnms.ac.rs*



Environmental pollution by wastewater represents one of the greatest challenges nowadays. The solution for this issue requires implementation of novel treatment methods. Therefore, enhanced techniques so-called Advanced oxidation processes (AOPs) are gaining increasing attention. Photocatalysis is a process based on the use of different types of irradiations on a pollutants adhered on a catalyst, driven by formation of radicals and oxidative species on the catalyst surface. Modern agricultural practice relies on use of different classes of pesticides, and to its, often, uncontrolled and excessive use. It leads to their widespread in the environment, with frequent detection in waterbodies and soil. Thiophanate-methyl (TPM) is benzimidazole fungicide, used in control of diverse groups of phytopatogenic fungus [1].

Specifically efficient and economically viable catalysts are TiO_2-based. Multiphase catalysts showed better results in the degradation of various pollutants, so TiO_2 P25 (Degussa) was used as a material that boosts photocatalytic decomposition. In order to advance and fasten the reaction, the surface of TiO_2 P25 was decorated with cerium (IV) oxide [2]. Surface and photochemical properties of newly obtained material are characterised by HR - TEM, HAADF - STEM; FTIR and UV - DRS methods.

In this study, the photocatalytic degradation of thiophanate-methyl (TPM) in the presence of CeO_2 - P25 was investigated. Different experimental conditions were varied, such as the concentration of the pesticide solution and the mass of the catalyst. Monitoring of the pesticide concentration in the reaction system was based on the decrease in absorbance using a Shimadzu 1800 UV spectrophotometer.

Results of textural and structural analyses prove decoration of P25 surface with particles of cerium (IV) oxide uniformly. Synthesised nanocatalyst CeO_2-P25 has lower band gap energy (2.90 eV) then P25 (3.30 eV).

The optimal experimental conditions were obtained using 0.07 g/L of CeO_2-P25 and 5 mg/L of TPM solution. Degradation reaction rate follows pseudo-first order law. Complete degradation was performed after 120 min. In experiments with TiO_2 P25 catalyst (Degussa) degradation time was 240 min. Hence, it can be concluded that the synthesized CeO_2-P25 catalyst has better performance.

Acknowledgements

This investigation was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No. 451-03-68/2022-14/200023, 451-03-9/2022-14/200214 and 451-03-9/2022-14/200135).

References

[1] G. Sharma *et al.* (2018) *Int. J. Biol. Macromol.*, 114, 295–305.

[2] T. M. Wandre *et al.* (2016) *J. Mater. Sci. Mater. Electron.*, 27(1), 825–833.

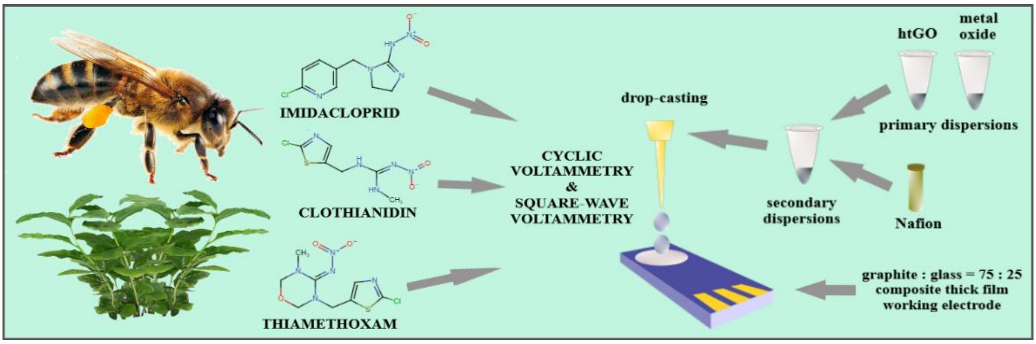
POSTER
(#2)

Optimization of Materials on a Graphite Glass Composite Thick Film Working Electrode for Voltammetric Detection of Neonicotinoids

M. Dekleva[1,], E. Gričar[1], G. Marolt[1], M. Kolar[1], B. Genorio[1], B. Repič[2], D. Kuščer[2], D. Belavič[2], K. Makarovič[2], M. Jerlah[2], H. Prosen[1]*

(1) Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia, (2) Electronic Ceramics Department, Jožef Stefan Institute, Ljubljana, Slovenia

**md2207@student.uni-lj.si*



Neonicotinoids (NNIs) are synthetic systemic pesticides with selective activity on acetylcholine receptors of insects. Due to their widespread use, NNIs have been detected in soils, waters and some foods, which may pose environmental and health risks. As established chromatographic methods for the determination of these insecticides have long procedure time, high price and use large amounts of solvents, a lot of recent research has been focused on fast and selective electrochemical sensor development. Usually, an improved electrochemical response is achieved by modifying the surface of working electrode [1,2].

In this work, we address the characterization of graphite-glass (GGE) working electrode, as well as optimization of materials for the modification of its surface. GGE was prepared with 100:0, 90:10, 75:25, and 50:50 weight ratios of graphite:glass. The electrochemical response of the GGE was studied by cyclic voltammetry in a phosphate buffer solution (pH = 7.4) using equimolar concentration of potassium hexacyanidoferrate(II)/(III) (HCF). Commercially available Ag/AgCl (3 M KCl) reference and platinum sheet counter electrodes were used for the measurement. According to characterisation results, the GGE with 75:25 weight ratio proved to be optimal for further development and three-electrode electrochemical test structures (TES) were prepared on alumina substrate using commercial Pt and Ag pastes for processing counter and reference electrodes, respectively, and GGE with 75:25 weight ratio for working electrode.

Simultaneously, using a commercially available screen-printed carbon electrodes (SPCE), materials for the modification of the working electrode were optimized. Dispersions of heat-treated graphene oxide (htGO), several metal oxide microparticles and Nafion were prepared in different volume ratios. Dispersion of htGO (1 mg/mL):MnO_2 (1 mg/mL):Nafion in volume ratio 6:3:1 proved to be optimal for the determination of thiamethoxam and clothianidin, whereas dispersion of htGO (1 mg/mL):Mn_2O_3 (1 mg/mL):Nafion in volume ratio 6:3:1 proved to be optimal for the determination of imidacloprid. Dispersions were used for the modification of the TES working electrode.

Modified electrodes were used to determine the concentration of imidacloprid, clothianidin and thiamethoxam in model solutions, using square-wave voltammetry (SWV). For the selected pesticides, we achieved good reproducibility over a wide linear range with detection limits of 2.68 – 4.40 mg/L.

Future research will be focused on optimising the deposit modification, while using smaller sized particles with the aim of achieving higher current response relative to the background, as well as testing of prepared electrodes on other NNIs.

Acknowledgements

This work was supported by Slovenian Research Agency (ARRS), grant number J2-3049.

References

[1] J. Ganesamurthi, M. Keerthi, S.M. Chen, R. Shanmugam (2020) *Ecotoxicology and Environmental Safety*, 189, 110035.

[2] S. Srinivasan, N. Nesakumar, J.B.B. Rayappan, A.J. Kulandaiswamy (2020) *Bull. Environ. Contam. Toxicol*., 104, 449 - 454.

POSTER
(#2)

Monitoring of Pesticides in Water Bodies from the Agricultural Region of South Banat District in Serbia

N. Zaric[1,*], *Lj. Stanisavljevic*[1], *M. Zaric*[2,3]

(1) University of Belgrade – Faculty of Biologyy, Studentski trg 12, Belgrade, Serbia (2) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoseva 12, Belgrade, Serbia, (3) Centre of Excellence in Environmental Chemistry and Engineering – ICTM, University of Belgrade, Belgrade, Serbia

[*] *nenad.zaric@bio.bg.ac.rs*

Pesticides are widely used in agriculture to protect crops against weed fungi and insect. Respectively they are divided into herbicides, fungicide and insecticides. Although they are very useful for protection of plants pesticides and their metabolites can be toxic to humans and animals.

When used on crops pesticides are spread throughout the environment. They can enter groundwater or they can be washed with rain and enter rivers or lakes in the vicinity of agricultural land.

Considering that they can be toxic it is very important to monitor their presence in the environment. Monitoring water for the presence of pesticides is a priority considering that it is essential for all living organisms. In addition, we use organisms from water as food (fish).

The aim of this study was to monitor pesticides in water bodies in an agricultural district of South Banat in Vojvodina, Serbia.

Water was collected from running water bodies (rivers), still water bodies (lakes) and underground water (wells). The sampling took place every month for a period of one year. Water was collected into clean plastic battles and was kept in the freezer at -20°C until analysis.

Before preparation all water samples were defrosted at room temperature. Pesticides were extracted using Solid phase extraction (SPE). C18 disks were preconditioned with 10 mL of acetone, 10 mL of ethyl acetate, 10 mL of methanol and 10 mL of water. Before the disk were dry the water samples were passed through the SPE disk using a vacuum manifold. Once the total sample is percolated, the disks were rinsed with 2 × 5 mL of deionized water. The disks were dried under vacuum. The analytes were eluted with ethyl acetate / dichloromethane. Extracts were evaporated to dryness under a gentle stream of nitrogen. Befor analysis the extracts were reconstituted with methanol.

The analysis was performed on a TSQ Quantis™ Triple Quadrupole Mass Spectrometer. A calibration curve was made with 283 pesticides.

Around 90 % of pesticides were not detected in water samples that were analyzed. Still water (lakes) had much more consistent presence of pesticides compared to running water. The qualitative and quantitative analysis of pesticides varied a lot in running water. This was expected because the samples were taken only once a month, and the water in rivers changes each time the samples were taken.

Acknowledgements

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

The Use of an Algal Micriobiotest to Assess the Toxicity of Degradation Products after Herbicide Photocatalysis

D. Josefova[1,*], *K. Hrda*[1]

(1) University of Pardubice, Studentska, Pardubice, Czech Republic

[*]*dominika.josefova@student.upce.cz*

Herbicides are an integral part of modern agricultural practices, and are used intensively to prevent, destroy, or mitigate undesirable vegetation, and their use has been increasing continuously over the past decades [1–3]. Unfortunately, the benefits generated by their use are accompanied by several negative effects on human health and the environment [4,5]. The extensive use of herbicides leads to soil and water contamination that is primarily due to agricultural runoff [2,3]. The presence of herbicides in aquatic ecosystems is concerning, as they can affect several levels of biological organization, from the molecular to the ecosystem level [6]. Systematic and selective chloroacetanilide herbicides represent one of the major classes of herbicides that are applied worldwide in the agricultural sector to control broadleaf weeds and annual grasses for crops such as corn, soybeans, sorghum, cotton, sugar beet, or sunflower [1,7,8].

Algae are the primary producers and the first level of the aquatic food chain. Therefore, any effect on algae will influence higher trophic levels. Although herbicides were generally designed to be toxic only to particular groups of organisms, nowadays there is undeniable evidence that herbicides, including chloroacetanilides, are not specific to their main target (weeds). As a result, chloroacetanilide herbicides can have considerable adverse effects on other aquatic non-target organisms and, in particular, on algae due to their similarity to plants, since both have the photosynthetic capacity [3,5,6,9]. In view of this fact, the freshwater alga *Chlorella kessleri* was chosen as a test organism for the evaluation of the toxicity of chloroacetanilide herbicides and the mixtures of their degradation products formed during heterogeneous photocatalysis. Species of the *Chlorella* genus (*Chlorophyceae*) are widespread throughout the world and can be found in a variety of aquatic environments, where they represent primary producers, contribute to the self-purification of water, and have many other important ecological functions [10].

Our work deals with the development and optimization of alternative tests on freshwater algae. The algal microbiotest is a miniaturized form of the classical algal bioassay, where microtiter plates are used instead of Erlenmeyer flasks. This significantly reduces the consumption of culture media, but above all limits the required amount of test sample. The test makes it possible to monitor not only the inhibitory (toxic) effects of substances, but also the stimulating effects, so-called trophic level. Due to the rapid growth of algae, it is possible to observe, in addition to the acute action, also the chronic effects of the tested substances (even for more than 96 hours).

The toxicity of the chloroacetanilide herbicides alachlor, acetochlor, and metolachlor to the freshwater alga *Chlorella kessleri* was investigated via a algal micribiotest. After 72 h of exposure, the growth inhibition increased with the increasing concentration of herbicides in the exposure medium. The results of toxicity testing in our study showed that *Chlorella kessleri* was the most vulnerable to the alachlor (14.07 μg/L), then to acetochlor (19.13 μg/L), and, in the presence of metolachlor, toxicity was an order of magnitude lower (115.10 μg/L). Our results showed that all herbicides were highly toxic to the freshwater alga *Chlorella kessleri.*

The toxicity of the resulting mixtures of herbicides and their photocatalysis degradation products increased or remained the same as that of the initial herbicide solutions.

References

[1] S.S. Mohanty, H.M. Jena (2019) *J. Water Process. Eng.*, 31, 100860.

[2] T. Huang, Y. Huang, Y. Huang, Y. Yang, Y. Zhao, C.J. Martyniuk (2020) *Chemosphere*, 243, 125345.

[3] M.D. Machado, E.V. Soares, (2021) *Ecotoxicol. Environ. Saf.*, 207, 111264.

[4] A. Thiam, R. Salazar, (2019) *Environ. Sci. Pollut. Res.*, 26, 2580–2591.

[5] M. Sigurnjak, Š. Ukić, M. Cvetnić, M. Markić, M. Novak Stankov, B. Rasulev, H. Kušić, A. Lončarić Božić, M. Rogošić, T. Bolanča (2020) *Chemosphere*, 240, 124973.

[6] M.D. Machado, E.V. Soares (2020) *Aquat. Toxicol.*, 222, 105449

[7] Y. Souissi, S. Bouchonnet, S. Bourcier, K.O. Kusk, M. Sablier, H.R. Andersen (2013) *Sci. Total Environ.*, 458–460, 527–534

[8] Z. Chen, Y. Chen, J. Vymazal, L. Kule, M. Koželuh (2017) *Sci. Total Environ.*, 577, 386–394.

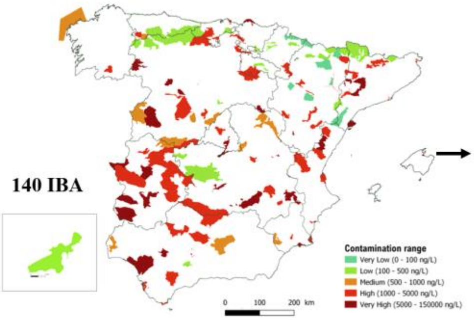
[9] K.H. Kim, E. Kabir, S.A. Jahan (2017) *Sci. Total Environ.*, 575, 525–535.

[10] P. Y. Caux, L. Ménard, R.A. Kent, R.A (1996) *Environ. Pollut.*, 92, 219–225.

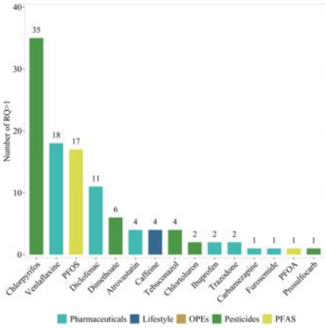
Risk Assessment of Water Organic Micropollutants in Important Bird and Biodiversity Areas

M. Dulsat-Masvidal[1*], C. Ciudad[2], O. Infante[2], R. Mateo[3], S. Lacorte[1]

(1) IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Spain. (2) SEO/BirdLife, Melquiades Biencinto, 34, 28053 Madrid, Spain. (3) IREC- CSIC-UCLM-JCCM, 13005 Ciudad Real, Spain
mariadulsat@gmail.com



$$\rightarrow RQ_{j,i} = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i} \rightarrow$$



Water pollution is an underestimated threat to natural surface water. The presence of organic micropollutants in surface water has a negative impact on living organisms and may directly lead to habitat degradation and loss of ecosystem services [1]. Therefore, water pollution is an important risk factor in the management of key biodiversity areas. This study aims to quantify, for the first time, the impact of organic micropollutants (OMP) detected in Important Bird and Biodiversity Areas (IBAs) in Spain.

In the present study, we performed a Tier I Environmental Risk Assessment (ERA) to identify the most concerning compounds in natural surface waters from Spain and to identify the IBAs most impacted by water pollution. The assessment was based on a previous monitoring scheme for the measurement of 59 OMP, including pharmaceuticals, pesticides, organophosphate esters (OPEs), and perfluoroalkyl substances (PFAS) in freshwaters of 140 IBAs.

Individual Risk Quotients (RQ) for each compound were calculated as the ratio between the Measured Environmental Concentration (MEC) and the lowest Predicted Non-Effect Concentration (PNEC) in freshwater from the NORMAN database. The most concerning compounds identified were the organophosphate pesticide chlorpyrifos, which was detected in 35 IBAs at high-risk concentrations (RQ>1) in freshwater. Followed by the antidepressant venlafaxine detected at high-risk concentrations in 18 IBAs, and perfluorooctanesulfonic acid (PFOS) in 17 IBAs. Optimised risk quotients (RQf) were used to identify the risk posed by substances in aquatic ecosystems.

The OMP in the surface waters of IBAs are present as mixtures of compounds. The chemical mixture risk for each IBA was calculated by summing the RQ for each target compound (i) at each site (j). Out of 140 IBAs, only 50 did not present any target compound at concentrations considered to be of concern for aquatic ecosystems (RQ<0.01). The other 90 IBAs presented a RQ of medium to high risk.

Finally, we have identified OMP levels that may pose at risk the conservation values of high relevant areas for conservation, such IBAs. This study serves to delineate the importance of water monitoring studies within IBAs and other natural areas as a first approach to contribute to pollution management actions and minimise the impact of pollutants on biodiversity.

Acknowledgements

The Spanish Ministry of Science and Innovation is acknowledged for financial support [PID2019-105732GBC21] from CIN/AEI/10.13039/501100011033 and for the Severo Ochoa project Grant CEX2018-000794-S funded by MCIN/AEI/ 10.13039/501100011033 to IDAEA-CSIC as Centre of Excellence.

References

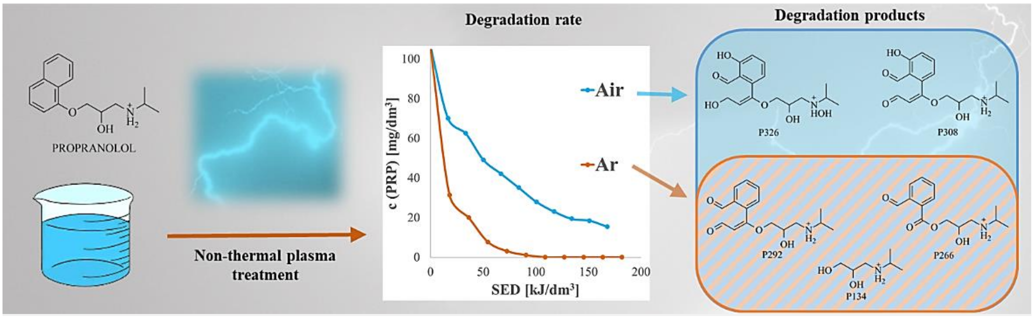
[1] L. Posthuma, W. Brack, J. van Gils, A. Focks, C. Müller, D. de Zwart, S. Birk (2019) *Sci. Eur.* 31.

POSTER
(#2)

Propranolol Degradation Products after Non-thermal Plasma Treatment using Coaxial DBD Reactor

S. Savić[1,], V. Kovačević[2], G. Sretenović[2], B. Obradović[2], G. Roglić[1]*

(1) University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia, (2) University of Belgrade, Faculty of Physics, Studentski trg 12, 11000 Belgrade, Serbia
[*]sladjana@chem.bg.ac.rs



Pharmaceuticals represent a considerable threat when they reach the environment. Propranolol (PRP), designed to be a biologically active compound, is a widely used beta-blocker prescribed for heart-related diseases. Due to its frequent use, PRP is detected in numerous aquatic environments and organisms. [1] To completely remove pharmaceuticals such as PRP, advanced oxidation processes (AOPs) are often employed, [2] like ozone, [3] or electrochemical oxidation [4]. Recently, the non-thermal plasma treatment has gained interest for water purification, due to *in situ* production of reactive oxygen species, such as hydroxyl radicals and superoxide anion radicals.

The aim of this paper was to investigate plasma treatment for PRP removal from water. To achieve that, the dielectric barrier discharge (DBD) non-thermal reactor was used. This DBD reactor was already tested for degradation of different organic compounds. [5, 6] In this study, PRO solution (100 mg/dm^3) was recirculated through the DBD reactor, while plasma was generated using ambient air and argon. The PRP degradation rate was monitored on HPLC-DAD, and the specific energy density (SED) was used to compare plasma effects on PRP degradation. SED was calculated by dividing the power (kept at 35 W and multiplied by the number of cycles of treatment) by the flow rate (held constant at 7.5 dm^3/h).

The single most striking observation is that pure argon contributes to faster PRP degradation. Namely, at 75 kJ/dm^3, there was less than 5% of PRP left when treated with Ar non-thermal plasma, while only around 35% was achieved at the same point with ambient air.

As for the degradation products, several compounds were identified (P326, P308, P292, P266, and P134). Interestingly, all compounds were spotted in air-treated PRP solution, but P326 and P308 were not found in samples treated by Ar-generated plasma.

In summary, both decomposition rate experiments and detected degradation compounds imply that Ar may be a better plasma gas for PRP treatment. A possible explanation is a fact that reactive oxygen species in air plasma are partly consumed to generate reactive nitrogen species, while there is no such phenomenon in Ar-plasma. [7]

The study confirmed that the non-thermal plasma treatment can be considered promising due to effective and rapid degradation of waterborne organic pollutants, with no catalysts added.

Acknowledgements

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

References

[1] J.P. Sumpter, T.J. Runnalls, R.L. Donnachie, S.F. Owen (2021) *Science of The Total Environment*, 793, 148617.

[2] K. Kovács, T. Tóth, L. Wojnárovits (2021) *Water Science and Technology*, 85, 685–705.

[3] M.L. Wilde, S. Montipó, A.F. Martins (2014) *Water Research*, 48, 280–295.

[4] J.D. García-Espinoza, P. Mijaylova Nacheva (2019) *Environ Sci Pollut Res*, 26, 6855–6867.

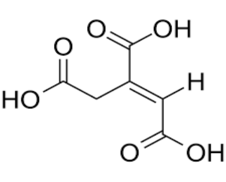
[5] J. Krupež et al., (2018) *J. Phys. D: Appl. Phys.*, 51, 17.

[6] M. S. Jović et al., (2014) *Chemical Engineering Journal*, 248, 63–70.

[7] V.V. Kovačević, B.P. Dojčinović, M. Jović, G.M. Roglić, B.M. Obradović, M.M. Kuraica (2017) *J. Phys. D: Appl. Phys*., 50, 15, 155205.

Thermodynamic Solution Properties of Trans-Aconitic acid and Its Sequestering Ability Toward Cd^{2+}, Pb^{2+} and Mn^{2+} at Different Experimental Condition

A. Irto[*], *G. Lando, P. Cardiano, C. De Stefano, C. Bretti*
CHIBIOFARAM Department, University of Messina, V.le F. Stagno d'Alcontres, 31 – 98166 Messina (Italy)
**airto@unime.it*


Trans-Aconitic acid

Trans-Aconitic acid (TA, propene-1,2,3-tricarboxylic acid), an unsaturated organic acid containing a double bond, is obtained from renewable and inexpensive sources like cane molasses and sweet sorghum syrup. According to the United States Department of Energy, TA is one of the top 30 value-added chemicals due to its use in industry as a chemical building block and precursor for other important chemicals and polymers [1]. The aim of this work is to explore the potential of TA as a green chelating agent towards various metals in aqueous solution, in order to assess its potential for the removal and recovery of different metal cations. Despite TA importance, few thermodynamic data are available in literature, and therefore new experiments may be useful, for example, to determine which are the best conditions (pH, ionic strength, concentration) at which TA can be efficiently exploited. In this light, the evaluation of species formation and their relative stability, as well as the determination of the chelation thermodynamics of TA toward Cd^{2+}, Pb^{2+} and Mn^{2+} is crucial to specifically design a sequestration strategy in view of practical heavy metal decontamination. Accordingly, a systematic study on the thermodynamics of the interaction of TA with protons, reporting data in a standard state (i.e., infinite dilution) and parameters to calculate protonation constants in different ionic media (NaCl, KCl, and $(C_2H_5)_4NI$) at different temperatures and ionic strengths, is here presented. To better understand the TA thermodynamic behaviour, the formation constants and sequestering ability towards Cd^{2+}, Pb^{2+} and Mn^{2+} were determined in a wide range of experimental conditions and also compared to data reported for other chelating agents (citric acid, EDTA, GLDA, EDDS). The assessment of the sequestering ability of a "ligand" towards metals is decisive for remediation processes, chemical treatment of waters (soil washing) and for applications involving the use of a chelating agent.

References

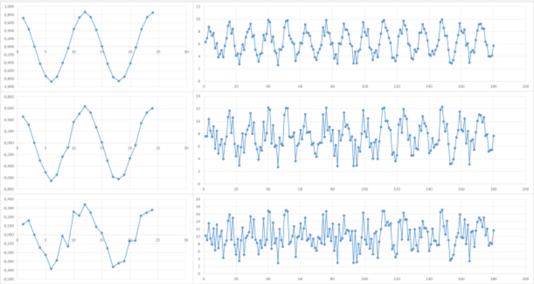
[1] T. Werpy, G. Petersen (2004). Top Value Added Chemicals from Biomass, Volume I: Results from Screening for Potential Candidates from Sugars and Synthesis Gas; Pacific Northwst National Laboratory and the National Renewable Energy Laboratory: Washington, DC, USA, 2004.
[2] A. Kanitkar, G. Aita, L. Madsen (2013) *J. Chem. Technol. Biotechnol*, 88, 2188–2192.

POSTER
(#2)

Potential of Correlograms to Detect and Characterise Autocorrelation in Water Monitoring Data

K. Ilijević[1,*], *B. Milovanović*[1], *J. Orlić* [1]

(1) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia
[*]*kilijevic@chem.bg.ac.rs*



Data autocorrelation is often observed within the values of ecochemical parameters that are continuously monitored as part of environmental monitoring. Its presence significantly complicates statistical data processing, which is necessary to adequately interpret the monitored ecochemical parameters. Therefore, it is very important to determine the presence of autocorrelation, as well as the degree and cause of its presence in the data.

Correlograms are a useful tool for monitoring autocorrelation for several reasons. Their drawing does not require higher levels of statistical knowledge, the interpretation is also relatively simple, and they can provide information not only about the degree of autocorrelation, but also about the causes that led to its appearance in the analyzed data.

The goal of this research is to develop several theoretical models with specific data traits and to explore how they affect shape and values of related correlograms.

Theoretical models combined different levels of data randomness with:

1. linear trend in the data
2. seasonal oscillations
3. discontinuity (which is reflected in a sharp growth in a certain part of the data set).

In addition to these individual factors, it is important to determine how the correlograms are be affected by combinations of the examined factors.

It was observed that each of investigated traits produces specific shape in the correlogram which is noticeable even when tested factors are not easily observed in data by visual inspection.

Correlograms potential to discover autocorrelation was compared with the results of Durbin Watson test which is routinely used for the same reason.

Lastly, correlograms were produced from data base which contained data collected from monitoring program of the Danube River over period of 15 years for several ecochemical parameters: total dry solids, residue after ignition, electroconductivity, suspended matter, COD, BOD-5, UV extinction at 254 nm, dissolved oxygen, oxygen saturation, nitrates, total N, phosphates, total P, ammonia, pH and free carbon-dioxide.

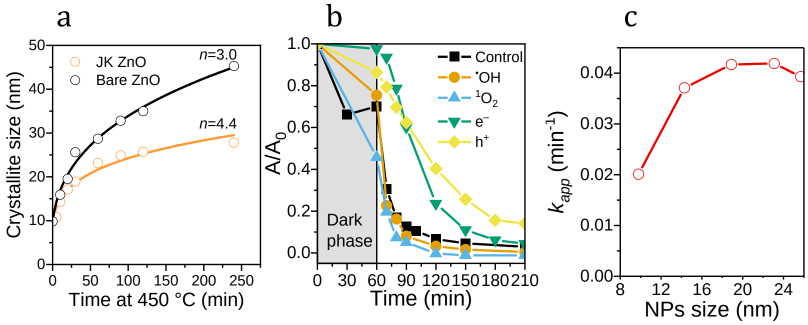
Acknowledgements

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

Synthesis of Zinc Oxide Nanoparticles Using a Japanese Knotweed Root Extract

M. Ravbar[1,], , S. Smole Možina[3], A. Šuligoj[1,2]*

(1) Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia, (2) National Institute of Chemistry, Ljubljana, Slovenia, (3) Biotechnical faculty, University of Ljubljana, Ljubljana, Slovenia
**Miha.Ravbar@fkkt.uni-lj.si*



Due to ever increasing environmental concerns, a lot of research is being done on the topic of photocatalytic degradation of organic pollutants in water [1]. While titanium dioxide is still the most popular of these photocatalysts, increasing amount of research is being directed toward others, such as zinc oxide, which has comparable electronic, physical and chemical properties and a more facile synthesis [2]. Although green synthesis of ZnO nanoparticles (NPs) using different plant extracts has been reported extensively, the attention is usually given to the synthesis route and antimicrobial and photocatalytic properties of NPs [3]. The effect of plant extracts on morphological and electronical properties, and the role plant extracts play in these changes is seldomly reported.

Herein, we synthesized ZnO nanoparticles (NPs) via a facile synthesis using ethanolic extracts from roots of Japanese knotweed (lat. Fallopia japonica). Such NPs were characterized by slower and more controllable crystallite growth upon thermal annealing at 450 °C (Figure a) as well as comparable long-term photocatalytic activity for the degradation of ciprofloxacin. In addition, the modified synthesis route using plant extracts resulted in better antimicrobial activity against both Gram-positive bacteria e.g., *Staphylococcus aureus* and Gram-negative bacteria e.g., *Escherichia coli* and *Campylobacter jejuni*. The materials were further tested for their antimicrobial activity against S. aureus under UV-illumination where, again, the photocatalyst prepared with plant extracts was proven to be superior. The main culprit for the observed differences was identified to be the leftovers of plant extract molecules on the surface of the catalyst and was studied extensively by means of thermal gravimetry coupled with mass spectrometry. For slowing the particle growth, a synergistic effect between different extract components was needed. Furthermore, synergy between the extract and nanoparticles was required for enhanced antimicrobial activity.

Acknowledgements

Slovenian research agency (ARRS) is acknowledged for funding the young researcher program.

References

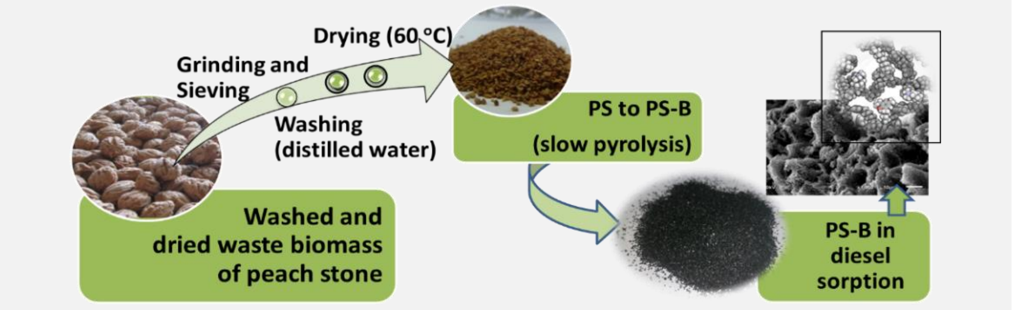
[1] Y. Zhao, Y. Li, L. Sun (2021) *Chemosphere*, 276, 130201.
[2] S. Murgolo, C. De Ceglie, C. Di Iaconi, G. Mascolo (2021) *Curr. Opin. Green Sustain. Chem.*, 30, 100473.
[3] P. Basnet, T. Inakhunbi Chanu, D. Samanta, S. Chatterjee (2018) *J. Photochem. Photobiol. B Biol.*, 183, 201.

Sorption of Diesel from Aqueous Solution on Biochar

J. Avdalović[1], Z. Lopičić[2], S. Miletić[1], S. Spasić[1], N. Lugonja[1], M. Lješević[1], V. Beškoski[3]

(1) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, (2) Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše Deperea 86, Belgrade, Serbia, (3) Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia

*jelena.avdalovic@ihtm.bg.ac.rs



Water contaminated with petroleum hydrocarbons has become a one of the major problems worldwide. Sorption is one the most commonly used technique for treatment of contaminated water. The sorption potential of peach stone biochar (PS-B) as a sorbent for diesel fuel from aqueous solution was explored.

Biochar preparation

Peach stones (Prunus persica L.) were obtained from Juice Factory “Vino Župa” Aleksandrovac, Serbia. The peach stones were washed with tap water in order to remove dirt from its surface, and dried at room temperature. Dried stones were further grinded using vibrating disk mill ”Siebtechnik – TS250” (Siebtechnik GmbH, Germany), and sieved into different particle sizes. For the purposes of these investigations, class between 0.1 to 0.5 mm was used. The ground peach samples (PS) were further pyrolysed at 500 °C under oxygen-limited conditions in Nabertherm 1300 muffle furnace with heating rate of 10 °C min^{-1}, for 1 h. Finally, the obtained biochar (PS-B) was stored in closed vials with polypropylene caps.

Sorption batch experiments

The sorption experiments were performed in batch system with mixing, with a constant amount of sorbent of 0,1 g mixed with 100 ml of water contaminated with diesel at concentrations of 2 mg/L 4 mg/L, 8 mg/L, 12 mg/L and 16 mg/L at 25 °C, and placed at horizontal shaker where the speed was 160 rpm. The solid and liquid phases in all experiments were separated in a centrifuge at 4000 rpm. Finally, diesel concentration in the liquid phase was detected according to SRPS EN ISO 9377-2:2009 method, by gas chromatographic analyses conducted on an Agilent 7890A gas chromatograph.

Ecotoxicity test

Bacterial strain *A. fischeri* NRRL B-11177 (Macherey-Nagel GmbH & Co. KG, and Duren, Germany) was used for the evaluation of acute ecotoxicity of water contaminated with diesel fuel before and after treatment with biochar. The test was performed according to the ISO 11348 standard, using freeze-dried bacteria and BioFix® Lumi-10 (Macherey-Nagel GmbH & Co. KG, Duren, Germany) **[1]** .

Results and conclusions

The application of peach stone biochar (PS-B) resulted in more than 92% removal of diesel in whole concentration range, with equilibrium reaching after 3 h of contact. After sorption process was completed, ecotoxicology tests were conducted using initial and purified water samples. Ecotoxicology tests have shown a decrease of toxicity of contaminated water on *A. fischeri* after the treatment of water by biochar sample. Therefore, these forms of carbon based sorbents have great potential to be good sorbents of diesel and can be successfully applied for their removal in water treatments.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no 451-03-68/2022-14/200026, grant no 451-03-68/2022-14/200023 and grant no 451-03-68/2022-14/200168).

References

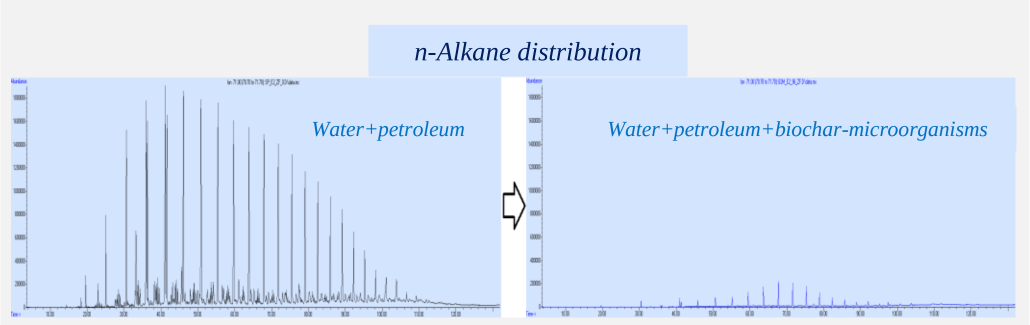
[1] Z. Lopičić, J. Avdalović, J. Milojković, A. Atanasković, M. Lješević, N. Lugonja, T. Šoštarić (2021) *Hemijska Industrija*, 75(6), 329–339.

Sorption and Biosorption of Petroleum Pollutants from Water Samples Using Biochar, Hydrocarbon Degrading Microorganisms and Their Combination

I. Despotović[1], N. Lugonja[2], S. Miletić[2], O. Mašek[3], V. Beškoski[1], B. Jovančićević[1], G. Gajica[2,]*

(1) University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia, (2) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Studentski trg 12-16, Belgrade, Serbia, (3) University of Edinburgh, School of GeoSciences, The King's Buildings EH9 3FF Edinburgh, UK

**gordana.gajica@ihtm.bg.ac.rs*



Petroleum pollutants and organic waste are both important environmental issues. Biochar is a highly complex and heterogenous material consisting of both organic and inorganic compounds obtained by thermal degradation of organic wastes [1, 2]. Using biochar for removal of petroleum pollutants could decrease the environmental impact of both petroleum pollutants and organic waste. Furthermore, immobilising microorganisms on biochar could increase removal trough the effect of biosorption and eventually biodegradation.

The aim of this research was to examine the efficiency of removal of petroleum hydrocarbons using biochar, microbial consortium and their combination. Microorganisms were isolated from soil polluted with hydrocarbons and enriched on media supplemented with diesel, while two biochar samples (made from wheat straw pellets and sewage sludge) were used as adsorbers and carriers for immobilization of these hydrocarbon degrading microorganisms.

The remediation study was performed on water samples prepared in laboratory condition by adding crude oil and minerals into the distilled water. The period of the remediation was 96 days, while the analysis of the removal and degradation of petroleum pollutants was performed every 32 days for each sample.

Measurement of the removal of total petroleum pollutants was followed gravimetrically measuring fraction of extracted soluble organic matter, separated saturated and aromatic fractions of crude oil that remained in water phase. Furthermore, saturated and aromatic fractions were analysed by GC-MS. From the obtained results it can be seen that more than 99% of crude oil was removed from numerous water samples and that microorganisms primarily degrade *n*-alkanes over other groups of compounds.

In further studies, if method effectiveness proven successful, should be tested on real samples and it should be scaled up for industrial purposes.

Acknowledgements

The study was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (451-03-68/2022-14/200168, 451-03-68/2022-14/200026).

References

[1] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok (2014) *Chemosphere*, 99, 19–33.

[2] Biochar for Environmental Management: Science and Technology. J. Lehmann, S. Joseph, 1st. Edition, London (United Kingdom), Routledge Ltd. 2009.

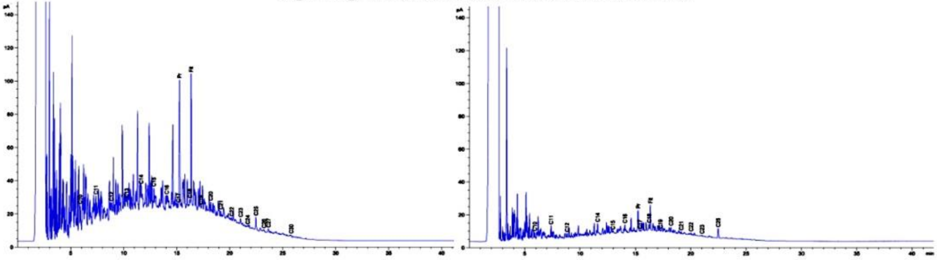
Engineered Bioremediation - Technology of Choice for Treatment of Aquifer Contaminated with Oil Pollutants

S. Miletić[1,*], *J. Avdalović*[2], *S. Spasić*[1], *N.Lugonja*[1], *M. Lukić*[2], *M. Ilić*[1], *M.M. Vrvić*[3]

1) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, (2) Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia (3) BREM GROUP Ltd., Oslobođenja 39b, Belgrade, Serbia

**srdjan.miletic@ihtm.bg.ac.rs*

Gas chromatogram of the total petroleum hydrocarbons extracted from aquifer at the beginning and at the end of *in situ* bioremediation



Aquifers contaminated by petroleum hydrocarbons is a major problem worldwide. During the exploitation, processing, accidental spills, transport, distribution, storage and use of crude oil and its products, these may be released into the hydrosphere in an uncontrolled manner. Bioremediation is a method of reducing petroleum pollution from environment which has been widely used in the last years. Bioremediation is a process which is based on the natural capacity of microorganisms to decompose toxic waste from the environment into harmless products. Engineered bioremediation is a preferable approach because it involves modification of polluted sites at desirable time intervals to accelerate the degradation of contaminants. This modification is achieved by biostimulation (providing nutrients, electron acceptors, biosurfactants, biopolymers, and slow-release fertilizers for increasing the microbial activity) **[1]**, and bioaugmentation (addition of microbial biomass, preferably a consortium, for its greater degradation capacity, synergistic performance, and co-metabolic events)

This paper presents the engineered bioremediation of aquifers contaminated by petroleum hydrocarbons, in the process which lasted for 12 months. The contaminated area was located near the city of Belgrade (Serbia), on the terrace sediments of the Sava River. This remediation treatment was performed within the closed bipolar system (one extraction and two injection wells), with adsorption in the external unit.

In situ engineered bioremediation was started with addition of nutrients from the reservoir through the injection well into the aquifer. Together with nutrients, in order to stimulate chemical oxidation and increase oxygenation of the aquifer, H_2O_2 was added. Finally, zymogenous hydrocarbon-degrading microbial consortia was added via the same injection well **[2]**. The zymogenous consortium of hydrocarbon-degrading microorganisms initially contained $7x10^9$ CFU dm^{-3} microorganisms. Reinoculation with the prepared microbial consortium was performed at 30-day intervals. Recirculation was achieved by extraction of contaminated groundwater using the extraction well followed by filtration through the filtration/adsorption column filled with natural inorganic hydrophobic adsorbents and finally injection to the subsurface through the injection well **[2]**. During water filtration, a biofilm of zymogenous microorganisms was formed on the material of the adsorption column.

During the engineered bioremediation, the content of petroleum hydrocarbon in aquifer decreased by 88% of the initial level. This indicates that the process was performed successfully.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no 451-03-68/2022-14/200026).

References

[1] T. Sayara, A. Sánchez (2020) *Applied Sciences*, 10, 3684.

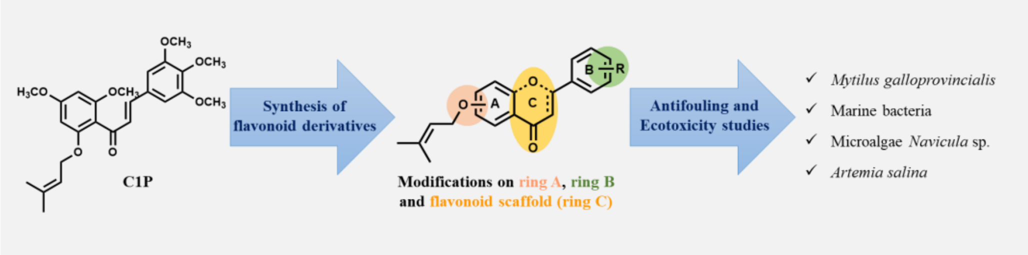
[2] N. Marić, M. Ilić, S. Miletić, G. Gojgić-Cvijović, V. Beškoski, M.M. Vrvić, P. Papić (2015) *Environmental Earth Sciences*, 74, 5211-5219

Potential of Nature-Inspired Prenylated Flavonoids as a Sustainable Alternative to Commercial Biocides Against Marine Biofouling

D. Pereira[1,2,*], *V. Vasconcelos*[2,3], *M. Pinto*[1,2], *J. R. Almeida*[2], *M. Correia-da-Silva*[1,2], *H. Cidade*[1,2]

(1) Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313, Porto, Portugal, (2) CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n 4450-208 Matosinhos, Portugal, (3) Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4069-007 Porto, Portugal

[*] *up200904461@edu.ff.up.pt*



The settlement and accumulation of marine organisms, such as bacteria, diatoms, bryozoans, and mussels on submerged surfaces, known as marine biofouling, causes enormous material and economic losses for maritime industries. Moreover, this phenomenon has ecological implications, since can be detrimental to marine biodiversity. Until recently, the use of tributyltin (TBT) or copper-based substances, were the most useful antifouling solutions. Nevertheless, TBT use was banned due to the toxicity against target and non-target organisms. As an alternative to TBT, the use of copper/zinc and booster biocides in antifouling paints come to be more frequent, however, despite these compounds being less harmful to the environment than TBT, some studies also reported problems of toxicity and accumulation in the marine environment [1,2]. Considering that natural compounds, including flavonoids, have potential activity as antifoulants [3], our research group has been focused on the synthesis and evaluation of antifouling activity of nature-inspired flavonoids [4,5]. From the results of our studies, one prenylated chalcone (C1P) was identified as a promising antifoulant [5]. Based on these results, and in an attempt to develop more effective antifoulants, a series of chemically related flavonoid analogues was prepared and evaluated for the antifouling activity. Then, the antifouling activity was assessed using the *in vivo* anti-settlement bioassay with *Mytilus galloprovincialis* larvae and marine biofouling microorganisms, and some flavonoid derivatives with antifouling activity were identified. Further, ecotoxicity studies were performed in *Artemia salina*, to evaluate their toxicity against non-target marine organisms. With this work, the relevance in obtaining novel nature-inspired compounds, namely flavonoid derivatives, as new non-toxic antifoulants to prevent marine biofouling was reinforced.

Acknowledgements

This research was supported by national funds through FCT (Foundation for Science and Technology) within the scope of UIDB/04423/2020, UIDP/04423/2020, and under the project PTDC/CTA-AMB/0853/2021 by FCT through national funds. D.P. acknowledges FCT for the Ph.D. scholarship (grant number SFRH/BD/147207/2019).

References

[1] P.A. Vinagre, T. Simas, E. Cruz, E. Pinori, J. Svenson (2020) *Journal of Marine Science and Engineering*, 8, 495.

[2] J. Gomez-Banderas (2022) *Frontiers in Marine Science*, 9, 858757.

[3] K.-L. Wang, Z.-R. Dou, G.-F. Gong, H.-F. Li, B. Jiang, Y. Xu (2022) *Marine Drugs*, 20, 90.

[4] J.R. Almeida, M. Correia-da-Silva, E. Sousa, J. Antunes, M. Pinto, V. Vasconcelos, I. Cunha (2017) *Scientific Reports*, 7, 42424.

[5] J.R. Almeida, J. Moreira, D. Pereira, S. Pereira, J. Antunes, A. Palmeira, V. Vasconcelos, M. Pinto, M. Correia-da-Silva, H. Cidade (2018) *Science of The Total Environment*, 643, 98-106.

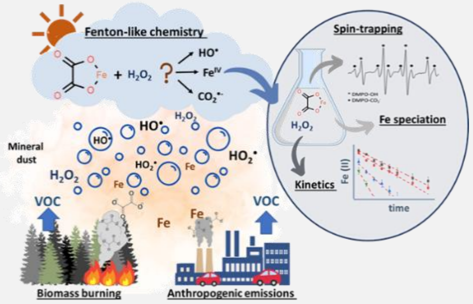
SESSION 3: Atmosphere

ORAL
(#3)

Insights into Fenton-Like Reactions in the Presence of Oxalate Complexes and Implications for the Atmospheric Aqueous Phase

D. Scheres Firak[*], *T. Schaefer, H. Herrmann*

Leibniz Institute for Tropospheric Research (TROPOS), Permoserstraße 15, 04318 Leipzig, Germany
[*]*firak@tropos.de*



Fenton reactions play important roles in atmospheric oxidation cycles and are based on the decomposition of hydrogen peroxide catalyzed by Fe(II). The Fe that participates in these reactions does not occur freely in the aqueous phase due to the presence of organic ligands, which typically originate from the chemical oxidation of volatile organic compounds and incomplete combustion processes [1,2]. Dicarboxylic acids, in special oxalic acid (OXL), have been measured in concentrations of hundreds of ng m^{-3} in urban regions and thousands of ng m^{-3} during biomass burning events [1,3].

Although the ubiquitous presence of Fe complexes in the atmospheric aqueous phase is recognized [3], the resulting Fenton-like mechanisms are not fully understood. Organic ligands can modify the reactivity of Fe towards H_2O_2, and reported rate constants for the Fenton-like reaction in the presence of OXL are in the order of 10^3 and 10^4 L mol^{-1} s^{-1} [4], much higher than those measured in the conventional Fenton reaction (40 to 80 L mol^{-1} s^{-1}) [5]. The mechanisms that lead to the formation of reactive species during Fenton-like processes in the presence of Fe ligands are debatable and involve the formation of $HO^\bullet$, carbon-centered radicals, and higher valence Fe species [4,5].

Herein we report the investigation of the Fenton-like reaction in the presence of Fe-OXL complexes in conditions that are relevant to the atmospheric aqueous phase. Using a modification of the phenanthroline method for the determination of iron in aqueous samples [6] and electron paramagnetic resonance (EPR) spectroscopy, we have observed, for the first time, an increase in the rate constant of the Fenton-like reaction upon successive additions of OXL and a decrease in the formation of $HO^\bullet$.

The rate constants of Fenton-like reactions catalyzed by Fe-OXL complexes increased if compared to the conventional Fenton reaction, particularly at higher pH values, as seen in Table 1. At pH 5, the formation of $HO^\bullet$ decreased by 36% in reactions conducted in a Fe:OXL ratio of 1:3.

Table 1. Second-order rate constants measured for the Fenton-like reactions in the presence of different pH and Fe:OXL ratios.

Fe:OXL	*pH 3*	*pH 4*	*pH 5*
1:0	60 ± 6	59 ± 3	63 ± 7
1:1	65 ± 2	73 ± 5	76 ± 5
1:2	82 ± 6	113 ± 7	117 ± 9
1:3	149 ± 10	318 ± 7	380 ± 44

These results indicate a change in the reaction mechanism that can affect the Fenton-like chemistry happening in the atmospheric aqueous phase, particularly in less acidic conditions usually encountered in cloud systems.

References

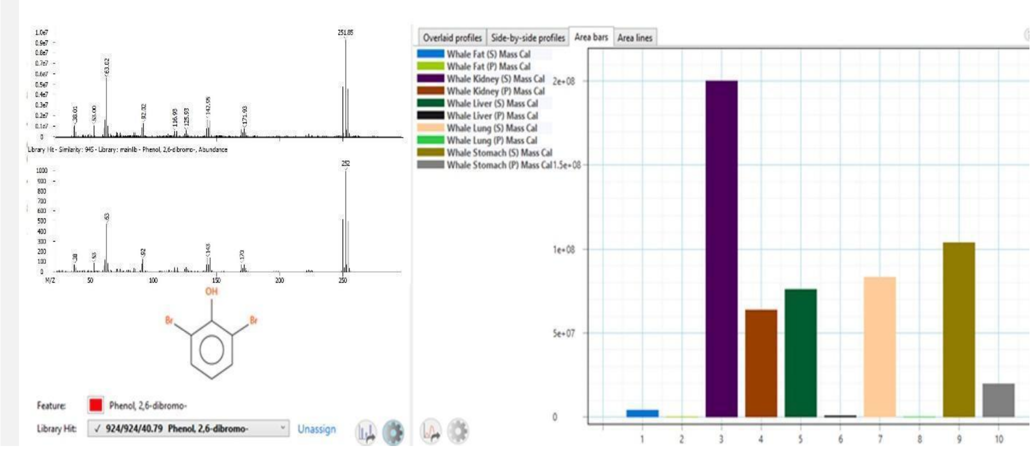
[1] S. Myriokefalitakis et al., (2011) *Atmospheric Chemistry and Physics* 11, 5761–5782.
[2] S. Kundu et al., (2010) *Atmospheric Chemistry and Physics*, 10, 2209-2225.
[3] A. G. González et al (2022) *Science of The Total Environment*, 829, 154642.
[4] J.S.B. Park et al., (1997) *Free Radical Research*, 27, 447–458
[5] J.J Pignatello, E. Oliveros and A. Mackay (2006) *Critical Reviews in Environmental Science and Technology*,36, 1-84.
[6] *Standard methods for the examination of water and wastewater.* APHA. 21st Ed. 2003.

Solving the Mystery of the Chukotka Stinky Gray Whales

O.V. Polyakova[1], O.A. Filatova[2,8,9], I.D. Fedutin[2], D.I. Litovka[3], B. Bukenov[4], V.B. Artaev[5], E.M. Humston-Fulmer[5], J. Binkley[5], D.S. Kosyakov[6], A.T. Lebedev[1,7,]*

(1) Department of Chemistry, Lomonosov Moscow State University; Moscow, Russia, (2) Department of Biology, Lomonosov Moscow State University; Moscow, Russia, (3) ANO "Chukotka Arctic Scientific Center"; Anadyr, Chukotka, Russia, (4) Center of Physical Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University; Almaty, Kazakhstan, (5) LECO Corporation; St. Joseph, MI, USA, (6) Core Facility Center "Arktika", Lomonosov Northern (Arctic) Federal University; Arkhangelsk, Russia, (7) MASSECO d.o.o.; Postojna, Slovenia, (8) Beringia National Park; Provideniya, Chukotka, Russia, (9) Department of Biology, University of Southern Denmark; Odense, Denmark.

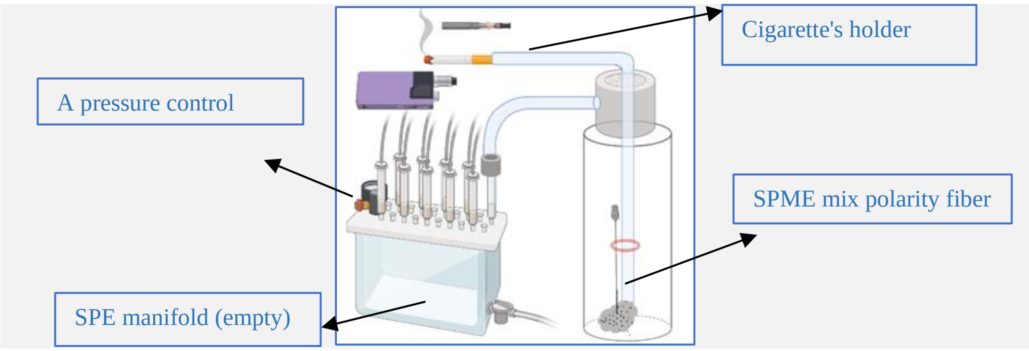
[*]mocehops@gmail.com



Gray whales (*Eschrichtius robustus*) constitute an important part of the diet of Chukotka Native population, reaching 30% of consumed food for the inland Chukchas. Over one hundred licenses for whale hunting are issued on an annual basis. After the USSR collapse natives had to hunt whales near the shore from the small boats. The problem of "stinky" whales arose immediately, as the meat of some harvested species possessed a strong medicinal/chemical odour. The hypotheses explaining the phenomenon ranged from biotoxins[3] to oil spills. To understand the problem, various tissues of normal and stinky Gray whales were collected in 2020-2021 and analyzed using headspace solid phase microextraction with Gas Chromatography – Mass Spectrometry. A prototype software, ChromaTOF Sync (LECO Corporation, USA), was used to process the data for the full set of samples and to find the differences in the composition of organic compounds between the "stinky" and normal whale per tissue type. The obtained results were filtered to leave the analytes with tentative IDs (by similarity score >700 and matching Retention Indices (RI) and that had odor descriptors that may be consistent with a "chemical" smell. 86 smelly organic compounds were identified among over 500 compounds detected. The most interesting analytes related to the off odour are bromophenols. The most probable suspect is 2,6-dibromophenol with strong iodoformic odour, perfectly matching that of the "stinky" whales. Quantitative results demonstrated its levels were up to 500-fold higher in the "stinky" whales´ tissues. The source of 2,6-dibromophenol is likely polychaetes, producing 2,6-dibromophenol and colonising near shore waters where whales feed. Therefore, the mystery of the stinky whales may be considered resolved.

Comparing Smoke and Aerosols from Classic and Electronic Cigarettes, and from »Heat-not-Burn« Devices

B. Poljšak[1], R. Gošnak Dahmane[1], L. Podobnik[2], M. Bavcon Kralj[1,]*
(1) Faculty of Health Sciences, Zdravstvena pot 5, Ljubljana, Slovenia, (2) Knauf Insulation, Trata 32, Škofja Loka, Slovenia
**mojca.kralj@zf.uni-lj.si*



Smoking tobacco and related products is one of the world's major public health problems. The tobacco industry is constantly launching new alternatives to classic cigarettes, such as e-cigarettes and heat-not-burn (HNB) devices, which are claimed to be less harmful to health. The purpose of this research was to develop a method, which will allow a comparison between the identified volatile organic compounds (VOCs) detected in cigarette's smoke, e-cigarette's aerosol and HBN device aerosol.

The use of an empty solid phase extraction (SPE) manifold with a pressure control enabled a constant pulsed puffes. VOCs were retained on a solid phase microextraction (SPME) fibre of mixed polarity and then detected by gas chromatography-mass spectroscopy (GC-MS). A further step was then the toxicological profile of selected VOCs and comparison between the different types of smoking.

A total of 24 chemicals were identified in the samples, 5 of which are classified as hazardous or harmful (nicotine, nicotyrine, toluene, naphthalene, and paraxylene). Most of these substances were found in traditional cigarette smoke and some of them in the vapor from the HNB device. The e-cigarette aerosol was free of harmful chemicals according to the method used. Nicotine, naphthalene, and D-limonene were measured in the smoke of classic cigarettes and in samples from the HNB device. Toluene and paraxylene were measured only in the smoke of classic cigarettes. Glycerol and diglycerol were detected in aerosol samples from e-cigarettes, as well as other compounds such as β-linalool, α-terpineol, glyceryl diacetate, benzyl acetate, persicol, 3-hexen-1-ol, and diethoxydimethylsilane. Newly reported compounds present only in the e-cigarettes aerosol were: β-linalool, α-terpineol, glyceryl diacetate, benzyl acetate, persicol, and 3-hexen-1-ol. Butylated hydroxytoluene (BHT) was the only chemical detected in all samples.

Attempts have been made to assess health risk, but little or no toxicological data are available for most of the identified compounds [1,2]. There are even fewer data on exposure to these compounds by inhalation, a point that has been made elsewhere [3,4]. The health effects assessment was therefore performed only for nicotine, which was measured most frequently in the HNB device aerosol samples, 60% more frequently than in the conventional samples of cigarette smoke. It was calculated that an average smoker exceeds the safe nicotine intake by 43% when using conventional cigarettes and by 275% when using the same heating sticks as in the study. We note that the result depends entirely on the products used and could be different if we used a different brand of cigarette. However, the experimental setup that allows the comparison between completely different smoking types, was finally developed and presented.

Acknowledgements

Slovenian Research Agency, the research core funding No. P3-0388 (Mechanisms of Health Maintenance).

References

[1] C. A. Lerner, /…/ I. Rahman (2015) *PLOS ONE*, 10(2).
[2] S. Munakata, /…/ S. Ito (2018) *Regulatory Toxicology and Pharmacology*, 99, 122–128.
[3] A. Larcombe, /…/ B. Mullins (2021) *Medical Journal of Australia*, 216(1), 27–32.
[4] B. Blount, /…/ J.L. Pirkle (2020) *New England Journal of Medicine*, 382(8), 697–705.

ORAL
(#3)

Air Quality Mobile Monitoring Campaign in Novi Sad Urban Area in Winter and Summer 2022

D. Kleut[1], M. Davidović[2], S. Dmitrašinović[3], M. Živković[1], D. Stojanović[1], M. Budimir[1], I. Lazović[1], M. Jovašević-Stojanović[1], M. Davidović[1,]*

(1) Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Serbia, (2) Faculty of Civil Engineering, University of Belgrade, Serbia, (3) Faculty of Technical Sciences, University of Novi Sad, Serbia

**davidovic@vinca.rs*

The goal of this study is to significantly contribute to solving the problem of low spatial resolution of data on pollution in the form of particles in Novi Sad urban area. Existing (state, regional, local) monitoring networks cannot provide a complete picture of air pollution, primarily due to the limited number of measuring points on a large area of interest.

Campaigns of measuring particulate matter (PM) pollution with TSI particle counters and sizers Nanoscan 3910 and OPS 3330 were conducted during heating and non-heating season in the urban area of Novi Sad, with high temporal resolution at the route of moving vehicle. This experimental design enables analyses of the spatio-temporal variation of PM, including ultrafine particles (UFP), with a high spatial and temporal (at minute and even second) resolution. As a result, zones, periods and scenarios where the highest concentrations of wide range of PM fractions as well as locations with the lowest concentrations of PM were identified.

The results include the assessment of the level and characteristics of daily and weekly mass, number concentration and specific surface area of fractions of ambient particles in the range from 10 nm to 10 μm.

Collected and prepared data are to be further used for the production of high-resolution maps related to respirable particles during a specific season, as well as preliminary maps of particle pollution in the territory of the City of Novi Sad using data available for the area.

All of this contributes to an improved quality of the environment, health and well-being for the citizens of Novi Sad.

Acknowledgements

The researchers acknowledge the funding of the project "*Spatio-temporal variations of the level of respirable particles in the urban area of Novi Sad - mobile monitoring, modelling and creation of high-resolution maps*" (City Administration for Environmental Protection Novi Sad project no. VI-501-2/2021-19в-19), MNTR of Republic of Serbia, project no. 451-03-68/2020- 14/200156, as well as the *VIDIS project* funded by the European Union's Horizon 2020 Research and Innovation programme under grant agreement No 952433.

References

[1] M. Davidović, M. Davidović, S. Dmitrašinović, M. Srećković, M. Jovašević-Stojanović, *ZBORNIK RADOVA, LXVI KONFERENCIJA ETRAN*, Novi Pazar 6 - 9. juna 2022., SSHE 1.2

[2] M. Davidović, Abstracts of Keynote lectures and contributed papers from the *VII International WEBIOPATR Workshop & Conference Particulate Matter: Research and Management*, 1st to 3rd October, 2019.

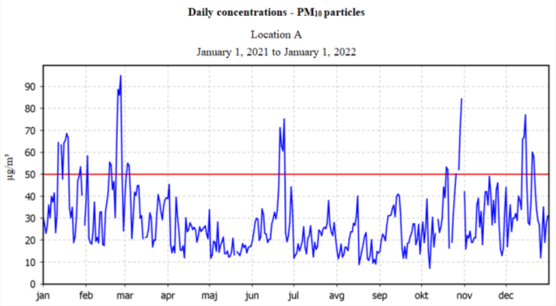
[3] M. Davidović, M. Davidović, M. Jovašević-Stojanović, *Proceedings from the 6th WeBIOPATR Workshop & Conference Belgrade, Serbia*, Belgrade 2019 pp. 175-179 (ISBN: 978-86-7306-152-8)

[4] https://vidis-project.org/index.php/about/vidis-synergistic-projects/novi-sad-mobile-monitoring-project/

Characterization of Atmospheric Aerosols (PM_{10} and $PM_{2.5}$) in the Area of the Republic of Slovenia

M. Ivanovski[1,2,*], *E. M. Barbarič*[3], *E. Marčenko*[2], *K. Alatič*[2], *M. Djurica*[2], *D. Goričanec*[1], *D. Urbancl*[1], *R. Vončina*[2]

(1) University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, (2) Elektroinštitut Milan Vidmar, Ljubljana, Slovenia, (3) University of Maribor, Faculty of Science and Mathematics, Maribor, Slovenia
maja.ivanovski@eimv.si



Air pollution can have a significant effect on human health [1]. Air pollution is defined as contamination of the indoor or outdoor environment by any chemical, physical, or biological agent that modifies the natural characteristics of the atmosphere [2]. In the last decade, it became the second biggest environmental concern after climate change, particularly in urban areas [3]. Air quality changes from day to day, which therefore needs to be properly monitored and analyzed [4]. Aerosols, such as particulate matter (PM10 and PM2.5), are being among the most polluting agents [5], [6]. The main objective of this work is the characterization of the PM10 and PM2.5 aerosol mass in the atmosphere. Firstly, the concentrations of PM10 and PM2.5 in the Republic of Slovenia (RS) were studied and analyzed in the period from 2020 to 2021, later the characterization via WD-XRF occurred. A morphological structural analysis (SEM) was also carried out to identify the probable sources of atmospheric aerosols in the country. Part of results was obtained from the publicly available data. Two monitoring stations (A - urban and B - industrial) were chosen as representatives of Slovenian air quality database. The findings revealed that the difference in concentrations of PM10 and PM2.5 in the studied period is negligible as the levels are still high, especially in winter time, due to domestic heating. The SEM-EDS characterization revealed the presence of heavy metals in PM10 and PM2.5. Cadmium, lead, and mercury elements with anthropogenic and natural origins were identified in the studied samples.

References

[1] S.Y. Kyung, S.H. Jeong (2020) *Tuberc. Respir. Dis. (Seoul),* 83, 2, 116–121.

[2] WHO, "World Health Organization - Air Pollution," 2021.

[3] European Commission, "Roadmap 2050," *Policy*, no. April, pp. 1–9, 2012, doi: 10.2833/10759.

[4] Ö. Zeydan, M. Pekkaya (2021) *Atmos. Pollut. Res.*, 12, 5..

[5] W. Yang, D. Pudasainee, R. Gupta, W. Li, B. Wang, L. Sun (2021) *Fuel Process. Technol.*, 213, 106657.

[6] A. Republike, S.L.O. Venije, "http://www.arso.gov.si/zrak/kakovost%20zraka/poro%c4%8dila%20in%20publikacije/kakovost_letna.html," pp. 1–2, 2011.

POSTER
(#3)

Influence and Contribution of Traffic on $PM_{2.5}$ Concentrations During Four Seasons in Novi Sad

S. Dmitrašinović[1,], J. Radonić[1], M. Davidović[2], M. Jovašević Stojanović[2], M. Turk Sekulić[1], S. Radović[1]*

(1) Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, (2) Vinča Institute of Nuclear Sciences, Mike Petrovića Alasa 12-14, Belgrade, Serbia

[*]dmitrasinovic@uns.ac.rs

Background and Aims

Air quality in Novi Sad is deteriorated by domestic heating and traffic. The aim of this study was to determine the influence of passenger cars and vans (A), lightweight trucks and trucks (B), and buses (C), on fine particle matter concentrations ($PM_{2.5}$) in ambient air during morning (MR), afternoon (AF), evening (EV), and night (NI) of one week in spring (SPR), summer (SUM), autumn (AUT) and winter (WIN) in 2020, as well as traffic emission contributions (EC) to $PM_{2.5}$ concentrations (conc.) during all four seasons.

Data and Study area

$PM_{2.5}$ data have been collected by the National Serbian Environmental Protection Agency (traffic site, TrS) and City Administration for Environmental Protection (background site, BCG). Traffic count data have been collected from traffic counters placed near the TrS.

Results of the study

One-hour $PM_{2.5}$ conc. during one week of SPR, SUM, AUT, and WIN on TrS were within the range from 4.39-28.4, 5.08-27.3, 4.15-48.9, and 6.4-72.7 μg/m^3, respectively. On the BCG site, $PM_{2.5}$ 24 hour conc. during same season order, ranged from 11-16, 6-13, 6-18, and 11-21 μg/m^3, respectively. During each week, correlation (corr.) analysis was conducted between MR, AF, EV, NI $PM_{2.5}$ conc., and A, B, and C vehicle count class. Comparation showed high and very high positive and negative corr. present on certain days during each week of the season, depending on whether it is MR, AF, EV or NI. $PM_{2.5}$/A,B,C corr. were detected usually during MRs, EVs and NIs. In the SPR and SUM, negative $PM_{2.5}$/A,B,C corr. were mostly during MRs, with corr. coefficients (R) from 0.73-0.98, 0.71-0.91 and p-values (p) from <0.001-0.037, 0.001-0.04. Positive $PM_{2.5}$/A,B,C corr. were present during NI with R and p within the intervals 0.9-0.91 and 0.004-0.005, for SPR, and 0.08-0.96 and 0.004-0.005 for SUM. In AUT, positive corr. were present during the most parts of the day, and R and p ranged from 0.95-0.99 and 0.002-0.04 during EVs ($PM_{2.5}$/A,B), and 0.79-0.89 and 0.01-0.09 during NI ($PM_{2.5}$/A,B,C). In the WIN, positive $PM_{2.5}$/A,B,C corr. were during MRs with R and p from 0.78-0.81 and 0.01-0.02, and 0.76-0.85 and 0.02-0.05 during NI. EC to $PM_{2.5}$ from traffic was 5.68, 5.34 and 12.62 μg/m^3 for SUM, AUT and WIN, respectively. SPR $PM_{2.5}$ conc. levels were higher on BCG site than on TrS.

Multiple positive corr. in AUT and WIN during MR, EV and NI showed higher traffic influence on $PM_{2.5}$, but vast corr./no corr. variations could be a consequence of the COVID-19 pandemic. Based on full seasonal data sets and smaller data resolution analysis, $PM_{2.5}$ conc. levels and air quality on typical urban TrS in 2020 were influenced to a small extent by the traffic density in Novi Sad.

Acknowledgments

This research (paper) has been supported by the Ministry of Education, Science and Technological Development through project no. 451-03-68/2020-14/200156 and the City Administration for Environmental Protection Novi Sad through project no. VI-501-2/2021-19в-19.

References

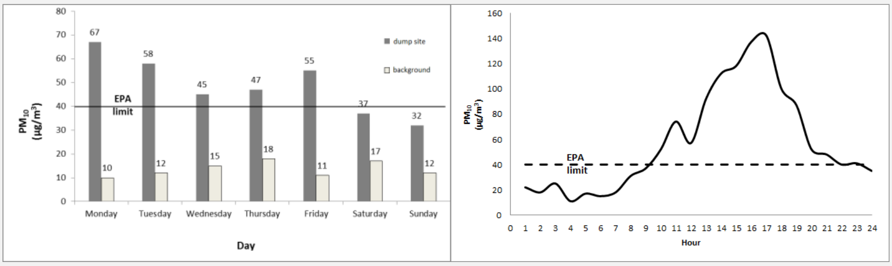
[1] F. Wang, et al. (2010) *Atmospheric Chemistry and Physics*, 10, 2745–2764.

Unregulated Landfills as Sources of PM Emissions

D. Adamović[1,], M. Turk Sekulić[1], J. Radonić[1],S. Adamović[1]*

(1) Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia

[*]draganadamovic@uns.ac.rs



Open dumping of solid waste is a major public health concern and a source of environmental degradation in Serbia and other developing countries. Effective solid waste management (SWM) is a principal challenge in urban areas. Furthermore, living close to landfill sites is a known health threat. Population living and working in the vicinity of solid waste processing and disposal facilities are exposed to environmental health threats [1].

Inappropriate and inefficient handling of waste disposal causes a damaging impact on the environment and human health.

Although landfills generate odor problems, open dumpsites' major health and safety challenges may be the emission of dangerous but odorless gases. These ‘invisible’ gases are also accompanied by visible emissions of dust and airborne particulate matter (PM_{10}). PM_{10} is found in the exhaust fumes of the trucks that transport waste to the landfill and leachate away from the landfill [2]. Dust and PM_{10} emissions are also generated from the movement of trucks and other vehicles that travel on the unpaved access roads to most landfills.

Inhabitants living close to landfill sites show concern due to several hazardous pollutants from landfills. Some other contaminants associated with the deposition of waste in landfills include dust, spare rodents, accidental landfill fires, etc [3].

In the European Union (EU), the roles, goals, and methods of air quality management are determined by EU directive 96/62/EC and the later daughter's directives that describe the objectives for air protection policy and standards for EU member states as well as candidate states, like Serbia, as the platform for air quality assessment. For PM10, the obligatory standards have been established at levels of 40 μg/m^3 (annual limit value for the protection of human health) and 50 μg/m^3 PM_{10}, not to be exceeded more than 35 times within a calendar year (24-h limit value for the protection of human health) [4].

In the current study, the PM10 concentrations in a open dump site are measured, and the importance of different PM_{10} sources are examined. Comparison has been also performed for PM_{10} concentrations in a background site several kilometres away from the dump.

Particulate matter measurements were performed simultaneously on three locations at the open dumping site and at a background location located 1 km away from the site in order to create background reference values for the PM_{10} concentration levels in the general area of the dumping site.

The influence of meteorological parameters on the concentration levels of PM_{10} in the air and the impact of high PM_{10} concentrations at the dumpsite on the immediate environment at the background location were analyzed.

Acknowledgements

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

References

[1] M. Palmiotto, E. Fattore, V. Paiano, G. Celeste, A. Colombo, E. Davoli (2014) *Environ. Int.*

[2] E. Chalvatzaki, T. Glytsos, M. Lazaridis (2015) *Int. J. Environ. Health Res.*

[3] C. U. Okeke, A. Armour (2000) *Appl. Geogr*.

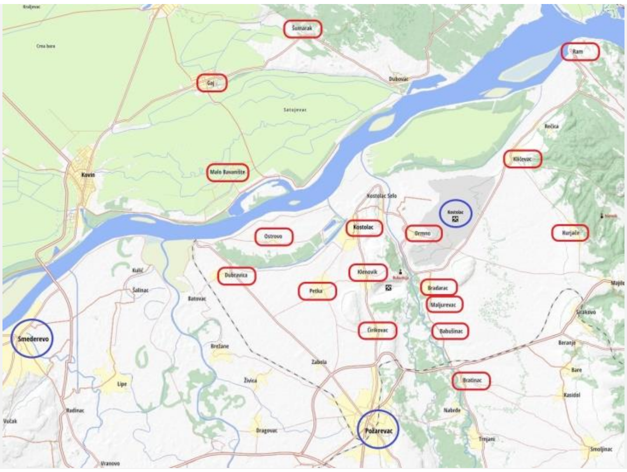
[4] M. Iriti, P. Piscitelli, E. Missoni, A. Miani (2020) *Int. J. Environ. Res. Public Health*.

Road Dust Enrichment of Rare Earth Elements Collected in the Vicinity of the Coal Combustion Power Plant

J. Orlić[1,], N. Zarić[2], M. Aničić Urošević[3], I. Zinicovscaia[4], K. Vergel[4], K. Ilijević[1]*

(1) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia, (2) University of Belgrade - Faculty of Biology, Studentski trg 16, Belgrade, Serbia, (3) Institute of Physics University of Belgrade, Pregrevica 118, Belgrade, Serbia, (4) Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

**jovanaorlic@chem.bg.ac.rs*



Rare earth elements (REE) content in road dust can provide clues to the origin of dust and potential sources of environmentally deleterious materials [1]. Elevated concentration of metals and other pollutants on roads can come from wide range of human activities, such as traffic emission, disintegration of vehicle brakes and tires, wear of road surface, atmospheric deposition, coal combustion, industrial solid waste dissipation and individual heating [2].

Road dust samples which were collected at 17 locations in the coal combustion power plant Kostolac area (mine, power plant, ash disposal site) and near to steel factory "Železara Smederevo", are able to cover all of the aforementioned sources of pollution. In addition to urban sites (Kostolac and Požarevac towns), samples were also collected in rural areas (villages in a 15 km radius). Moreover, dust samples were collected from the main roads, but also from the side roads at each site.

Approximately 0.1 g of the road dust samples (fraction < 63 μm) was pelletized and taken for measurements of long-lived isotopes (Na, K, Sc, Cr, Fe, Co, Ni, Sb, Zn, As, Rb, Sr, Rh, Pd, Pt, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Hf, W, Th, U). The samples were packed in aluminium cups and irradiated for 3 days. Gamma-ray spectra were measured using an HP Ge detector. Instrumental neutron activation analysis (INAA) was performed at the pulsed fast reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia.

For assessment of the REE pollution of road dust and the probable contribution of anthropogenic sources, the enrichment factor (EF) was calculated [3]. To minimize the variations caused by heterogeneous samples, these factors are usually normalized using a reference element (Al or Mn).

Acknowledgements

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

References

[1] T. Kolawole, O. Olatunji, O. Ajibade, C. Oyelami (2021) *Journal of Health & Pollution*, 11(30), 210611.

[2] S. M. Atiemo, F. G. Ofosu, I. J. Kwame Aboh, O.C. Oppon, *John Wiley & Sons*, 41 (2012) 105-110.

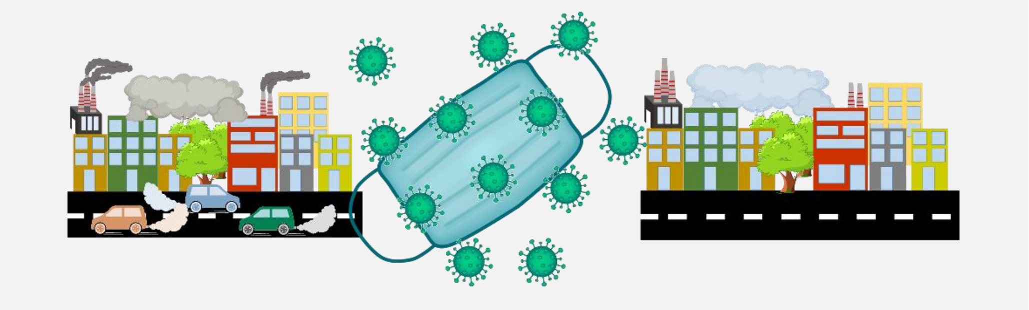
[3] A. Logiewa, · A. Miazgowicz, · K. Krennhuber. · C. Lanzerstorfer (2020) *Archives of Environmental Contamination and Toxicology*, 78, 46-59.

Effects of COVID-19 Lockdown on Particulate Matter and Trace Elements Levels in the Ambient Air of Urban and Rural Location in Extremadura (Spain)

S. Carretero-Peña[1], *L. Calvo-Blazquez*[1,*], *E. Pinilla-Gil*[1]

(1) Departamento de Química Analítica e IACYS, Facultad de Ciencias, Universidad de Extremadura, Avda. de Elvas, s/n, 06006, Badajoz, España

[*]lorcalvo@unex.es



In 2020, the outbreak of the Covid-19 virus triggered a global pandemic, as a result of which a state of lockdown, characterized by restrictions on mobility and productive and human activity, was decreed for the population. Air pollution is closely linked to the three factors indicated through the emission of air pollutants in all of them. Therefore, the main objective of this research is to know the evolution of the concentrations of particulate matter (PM) and trace elements in the ambient air of rural and urban areas of Extremadura during the period of lockdown by Covid-19.

The methodology applied was based on the statistical comparison of the average concentrations of each pollutant obtained in five stations of the Air Quality Surveillance Network of Extremadura (REPICA), corresponding to two defined periods [1]. The lockdown period (LDD, lockdown data) was defined for the data obtained between March 15 and April 30, 2020, and the reference lockdown period (LRD, lockdown reference data) for the data obtained between March 15 and April 30, 2017, 2018 and 2019.

The average levels of PM10 and PM2.5 showed, in general, concentrations during the lockdown period significantly lower than those of the reference lockdown period for all the urban stations analyzed, possibly due to the reduction of emissions from road traffic, as happened in cities such as Madrid and Zaragoza [2], and in many other cities of the world. In the rural station of the Monfragüe National Park, the concentration during the lockdown was lower than in previous years, but not significantly due to the low exposure of the monitoring station to anthropogenic sources.

As for the trace elements, the ambient air levels of As, Cd, Pb, Cu, Mn and V were studied. Among them, the results obtained for Cu stand out, since there was a decrease in its levels during the lockdown to values below detection limit (0.9 ng/m^3) throughout the period, probably related to the reduction of road traffic, especially in suburban stations. There was also a significant decrease in V levels during confinement in all monitoring stations, again related to the decrease in anthropogenic sources associated with traffic (burning of fuels) that took place.

The elements As, Pb and Mn did not follow a clear pattern of variation, presenting levels during confinement that depended on the sampling location. Finally, the Cd did not experience significant variations in any location or PM fraction.

Acknowledgements

We acknowledge support from Junta de Extremadura, Spain (projects GR21076 and IB20081), and the Air Quality Surveillance Network of Extremadura (REPICA) (1855999FD022), all partially financed by European Union Funds for Regional Development (ERDF).

References

[1] M. Cerrato-Alvarez, C. Miró-Rodríguez, E. Pinilla-Gil (2021) *Rev. Int. Contam. Ambient*, 37, 237-247.

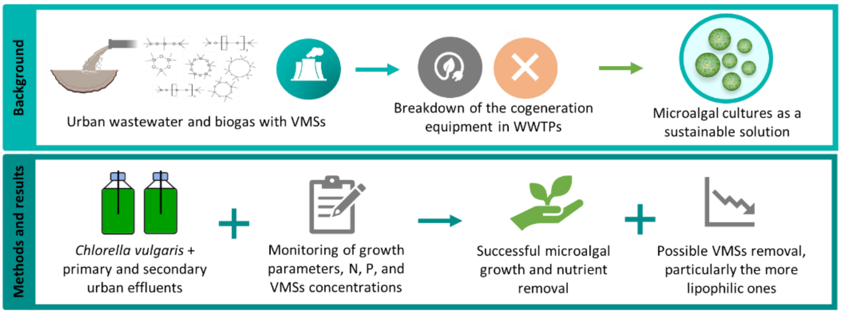
[2] X. Querol, A. Alastuey, T. Moreno, G. Gangoiti, E. Mantilla, J.J. Duéguez, M. Escudero (2021) *Sci. Total Environ.*, 779, 146380.

SESSION 4: Sustainability

Urban Wastewater Treatment and Volatile Methylsiloxanes Removal with Microalgal Cultures

E.M. Salgado[1,2,], A.L. Gonçalves[1,2,3], F. Sánchez-Soberón[1,2], N. Ratola[1,2], J.C.M. Pires[1,2]*

*(1) LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (2) ALICE – Associate Laboratory in Chemical Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (3) CITEVE – Technological Centre for the Textile and Clothing Industries of Portugal, Rua Fernando Mesquita, 2785, 4760-034 Vila Nova de Famalicão; *Correspondence: up201606419@fe.up.pt; Tel.: +351-91-063-2337*



Volatile methylsiloxanes (VMSs) are oligomeric alkyl silicones nowadays considered contaminants of emerging concern (CECs). Due to their ample use in personal care products, these compounds are typically found in wastewaters, ending up in biogas and forming SiO_2 precipitates in its combustion. These particles cause the breakdown of the cogeneration equipment in wastewater treatment plants and decrease the process yield [1]. Biological VMSs removal from wastewaters could be a sustainable solution. Microalgae are a diverse group of photosynthetic microorganisms with a notable potential in secondary and tertiary wastewater treatment since they can remove and/or degrade several pollutants [2]. Hence, this study aims to evaluate the remediation of primary (PE) and secondary (SE) urban effluents and possible VMSs removal using *Chlorella vulgaris* cultures. The following assays were conducted: (i) a positive control with microalgae in modified OECD test medium; (ii) a negative control with PE; (iii) an experiment with microalgae and PE (PE assay); (iv) a negative control with SE; and (v) an assay with microalgae and SE (SE assay). The microalgal growth, nitrogen, phosphorus, and VMSs concentrations were monitored over the course of the experiments. Overall, *C. vulgaris* grew successfully and efficiently removed nitrogen and phosphorus from the effluents, evidencing that these wastewaters can be a suitable culture medium for this microalga. The VMSs concentration was evaluated not only in the effluents but also in the microalgal biomass. Four cyclic VMSs were detected in the effluents and dodecamethylcyclohexasiloxane (D6) was the one that accumulated the most in the microalgal biomass from the PE assay. D6 might have adsorbed onto the surface of *C. vulgaris* to a greater extent due to its physicochemical properties, as it is one of the most lipophilic VMSs, with very low water solubility. Moreover, the results suggest that PE appears to be more adequate for the study of VMSs removal using microalgal cultures. In conclusion, this study confirms the extraordinary potential of microalgae in urban wastewater treatment and indicates a possible removal of certain VMSs, particularly the more lipophilic ones.

Acknowledgements

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE) and UIDB/00511/2020-UIDP/00511/2020 (LEPABE) funded by national funds through FCT/MCTES (PIDDAC); (ii) Project LANSILOT (ref. PTDC/CTA-AMB/32084/2017; POCI-01-0145-FEDER-032084), project PhotoBioValue (ref. PTDC/BTA-BTA/2902/2021), and project HealthyWaters (ref. NORTE-01-0145-FEDER-000069), funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; and (iii) E.M. Salgado thanks FCT for the 2021 PhD Research Scholarship - [2021.07412.BD].

References

[1] G. Wang, Z. Zhang, Z. Hao (2019) *Critical Reviews in Environmental Science and Technology*, 49(24), 2257-2313.

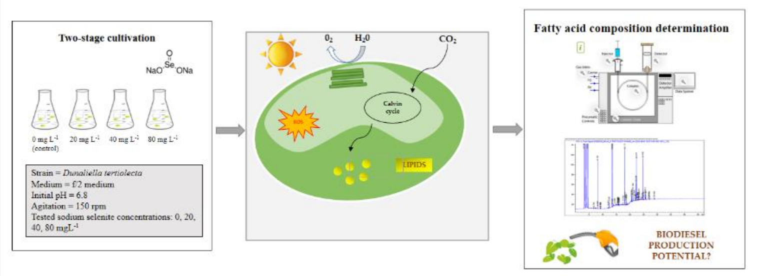
[2] E.M. Salgado, A.L. Gonçalves, F. Sánchez-Soberón, N. Ratola, J.C.M. Pires (2022) *International Journal of Environmental Research and Public Health*, 19, 2634.

ORAL
(#4)

Fatty Acid Profile of *Dunaliella tertiolecta* in response to Different Selenium Concentrations

M. Galić Perečinec[1,2,*], *L. Čižmek*[1,2], *S. Babić*[1,2], *N. Topić Popović*[1,2], *I. Strunjak-Perović*[1,2], *R. Čož-Rakovac*[1,2]

(1) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (2) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia
**mgalic@irb.hr*



Due to the increasing human population and the negative impact of fossil fuel combustion on the environment, there is an ever-increasing need for sustainable energy development [1]. Since microalgae offer several advantages (high growth rate, high oil content, etc), they have been considered as a promising candidate for alternative renewable fuel sources (biodiesel, bioethanol, etc.). The two most important factors affecting biodiesel production, oil content and microalgal fatty acids profile, are highly dependent upon the used microalgae species and cultivation conditions. Furthermore, studies have confirmed the beneficial effect of trace elements (Co, Cr, Mn, Mo, Cu, Fe, Zn) on microalgal growth and lipid content [2].

This research aimed to assess the dependence of total fatty acids content and profile in marine microalgae *Dunaliella tertiolecta* upon exposure to different concentrations of sodium selenite (Se) during two-stage cultivation. Total lipids were determined as total fatty acid methyl esters (FAME) by in-situ transesterification, while the FAME content was determined using gas chromatography [3]. According to the obtained results, the total FAME content of the control treatment group (no Se addition) was approximately 2-fold higher compared to the 20.00, 40.00 and 80.00 mg L^{-1} selenite treatment groups, which can be explained by the excessive exposure time of microalgae cells to Se which leads to a decrease in lipid synthesis. Furthermore, it was reported that in the control medium, γ-linoleic acid (C18:3 (c6, c9, c12) and palmitic acid (C16:0) were present in a higher proportion. Increasing the Se concentration in the culture medium increases the proportion of C16:0, while the proportion of C18:3 (c6, c9,c12) decreases, which indicates that the addition of Se in a culture medium, as a stress factor, contributes to the synthesis of monounsaturated fatty acids (MUFA).

Since highly saturated fatty acids (e.g. C16:0) contribute to the satisfactory value of cetane number and oxidative stability parameters, which represent important biodiesel standards, it can be concluded that the present study reports valuable data regarding the influence of Se on fatty acids content and profile in microalgae *D. tertiolecta* and therefore potentially sustainable biodiesel production.

Acknowledgements

This research was funded by the Croatian Government and the European Union through the European Regional Development Fund—the Competitiveness and Cohesion Operational Programme (KK.01.1.1.01) through the project Bioprospecting of the Adriatic Sea (K.K.01.1.1.01.001) granted to The Scientific Centre of Excellence for Marine Bioprospecting—BioProCro

References

[1] A. Udayan, A.K. Pandey, R. Sirohi, N. Sreekumar, B. I. Sang, S.J. Sim, A. Pandey (2022) *Phytochemistry Reviews*, 1-28.

[2] M.G. Perečinec, S. Babić, L. Čižmek, A. Selmani, N. Topić Popović, M. Dutour Sikirić, R. Čož-Rakovac (2022) *Applied Biochemistry and Biotechnology*, 194(2), 930-949.

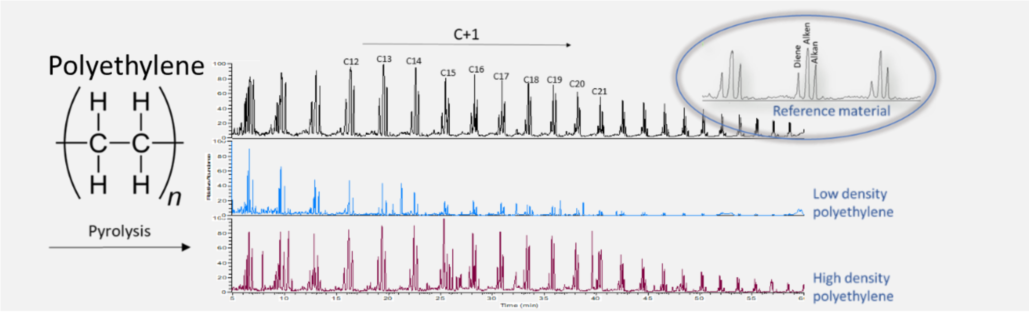
[3] S. Van Wychen, K. Ramirez, K., L.M. Laurens (2016) National Renewable Energy Lab. (NREL), Golden, CO (United States).

Plastic Waste Material as a Sustainable Source of Alternative Fuels and Valuable Chemicals

I. Jovancicevic [1,*], J. Schwarzbauer[1]

Institute for Geology and Geochemistry of Petroleum and Coal, RWTH, Lochnerstr. 4-20, Aachen, Germany

**Ivana.Jovancicevic@emr.rwth-aachen.de*



The use of conventional fossil fuels leads to increasing environmental pollution associated with high emission levels of carbon, nitrogen and sulphur oxides, among other pollutants [1]. Therefore, it is important to consider other renewable resources to reduce the dependence on petroleum-based means.

The demand for plastic production is increasing at an alarming rate every year [2]. Unfortunately, improper dispose of plastic waste makes plastic a major environmental problem [2]. However, considering the high carbon and hydrogen content of these materials, pyrolysis into valuable biofuels could provide a sustainable method for recovering the organic content of plastic waste [3]. Moreover, thermal decomposition could expand the options for plastic waste disposal and in that way protect the environment [3].

This study was conducted to identify optimal experimental conditions for pyrolysis and copyrolysis of plastic waste materials, in order to obtain high quality oil that has the potential to be commercialized as biofuel or as a source for chemical raw materials. Therefore, most abundant polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) or poly(ethylene terephthalate) (PET) as well as corresponding waste material consisting of these polymers were pyrolyzed at different temperatures. For this purpose, an online Curie-Point-Pyrolizer 1040 PSC directly coupled to a gas chromatograph GC 8000 series and a Finnigan Trace Mass Spectrometer as well as an offline MTF 10/15/130 model Carbolite tube furnace were used. However, in order to determine whether co-pyrolysis of these polymers would lead to changes in the chemical composition of individual polymers, four different two-component mixtures of polymers were pyrolyzed at different temperatures (PP:PS; PE:PET; PP:PET; and PE:PS) in the ratios of 1:1, 1:3, and 3:1.

Polyethylene reference material was pyrolyzed to reveal a series of triplets corresponding to alkadienes, alkenes, and alkanes respectively in the order of increasing the carbon number by one. In addition, thermal degradation of polypropylene demonstrated a mainly aliphatic composition of the degradation products, consisting of a number of alkanes and alkenes and a variety of isomers. On the other hand, pyrolysis of polystyrene and polyethylene-terephthalate revealed mainly phenyl-like degradation products such as α-methylstyrene, 1-propenylbenzene, benzaldehyde, vinyl benzoate, etc. However, due to the different types of stabilizers, fillers and pigments contained in the plastic waste, several unknown degradation products were detected during pyrolysis of the corresponding waste material, which are not typical for polymers themselves.

This work covers significant aspects in terms of sustainable development and environmental protection. The results obtained in this work indicated a good potential for synthetic polymers to be used in the petrochemical industry as feedstock for the production of new plastics or refined fuels.

References

[1] A.S. Nizami, M. Rehan, M. Waqas, M. Naqvi, O. Ouda, K. Shahzad, R. Miandad, M.Z. Khan, M. Syamsiro, I. Ismail, D. Pant (2017) *Bioresource technology*, 241, 1101–1117.

[2] D.S. Achilias, C. Roupakias, P. Megalokonomos, A.A. Lappas, E.V. Antonakou (2007) *Journal of Hazardous Materials*, 149 (3), 536-542.

[3] L. Zhang, Z. Bao, S. Xia, Q. Lu, K.B. Walters, (2018) *Catalysts*, 8, 659.

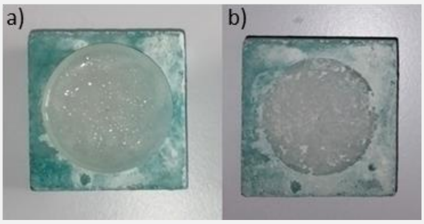
ORAL
(#4)

Development of Ionic Liquid Based Hydrogels for Iron and Cooper Metallic Patinas on Stone Surfaces

P. Irizar[1,], O. Gomez-Laserna[1], I. Martínez-Arkarazo[1], G. Arana[1], J. M. Madariaga[1]*

(1) Department of Analytical Chemistry, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, E-48080, Leioa, Bizkaia, Spain

[*] Pablo.irizar@ehu.eus



a) Hydrogel loaded with ionic liquids application over a marble surface affected by a cooper patina. b) Result of the clean-up process.

Over time, stone materials with metallic artefacts or structures tend to develop chromatic alterations as a result of the environmental stressors attack, mainly when they are regularly exposed to acid rain. The lixiviation and oxidation processes suffered by the metallic composition generate degradation compounds, oxides and salts, which cause a non-aesthetic metallic patina over all the stone matrix where the metals are placed. In addition to this, biodeterioration factors can affect to stone materials and cause colour changes on the surface as consequence of the growth of different kind of bacteria and fungus. In both cases, the patinas not only produce aesthetic changes but are also the beginning of much more serious stone pathologies. With the purpose of developing cleaning procedures that prevent long-term damage, different acids like citric acid or EDTA in solid supports like agarose [1] and cellulose have been previously used to perform metal extractions from stone surfaces. Unfortunately, these treatments have the potential to leave microscopic damages in the stone, especially if it has an alkaline nature. However, new technologies based on Ionic liquids (ILs) have recently demonstrated impressive capabilities to dissolve and extract metals on liquid-liquid exchanges, in addition to its biocidal potential [2].

Accordingly, in this work, different ILs were embedded into agarose hydrogels as the extracting component for patina clean up processes. Concretely, bis (2-ethylhexyl) phosphate and a mixture of methyltrioctylammonium chloride and trihexyltetradecylphosphonium [3], at different concentrations, with the aim to develop a multifunctional product that can effectively clean up copper and iron patinas from stone materials and also prevent further biological deterioration thanks to their inherent biocidal properties.

For this purpose, iron and cooper patinas were generated on white calcite marble test samples by spraying artificial acidic rain over CorTen steel and bronze pieces. The lixiviates were allowed to precipitate on the stone surface generating the characteristic ocre and green patinas, respectively. For the assessment of the clean-up process, inductively coupled plasma mass spectrometry (ICP-MS) analysis of the hydrogel applied and energy dispersive μ-X-Ray fluorescence imaging studies of the stone surface, pre- and post-treatment, were used to examine the elemental sequestration ability of each hydrogel developed. Additionally, an innovative Raman imaging study was used for the most promising formulations in order to characterize the patinas and find out, quantitatively, the cleaning effectiveness according to the specific molecular composition, thanks to the applications of chemometric models based on direct classical least squares (DCLS).

Finally, the hydrogels were tested on outdoor naturally formed patinas and CIE Lab colorimetric measurements were used to evaluate the clean-up effectiveness.

Acknowledgements

This work has been financially supported by the project DEMORA (PID2020-113391GB-I00) from the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) and by the European Regional Development Fund (FEDER). P. Irizar gratefully acknowledges his predoctoral grant from the MINECO (PRE2018-085888).

References

[1] N. Prieto-Taboada, C. Isca, I. Martínez-Arkarazo, et al. (2014) *Environ. Sci. Pollut. Res.*, 21, 12518–12529

[2] J. N. Pendleton, B. F. Gilmore, (2015) *Int. J. Antimicrob. Agents*, 46, (2) 131-139

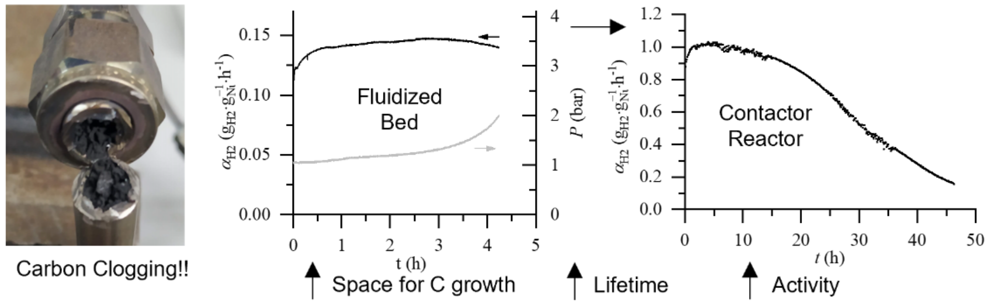
[3] G. Lando, O. Gomez-Laserna, E. Proverbio, et al. (2021) *Environ. Sci. Pollut Res.*, 28, 51072–51087 .

New Reactor Approach for Low-Temperature Catalytic Methane Decomposition

V. Pereira[1,2,*], *L. Alves*[1,2], *P. Dias*[1,2], *F. Pereira*[2,3], *T. Lagarteira*[1,2], *A. Mendes*[1,2]

(1) LEPABE - Laboratory for Process Engineering, Environmental, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, (2) ALiCE – Associated Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, (3) LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[*]up201305593@fe.up.pt



Hydrogen is expected to be a key energy carrier in the current energy transition and catalytic methane decomposition (CMD) at low temperature (500 – 650 ºC) can make it smoother and swifter, compared to water electrolysis. Hydrogen produced from CMD is also CO_x-free, less energy demanding and can use the current natural gas infrastructure, making it much more economically attractive [1]. So far, catalyst deactivation, reactor clogging, and pressure build-up have hindered the stability and long-term operation of standard reactors, requiring the development of alternative designs. The present work proposes the application of the catalyst over a porous slab, as a contactor reactor, which allow methane to reach catalyst active sites and provide sufficient space for carbon growth before this causes irreversible clogging [2].

CMD was tested in different reactor configurations at 550 °C. A commercial Ni/SiO_2-Al_2O_3 catalyst (Sigma Aldrich) was used in all experiments. Fixed and fluidized bed reactors were run for 35 min and 4 h, respectively, at *ca.* 0.15 $g_{H2}\cdot g_{Ni}^{-1}\cdot h^{-1}$. Carbon clogging caused rapid defluidization and pressure build-up, which ultimately rendered these reactors unviable. Alternatively, a wall-coated reactor was developed by dip-coating the inner walls of a tubular steel reactor. Here, the operation was extended to 11.5 h with a similar activity. However, carbon growth caused inevitable pressure build-up. The best performing reactor, equipped with an alumina tubular porous support, was prepared by dip coating and showed a stability of *ca.* 45 h, with a maximum activity of 1 $g_{H2}\cdot g_{Ni}^{-1}\cdot h^{-1}$ and no signs of clogging.

Contactor reactors equipped with porous slab supports or equivalent, showed remarkable improvements compared to the traditional reactors for long term CMD. Additionally, they present easy scalability and further developments can be implemented such as cyclic carbon removal or regeneration of the catalyst.

Acknowledgements

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), UIDB/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). The authors acknowledge the European Commission through the European Union's Horizon 2020 programme - FET Proactive research and innovation action - under grant agreement No. 952219 (112CO2). Vítor Pereira, Luís Alves and Paula Dias acknowledge the Portuguese Foundation of Science and Technology (FCT) support for their grants SFRH/BD/143218/2019, 2020.10008.BD and CEECIND/02862/2018, respectively.

References

[1] L. Alves, V. Pereira, T. Lagarteira, A. Mendes (2021) *Renew. Sustain. Energy Rev.*, 137, 110465.

[2] Westermann T, Melin T (2009) Chem Eng Process Process Intensif, 48, 17-28

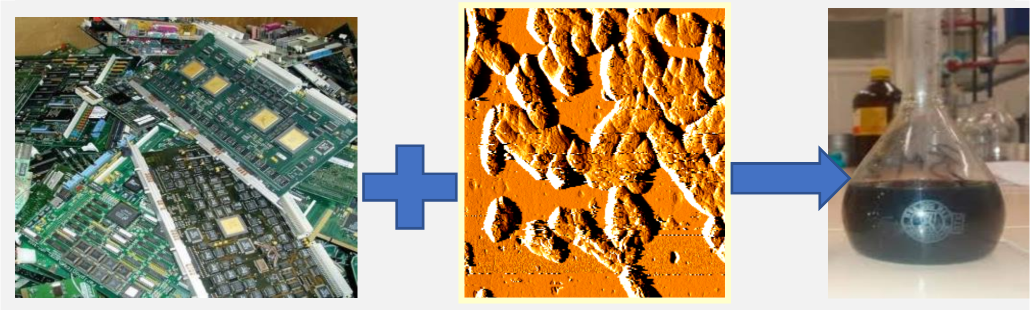
POSTER
(#4)

Biohydrometallurgical Methods for Cobal and Nickel Recovery from Printed PC Motherboard

J. Avdalović[1,*], S. Miletić[1], S. Spasić[1], N. Lugonja[1], B. Dojćinović[1], J. Milić[1], V. Conić[3]

(1) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, (2) Mining and Metallurgy Institute Bor, Zeleni bulevar 35, Bor, Serbia

[*]jelena.avdalovic@ihtm.bg.ac.rs



E-waste is one of the fastest growing waste. E-waste contains lots of valuable resources together with plenty of heavy metals and hazardous materials, which are considered both an attractive polymetallic secondary source and an environmental contaminant. Therefore, recycle of valuable metallic from them are necessary and compulsory in many developed/developing countries [1].

The aim of our study was to investigate the potential of using the *Acidithiobacillus* sp. B2, to recovery Co and Ni from printed PC motherboard.

Methodology

Chemical analysis of electronic waste and pyrite

The electronic waste (after separating of the plastic parts) and pyrite were pulverized and sieved through a 63 μm stainless steel sieve in preparation for chemical and leaching studies.

Electronic waste preparation for the leaching experiment

The presence of alkali components in electronic waste is considered inconvenient for the reaction between the electronic waste and the acidic iron(III) sulphate solution. Hence, it is necessary to neutralize the electronic waste before adding the bacterial culture which would generate the oxidant. Before the leaching experiment, electronic waste was dispersed in 0.05 M H_2SO_4 solution, shaken for 48 h, filtered from the solution, washed out with deionized water and dried at 110 °C [2].

Leaching experiments

The leaching experiments were carried out with bacterium *Acidithiobacillus* sp. B2. Experimental conditions were: leaching period of 20 d, 50 ml leaching solution (g/dm^3): $FeSO_4 \times 7H_2O$ (44.8) $(NH_4)_2SO_4$ (3), K_2HPO_4 (0.5), $MgSO_4 \times 7H_2O$(0.5), KCl (0.1), $Ca(NO_3)_2$ (0.01), at a pH of 2.5 in 150 mL Erlenmeyer flasks at a pulp density of 10% (m/V) (5 g leaching substrate in 50 ml solution). The pH of the leaching solution was maintained at a constant value during the leaching process. The initial number of microogranisms was 10^9 per mL, determined by the Most Probable Number method. The control suspension had the same chemical content and pH value as the suspension with *Acidithiobacillus* sp. B2 but the *Acidithiobacillus* sp. B2 culture had been inactivated by sterilization. The study was realized on a horizontal shaker. The incubation temperature was 28 °C [2].

Results and conclusions

The results of the effective metal leaching (calculated by subtraction of percentage metal leaching in the control suspension from that in the *Acidithiobacillus* sp. B2 suspension) are as follows: Ni(36%)>Co(15%). E-waste recycling will be a very important sector in the near future from economic and environmental perspectives. Recycling technology must ensure that e-waste is processed in an environmentally friendly manner. Authors feel that biohydrometallurgical method will be a key player in the metal recovery.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant no. 451-03-9/2022-14/200026 and Grant no. 451-03-68/2022-14/ 200052).

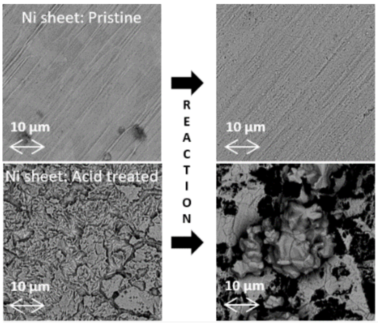
References

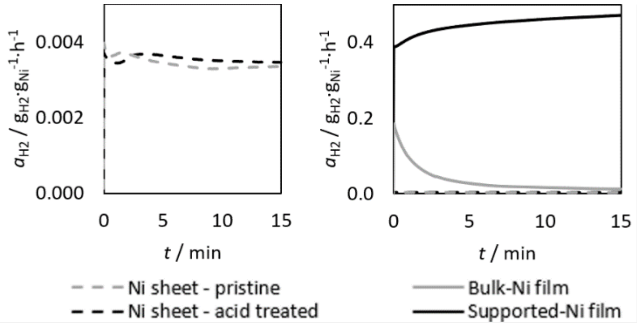
[1] M. Kaya (2016) *Waste Management*, 57, 64-90.
[2] J. Jekić, V. Beškoski, G. Gojgić-Cvijović, M. Grbavčić, M.M. Vrvić (2007) *Journal of the Serbian Chemical Society*, 72, 615-619.

The Role of Ni Film Structure on Catalytic Methane Decomposition

L. Alves[1,2,*], *V. Pereira*[1,2], *T. Lagarteira*[1,2], *P. Dias*[1,2], *G. Prieto*[3], *A. Mendes*[1,2]

(1) LEPABE - Laboratory for Process Engineering, Environmental, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, (2) ALiCE – Associated Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, (3) ITQ - Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Av. Los Naranjos, s/n, 46022 Valencia, Spain
**up201404142@fe.up.pt*





Catalytic methane decomposition can produce cost competitive H_2, from methane, while avoiding direct emissions of CO_2 [1]. This technology may revolutionize the energy sector, promoting a swift transition from carbon-based to hydrogen-based energy. However, methane decomposition is currently hindered by catalyst deactivation and clogging of catalyst beds, in conventional reactor designs, requiring research on alternative catalytic systems. Catalytic films, typically used in membrane reactors, are one of such alternatives [2]. In this work, methane decomposition was promoted by catalytic Ni-based films, namely, dense Ni sheets, bulk-Ni porous film and SiO_2-Al_2O_3-supported Ni porous film. It was demonstrated that the Ni sheet has very low H_2 production activity, a_{H2}, which can be attributed to its low specific area. Hence, a similar sheet was treated in *aqua regia* for 12 h to increase surface area and the dispersion of active sites. However, no significant differences on a_{H2} were observed. Severe sintering caused the treated surface to form large agglomerates with very low specific area. Consequently, the use of Ni sheets under these conditions was found ineffective to promote methane decomposition reaction. The fabrication of catalytic films was also considered, through the dip-coating of catalytic powders on porous tubular α-Al_2O_3 substrates. NiO powder was deposited and then reduced *in situ* to bulk-Ni. This catalytic film displayed higher a_{H2}, when compared to the Ni sheets, but the conversion decreased at a fast rate, due to carbon formation over the catalyst active sites. As supported Ni nanoparticles are known to be both more active and stable than bulk-Ni [3], a new film was prepared by dip-coating the substrate with nanoparticles of Ni/SiO_2-Al_2O_3. The Ni/SiO_2-Al_2O_3 film almost doubled the initial activity, when compared to bulk-Ni, and proved to be stable for more than 30 h (>0.4 $g_{H2} \cdot g_{Ni}^{-1} \cdot h^{-1}$). To the best knowledge of the authors, this result outperforms most of those reported in the literature, while being easily scalable and enabling easy carbon removal [2]. Even so, carbon was grown through the porous matrix of both the bulk-Ni and supported-Ni films, affecting the mechanical integrity of the films as the reaction progressed. Further work on this type of systems should be performed to address this issue and increase the industrial prospects of the technology.

Acknowledgements

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC). The authors acknowledge the European Commission through the European Union's Horizon 2020 programme - FET Proactive research and innovation action - under grant agreement No. 952219 (112CO2). Luís Alves, Vítor Pereira and Paula Dias acknowledge FCT support for their grants 2020.10008.BD, SFRH/BD/143218/2019 and CEECIND/02862/2018.

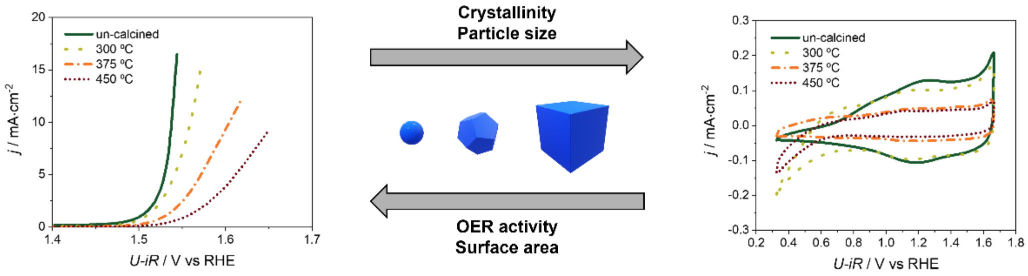
References

[1] B. Parkinson, P. Balcombe, J. Speirs, A. Hawkes, K. Hellgardt (2019) *Energy Environ. Sci.*, 12, 19-40.
[2] L. Alves, V. Pereira, T. Lagarteira, A. Mendes (2021) *Renew. Sustain. Energy Rev.*, 137, 110465.
[3] A. Gili, L. Schlicker, M. Bekheet, O. Görke, D. Kober, U. Simon, et al. (2019) *ACS Catal*. 9, 6999-7011.

Effect of Calcination Step in the Activity of Ir/M-SnO_2 Catalysts for PEM Technology

R. Marques[1,2], S. Delgado[1,2], L. Alves[1,2,], T. Lagarteira[1,2], T. Lopes[1,2], A. Mendes[1,2]*

*(1) LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (2) ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal *up201404142@fe.up.pt*



PEM electrolysis is considered a promising route to produce high-purity green hydrogen, which is expected to be a key technology for the swift transition to a carbon-neutral economy. However, for practical implementation, anode catalysts must be improved towards providing high activity with less amount of precious group metals (PGMs) [1].

Iridium oxide is the state-of-the-art catalyst for conducting the oxygen evolution reaction (OER). To decrease the Ir loading, an interesting strategy is to disperse Ir particles on electrical conductive supports that can lead to smaller average particle size and subsequently higher OER mass-specific activity. Doped tin oxides (M-SnO_2) are noteworthy electrocatalyst support candidates due to their high electrical conductivity and corrosion resistance [2].

The polyol method has been widely reported as a low-cost and easily scalable technique to produce Ir-supported catalysts. However, few studies report the influence of a calcination step after the synthesis. Since this step can deeply influence the catalyst morphology, it is critical to evaluate the impact of a heat-treatment procedure on OER activity [3].

In this work, iridium particles were supported in antimony-doped tin oxide (SnO_2:Sb_2O_5 – ATO) and indium-doped tin oxide (SnO_2:In_2O_3 – ITO) via polyol method. Subsequently, the catalysts were subjected to a calcination step at different temperatures (300 ºC, 375 ºC and 450 ºC) for 3 h.

Electrochemical results show that as the calcination temperature increases, the overall catalytic performance decreases. This can be related to the sintering and crystallisation of Ir particles, which leads to a drop in measured current density and a severe decrease in the electrochemical active area, particularly for the samples calcined above 300 ºC.

Therefore, the best OER activity and Ir utilisation was accomplished with the lowest calcination temperature (300 ºC), which is assigned to amorphous Ir particles. As future work, calcination step at lower temperatures (below 300 ºC) is envisioned. Additionally, the application of the calcination step to the supports before adding the iridium should also be studied.

Acknowledgements

This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); project Baterias 2030, with the reference POCI-01-0247-FEDER-046109, co-funded by Operational Programme for Competitiveness and Internationalisation (COMPETE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). R. Marques, S. Delgado and L. Alves are grateful to the Portuguese Foundation for Science and Technology (FCT) for the doctoral grants (refs. 2021.06496.BD, SFRH/BD/144338/2019 and 2020.10008.BD, respectively).

References

[1] S. Kumar, et al. (2019) *Mater. Sci. Technol.*, 2(3), 442-454.
[2] H. Ohno, et al. (2018) *Catalysts*, 9(1), 74.
[3] F. Karimi, et al. (2017) *J. Electrochem. Soc.*, 164(4), F464-F474.

Synthesis of Iodine monochloride Using a Chlorine Solution in Glacial acetic acid with Simultaneous Disinfectant Generation

N. Radović[1,], K. Stojanović[1], S. Savić[1]*

(1) University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia
[*]nradovic@chem.bg.ac.rs

Iodine monochloride is an interhalogen compound that acts as an iodinating reagent for aromatic compounds, a halogenating agent for unsaturated compounds and for cleavage of carbon-metal bonds [1]. The direct synthesis of solid iodine monochloride from elements is a very hazardous procedure in the laboratory due to the high toxicity of chlorine and iodine.

In this paper, a safer method for obtaining a solution of iodine monochloride in glacial acetic acid, which is used as a reagent for determination of the iodine value of fats and oils, is presented. Laboratory preparation of iodine monochloride solution in glacial acetic acid is described in AOAC Official Method 993.20 - Iodine Value of Fats and Oils [2]: chlorine gas passes through the iodine solution in acetic acid until a change in the colour of the solution is observed. If excess of chlorine is present in the resultant solution, it must be neutralised by adding of iodine solution in acetic acid. The main disadvantage of this method is the barely noticeable change in colour from brown to reddish brown and the lack of a procedure for the safe removal of chlorine excess after preparing the reagent. Considering the fact that chlorine gas is soluble in glacial acetic acid [3], we have overcome the mentioned deficiencies of AOAC Official Method 993.20 by introducing chlorine gas into the glacial acetic acid at 298K. The figure shows the process to obtain a chlorine solution in glacial acetic acid. The necessary volume of concentrated hydrochloric acid is added to the solid potassium permanganate in the reactor vessel (A) and the container is immediately closed. Chlorine gas is released, which flows through concentrated sulphuric acid (B) to remove moisture. After that, the chlorine is introduced into a vessel filled with glacial acetic acid (C). The excess chlorine is then dissolved in a 10% (w/v) sodium hydroxide solution (D) to produce a mixture of sodium hypochlorite and sodium hydroxide, which requires dilution with an appropriate volume of water to obtain an alkaline hypochlorite solution, which has strong disinfectant properties [4].

The chlorine content in the glacial acetic acid solution is determined by iodometric titration [5]; the same technique is used for determining the hypochlorite content after absorbing the excess chlorine in the sodium hydroxide solution. The final solution of iodine monochloride is prepared simply by adding a calculated volume of chlorine solution in glacial acetic acid to a specified volume of iodine in the same solvent. The results of our study demonstrate that the reaction of 0.12 mol potassium permanganate with 80 cm^3 concentrated hydrochloric acid produce 200 cm^3 of 0.85 mol/dm^3 chlorine solution in glacial acetic acid and 250 cm^3 of 0.34 mol/dm^3 alkali sodium hypochlorite solution. This amount of chlorine solution in glacial acetic acid is sufficient to prepare approximately 3 dm^3 of 0.1 mol/ dm^3 iodine monochloride solution in the same solvent.

Acknowledgements

This study was financed by the Ministry of Education, Science and Technological Development of Republic of Serbia (Contract number: 451-03-68/2022-14/200168).

References

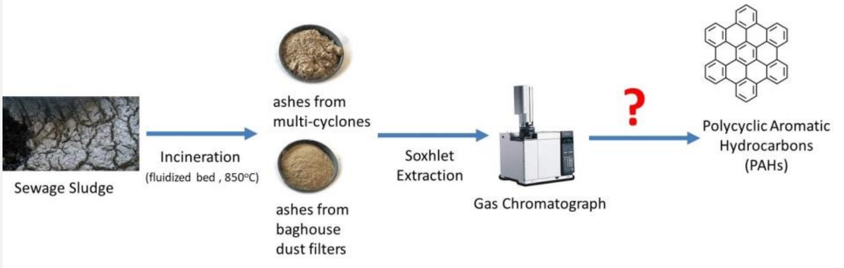
[1] R.G. Brisbois, R.A. Wanke, K.A. Stubbs, R.V. Stick, U. Ellervik, in Encyclopedia of Reagents for Organic Synthesis, A. Charette, T. Rovis, J. Bode (Eds.), New York (USA), Wiley, 2013, 1-6.
[2] Official Methods of Analysis of AOAC International. W. Horwitz, 17. Edition, Gaithersburg (USA), AOAC International, 2000, Chapter 41, 7-9.
[3] Solubility Data Series, Volume 12. C. Young (Ed.), Exeter (GB), IUPAC, 1983, 386-387.
[4] S. Fukuzaki (2006) *Biocontrol Science*, 11, 147-157.
[5] Quantitative Analytical Chemistry. D. C. Harris, 8. Edition, New York (USA), W.H. Freeman & Company, 2010, 351-356.

Determination of PAHs in Flying Ashes from Multi-cyclones and Baghouse Dust Filters

I. Gevinc[1], G. Salihoglu[1], D. Mazur[2], R. Gošnak Dahmane[3], P. Trebše[3,]*

(1) Bursa Uludag University, Faculty of Engineering, Environmental Engineering Department, Bursa, Turkey, (2) Moscow State University, Chemistry Department, Moscow, Russia (3) University of Ljubljana, Faculty of Health Sciences, Zdravstvena pot 5, Ljubljana, Slovenia

[*]polonca.trebse@zf.uni-lj.si



Sewage sludge, a semi-solid material, is an inevitable residue of wastewater treatment process. It is generated in large amounts. The total amount of sewage sludge generated by 27 EU countries ranged between 2852 and 7844 tons of dry matter (DM), while the mean level was 5680 ± 1231 tons of DM, between years 2006 and 2017 [1]. Mean specific sludge production is estimated to be 21.9 kg/population equivalent/year in the European Union (EU) [2]. Incineration is a commonly preferred method in sewage sludge management because of its high volume reduction capacity. However, a waste, namely sludge ash is being generated in considerable amounts as a result of incineration.

Most of the studies on sewage sludge have focused on heavy metal residue, so there are not many studies about organic pollutants, such as polychlorinated dioxins, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and others. Sewage sludge pollution due to PAHs is quite common [3]. PAHs are hydrophobic and can easily be removed from sewage and absorbed by solid particles during the activated sludge treatment process of wastewater. The EU has enacted legislation controlling the total concentration of PAHs in sewage sludge for agriculture use. According to this protocol the concentration should not exceed 6.0 mg/kg.

In this study, two types of sewage sludge incineration ashes from multi-cyclones and baghouse dust filters have been investigated in order to identify the levels of PAHs.

Sewage sludge incineration ashes were obtained from the fluidized bed incinerator (>850°C) plant of Bursa city, which has a capacity to incinerate 400 tons dry matter sludge/day. The sewage sludge that the plant incinerates is the end product of Bardenpho process.

For the extraction of fly ash sample, Soxhlet extraction was used. The extraction solvent used was mixture of acetone and hexane (1:1). Sample of fly ash (10 g) was placed into extraction thimble, covered with cotton and left for boiling. Period of the experiment was 3 days, 6 hours/day with 6 cycles/hour. The extraction mixture was evaporated, then 2 mL of CH_2Cl_2 was added and filtered through 45 um filter for GC-MS analysis.

The extracts were analyzed with with Pegasus® GC-HRT$^+$ 4D high resolution time-of-flight mass-spectrometer (LECO Corporation) coupled to gas chromatograph Agilent 7890A (Agilent Technologies). Identification and quantification of PAHs was done using standard mixture of PAHs (Restek) and naphthalene-D8 as internal standard.

The results have shown the presence of acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene in the case of bag filter, and additionally naphthalene in the case of multi-cyclon filter ash.

References

[1] EUROSTAT, 2020. Sewage sludge production and disposal from urban wastewater. In: Comission, E. (Ed.). https://ec.europa.eu/eurostat/databrowser/view/TEN00030/default/table, Luxembourg.

[2] A. Kelessidis, A.S. Stasinakis (2012) *Waste Manage*, 32(6):1186–1195.

[3] D. Bodzek, B. Janoszka, C. Dobosz, L.Warsecha, M.Bodzek (1997) *Journal of Chromatography A*, 774 (1-2), 177-192.

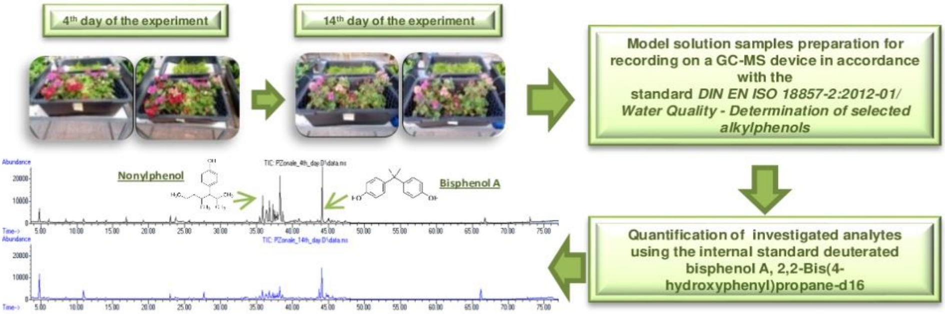
POSTER
(#4)

Phytotoxicity of Endocrine Disrupters Nonylphenol and Bisphenol A in *Pelargonium Zonale*

K. Antić[1,], M. Stošić[2], J. Radonić[2], T. Šolević Knudsen[1]*

(1) University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia, (2) University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Novi Sad, Serbia

**katarina.antic@ihtm.bg.ac.rs*



Model solution samples preparation for recording on a GC-MS device in accordance with the standard *DIN EN ISO 18857-2:2012-01/ Water Quality - Determination of selected alkylphenols*

Quantification of investigated analytes using the internal standard deuterated bisphenol A, 2,2-Bis(4-hydroxyphenyl)propane-d16

Introduction

The phytotoxicity of individual plant species utilized in phytoremediation systems must be assessed in order to improve the systems [1]. This study investigated the phytotoxicity of endocrine disruptors Nonylphenol and Bisphenol A in the plant species *Pelargonium Zonale*.

Materials and methods

The research was conducted over a 14-day period in a model solution under laboratory settings. Greenhouse conditions were reproduced, with a temperature ranging from 20 to 30 °C and an air humidity of 45 %.

The model solution, which consisted of 20 L of tap water and 2 L of Hoagland's solution with a pH of 6.8, was placed in plastic trough. The plastic trough was then filled with 1 kg of *Pelargonium Zonale* seedlings secured with a metal mesh to ensure semi-submerged conditions. Finally, the model solution was spiked with 2 mg each of Nonylphenol, Tech. and Bisphenol A, 99+ %, standard solutions made by Sigma-Aldrich, diluted in 3 mL of Methanol. Aeration was added into the system utilizing a Champion CX-0098 air pump on the third day of the experiment. After the experiment was set up, 2 L of model solution was sampled on the fourth and fourteenth days.

The model solution samples were prepared for analysis on a GC-MS device in accordance with the standard DIN EN ISO 18857-2:2012-01. The investigated analytes were quantified using the internal standard *deuterated bisphenol A, 2,2-Bis(4-hydroxyphenyl)propane-d16*.

Results

Following the completion of the 14-day experiment, the efficiency of removing the Bisphenol A from the model solution using the plant species *Pelargonium Zonale* was 74 %, while the efficiency of removing Nonylphenol was 67 %. The course of reduction of the concentrations of the analysed analytes during the experiment is detailed in **Table 1**.

Table 1. Reduction of the concentrations of the analysed analytes during the experiment

	C_{BPA} [mg L^{-1}]	C_{NP} [mg L^{-1}]
0. day	0.091	0.091
4. day	0.030	0.046
14. day	0.024	0.030

On the final day of the experiment, phytotoxicity characteristics such as leaf speckling, leaf margin necrosis (browning) and chlorosis (yellowing), leaf cupping, plant stunting, and even mortality of a few seedlings were observed.

Conclusion

The experiment demonstrated a considerable degree of phytotoxicity as well as a high success rate in reducing the concentrations of Bisphenol A and Nonylphenol utilizing the plant species *Pelargonium Zonale*, whose optimization for the goal of application requires additional testing.

References

[1] J.-M. Kim, J. Ha, K.-H. Kim, T. Lee, J. Heo, J. Jung, J. Lee, S. Kang (2021) *Journal of Pesticide Science*, 46(2), 168-172.

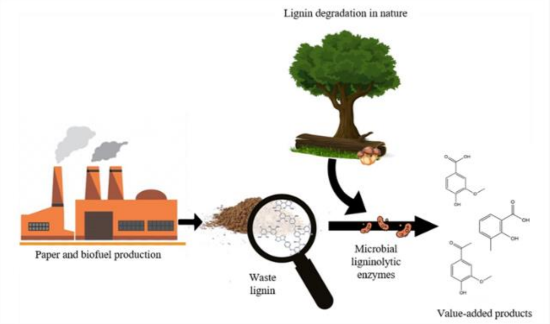
POSTER
(#4)

Determination of the Products of Bacterial Lignin Degradation: Targeted and Non-Targeted Screening

H. Plešnik[1,2], Ž. Tkalec[2], M. Zugan[1,2], A. Lapanje[1], T. Kosjek[1,2]*

(1) Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia, (2) International Postgraduate School Jožef Stefan, Jamova cesta 39, 1000 Ljubljana, Slovenia

*helena.plesnik@ijs_si



Lignin is a complex heterogeneous aromatic biopolymer, found in plant cell walls as one of the components of lignocellulose [1]. Though primarily present in nature, large quantities are daily generated as a waste product in paper and biofuel industries. To date, lignin is still mostly burned as low-quality fuel despite its considerable potential for transformation into value-added chemicals as it is a rich source of aromatic molecules. [2] This is mainly due to its heterogeneous composition and resistance to degradation, which makes any refinement very complex, but also because of the extensive purification, required by the obtained products. [3] As a result of the recent energy crisis, interest in lignin and its valorization has grown considerably in the last few years, mainly focusing on more environmentally friendly degradation by microorganisms. The majority of research has so far been done on fungi, though it was later concluded that they are unsuitable for large-scale use due to the complexity of their enzymes. [4]

We studied the less researched bacterial degradation, focusing on selected strains of the species *Paraburkholderia jirisanensis sp.*, which holds a gene for the production of ligninolytic enzymes of the laccase class. The bacteria were incubated with lignin as an energy source and the resulting product mix was subjected to analyses comprising target and non-targeted LC-MS/MS and LC-HRMS screening. The target analytical method was developed using 14 monomeric phenolic compounds that have been reported in the literature as degradation products. Results showed that four of them appeared in the product mixture which implies that they are in fact produced by bacteria during the incubation time.

As lignin and consequently also the degradation product mixture are very heterogeneous and a targeted method cannot be expected to cover the full range of compounds present, LC-HRMS-based non-targeted screening was performed. Comparing the acquired data to HRMS databases, tentative structures of further compounds have been proposed.

The obtained results clearly demonstrate the ability of *Paraburkholderia jirisanensis sp.* to degrade lignin, therefore holding a potential for environmentally friendly lignin valorization.

Acknowledgements

The research was carried out under the Applause (Grant Agreement No UIA02-228), Greener (Grant Agreement No 826312) and SurfBio (Grant Agreement No 952379) projects and the Slovenian Research Agency programme group (P1-0143).

References

[1] S. Schoenherr, M. Ebrahimi, P. Czemrmak (2018) *Lignin-Trends Appl*., 29-64.

[2] Z. Chen, C. Wan (2018) *Renewable and sustainable energy reviews*, 73, 610-621.

[3] T. Bugg, M. Ahmad, E. Hardiman, R. Rahmanpour (2011) *NPR*, 28, 1883-1896.

[4] G. De Gonzalo, D. I. Colpa, M. H. Habib, M. W. Fraaije (2016) *Journal of Biotechnology*, 236, 110-119.

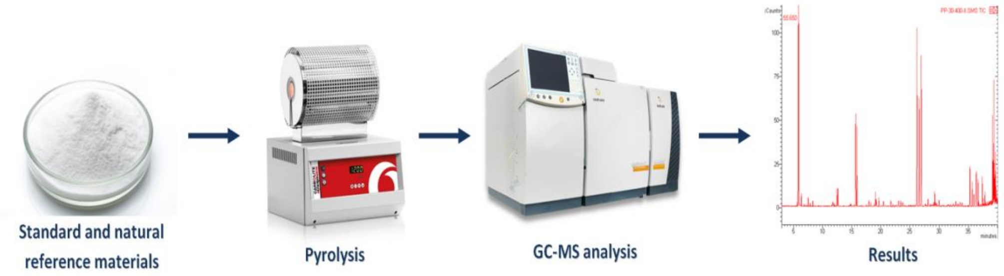
POSTER
(#4)

GC-MS Analysis of Liquid Fractions Obtained by Off-Line Pyrolysis of Reference Synthetic and Natural Polymers

D. Savić^{1,*}, J. Isailović^{1}, E. Vukićević^{2}, I. Jovančićević^{3}, G. Gajica^{4}, M. Antić^{1}, B. Jovančićević^{2}, J. Schwarzbauer^{3}, V. Antić^{1}

(1) University of Belgrade - Faculty of Agriculture, Nemanjina 6, Belgrade, Serbia, (2) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia, (3) Institute for Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstr. 4-20, 52056 Aachen, Germany, (4) Institute of Chemistry, Technology and Metalurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia

**dajana.savic@agrif.bg.ac.rs*



When waste biomass or plastic residues are stored or landfilled without control, they can represent a significant environmental problem. The idea of this paper was to examine the liquid fraction obtained by pyrolysis of some reference synthetic and natural polymers to evaluate their potential for generating valuable chemicals in further co-pyrolysis of agricultural and plastic waste materials. Pyrolysis is a frequently used process of thermochemical conversion, which involves heating the sample without the presence of oxygen. Pyrolysis can be used to solve accumulated agricultural and plastic waste materials in order to obtain valuable products, such as biofuel or some compounds of importance in the pharmaceutical and food industry [1, 2]. However, before any analysis of real samples, it is crucial to examine the pyrolysis of reference polymers, which can be found in actual plastic and biomass samples.

The pyrolysis of the following reference synthetic polymers was performed in this work: polypropylene (PP), polystyrene (PS), and poly(methyl methacrylate) (PMMA). Natural reference polymers, the constituents of agricultural waste, were also pyrolyzed, such as lignin, hemicellulose, cellulose, and hydroxyethyl cellulose. The liquid fractions were analyzed using gas chromatography-mass spectrometry (GC-MS). Pyrolysis of each reference polymer was performed at different temperatures and during different periods to examine the influence of these parameters on the composition of obtained products. The pyrolysis temperatures were selected based on the thermogravimetric curves for the corresponding reference polymers, and each pyrolysis was performed for 90 minutes. [3] The ratio of the areas of the most intensive peaks in GC-MS spectra was calculated in order to examine the influence of temperature and time. Many valuable compounds were identified in liquid fractions, such as various solvents, precursors of compounds beneficial for the food industry, and compounds that can be used as pesticides, herbicides, etc.

Based on the obtained results, it can be concluded that the temperature and time change did not hugely impact the pyrolysis products. After identifying the acquired products, further co-pyrolysis experiments are planned, to examine the synergy of synthetic and natural polymers in this process.

Acknowledgements

This work is supported by the project “Agricultural residues and plastic waste materials as a sustainable source of alternative fuels and valuable chemicals” (AGRIPLAST), grant No. 01DS21008.

References

[1] Y. Zhenga, L. Taob, X. Yanga, Y. Huanga, C. Liua, Z. Zhenga (2018) *Journal of Analytical and Applied Pyrolysis*, 133, 185-197.

[2] B. B. Uzoejinwaa, X. Hea, S. Wanga, A. Abomohraa, Y. Hua, Q. Wanga (2018) *Energy Conversion and Management*, 163, 468-492.

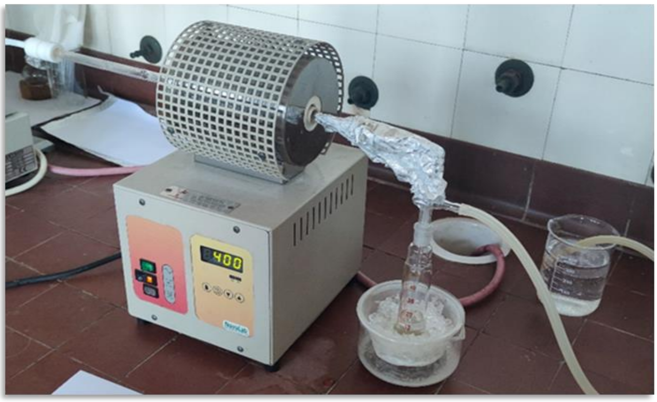
[3] M.V. Navarro, J.M. Lopez, A. Veses, M.S. Callen, T. García (2018) *Energy*, 165, 731-742.

Comparison of Off-Line Pyrolysis of Commercial Biopolymers and Biomass Samples

J. Isailović[1,*], *D. Savić*[1], *E. Vukićević*[2], *I. Jovančićević*[3], *G. Gajica*[4], *M. Antić*[1], *B. Jovančićević*[2], *J. Schwarzbauer*[3], *V. Antić*[1]

(1) University of Belgrade - Faculty of Agriculture, Nemanjina 6, Belgrade, Serbia, (2) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia, (3) Institute for Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstr. 4-20, 52056 Aachen, Germany, (4) Institute of Chemistry, Technology and Metalurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia

jelena.isailovic@agrif.bg.ac.rs



In off-line conditions, four biopolymer standards and three biomass samples were pyrolyzed in this work. Biopolymer standards: hemicellulose, cellulose, lignin, and hydroxyethyl cellulose were pyrolyzed at two different temperatures, which were chosen based on thermogravimetric results. For the first temperature, the middle of the thermogravimetric curve was taken, while the end of the same curve was used for the second temperature. [1] The temperatures at which the biopolymer standards were pyrolyzed were: hemicellulose at 315 and 400 °C, cellulose at 350 and 400 °C, lignin at 400 and 600 °C, and hydroxyethyl cellulose at 300 and 400 °C. All samples were pyrolyzed for 30 and 60 minutes in duplicate. The weights of the samples were about 100 mg.

Three different agricultural residues (waste biomass), i.e., tobacco, tomato, and corn stalks, were pyrolyzed at the same temperatures. [2, 3] After each pyrolysis, the weight of the solid residue was measured. The amount of solid residue after pyrolysis of biomass was compared with the amount of solid residue after pyrolysis of polymer standards. The chemical composition of liquid fractions obtained by pyrolysis of biopolymer standards and waste biomass were compared by applying gas chromatography-mass spectrometry (GC-MS) analysis. The most abundant compounds in all pyrolyzates were identified.

Based on the obtained results, it can be concluded that after the pyrolysis of natural polymers, a large amount of solid residue remains, and the yield of solid residue decreases with increasing pyrolysis temperature. The results also showed that pyrolysis oil from agricultural waste rich in alkaloids (tobacco, tomato) is a source of valuable chemicals, especially agrochemicals and pharmaceutical products.

Acknowledgements

This work is supported by the project “Agricultural residues and plastic waste materials as a sustainable source of alternative fuels and valuable chemicals” (AGRIPLAST), grant No. 01DS21008.

References

[1] A. O. Oyeduna, C. Z. Teeb, S. Hansonb Chi, W. Huia (2014) *Fuel Processing Technology*, 128, 471-481.

[2] G. Wang, Y. Dai, H. Yang, Q. Xiong, K. Wang, J. Zhou, Y. Li, S. Wang (2020) *Energy Fuels*, 34 (12), 15557–15578.

[3] B. Yan, S. Zhang, W. Chen, Q. Cai (2018) *Journal of Analytical and Applied Pyrolysis*, 136, 248-254.

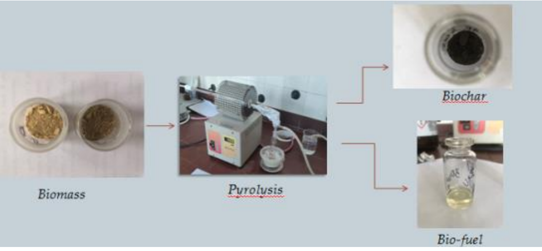
POSTER
(#4)

Physicochemical Characterization of Biomass Samples Used for Pyrolysis and Co-Pyrolysis for Pyrolytic Processes

E. Vukićević[1,], D. Savić[2], J. Isailović[2], I. Jovančićević[3], G. Gajica[4], M. Antić[2], B. Jovančićević[1], J. Schwarzbauer[3], V. Antić[2]*

(1) University of Belgrade - Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia, (2) University of Belgrade - Faculty of Agriculture, Nemanjina 6, Belgrade, Serbia, (3) Institute for Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstr. 4-20, 52056 Aachen, Germany, (4) Institute of Chemistry, Technology and Metalurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia

**emilija@chem.bg.ac.rs*



Agricultural countries should focus on reusing agricultural waste because this waste is managed mainly by incineration, which leads to increasing environmental pollution.

The most common agricultural waste is biomass, which can be converted by the pyrolysis process into liquid products (bio-oil), gases and lignite-type coal called bio-char, which is suitable for various purposes. In this way, environmental pollution caused by waste biomass is prevented. Biomass samples used in this research are corn, tomato and tobacco stalks. The stalks are a rich source of biomass that is otherwise treated as Physico-chemical characterization aims to determine important characteristics of biomass samples before their pyrolysis and further analysis, such as moisture and dry matter, pH, ash, lignin, cellulose, hemicellulose, elemental analysis and calorimetry. Samples should meet certain conditions to be pyrolyzed and give the desired products by pyrolysis. Dry matter and moisture content included oven drying at 105 °C. In contrast, ash determination involved burning the samples in an oven at 750 °C. The method used to determine the content of lignin, cellulose and hemicellulose was based on the solubility of these substances in different solvents [2]. The elemental analysis included the analysis of C, H, N and S content in the samples, while the caloric value was measured by the standard calorimetric method.

After drying in air, all samples had a low percentage of moisture (about 5-6 %) and, therefore, a high content of dry matter, which enabled their use in the pyrolysis process for the production of bio-oil and bio-char. The determined pH values showed that all samples were slightly acidic, ranging from 6 to 6.5. It was observed that good homogenization is required due to the different pH values of parts of the same plant (e.g. leaves and stems). The ash content was about 4 %, except for tomatoes, which amounted to about 7 %. Hemicellulose was the most abundant in the biomass samples, followed by cellulose and the least abundant lignin. The elemental analysis confirmed that the examined samples are suitable for pyrolysis due to the high percentage of carbon (40-45 %). The high proportion of S (18 %) in one maize variety is attractive, which may be a consequence of the different compositions of the soil on which the crops were grown. The calorific value of the biomass samples was about 17-18 MJ/kg, which is in the range of the heating value of wood (18-22 MJ/kg).

Based on the obtained results, it can be concluded that adequately prepared biomass based on agricultural residues can be used for pyrolytic experiments to produce bio-oil and bio-char. Furthermore, biomass can be used in co-pyrolysis with other types of waste (e.g. waste plastic) to increase the quality of pyrolytic products.

Acknowledgements

This work is supported by the project “Agricultural residues and plastic waste materials as a sustainable source of alternative fuels and valuable chemicals” (AGRIPLAST), grant No. 01DS21008.

References

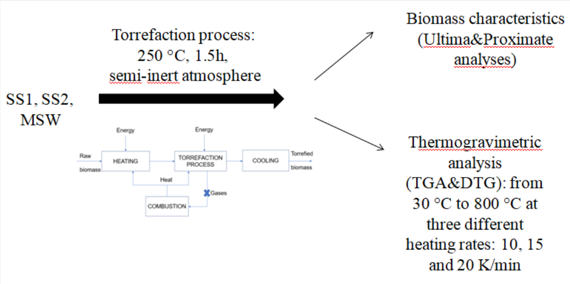
[1] L. Zhang, Z. Bao, S. Xia, Q. Lu, K. B. Walters (2018) *Catalysts*, 8, 659.
[2] A. M. Mansor, J. S. Lim, F. N. Ani, H. Hashim, W. S. Ho, (2019) *Chemical Engineering Transactions*, 72, 79-84.

Pyrolysis Characteristics of Sewage Sludge and Municipal Solid Waste Subjected to the Torrefaction Process

M. Ivanovski[1,2,], A. Petrovič[1], J. Stergar[1,3], R. Vončina[2], D. Goričanec[1], D. Urbancl[1]*

(1) University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, (2) Elektroinštitut Milan Vidmar, Ljubljana, Slovenia, (3) University of Maribor, Faculty of Medicine, Maribor, Slovenia

[*]maja.ivanovski@eimv.si



In the last years, torrefaction process of sewage sludge (SS) and municipal solid wastes (MSW) have gained much attention in the terms of reaching the climate and energy goals set up in the European Green Deal [1]. Torrefaction is defined as a pre-treatment method where biomass is heated up at temperatures ranging from 200 °C to 300 °C in dry and inert or non-inert atmosphere to improve physical and chemical properties of biomaterials [2, 3]. In this present work, the torrefaction process of above-mentioned biomass materials was studied in order to determine the general characteristics of obtained biomaterials. Different types of SS materials (SS1 and SS2) and MSW were thermally treated at 250 °C in semi-inert atmosphere for 1.5 h using Bosio furnace type EUP-K 6/1200. Proximate and ultimate analyses have been performed, together with TGA/DTG experiments. Thermal stability of torrefied samples was carried out using a thermogravimetric analysis (Mettler TGA thermogravimetric analyzer TGA/SDTA, 851^e and TGA 2, (Mettler Toledo, Switzerland)) under an air atmosphere. Samples were taken in a 70 µL aluminium crucibles (Al_2O_3) and heated to raise the temperature from 30 °C to 800 °C at three different heating rates: 10, 15 and 20 K/min. The findings revealed that SS and MSW degrade faster at the same temperatures than lignocellulosic biomass, and that mass yields are lower compared to the woody biomass. Moreover, the optimal temperature has been determined to be around 260 °C. The obtained results will be useful in the future when kinetics of biomass will be investigated [4, 5].

References

[1] European Commission, "COM(2019) 640 final," *Eur. Green Deal*, vol. 53, no. 9, pp. 1689–1699, 2019, doi: 10.1017/CBO9781107415324.004.

[2] A. T. Hoang *et al.* (2021) *Fuel Process. Technol.*, 223, 106997.

[3] M. Ivanovski, D. Goricanec, J. Krope, D. Urbancl (2021) *Energy*, 122483.

[4] R.K. Singh, T. Patil, A.N. Sawarkar (2020) *Bioresour. Technol. Reports*, 12, 100558.

[5] M. Ivanovski, A. Petrovic, I. Ban, D. Goricanec, D. Urbancl (2021) 1–22.

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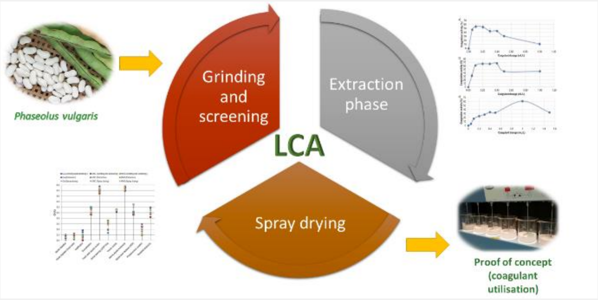
Life Cycle Assessment of Nature-Based Solution for Wastewater Treatment

S. Radovic[1,], M. Turk Sekulic[1], S. Pap[1,2], B. Agarski[1], D. Vukelic[1], J. Radonic[1], S. Dmitrasinovic[1], J. Prodanovic[3]*

(1) Department of Environmental Engineering and Occupational Safety and Health, Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovića 6, 21 000 Novi Sad, Serbia, (2) Environmental Research Institute, UHI North Highland, University of the Highlands and Islands, Thurso, Caithness, Scotland, KW14 7JD, UK; (3) Faculty of Technology in Novi Sad, University of Novi Sad, Bulevar cara Lazara 1, 21 000 Novi Sad, Serbia
[*]sanjaradovic@uns.ac.rs



Coagulation/flocculation technology is commonly used in wastewater treatment systems. However, commercially utilised coagulants based on aluminium (Al) and iron (Fe) salts can cause environmental and health problems. One of the possible solutions to overcome mentioned problems is usage of new coagulants of "green" origin, as one of the specific nature-based solution for wastewater remediation [1]. Alternative coagulants are yet to be understood and evaluated before their commercial application. As a step forward, this work evaluates ecological aspects of the production of three coagulant types obtained from the common bean seeds (*Phaseolus vulgaris*).

All coagulants were obtained using the same extraction agent, i.e., 0.5 M NaCl solution, but with different extraction procedures: conventional solid-liquid (KNO coagulant) and ultrasound extraction (UNO and GA coagulants). Conversion of liquid into powdered coagulants was achieved by spray drying process without (KNO and UNO coagulants) or with addition of carrier materials (GA coagulant) [2].

In order to evaluate environmental aspects of three coagulants production, determine their hot-spots and discover the most *eco-friendly* one, a life cycle assessment (LCA) was performed. Produced coagulants were additionally tested for their viability to treat waters with elevated turbidity values.

Comparing both ecological and performance aspects of each coagulant, several conclusions can be highlighted:

- In general, the production process was simple (three-step), not chemically demanding and all obtained coagulants showed high performances in terms of turbidity removal (55.2-68.3 %);
- The lowest impact on the environment, per declared unit (DU), was observed for GA coagulant production due to addition of carrier material in spray drying phase;
- Extraction type did not significantly influence results of LCA, i.e., negligible differences in environmental impact were spotted for KNO and UNO coagulant;
- The main hot spot in all three coagulant production processes was the electricity consumption within spray drying process (90% of all impact categories);
- Scale-up of the production process could lead to process optimisation.

Acknowledgements

The research has been supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, through the project number 451-03-68/2022-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain" and by the Innovation Fund, Republic of Serbia, ID 5156 through the project Proof of Concept.

References

[1] W.L. Ang, A.W. Mohammad (2020) *Journal of Cleaner Production*, 262:121267

[2] S. Radovic, M. Turk Sekulic, B. Agarski, S. Pap, D. Vukelic, I. Budak, J. Prodanović (2022) *International Journal of Environmental Science and Technology*, ISSN 1735-1472

Environmental Bioremediation is the Technology of the Future in Sustainable Development

S. Miletić[1,*]*, S. Spasić*[1]*, J. Avdalović*[1]*, N. Lugonja*[1]*, A. Žerađanin*[1]*, M. Vrvić*[2]*, V. Beškoski*[3]

(1) University of Belgrade-Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade, Serbia, (2) BREM GROUP Ltd., Oslobođenja 39b, Belgrade, Serbia (3) University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia

[*]*srdjan.miletic@ihtm.bg.ac.rs*

Soil pollution may arrive from many sources. These can be discrete and point sources of pollution, diffusion sources, pollution due to fertilization, accidental situations such as oil spills. The main sources of soil pollution are agrochemical, urban, industrial, atmospheric, and incidental.[1] Pesticides, heavy/toxic metals, hydrocarbons and nuclear waste are distinguished by their toxicity.[2]

Remediation is a logical continuation that results from the fact that in some habitat there are concentrations of pollutants in illegal amounts. The goal of remediation is to bring the polluted habitat into a sustainable environment, whereby the concentration of pollutants is reduced below the maximum permitted by law.[1] Of all the remediation technologies, the use of microorganisms in the bioremediation process is considered the most eco-friendly due to its efficiency. This is, among other things, because no additional waste is created during bioremediation, but the existing waste is broken down or converted into a less toxic form (for heavy metals).

In addition, in the process of soil bioremediation, there is an increase in the content of humic acids, which are an indicator of soil quality.[3]

In order to ensure the acceleration of natural degradation processes, primarily oil hydrocarbons, enhanced bioremediation technology is often resorted to, which involves the addition of nutrients (biostimulation) and the addition of microorganisms (bioaugmentation).[4]

In our research, we examined the content of total petroleum hydrocarbons and the content of humic acids found in oil-polluted soil before and after 150 days of bioremediation. Bioremediation was performed with a consortium of microorganisms isolated from contaminated soil, and the procedure itself was described in earlier works.[5]

After the end of the enhanced bioremediation, there was a significant reduction in the total petroleum hydrocarbons (up to 94%), while the content of humic acids increased (up to 47%).

These results are just one more of many confirmations that bioremediation is a technology to restore polluted environment with the help of biological agents such as bacteria, fungi and other microorganisms and their enzymes. This is a good example of green technology where microorganisms decompose toxic substances from the environment, creating useful molecules and restoring the environment.

Acknowledgements

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Contract number: 451-03-68/2022-14/200026) for financial support.

References

[1] Soil Pollution. I. A. Mirsal, 2nd Edition, Berlin, Heidelberg, Springer, 2008.

[2] C.C. Azubuike, C.B. Chikere, G.C. Okpokwasili (2016) *World Journal of Microbiology and Biotechnology*, 32, 180.

[3] A. Boveiri Dehsheikh, M. Mahmoodi Sourestani, M. Zolfaghari, N. Enayatizamir (2020) *Journal of Cleaner Production*, 256, 120439.

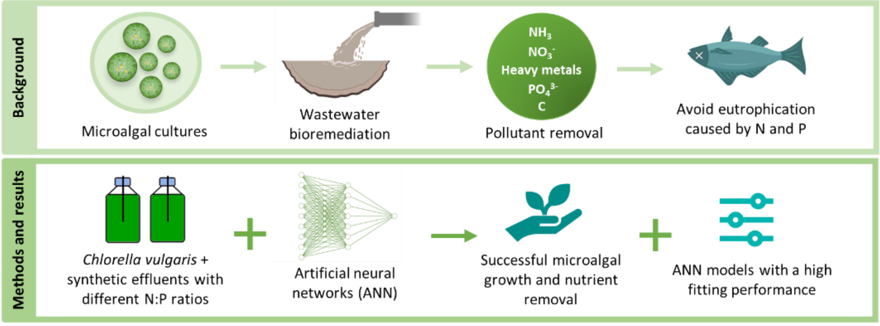
[4] F. Wang, W. Dong, H. Wang, Y. Zhao, Z. Zhao, J. Huang, T. Zhou, Z. Wu, W. Li (2022) *Chemosphere*, 291, 132770.

[5] V. P. Beškoski, G. Gojgić-Cvijović, J. Milić, M. Ilić, S. Miletić, T. Šolević, M.M. Vrvić, T. Solević, M.M. Vrvić, T. Šolević, M.M. Vrvić (2011) *Chemosphere*, 83, 34–40.

Microalgal Cultures for Wastewater Polishing: Application of Artificial Neural Networks for Process Modelling and Control

E. M. Salgado[1,2,*], *A. F. Esteves*[1,2], *A. L. Gonçalves*[1,2,3], *J. C. M. Pires*[1,2]

(1) LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (2) ALiCE – Associate Laboratory in Chemical Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (3) CITEVE – Technological Centre for the Textile and Clothing Industries of Portugal, Rua Fernando Mesquita, 2785, 4760-034 Vila Nova de Famalicão
[*]up201606419@fe.up.pt; Tel.: +351-91-063-2337



Microalgae are a diverse group of photosynthetic microorganisms with an extraordinary potential for wastewater treatment due to their rapid growth rate, CO_2 fixation ability and efficient removal of numerous pollutants such as nitrogen and phosphorus [1]. Nevertheless, wastewater composition can greatly vary depending on the source, location, and season of collection. When using microalgal systems for wastewater bioremediation, it is crucial to comprehend how variations in the nitrogen and phosphorus levels can impact their growth and nutrient removal efficiency. Therefore, this work aimed to evaluate the effect of different initial nitrogen to phosphorus (N:P) molar ratios on these parameters. Moreover, artificial neural networks (ANNs) were developed to evaluate their potential for predicting biomass productivity and nutrient removal rates based on the initial and instantaneous concentrations of biomass and nutrients. The structure of ANN models was optimised based on the Akaike information criterion. For this purpose, *Chlorella vulgaris* was cultured in synthetic wastewater with different nitrogen and phosphorus concentrations to simulate the composition of real wastewater. Different assays were conducted with N:P molar ratios between 2 and 67 to comprise values reported in the literature for various real wastewaters. Microalgal growth parameters and nutrient concentrations were monitored for each experiment. Overall, the studied microalga was able to grow in all the experimental conditions, with a similar growth behaviour between the assays. Regarding nutrient removal, *C. vulgaris* efficiently removed nitrogen and phosphorus from the synthetic wastewater. For ratios 2-19, the nitrogen removal rates increased with the increase of the initial nitrogen concentration. The same correlation was found in the phosphorus removal rates for ratios between 19 and 67: increasing phosphorus concentration increased the removal rate. Moreover, the results showed that with low N:P ratios, nitrogen concentration could limit phosphorus uptake by microalgae, while phosphorus concentration might limit nitrogen uptake with high ratios. ANN models presented a high fitting performance, being a relevant tool for process modelling and control. The combined effect of each pair of input variables on the output variables was also analysed based on the determined ANN model. Lastly, the present work suggests that microalgal-based systems can be a reliable, sustainable, and efficient technology for wastewater bioremediation.

Acknowledgements

This work was financially supported by: (i) LA/P/0045/2020 (ALiCE) and UIDB/00511/2020-UIDP/00511/2020 (LEPABE) funded by national funds through FCT/MCTES (PIDDAC); and (ii) Project PhotoBioValue (ref. PTDC/BTA-BTA/2902/2021), funded by FEDER funds through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. A.F. Esteves and E.M. Salgado thank FCT for the financial support of their work through the FCT PhD Research Scholarships 2020.05477.BD and 2021.07412.BD, respectively.

References

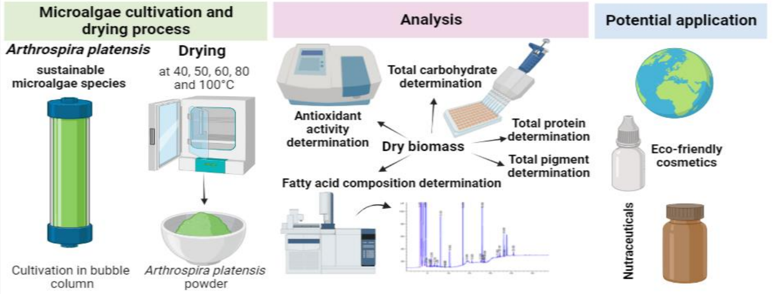
[1] E.M. Salgado, A.L. Gonçalves, F. Sánchez-Soberón, N. Ratola, J.C.M. Pires (2022) *International Journal of Environmental Research and Public Health*, 19, 2634.

Arthrospira platensis as a Highly Sustainable Ingredient for Eco-friendly Cosmetics

*A. Martić[1, *], L. Čižmek[1,2], M. Baković[1], M. Galić Perečinec[1,2], E. Djedović[1], N. Topić-Popović[1,2], T. Vujović[1], R. Čož-Rakovac[1,2]*

(1) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (2) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

**amartic@irb.hr*



Arthrospira platensis is a promising and sustainable microalga characterized by easy growth without the need for herbicide or pesticide usage, and a possibility to utilize the whole microalgae without waste and harmful greenhouse gas emissions. It represents a valuable source of bioactive compounds with different health-promoting properties which makes *A. platensis* an attractive ingredient for the formulation of eco-friendly cosmetics [1].

As dehydration is one of the crucial production steps in the cosmetic, pharmaceutic, and food industries, the aim of this work was to investigate the influence of different drying temperatures on the chemical composition of *A. platensis*. Antioxidant activity of methanol: dichloromethane (1:1) extracts from differently dried (40, 50, 60, 80, and 100°C) samples was analyzed using 2,2-diphenyl-1-picryl-hydrazyl (DPPH), reduction of the radical cation (ABTS), ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC) assays. The influence of drying temperature on total protein, carbohydrate, pigment, and lipid content was evaluated, while gas chromatography was carried out to determine fatty acid composition.

By implementing ABTS and DPPH methods, the highest antioxidant activity was observed for the sample dried at 40°C followed by 50 and 80°C dried samples with 1.5- and 2.5-fold lower activity ($p<0.005$). ORAC results showed the highest activity for samples dried at 50°C when compared to other samples ($p<0.0001$) while FRAP assay revealed high activity off all tested extracts indicating electron transfer as the main mechanism, with the highest activity for samples dried at 40°C and 100°C among which no statistically significant difference was observed. The highest lipid content was around 2% for samples dried at 40 and 50°C. Fatty acid composition revealed a similar qualitative and quantitative distribution of fatty acids in all samples. Saturated fatty acids were the most represented, followed by monounsaturated and polyunsaturated fatty acids, among which essential omega-6 (linoleic acid) and omega-3 (docosahexaenoic acid) fatty acids were found. Total protein, carbohydrate, and pigment contents are influenced by drying temperatures with differences between samples.

Duration of drying along with an increase in temperature has shown to have an impact on chemical composition and activity among samples. Overall results point out that *A. platensis* can be utilized by different industries in an economically and eco-friendly manner by using intermediate temperatures of drying while preserving the beneficial properties of this microalga.

Acknowledgments

This study was financially supported by: Development of Innovative Biobased Products by in silico Assessment of Microalgae Bioactivity (KK.01.2.1.02.0015), financed by the European Union through the European Regional Development Fund—the Competitiveness and Cohesion Operational Program.

References

[1] I. Ragusa, G.N. Nardone, S. Zanatta, W. Bertin, E. Amadio (2021) *Cosmetics*, 8, 7.

[2] I. Jerković, A.M. Cikoš, S. Babić, L. Čižmek, K. Bojanić, K. Aladić, N.V. Ul'Janovskii, D.S. Kosyakov, A.T. Lebedev, R. Čož-Rakovac, P. Trebše, S. Jokić (2021) *Marine drugs*, 19, 235.

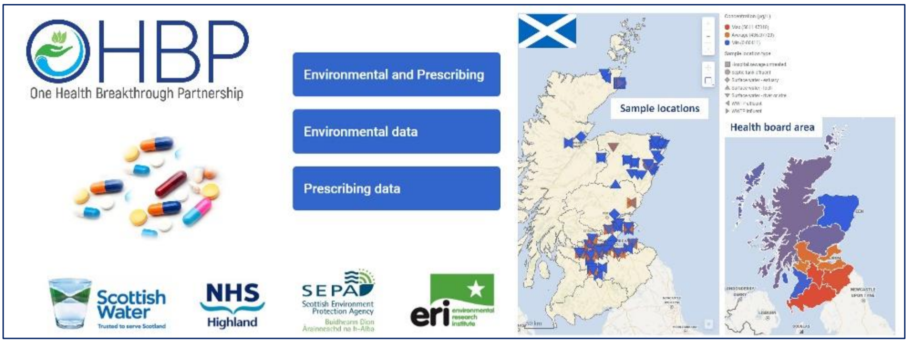
SESSION 5: One health

Innovative Data Visualisation Tool to Aid Addressing Pharmaceutical Pollution in the Scottish Water Environment

L. Niemi [1,*], *S. Gibb*[1], *S. Pfleger*[2], *E. Cartmell*[3], *B. Homer*[3], *F. Whyte*[4], *L. Green*[4]

(1) Environmental Research Institute, University of the Highlands and Islands, Castle Street, Thurso KW14 7JD, UK; (2) NHS Highland, John Dewar Building, Highlander Way, Inverness IV2 7GE, UK; (3) Scottish Water, 55 Buckstone Terrace, Edinburgh EH10 6XH, UK; (4) Scottish Environment Protection Agency, 10 Fodderty Way, Dingwall IV15 9XB, UK.

*lydia.niemi@uhi.ac.uk



The presence of pharmaceutical residues in the aquatic environment is recognised internationally as an important public health and environmental issue. Due to extensive prescribing and use, pharmaceuticals have been widely detected in effluent-receiving surface water and aquatic environments following incomplete removal within wastewater treatment plants. The environmental fate and risks are not fully characterised, but many compounds are of ecotoxicological and regulatory concern due to the effects in non-target organisms at trace, environmentally relevant concentrations.

To address this in Scotland, four organisations representing the environment, water, and healthcare sectors have formed the One Health Breakthrough Partnership (OHBP). The OHBP brings together key regional and national stakeholders committed to reducing pharmaceutical pollution in the environment through innovation, cross-sector engagement, and knowledge exchange. Recently the OHBP worked with researchers to perform a baseline assessment of pharmaceuticals in Scotland's water environment [1]. The database has been collated into an innovative data visualisation tool developed by the Scottish Environment Protection Agency (SEPA) with the OHBP [2].

This tool is the first open access interactive data source to combine national environmental data and prescribing data on pharmaceuticals. Users can navigate dataframes to access environmental data matched to standardised quantities of drugs prescribed, by health board, GP practice and drainage operational area. The OHBP is working to interrogate this tool with researchers, health professionals and environmental scientists to develop a better understanding of the link between medicine use and pharmaceutical pollution, and the impact pharmaceuticals may have on Scotland's water environment. This will include assessing environmental spatiotemporal trends and prescription trends, and modelling to predict future environmental risk related to population demographics, prescription frequency and changing weather patterns.

Acknowledgements

The OHBP acknowledges funding from the Scottish Government Water Industry Division, and the Centre of Expertise for Waters (CREW). Data visualisation tool developers include the OHBP, and Graeme Cameron and Lauren Fuller (SEPA Data Informatics Team).

References

[1] Helwig, K., Aderemi, A., Donnelly, D., Gibb, S., Harrower, J., Helliwell, R., Hunter, C., **Niemi, L.,** Pagaling, E., Roberts, J., & Zhang, Z., CREW report, 2022, *"Pharmaceuticals in the water environment: Baseline assessment and recommendations"*.

[2] SEPA online resource, 2022, https://informatics.sepa.org.uk/EnvironmentalPharmaceuticals/.

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Assessing Particle Toxicity of Two African Cities Using the Ascorbic Acid Assay

E. J. S. Souza[*], *N. Deabji, K. W. Fomba, H. Herrmann*

Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Leipzig, Germany

[*]*souza@tropos.de*

Africa

Praia, Cape Verde

Dust events: 281 pmol min^{-1} m^{-3}
Non-dust events: 93 pmol min^{-1} m^{-3}

Fez, Morocco

Anthropogenic emissions
269 pmol min^{-1} m^{-3}

Oxidative potential (OP) is a reliable metric to assess the health effects of exposure to particulate matter (PM). PM has shown an interesting capacity to generate reactive oxygen species (ROS) by redox reactions under incubation with body antioxidants or probes. Moreover, an excess in the concentration of oxygen molecules in the lung makes these PM-redox catalysts donate electrons to O_2, promoting ROS generation [1]. Cognizant of this, this study aims to assess particle toxicity based on OP assays of two African cities, Fez (Morocco) and Praia (Cape Verde), which are more impacted by anthropogenic and natural emissions, respectively. Furthermore, investigations of the differences in the chemical composition of both atmospheres and their impact on human health by applying the ascorbic acid (AA) assay (OP^{AA}) were performed.

Sampling campaigns were carried out in both cities from Jan-Feb 2020 in Praia and Sep-Oct 2019 in Fez. After sampling, PM samples were stored at -20 °C until analyses. The extraction of PM content was carried out by using 10 mL of a phosphate buffer solution (PBS). From ten PM_{10} samples of each sampling site (N=20), a chemical assay using OP^{AA} was investigated. An aliquot of 2 mL was incubated with AA to investigate the redox mechanism between PM redox catalysts and AA. The depletion of AA (265 nm) over 25 min was monitored by using UV-vis. The human exposure, was obtained by normalizing the OP values by the sampling volume (nmol min^{-1} m^{-3}).

The average OP^{AA} values from both sites was 269 ± 50 and 93 ± 12 pmol min^{-1} m^{-3} for Morocco and Cape Verde, respectively. However, OP^{AA} values of aerosol samples during dust storms in Cape Verde reached average OP values of 281 ± 46 pmol min^{-1} m^{-3}. Using Spearman correlation, water-soluble (WS) Mn (0.61) and Cu (0.61) correlated better with the OP^{AA} values from Fez, while Fe (0.59) and Zn (0.49) correlated better with those from Praia. The high correlations of WS-Cu, and WS-Mn, with the OP values from Fez samples, indicate that these metals can influence ROS formation through redox reactions which are explained by individual or synergistic and antagonistic effects.

The OP values of the PM samples from Fez were not correlated with PM mass concentration (-0.28), but those from Praia showed a strong correlation (0.90) during dust events. This could be connected to the higher Mn, Fe, and Zn contents of these samples during dust storms. In other hand, the divergences in OP values could also be connected to anthropogenic activities in Fez that may emit significant contribution of quinones and PAHs, which are also known to affect OP. During non-dust events in Praia, the OP values are about nine times lower than those from Fez, which may be connected to the lower concentration of PM-redox catalysts. But during dust events, the OP values increased significantly due to the increase in oxidizing agents. Human exposure to PM is more affected in Fez than in Praia city during non-dust events. However, dust events can make the OP increase significantly, providing even more health risks in Praia than Fez.

References

[1] J. Bates et al. (2019) *Environmental Science and Technology,* 53, 4003 – 4019.

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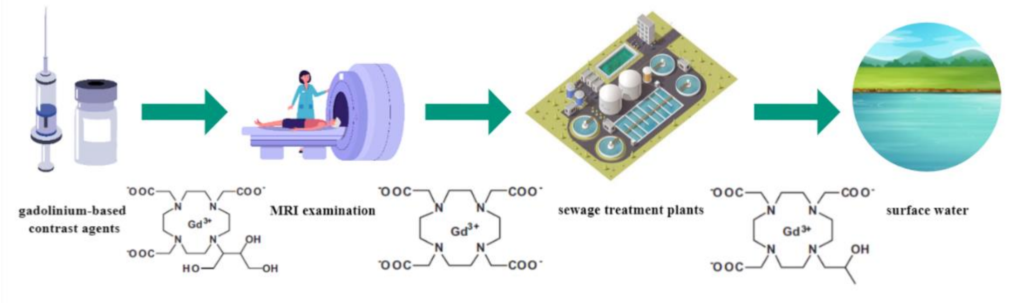
Mass Flow Balance of Gadolinium-Based Contrast Agents in Workplaces with Magnetic Resonance Imaging Services

F. Mišíková[*], *P. Kubitová, A. Krejčová*

University of Pardubice, Studentská 573, Pardubice, Czech Republic

[*]*frederika.misikova@student.upce.cz*



Gadolinium is one of the rare earth elements and occurs in nature in mixed minerals [1]. It is used in technology, industry and agriculture [2] but also in medicine in gadolinium-based contrast agents (GdCA) for magnetic resonance imaging (MRI), where its paramagnetic properties are used. Worldwide, it is estimated that 40 to 50% of MRI examinations are performed using contrast agents and their number should increase in the future [1]. GdCA are Gd chelates where the Gd(III) ion is bound to an organic ligand, usually with a polyaminocarboxylic acid, and forms a stable complex due to the high toxicity of the ion in the hydrated form [1,3].

Due to the widespread use of Gd, the content of anthropogenic Gd in the environment is increasing compared to geogenic ones, thus creating a Gd anomaly [3]. Anthropogenic Gd accumulates both in wastewater and surface water, as well as in the soil. The discovery of the Gd anomaly is linked to the finding of Gd complexes in sewage treatment plants. Since the 1980s, when the Gd anomaly was first described, nowadays it is detected in many locations around the world (Japan, Germany, the Czech Republic, etc.) [4]. According to specific environmental conditions, Gd compounds can be immobilized, mobilized [5] or bioaccumulated in organisms and thus enter food chains and can cause a health risk. [6].

The study aimed to investigate the mass flow balance of GdCA at selected workplaces with MRI services, i.e. to find out information about the amount of GdCA consumed, the amount of MR examinations performed during the selected period, and the method of waste management. Another aim was to evaluate the amount of unused waste GdCA over a period of time from samples of waste ampoules and syringes after the application to patients during MR examinations.

For the study, samples of waste ampoules were obtained, which were collected for one month at 3 MRI workplaces (Pardubice and Hradec Králové, Czech Republic). At the same time, a questionnaire survey was carried out at these workplaces. Analysis of Gd content was performed using inductively coupled plasma optical emission spectrometry (ICP-OES).

The following were evaluated: the mass flow balance of GdCA at individual MRI workplaces, the necessary amount of water rinsing of empty waste ampoules to remove all residues of GdCA, and also the amount of GdCA that would normally end up in the waste. The amount of GdCA intended for disposal was from 3 to 6% of the total volume per month.

Acknowledgements

Acknowledgement belong to MRI workplaces in Nemocnice Pardubického kraje, Multiscan s.r.o. and Fakultní nemocnice Hradec Králové.

References

[1] M.F. Bellin, A.J. Van Der Molen (2008) *European Journal of Radiology*, 66, 160-167.
[2] V. González, D.A.L. Vignati, M.N. Pons, et al. (2015) *Environmental Pollution*, 199, 139-147.
[3] L. Telgmann, M. Sperling, U. Karst (2013) *Analytica Chimica Acta*, 764, 1-16.
[4] L. Bendakovská, A. Krejčová, T. Černohorský, J. Zelenková (2016) *Chemical Papers*, 70, 1155-1165.
[5] A. Menahem, I. Dror, B. Berkowitz (2016) *Chemosphere*, 144, 713-720.
[6] X. Li, Z. Chen, Z. Chen, Y. Zhang (2013) *Chemosphere*, 93, 1240-124.

ORAL
(#5)

Gasoline Additives in Groundwater in Paraguay - Case Study: Methyl t-Butyl Ether in the Patiño Aquifer

*J. F. Facetti**, *R. León-Ovelar, C. Bernal, J. Ojeda, R. Núñez, F. Carvallo*

Universidad Nacional de Asunción, Facultad de Ingeniería, San Lorenzo- Paraguay
**jfacetti@ing.una.py*

In Paraguay, the Patiño aquifer is an important source of supply for human consumption, for industry and for agriculture production. Nearly two million people directly depend on this resource. The overexploitation, climate change impact on hydrological regime as well as the increase of point source as gasoline stations in its area have raised critically their vulnerability. The possible infiltration of gasoline and their additives into its waters has been proposed. Methyl t-butyl Ether (MtBE) is an additive for gasoline that oxygenates and increases its octane number, its degradation products are t-butyl-alcohol (TBA) and t-butyl formate (TBF). A vulnerability map has been done, according to population density and the presence of gasoline stations. 90 wells located over the aquifer area have been selected with the criteria of distance to a potential point source of contamination. Two sampling campaigns were performed, one in a rainy season and other in the dry season and, with a geospatial analysis. Determination of MtBE and its by-products was performed by solid phase microextraction (SPME) and gas chromatography-mass spectrometry (GC/MS). In the rainy season, MtBE, TBA, and TBF were detected in 44, 21, and 13% of the wells, respectively, while in the dry season, 19, 2, and 74% of the wells showed MtBE, TBA, and TBF, respectively. The MtBE properties depend on environmental conditions. In the rainy season the concentration of MtBE ranged from 0.1 to 0.16 µg/l and in the dry season from 0.01 to 0.18 µg/l. TBA and TBF concentrations increased in the dry season reaching maximums of 1.16 and 4.8 µg/l. The increase in TBA and TBF in the second campaign it is according to the MtBE degradation and could presume they have a longer half-life, affected by the geology characteristics and presence of bacteria. Although the low concentrations in the rainy season could be due to the recharge of the aquifer and related to increased mobility of the compounds. It is possible to conclude that the presence of these contaminants in the waters of the Patiño aquifer confirms the infiltration of fuels as well as their persistence for years in said waters.

Keywords: Methyl t-butyl Ether (MtBE), t-butyl-alcohol (TBA), t-butyl formate (TBF), Patiño aquifer, contaminated groundwater

Acknowledgements
CONACYT finances this project through the PROCIENCIA Program with resources from the Fund for Excellence in Education and Research (FEEI) (INV-14-284).

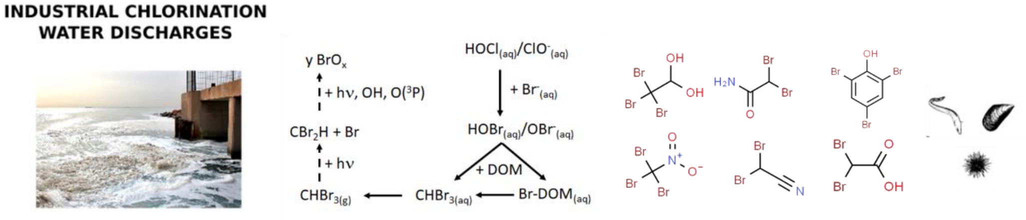
ORAL
(#5)

Assessing the Nature and the Impact of By-Products Issued from Industrial Chlorinated Discharges into the Sea

J-L. Boudenne[1,], J. Dron[2], C. Demelas[1], E. Quivet[1], L. Vassalo[1], B. Coulomb[1], S. Coupé[3], G. Revenko[2], P. Hôhener[1]*

(1) Aix Marseille University/CNRS, Laboratoire Chimie Environnement (UMR7376), Marseille, France, (2) Institut écocitoyen pour la connaissance des pollutions, Fos-sur-mer, France, (3) Aix Marseille Université, Université de Toulon, CNRS, IRD, MIO, Toulon, France

[*]jean-luc.boudenne@univ-amu.fr



Chlorination treatment of seawater in coastal and shipboard installations is a common process applied to control biofouling and/or to minimize the input of noxious or invasive species into the marine environment. The major concern related to the use of this process is, to some extent, dumping of chlorine in the environment with known impacts on fauna and flora but above all potential output of many halogenated compounds formed by complex reactions between the chlorine residual inorganic and organic constituents, natural and man present in the receiving environment [1]. Chlorine (as Cl_2 or HOCl form) can rapidly react with the bromide ions found in seawater to form instantly hypobromous acid (HOBr), compound known to be much more reactive than HClO with the organic matter [2].

A three-year survey was conducted in a heavily industrialized area (Gulf of Fos, Mediterranean Sea), where more than 3 million cubic meters of chlorinated seawater is released each day by various industrial plants, with the aims of monitoring chlorination by-products (CBP) formed in water, in air, in sediments and in biota (conger eel, mussel, ursin). Water samples were collected in 26 stations disseminated in the Gulf, at surface and at depth, following transects from known chlorinated discharges to the open sea. Passive samplings were also carried out by use of Chemcatchers® hanged from navigation buoys. Air monitoring was realized in two different ways, by use of canisters and by use of a laboratory truck equipped with a proton-transfer-reaction time-of-flight mass spectrometry analyzer (PTR-ToF-MS). Sediments, ursins, congers and mussels were collected throughout the Gulf of Fos.

Occurrence of CBP was determined by gas chromatography with electron capture detection (GC-ECD), after liquid-liquid extraction and/or esterification for water samples, after sonication extraction for marine organism and sediments, or after elution for passive samplers.

Various families of CBP have been identified and quantified during these fields campaigns in water samples, including trihalomethanes (THM), haloacetic acids (HAA), haloacetamides (HAM), haloacetonitriles (HAN), haloaledhydes (HAL), halobenzoquinones (HBQ), halophenols (HP), with values directly linked to chlorination doses applied in industrial plants. Among these compounds, two compounds emerge due to their environmental impacts. Bromoform ($CHBr_3$) has been found up to 34.6 µg L^{-1} in water and up to 3.9 ppbv in air. $CHBr_3$ is known to have direct harmful impacts on marine organisms [3], but also, once in air, known to impact atmospheric chemistry by being either photolyzed in the atmosphere into bromine radicals or being reacted with hydroxyl radicals to form reactive bromine species [4]. 2,4,6-tribromophenol (TBP) has been found in all marine organisms sampled, with highest levels in mussels (1500 to 2000 ng g^{-1} lipid weight, in average).

Acknowledgements

This work was supported by the French National Research Agency (ANR) within the project FOS-SEA (ANR-16-CE34-0009) and by the Conseil Regional Provence Alpes Côte d'Azur (Regional Council SUD-PACA).

References

[1] M. Grote, J.-L. Boudenne, J.-P. Croué et al. (2022) *Water research*, 217, 118383.

[2] M. Deborde, U. von Gunten (2008) *Water Research*, 42, 13-51.

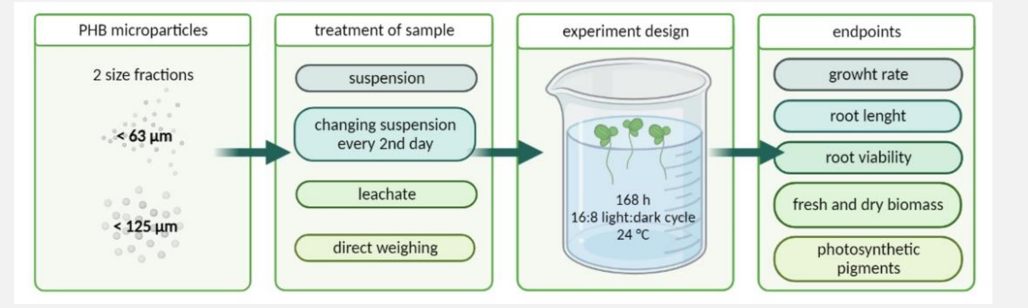
[3] K. Lebaron, L. Mechiri, S. Richard et al. (2019) *Environmental Science & Pollution Research*, 26(20), 20573-20580.

[4] B. Quack, D.W.R. Wallace (2003) *Global Biogeochemical Cycles*, 17, GB1023.

Impact of Polyhydroxybutyrate Microparticles on the Floating Freshwater Plant Duckweed *Lemna minor*

P. Procházková[1*], S. Mácová[1], J. Kučerík[1], H. Zlámalová Gargošová[1]

(1) Brno University of Technology, Faculty of Chemistry, Purkyňova 118, Brno 620 00, Czech Republic
*Petra.Prochazkova1@vutbr.cz



Considering the superior properties of plastics, such as low cost, lightweight, durability, waterproof, etc., plastic production has been growing rapidly for wide possibilities of the use of plastic materials [1]. Plastics accumulate in the environment due to their resistance, improper disposal of plastic waste, and widespread use of plastic products [2]. In the environment, larger plastic fragments – macroplastics - are gradually broken down by weathering, degradation, and microbial-mediated factors, into small plastic particles called microplastics (MPs) [3]. MPs can be defined as solid synthetic particles or polymer matrices with regular or irregular shapes and with a size in the range of 1 µm to 5 mm. These particles are insoluble in water [4].

Conventional MPs are not biodegradable in the environment, and therefore biodegradable materials are increasingly becoming a focus of interest. Biodegradable plastics (BDPs) have an appeal in ensuring the safe return of carbon to ecosystems by complete assimilation of the degraded product as a food source for soil or aquatic microorganisms. The material to produce BDPs can be renewable raw materials, petrochemicals, or mixtures. BDPs have found applications in medicine, agriculture, and packaging materials. The advantage is that most of the modified conventional polymer processing techniques can be used to process BDPs [5]. One of the most important groups of biobased and biodegradable polymers is polyhydroxyalkanoates.

The aim of this study was to investigate the effect of polyhydroxybutyrate (PHB) microparticles on duckweed (*Lemna minor*) the freshwater floating plant. We tested the effect of two size fractions (particles <63 µm and <125 µm) of PHB in differently prepared samples – (a) suspension of MPs, (b) suspension of MPs with the recovery of media every second day, (c) direct weighing of MPs into the test vessel and subsequent addition of media, and (d) leachate from MPs. The effect of these samples on the specific leaf growth rate, root length, root cell viability, fresh and dry weight of biomass, and content of photosynthetic pigments (chlorophyll *a* and *b*, carotenoids) were assessed.

Acknowledgements

This work was supported by the project FCH-S-22-8001 of Ministry of Education, Youth and Sports of the Czech Republic.

References

[1] W. Xiang, H. Huijie, et al. (2022) *Journal of Hazardous Materials*, 422, 126834.
[2] M. C. Rillig (2012) *Environmental Science and Technology*, 46 (12), 6453-6454.
[3] M. Cole, P. Lindeque, C. Halsband, T.S. Galloway (2011) *Marine Pollution Bulletin*, 62 (12), 2588-2597.
[4] G. Kalčíková, A. Ž. Gotvajn, A. Kladnik, A. Jemec (2017) *Environmental Pollution*, 230, 1108-1115
[5] K. Gosh, B. H. Jones (2021) *ACS Sustainable Chemistry and Engineering*, 9 (18), 6170-6187.

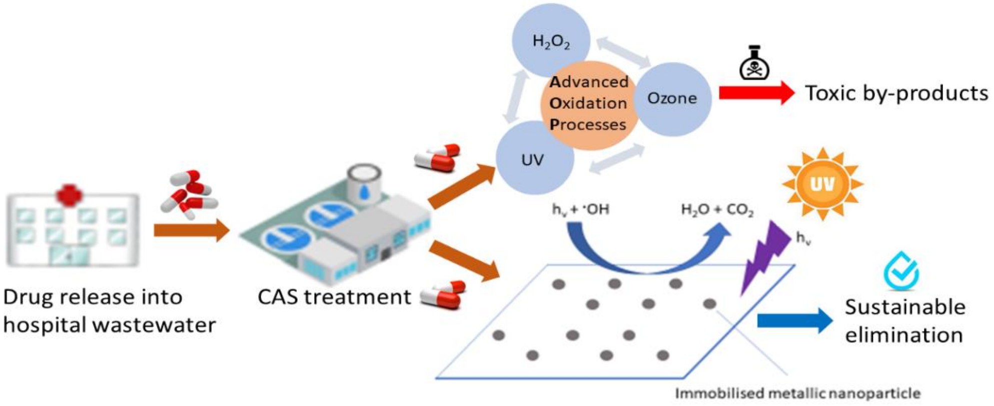
ORAL
(#5)

At-Source Hospital Wastewater Treatment to Eliminate Harmful Pharmaceuticals: A Novel Approach Using UV-LED Activated Photocatalytic Nanomaterials

M. Valdivia[1,*], *M. A. Taggart*[2], *S. Pap*[2], *A. Kean*[1], *I. Megson*[1]

(1) Division of Biomedical Sciences, Institute of Health Research and Innovation, University of the Highlands and Islands, Old Perth Road, Inverness IV2 3JH, United Kingdom, (2) Environmental Research Institute, University of the Highlands and Islands, Castle Street, Thurso KW14 7JD, United Kingdom

manuelthomas.valdivia@uhi.ac.uk



Healthcare interventions are a globally challenging task. Novel disease patterns require adequate pharmacological responses and continuous revision of prescribing rates and drug formularies. Targeted drug interventions against a multitude of diseases are primarily delivered at hospitals.

After administration, many pharmaceuticals are partially absorbed by the human body and excreted into hospital wastewater as biologically active parent compounds or metabolites. Until recently, these pharmaceutical residues were thought to be harmless due to their high dilution as they pass into sewage, rivers and lakes. However, non-biodegradable active pharmaceutical ingredients can persist in the aquatic environment. Toxicity studies have demonstrated that pharmaceutical residues in nature can cause harmful effects on aquatic organisms even at these minute concentrations. Conventional wastewater treatment can efficiently eliminate most biodegradable drugs, but many drugs remain in water bodies as a mixture of toxic parent compounds and metabolites.

Pilot-scale tertiary wastewater treatment such as ozone or UV-irradiation have shown some success in eliminating most harmful pharmaceuticals but may produce toxic by-products or are very expensive at large-scale.

A novel laboratory-scale wastewater treatment design, using energy saving UV-light LEDs to initiate a chemical reaction on the surface of a reusable, non-toxic, metallic nanomaterial, has been designed to show proof of principle for the concept of a highly effective means of oxidising a diverse range of pharmaceuticals in water.

This talk will highlight the tremendous potential of this technique as a future-proof approach to purify pharmaceutical polluted wastewater at hospitals.

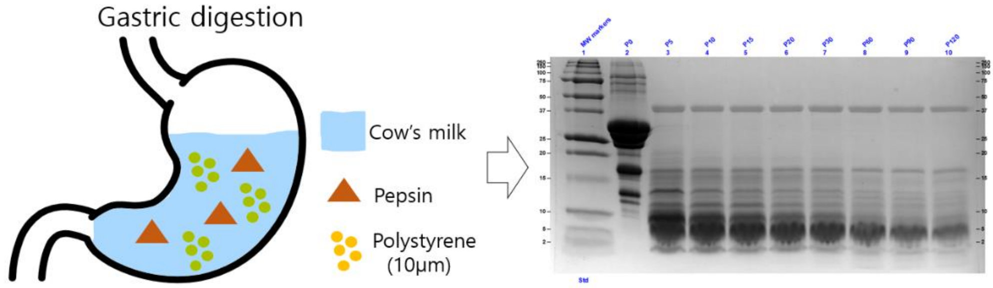
Acknowledgements

The authors would like to gratefully acknowledge the Scottish Government’s Hydronation Scholars Programme for a PhD studentship to Manuel-Thomas Valdivia.

Implications of Polystyrene Microplastics on the Gastric Digestion of Bovine Milk

MK. de Guzman[1,2,*], *L. Wimmer*[3], *LA. Dailey*[3], *S. Van Haute*[1,2], *T. Cirkovic Velickovic*[1,2,4,5]

(1) Center for Food Chemistry and Technology, Ghent University Global Campus, Incheon, South Korea, (2) Department of Food Technology, Safety, and Health, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium, (3) Department of Pharmaceutical Technology and Biopharmacy, University of Vienna, Vienna, Austria, (4) Faculty of Chemistry, Centre of Excellence for Molecular Food Sciences, University of Belgrade, Belgrade, Serbia, (5) Serbian Academy of Sciences and Arts, Belgrade, Serbia
[*]mariakrishna.deguzman@ugent.be



The prevalence of microplastics (MP) pollution in different zones of the environment has been established by several studies [1]. Due to its widespread presence, MP have found its way into food items. Fish, shellfish, water, milk, salt, and sugar are just some examples of the food we commonly consume that are contaminated with MP [2]. Human ingestion of MP is already well-established but there is limited data regarding how MP affect human gastric digestion of food components, especially proteins.

In this study, we investigated the effects of polystyrene (PS) MP on pepsin, the major protease in human gastric digestion. Pepsin activity was tested during exposure to two different sizes -10 μm (PS10) and 100 μm (PS100), and three different quantities- low count (142 particles), moderate count (1420 particles), and high count (14200 particles), of PS using haemoglobin as substrate. Results showed that exposure to PS100 has no effect on enzyme activity. However, exposure to high count PS10 considerably reduced pepsin activity from 2957 ± 310 U/mg to 1674 ± 270 U/mg.

To test the effect on food digestion, high count PS10 was added to a sample of commercially available liquid bovine milk (defatted). In this case, the static in vitro simulation of gastric digestion was followed to mimic human digestion of food [3]. Milk digesta at different time points (5, 10, 15, 20, 30, 60, 90, 120 minutes) were obtained to monitor the progress of protein degradation.

SDS-PAGE showed no difference in the peptide bands from 30-120 minutes. However, bands corresponding to caseins were not observed at 5 minutes when PS10 was present. Additionally, 14 kDa fragments were not observed at 10-20 minutes.

Washing of the PS particles followed by SDS-PAGE revealed a faint pepsin band from all time points. At 5 and 10 minutes, faint peptide bands >10kDa were also observed. These suggest that pepsin and some milk peptides were adsorbed on the surface of PS10. Zeta potential analysis of PS revealed a slightly negative surface charge which could explain the adsorption and disappearance of peptide bands. This adsorption of pepsin on PS did not seem to affect its overall protease activity. However, the interaction of milk peptides with PS may reduce the nutrients human could acquire from milk.

Acknowledgements

This study was supported by Ghent University Global Campus; Special Research Fund (BOF) of Ghent University (grant number 01N01718) and IMPTOX European Union's Horizon 2020 research and innovation program (grant number 965173).

References

[1] S. Sharma, S. Basu, N. P. Shetti, M. N. Nadagouda, T. M. Aminabhavi (2021) *Chem. Eng. J.*, 408, 127317.
[2] K. D. Cox, G. A. Covernton, H. L. Davies, J. F. Dower, F. Juanes, S. E. Dudas (2019) *Environ. Sci. Technol.*, 53(12), 7068–7074.
[3] A. Brodkorb et al. (2019) *Nat. Protoc.*, 14(4), 991–1014.

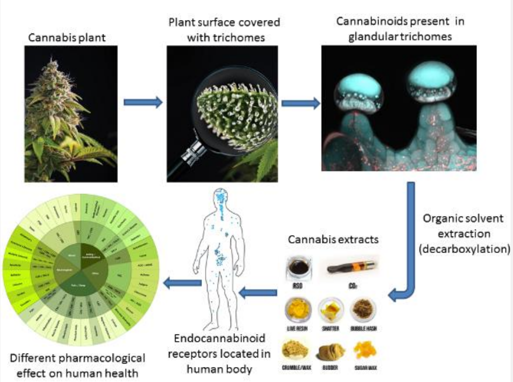
ORAL
(#5)

The Role of Secondary Metabolites from *Cannabis Sativa* L. in Health

R. Štukelj[1,*]*, B. Radišič*[2]

(1) Faculty of Health Sciences, University of Ljubljana, Zdravstvena 5, Ljubljana, Slovenia, (2) Research Nature Institute, Trubarjeva 66, Ljubljana, Slovenia

[*]*roman.stukelj@zf.uni-lj.si*



Cannabis Sativa L. has been cultivated for many centuries all over the world as an annual plant for various purposes (natural remedies, food and fiber). Prohibition, which began in the 1930s, prevented scientists from all over the world to do research and clinical studies on the broad range of plant components (secondary metabolites) and their benefits in human health.

In the literature we can find more than 1200 different compounds isolated from Cannabis plant. It is rich in essential nutrients, fibres, enzymes, vitamins, minerals, flavonoids, carotenoids, terpenes and acidic form of cannabinoids (eg. *trans*-Δ^9-tetrahydrocannabinol acid (THC-a), cannabidiol acid (CBD-a)). The term cannabinoids represent a group of C21 or C22 terpenophenolic compounds which are highly hydrophobic lipids, soluble in fats, alcohols and other non-polar organic solvents [1]. They are located in trichomes on the surface of cannabis flowers and are non-enzymatically decarboxylated into their corresponding active neutral forms upon heating after plant harvesting [2]. Decarboxylation process allows them to bind to the endocannabinoids receptors (CB1 and CB2) in human body which activates and influences several body systems suggesting utility in multiple diseases [3]. The pharmacological actions of CBD show that it could be used for the treatment of anxiety, epilepsy, central motor disorders, nausea, diabetes, schizophrenia and dementia, while THC shows good effect on pain management, muscle spasticity, nausea and vomiting, can stimulate appetite and is a good neuroprotectant [4].

Over the last decade, the use of cannabis and its extracts has increased significantly among Slovenian patients, particularly oncological, neurological, autoimmune and neurological patients. Since there is still little known about the dosages, quality of the products and the route of administration the cannabinoid profiling of this products is crucial. Moreover, it is of paramount importance for patients to be able to monitor the quality of the products they use. **We present the results of mapping of cannabis products from the industry and patients in a two-year period.**

Acknowledgements

Research was supported by Research Nature Institute.

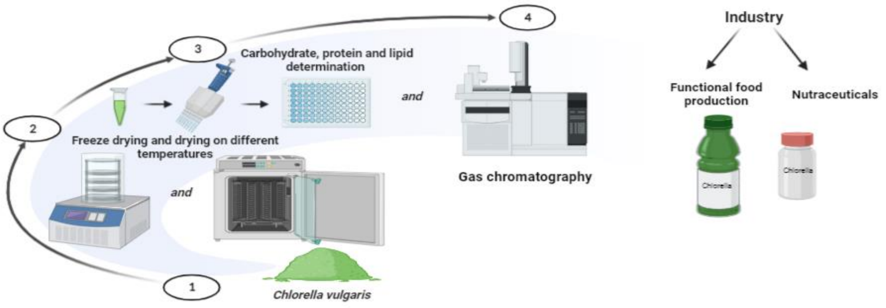
References

[1] R. Smith, C. Vaughan (1977) *Journal of Pharmacy and Pharmacology*, 29, 286-290.
[2] I.J. Flores-Sanchez, R. Verpoorte (2008) *Phytochemistry Reviews*, 7, 615-639.
[3] K.B. Walsh, et al. (2021) *Frontiers in Pharmacology*, 29:777804.
[4] R. Stukelj, M. Bencina, et al. (2019) *Materials and technology*, 53, 543–549.

Evaluation of *Chlorella vulgaris* Potential as Nutraceutical and Sustainable Food Supplement

*M. Baković[1, *], A. Martić[1], L. Perković[1], N. Topić-Popović[1,2], T. Vujović[1], M. Galić Perečinec[1,2], R. Čož-Rakovac[1,2]*

(1) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (2) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia
**mbakovic@irb.hr*



Chlorella vulgaris is a green unicellular that has been subjected to extensive studies within the last decade and has experienced imense applications in food and cosmetic industries [1]. *C. vulgaris* biomass represents a valuable and sustainable source of numerous bioactive compounds that can positively affect human health, such as proteins, vitamins, polysaccharides, microelements and polyunsaturated fatty acids (PUFA) [2]. Proteins and PUFAs recently gained a special interest of the nutraceutical sector due to their ability to accelerate wound healing, decrease blood pressure and cholesterol levels, but also improve bone health and neurological function [3]. For those reasons, particular focus is placed on the microalgal potential to enhance the nutritional value of conventional foods.

Drying harvested microalgae while at the same time preserving all beneficial activities has shown to be a challenging step for the industry. To deepen the knowledge gap, *C. vulgaris* biomass was dried at different temperatures (lyophilized, 25, 40, 60 and 100), followed by determination of protein, carbohydrate and lipid contents.

The highest protein value was observed for *C. vulgaris* dried at 25°C (58.5377±0.0007% (µg/µg), followed by samples dried at 40°C and 100°C. According to the findings, lower-temperature dried samples had higher levels of chlorophyll a and b, as well as their derivatives pheophytin a and b. The biomass dried at 40°C had the highest amount of carotenoids.

The lipid profile determined by gas chromatography analysis showed a predominance of monounsaturated and polyunsaturated fatty acids, in specific essential omega-6 (linoleic acid) and omega-3 (docosahexaenoic acid) fatty acids. The highest total lipid content of *C. vulgaris* was around 5% for samples dried at 60 and 100°C.

The results obtained confirmed *C. vulgaris* as a microalga with a great potential source of proteins, pigments and essential fatty acids, but also emphasized the importance of optimization of drying techniques.

Acknowledgments

This study was financially supported by: Development of Innovative Biobased Products by in silico Assessment of Microalgae Bioactivity (KK.01.2.1.02.0015), financed by the European Union through the European Regional Development Fund—the Competitiveness and Cohesion Operational Program.

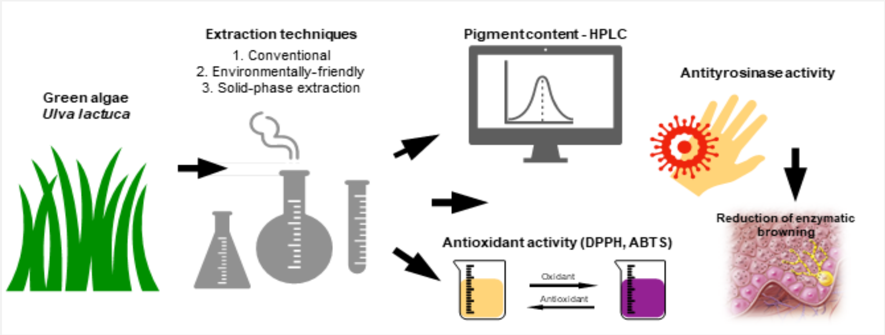
References

[1] L. Tomaselli (2004) The microalgal cell. In: A. Richmond (ed) *Handbook of Microalgal Culture: Biotechnology and Applied Phycology*, pp. 146–167. Blackwell Science Ltd, Oxford, UK.
[2] M. Görs, R. Schumann, D. Hepperle, U. Karsten (2009) *Journal of Applied Phycology*, 22(3), 265–276.
[3] R.R. Wolfe, S.L. Miller, K.B. Miller (2008) *Clinical Nutrition*, 27(5), 675–684.

Evaluation of Extraction Procedures to Yield the Highest Pigment content, Antioxidant and Antityrosinase activity from Green Algae *Ulva lactuca*

L. Krumpak[1], *L. Čižmek*[2,3,*], *R. Čož-Rakovac*[2,3], *P. Trebše*[1]

(1) Faculty of Health Sciences, University of Ljubljana, Zdravstvena pot 5, Ljubljana, Slovenia, (2) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (3) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia
[*]lcizmek@irb.hr



Green macroalgae *Ulva lactuca*, also known as marine green salad, has high amount of different biologically active compounds such as polysaccharides, pigments, terpenes etc. [1]. In this study, aim was to evaluate conventional (successive solvent extraction – hexane, chloroform, methanol) and modern (solid-phase extraction, SPE, using methanol and dichloromethane) extraction procedures, as well es environmentally-friendly option (ethanol, further fractionized using non-toxic solvents – hexane, chloroform, ethyl acetate and butanol) for purpose of extracting pigments such as lutein, chlorophylls, and others that could posses' activity against tyrosinase, an enzyme that has an important role in the melanogenesis and enzymatic browning [2].

High-pressure liquid chromatography (HPLC) was used for successful identification of lutein, chlorophyll b and canthaxanthin. The highest content of lutein was found in SPE methanolic fraction (3.422 ± 0.007 mg/g), followed by chloroform extract (1.638 ± 0.002 mg/g). Chlorophyll b was most abundant in ethyl acetate fraction (0.443 ± 0.001 mg/g), while the canthaxanthin content was also the highest in SPE methanol fraction (0.091 ± 0.000 mg/g). In SPE dichloromethane fraction and butanol fraction no pigments were identified.

Antioxidant activity using both DPPH and ABTS methods have shown to be the highest for SPE methanol fraction. The highest monophenolase activity was observed for ethanol extract (20.39 ± 8.01 %) followed by chloroform (14.36 ± 4.31 %) and hexane extracts (7.51 ± 1.02 %), while no activity was observed for all other extracts and fractions. Samples showed better diphenolase activity. The highest activity was observed for methanol extract (57.33 ± 2.53 %), followed by chloroform extract (54.09 ± 1.05 %) and methanol fraction (51.78 ± 0.95 %).

All the results suggest that not only pigments exert antityrosinase activity, but also other isolated molecules. SPE has shown to be the best used method for lutein isolation from *U. lactuca* and has shown to significantly contribute to the antioxidant activity.

Acknowledgements

This contribution was financially supported by Slovenian Research Agency (ARRS), grant number P3-0388 (Mechanisms of health maintenance) and by the European Regional Development Fund—the Competitiveness and Cohesion Operational Programme (KK.01.1.1.01) through the project Bioprospecting of the Adriatic Sea (K.K.01.1.1.01.001).

References

[1] S. Pappou, M. Myrto Dardavila, M.G. Savvidou, V. Louli, K. Magoulas, E. Voutsas (2022) *Applied Sciences*, 12, 2117.

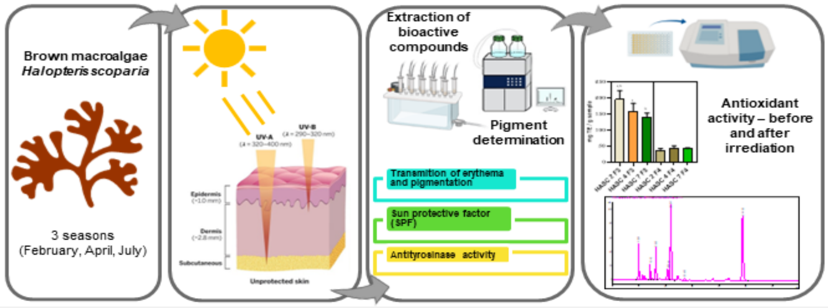
[2] S. Zolghadri, A. Bahrami, M.T.H. Khanb, J. Munoz-Munoz, F. Garcia- Molinad, F. Garcia-Canovas, A. Akbar Saboury (2019) *Journal of enzyme inhibition and medicinal chemistry*, 34, 279–309.

Photostability and Photoprotective Effects of Brown Macroalgae *Halopteris scoparia* Influenced by Seasonal Changes

L. Čižmek[1,2*], A. Martić[1], R. Čož-Rakovac[1,2], P. Trebše[3]

(1) Laboratory for aquaculture biotechnology, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (2) Center of Excellence for Marine Bioprospecting (BioProCro), Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (3) Faculty of Health Sciences, University of Ljubljana, Zdravstvena pot 5, Ljubljana, Slovenia

*lcizmek@irb.hr



Brown macroalgae have recently been in the focus of many research due to their composition and the accumulation of specific metabolites with several health benefits and biological activities [1, 2]. Additionally, the extracts of *Halopteris scoparia* (HASC) have shown to have a protective and preventive activity against human cancer cells [3].

In this study, evaluation of HASC against harmful ultra-violet (UV) light was done in regard to different activities, namely pigment determination by HPLC analysis, transmission of erythema (Te) and pigmentation (Tp), along with calculation of sun protective factor (SPF), antityrosinase and antioxidant activities. Antioxidant activity was also analysed before and after irradiation using UV-B light (8 W, 2000 μW cm^{-2}) for different time periods (30, 60 and 120 minutes). Analysis was performed on two different fractions obtained with solid-phase extraction (SPE) method, methanolic F3 and dichloromethane F4 fractions, from three different harvesting seasons (February, April, and June 2021).

HPLC analysis revealed several pigments in HASC samples. The most abundant were fucoxanthin, lutein, and β-carotene. The highest concentrations were found in sample from February. Interestingly, the less lipophilic pigments such as fucoxanthin, lutein, astaxanthin and canthaxanthin, were observed in F3 fraction, while F4 fraction contained more lipophilic pigments chlorophyll a and β-carotene. The highest antioxidant activity using DPPH and ABTS assays was also observed for February sample which could be explained by the presence of pigments such as β-carotene with known activity against free radicals. SPF was high for all HASC samples when compared to a known UV-filter Benzophenone-3 (BP-3). % Te and % Tp showed high protective effect for all samples, with the lowest transmission for HASC from February, especially F4 fraction which can be attributed to the presence of β-carotene. No significant difference was observed in antioxidant activity after UV-B irradiation for all tested time periods and samples. Only the HASC June samples have shown slight decrease in antioxidant activity after 120 minutes.

Additional chemical characterization of obtained extracts is in progress to further evaluate additional bioactive compounds present in samples that could influence photostability of this samples and could have application as natural sun-protective agents.

Acknowledgements

This research was funded by the European Regional Development Fund—the Competitiveness and Cohesion Operational Programme (KK.01.1.1.01) through the project Bioprospecting of the Adriatic Sea (K.K.01.1.1.01.001) granted to The Scientific Centre of Excellence for Marine Bioprospecting—BioProCro and by the Slovenian Research Agency (ARRS), grant number P3-0388 (Mechanisms of health maintenance)

References

[1] A-M. Cikoš, I. Flanjak, K. Bojanić, S. Babić, L. Čižmek, R. Čož-Rakovac, S. Jokić, I. Jerković (2021) *Molecules*, 26, 520.

[2] N.C. Afonso, M.D. Catarino, A.M.S. Silva, S.M. Cardoso (2019) *Antioxidants*, 8, 365.

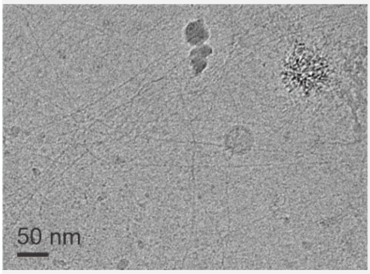
[3] A. Güner, A. Nalbantsoy, A. Sukatar, N.Ü.K. Yavaşoğlu (2019) *Cytotechnology*, 71: 687–704.

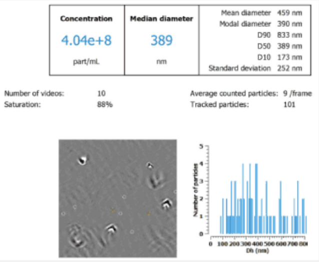
Determination of Hydrodynamic Radius of Extracellular Particles from Conditioned Media of Microalgae *Phaeodactylum Tricornutum* by Interferometric Light Microscopy

A. Romolo[1,], Z. Jan[1], V. Arrigler[2], A. Iglič[3], K. Kogej[2], V. Kralj-Iglič[1]*

(1) University of Ljubljana, Faculty of Health Sciences, Zdravstvena 5, Ljubljana, Slovenia, (2) University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 101, Ljubljana, Slovenia, (3) University of Ljubljana, Faculty of Electrical Engineering, Tržaška 25, Ljubljana, Slovenia

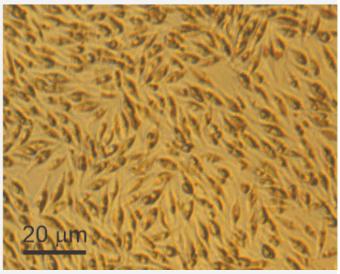
[*]romoloa@zf.uni-lj.si





Concentration	Median diameter		
4.04e+8	389	Mean diameter	459 nm
part/mL	nm	Modal diameter	390 nm
		D90	833 nm
		D50	389 nm
		D10	173 nm
		Standard deviation	252 nm

Number of videos: 10
Saturation: 88%
Average counted particles: 9 /frame
Tracked particles: 101



Extracellular particles (EPs) (e.g. protein aggregates, lipid droplets and viruses) are present in the environment and are suggested to be universal mediators of interaction between life domains. They can be isolated from samples (e.g. conditioned culture media) and characterized. However, as EPs are tiny and fragile, their harvesting and assessment presents a challenge. Recently, interferometric light microscopy (ILM) principle [1] for determination of EPs number density and hydrodynamic radius R_h was developed. In this work we used ILM to estimate number density and size of EPs isolated from conditioned culture media of microalgae *Phaeodactylum tricornutum* (CCAP 1052/1A from the Culture Collection of Algae and Protozoa (CCAP) of SAMS (Oban, Scotland)). Microalgae were grown in artificial seawater supplemented with Guillard's (F/2) Marine Water Enrichment Solution in a respirometer in borosilicate bottles, at controlled temperature, illumination and aeration. EPs were isolated by differential ultracentrifugation [2]. A 5 μL drop of sample was placed between cover glasses and illuminated by LED light. The light scattered on the particle was imaged by a bright-field microscope objective and allowed to interfere with the incoming light to spot the particles in the sample. The image of the particle was recorded by a complementary metal–oxide–semiconductor (CMOS) high-resolution high-speed camera to track the particle and assess its diffusion coefficient D. R_h was estimated by assuming that the particles were spherical and using the Einstein-Stokes relation $R_h = kT/6\pi\eta D$ where k is the Boltzmann constant, T is temperature and η is viscosity of the medium. Each particle was tracked and processed individually, and the respective incident light signal was subtracted from each image by using the associated software QVIR 2.6.0 (Myriade, Paris, France). We assessed 5 isolates and obtained the average number density of EPs $(3.97 \pm 1.64)\,.10^8$/mL and R_h (186±22) nm. The difference between the effective radius of EPs observed by cryo-TEM (smaller than 50 nm) [3] and R_h can be explained by the presence of thin filaments in the isolate [3] which hinder the motion of EPs. In this case, overestimation of R_h is suggested to be due to decreased diffusion coefficient D.

Acknowledgements

Authors acknowledge ARRS grants P3-0388, J3-3066, L3-2621.

References

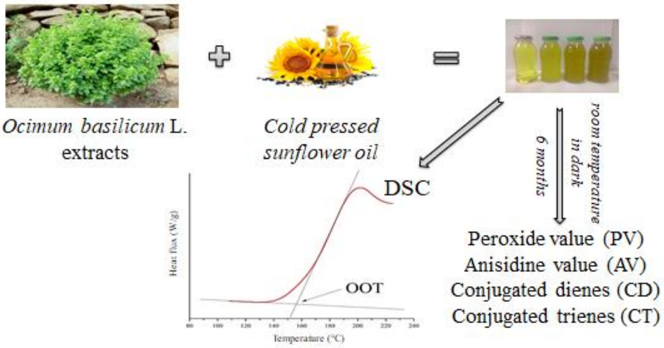
[1] M. Boccara, Y. Fedala, C. V. Bryan, et al., (2016) *Opt. Express* 7, 3736-3746.
[2] D. Škufca, D. Božič, M. Hočevar, et al., (2022) *Int. J. Mol. Sci.* 23, 8447.
[3] V. Kralj-Iglič, A. Bongiovanni, D. Božič, et al., *Zenodo.* (2022) https://doi.org/10.5281/zenodo.6976794.

The use of ethanolic extracts of basil to improve the oxidative stability of cold-pressed sunflower oil

A. Stojićević[1], *V. Rac*[2], *B. Rabrenović*[2], *M. Antić*[2, *]

(1) Academy of Applied Technical Studies Belgrade- Applied Engineering Sciences Požarevac, Nemanjina 2, Požarevac, Serbia, (2) University of Belgrade- Faculty of Agriculture, Nemanjina 6, Belgrade, Serbia

[*] *mantic@agrif.bg.ac.rs*



Lipid oxidation is one of the leading causes of the decrement in the shelf life of edible oils. This undesirable process leads to the loss of essential fatty acids and liposoluble vitamins. A decrease in the nutritional value of the oil is accompanied by a change in the sensory properties and the formation of potentially harmful products of oxidative degradation, which makes the oil unsuitable for consumption [1]. As there is a justified need to remove synthetic antioxidants from use, several methods have been developed to delay oxidative changes in the oil. In this sense, the use of antioxidants of plant origin is one of the most prevalent [2]. Of particular importance is the use of extracts of medicinal and herbal plants because they contain active components that can delay lipid oxidation [3].

Therefore, the subject of this work was to investigate the effect of adding basil extracts on the oxidative stability of cold-pressed sunflower oil during long-term storage. Extracts were prepared with 70 % ethanol solution using two methods - Soxhlet extraction (SE) and ultrasonic assisted maceration (UAM). Oil samples with the addition of extracts in a concentration of 250, 500 and 1000 ppm were stored in the dark for six months. Oxidative status parameters (peroxide value, anisidine value, conjugated dienes and conjugated trienes) were monitored monthly. An oil sample supplemented with BHT (200 ppm) and oil without additives were used as control samples. Oxidative stability of oil samples with the addition of extracts in the highest concentration was also tested by differential scanning calorimetry (DSC) in non-isothermal conditions.

The results indicate that basil extracts effectively suppress oxidative changes in cold-pressed sunflower oil during long-term storage. SE extracts were more potent antioxidants compared to UAM extracts. Regardless of the extraction method, the extracts in the highest concentration are equally effective as the synthetic antioxidant BHT so that basil extracts can be used as an effective, healthy and environmentally acceptable alternative to artificial additives.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract No: 451-03-68/2022-14/200116).

References

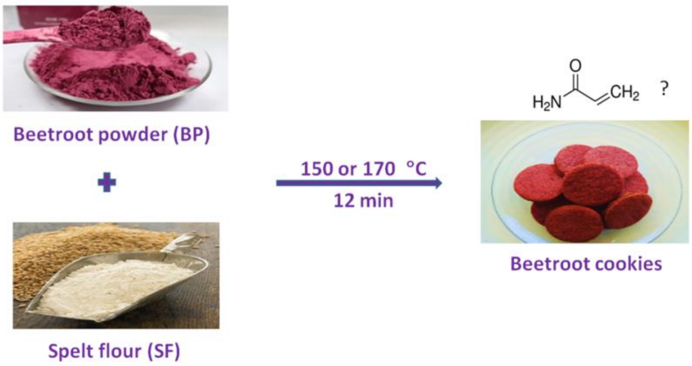
[1] F. Shahidi, Y. Zhong (2010) *Chemical Society Reviews*, 39(11), 4067–4079.
[2] M. Kiralan, M. Ulaş, A. Özaydin, N. Özdemır, G. Özkan, A. Bayrak, M. F. Ramadan (2017) *Journal of Food Biochemistry*, 41(1), e12272.
[3] Z. Sayyari, R. Farahmandfar (2017) *Food Science & Nutrition*, 5(2), 266–272.

Acrylamide Content in Cookies Based on Spelt Flour and Beetroot Powder

S. Mitrevski[1,2], D. Dj. Savić[2], D. N. Savić[3], N. Pantelić[2], M. Balaban[3], J. Laličić-Petronijević, V. Antić[2,]*

(1) Olea Health House, Karadjordjeva 8, Pančevo, Srbija, (2) University of Belgrade-Faculty of Agriculture, Nemanjina 6, Belgrade, Serbia, (3) University of Banja Luka, Faculty of Natural Sciences and Mathematics, Mladena Stojanovića 2, Banja Luka, Bosnia and Herzegovina

[*] *vantic@agrif.bg.ac.rs*



Acrylamide is an organic compound of low molecular weight, soluble in water, formed in Maillard reactions during thermal processing and food exposure to temperatures above 120 °C. Acrylamide is mainly found in baked or fried foods rich in carbohydrates. It is formed by reactions between the amino acid asparagine and reducing sugars such as glucose, fructose, and lactose at high temperatures. The acrylamide content depends on the time and temperature of baking/frying, the amount of asparagine, and the availability of sugar in the food. Foods such as chips, French fries, coffee, biscuits, and bakery products contribute the most to the total acrylamide intake in the human body. The European Food Safety Authority (EFSA) announced in 2015 that acrylamide in food is a public health concern based on the results of animal studies. EFSA warns that acrylamide content in food potentially increases cancer risk in people of all age groups [1]. Due to its harmful effects, it is necessary to reduce acrylamide's presence in food that, in raw form, contains its precursors.

In the last few years, several methods have been developed for identifying and quantifying acrylamide in food, based mainly on gas and liquid chromatography with different detectors [2, 3]. In this work, acrylamide was determined in cookies prepared with spelt flour and beetroot powder, using the GC-MS method preceded by derivatization via bromination or silylation. The silylation reagent was *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA). Earlier results showed that cookies prepared with beetroot powder had significantly improved antioxidant properties compared to a control sample without beetroot [4]. Here, the influence of beetroot powder content (15-25 % in the baking mixture) and baking temperature (150 and 170 °C) on acrylamide formation was investigated. It was found that a higher amount of acrylamide is formed in the examined cookies at a higher baking temperature.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract No: 451-03-68/2022-14/200116).

References

[1] EFSA CONTAM Panel (EFSA Panel on Contaminants in the Food Chain), 2015. Scientific Opinion on acrylamide in food. *EFSA Journal* (2015) 13(6):4104, 321 pp.

[2] Foodstuffs - Determination of acrylamide in food and coffee by gas chromatography-mass spectrometry (GC-MS), Ref. No. FprCEN/TS 17083:2017 E.

[3] J. Cooper, Simple and cost-effective determination of acrylamide in food products and coffee using gas chromatographymass spectrometry, Thermo Fisher Scientific, 2019.

[4] J. Ž. Mitrevski, N. Đ. Pantelić, J. J. Vulić, J. S. Kojić, J. G. Laličić-Petronijević, V. V. Antić, *Proc. of 58th Meeting of the Serbian Chemical Society*, Belgrade, Serbia, June 9-10, 2022, 175.

Preparation of PET Particles By Cryomilling and Potential Environmental Impact of Microplastics

E. Kameníková[1,], P. Procházková[1], A. Hrušková[1], J. Palovčík[1], J. Kučerík[1]*

(1) Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno
[*]Eliska.Kamenikova@vutbr.cz

Exposure of plastics to natural conditions and influences, such as light and heat, organisms, mechanical abrasion, etc., can cause degradation of plastics and the formation of microplastics and nanoplastics [1, 2].

These particles can subsequently contaminate the environment, to interact with all its components, in become a part of the food chain, bioaccumulate, or adsorb contaminants on their surface and release toxic substances used for their production into the environment.

After contamination of the environment, microplastics can have a significant effect on all environmental compartments, to cause damage to fauna and flora or influence soil properties (aggregation, free and bound soil water content, nutrient content), thus potentially affect soil quality and health [3].

Some studies have also shown that particle shape and size are key factors determining the behaviour of micro- and nanoplastics in the environment [2,4].

For environmental studies focused on investigation of microplastics' effects on environmental compartments, it is necessary to find a fast and robust method which will enable to produce particles of different sizes and shapes without significant changes in particle properties [5].

The aim of this study was to test cryomilling, i.e., milling with pre-cooling with liquid nitrogen, as a simple physical method for preparation of PET microplastics in laboratory.

Different conditions of this process (such as milling frequency and time, pre-cooling time, number of milling cycles and number of balls) and the effect of the milling process on the properties of PET particles were tested.

Furthermore, the suitability of this process for the preparation of particles for environmental studies and the potential effect on the activity of organisms were assessed.

Acknowledgements

The work was supported by the project FCH-S-22-8001 of Ministry of Education, Youth and Sports of the Czech Republic.

References

[1] M. C. Rillig (2012) *Environmental Science and Technology*, 46(12), 6453-6354.

[2] D. S. Machado, A. Abel, CH. W. Lau, J. Till, W. Kloas, A. Lehmann, R. Becker, M. C. Rillig (2018) *Environmental Science and Technology*, 52(17), 9656-9665.

[3] K. Vogel, R. Wei, L. Pfaff, D. Breite, H. Al-Fathl, Ch. Ortmann, I. Estrela-Lopis, T. Venus, A. Schulze, H. Harms, U.T. Borncheuer, T. Maskow (2021) *Science of the Total Environment*, 773, 145111.

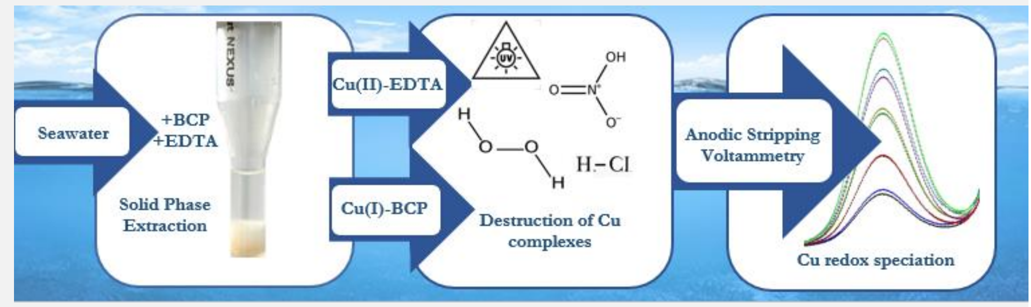
[4] D. S. Machado, A. Abel, Ch. W. Lau, W. Kloas, J. Bergmann, J. B. Bachelier, E. Faltin, R. Becker, A. S. Gorlich, M. C. Rillig (2019) *Environmental Science and Technology*, 53(10), 6044-6052.

[5] A. G. Rodríguez-Hernández, J. A. Munoz-Tabares, J. C. Aguilar-Guzmán, R. Vazquez-Duhalt (2019) *Environmental Science*, 6(7), 2031-2036.

Adaption of a Solid Phase Extraction Method for Copper (I) Determination in Marine Waters and Estuaries

D. Crmaric[1,*], *E. Bura-Nakic*[1]

(1) Ruder Boskovic Institute, Bijenicka cesta 54, Zagreb, Croatia
**dora.crmaric@irb.hr*



Copper (Cu) occurs in nanomolar concentrations in seawater and is an essential micronutrient to the most marine organisms, but its free ion is toxic to marine organisms at concentrations as low as 10-12 M [1, 2]. Copper in oxic environments such as oceans is primarily present as Cu (II), leading to speciation models assuming only Cu (II) as significant Cu state. Only few studies reported detectable amounts of Cu (I) in water, with Cu (I) ratio ranging from 5-10% of total dissolved copper in oceans and up to 80% of total dissolved copper in estuaries [3, 4, 5]. Marine organisms are producing Cu binding ligands as defence mechanism against free Cu toxicity, which are likely reducing Cu (II) to Cu (I) [6]. Since it is predicted that free Cu concentration in ocean will rise by 50 % by the end of century, better understanding of copper speciation is crucial to assess its negative effects [7]. In this work we will present adaption of solid phase extraction method for Cu (I) determination in seawater [5]. Cu (I) is retained on column as bathocuproine (BCP) complex, while Cu (II) is complexed with ethilendiamine (EDTA) and it is not retained on column. Cu (I) is eluated with acidic methanol, irradiated under UV lamp and mixed with concentrated HNO3, HCl and H2O2 in order to destruct Cu (I)- BCP complex. Cu concentrations are measured in both Cu (II) and Cu (I) fractions, as well as in seawater samples before column separation, using anodic stripping voltammetry (ASV) with hanging drop mercury electrode (HDME).

Acknowledgements

This research is supported by the Croatian Science Foundation project IPCH-2020-10-4965: „Understanding copper speciation and redox transformations in seawater”.

References

[1] W. G. Sunda, S. A. Hunstsman (1998) *Limnology and oceanography*, 43, 1055-1064.
[2] J. W. Moffet, R. G. Zika, L. E. Brand (1990) 37, 27-36.
[3] H. Xue, M. Goncalves, M. Reutlinger, L. Sigg , W. Stumm (1991) *Environmental Science and Technology*, 25, 1716–1722.
[4] J.W. Moffett, R.G. Zika (1988) *Geochimica et Cosmochimica Acta*, 52, 1849–1857.
[5] D. Buerge-Weirich, B. Sulzberger (2004) *Environmental Science and Technology*, 38, 1843–1848.
[6] A. Kungolos, P. Samaras, V. Tsiridis, M. Petala, G. Sakellaropoulus (2007) *Journal of Environmental Science and Health*, 41, 1509-1517.
[7] F. Millero, R. Woosley, B. DiTrolio, J. Waters (2009) *Oceanography* (Wash DC), 22 72–85.

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(#5)

Determination of Pollution Status of Urban Forest Obrenovački Zabran (Serbia) – Part A: Anion Concentrations in Soil and Sediments

S. Štrbac[1,], T. Tosti[2], S. Stojadinović[1], N. Antić[1], G. Veselinović[1], N. Živanović[4], M. Kašanin-Grubin[1]*

(1) Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia, (2) Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia, (3) Institute for Testing of Materials, Bulevar vojvode Mišića 43, Belgrade, Serbia, (4) Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, Belgrade, Serbia

**snezana.strbac@ihtm.bg.ac.rs*

Figure 1. Map of the „Obrenovački zabran” (Serbia).

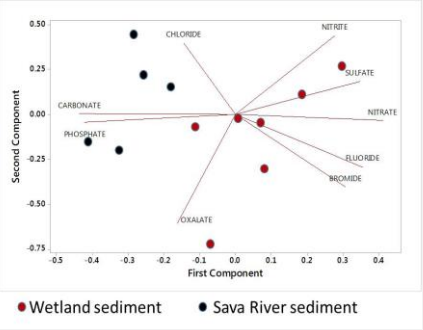

Figure 2. Multivariate analysis of the anion concentrations in „Obrenovački zabran” soil and sediments.

Inorganic anions play a vital role in the health of a water ecosystem. However, many agricultural activities increase nutrient levels of water due to runoff of large inorganic and organic materials into rivers and thus are transported over long distances (Michaud, 1994; Jake and Serge, 2010). The main objective of this study is to determine anion concentrations in soil and sediments from „Obrenovački zabran (OZ)” (Figure 1). OZ is a protected area of category III. It is located on the territory of the city municipality of Obrenovac, about 1.5 km east of Obrenovac and about 12 km southwest of the suburbs of Belgrade. The wider area where the protected area is located belongs to the plain terrain, that is, the alluvial plains of the Sava and Kolubara Rivers. Due to the presence of larger areas under agricultural crops in the immediate vicinity of the OZ, it is to be expected that increased use and spreading of certain amounts of various chemical substances in the form of artificial fertilizers, herbicides, pesticides, and other protective chemical agents.

A total of twelve soil and sediment samples from two different sites were analyzed. Soil samples were sampled from the forest that is flooded by the Kolubara River, and sediment was sampled from the Sava River. Analysis of the most abundant anions such as fluoride, chloride, nitrite, carbonate, sulfate, oxalate, bromide, nitrate, and phosphate was performed using an Ion chromatograph DIONEX ICS 3000. The Dionex ICS-3000 chromatographic set-up consisted of a single pump, a conductivity detector (ASRS ULTRAII (4 mm), recycle mode), and an eluent generator (potassium hydroxide) with a Chromeleon® Chromatography Work-station and Chromeleon6.7 Chromatography Management Software. All the separations were performed using an IonPac AS15 Analytical, 4 mm × 250 mm, and IonPac AG15 Guard, 4 mm × 50 mm columns. The flow rate of the mobile phase was 1.00 ml min concentration of 1000 ppm. The dilution was made according to the estimated concentration in solute. Concentrations and spatial distribution of characteristic anions are given in Figure 2.

However, there is a difference in anion concentrations between the two locations (Figure 2). The highest concentrations of chloride and phosphate were found in sediments from the Sava River, while the highest concentrations of fluoride, nitrite, carbonate, sulfate, oxalate, bromide, and nitrate were found in soil samples from the forest that is flooded by the Kolubara River.

Acknowledgments

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No: 451-03-68/2022-14/200026, 451-03-68/2022-14/200169).

References

[1] K. Jake, N.P. Serge (2010) *Journal of Analytical Chemistry*, 1, 24-28.
[2] J. Michaud (1994) *Journal of Ecology*, 36, 449-462.

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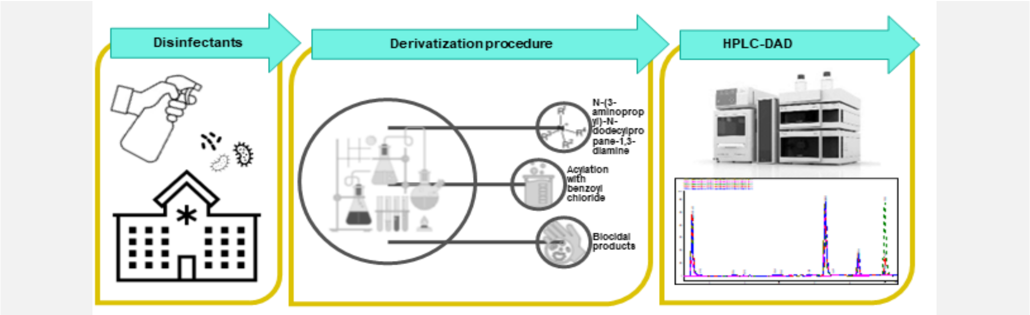
Development of Novel Method for Determination of Disinfection Agent N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine Using HPLC-DAD

L. Tomazin[1,*], *L. Čižmek*[2], *D. Mazur*[3], *P. Trebše*[4]

(1) Kimi d.o.o., Planjava 1, Trzin, Slovenia, (2) Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia, (3) Moscow State University, Chemistry Department, Leninskie gori 1, Moscow, Russia (4) University of Ljubljana, Faculty of Health Sciences, Zdravstvena pot 5, Ljubljana, Slovenia

[*]lovro.tomazin@kimi.si



Disinfectants are one of the key tools in the process of controlling the spread of hospital infections [1]. Given that there is a growing interest in the development of more environmentally and human-friendly, but also economically affordable agents, the reduction of active substances in prepared working solutions is desirable. At the same time, the prepared solutions must keep or even shorten needed contact times, which are necessary to achieve the required effects according to standardized efficacy testing procedures [2].

Quaternary ammonium compounds and amines represent one of the most common active group of substances used in preparations to disinfect surfaces, instruments, equipment or remaining medical devices. The reason for their widespread use is that these substances enable different ways of application, good compatibility with materials and generally proven effectiveness [3]. The problem of monitoring such large group of compounds in so many different media is need in an extremely large number of analytical methods, which include chromatography (liquid or gas coupled with various detectors), mass spectrometry, electrochemical and many other methods. Reliable analytical method is also vital in processes of proving compliance with legislation in the field of biocides, and especially in the field of medical devices.

Antimicrobial substance N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (BAPDA) is a novel compound used for the disinfection purposes. Methodologies for BAPDA detection such as HPLC-MS have already been developed, but our scope of research was oriented to the development of simple method, suitable for determination of residues on various hygienic and medical surfaces. We propose HPLC-DAD method with the prior derivatization of the amine, present in the sample.

The derivatization procedure was carried out as described earlier [4]. Briefly, amine was dissolved in a 0.1 M HCl aqueous solution or ethyl acetate. Sodium hydroxide (2 M) was added followed by addition of benzoyl chloride. The reaction took place at different temperatures for specific time interval. The acylation was stopped by adding saturated NaCl solution and performing further extraction with diethyl ether. The upper organic layer was dried and redissolved in methanol for HPLC analysis. Method optimisation included: selection of solvent for working solution, temperature, and derivatisation time optimisation. Obtained results showed that ethyl acetate was better initial solvent, 50 min as an optimal time at 30°C with a linear response curve for amine concentrations from 0.2 to 1 mg/ml. The method was evaluated on several biocidal products.

Acknowledgements

This research was supported by Slovenian Research Agency through the core foundlings No. P3-0388 (Mechanisms of health maintenance).

References

[1] J. Gebel, M. Exner, G. French, Y. Chartier, et al. (2013) *GMS Hygiene and Infection Control*, 8(1), 1-12.

[2] P.N. Humphreys (2011) *Journal of Hospital Infection*, 77(3), 193-198.

[3] K.R. Morrison, R.A. Allen, K.P.C. Minbiole, W.M. Wuest (2019) *Tetrahedron Letters*, 60(37), 1-12.

[4] D.F. Hwang, S.H. Chang, C.Y. Shiua, T. Chai (1997) *Journal of Chromatography B*, 693(1), 23-30.

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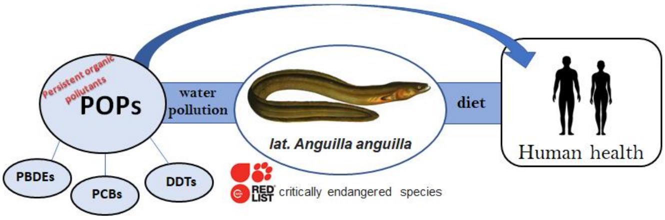
(#5)

Persistent Organic Pollutants in the European Eel from the Karstic River (Raša River, Croatia)

K. Jagić[1,*], *M. Dvoršćak*[1], *Z. Kljaković-Gašpić*[1], *D. Zanella*[2], *D. Klinčić*[1]

(1) Institute for Medical Research and Occupational Health, Ksaverska cesta 2, 10 000 Zagreb, Croatia, (2) University of Zagreb, Faculty of Science, Department of Biology, Rooseveltov trg 6, 10 000 Zagreb, Croatia

[*]*kjagic@imi.hr*



Polybrominated diphenyl ethers (PBDEs) and organochlorinated (OC) compounds such as polychlorinated biphenyls (PCBs) and DDT isomers are omnipresent in aquatic environments as a consequence of current anthropogenic activities or their use in the past. Due to their specific life cycle, eels are regularly used for biomonitoring contaminant concentrations reflecting environmental burden [1,2]. Monitoring levels of pollutants in eels is important because it is suspected that they have contributed to the decline of the eel population over the last few decades, as well as because of the impact on human health, as eels are widely included into typical diets among people living in the area of their habitat.

Persistent organic compounds (POPs) – PBDE congeners (BDE–28, −47, −99, −100, −153, −154, −183), indicator PCB congeners (PCB−28, −52, −101, −118, −138, −153, −180), and three DDT-type compounds (DDT, DDD, DDE) were analysed in 33 European eels (*Anguilla anguilla*) caught in the upper (S1) and middle (S2) course of the Raša River, an eastern Adriatic karstic river. Microwave-assisted extraction was used as the extraction technique followed by GC-µECD.

According to the results, a low level of PBDE contamination of eels was observed, with a median total concentration (∑PBDE) of 1.76 ng g^{-1} lipid weight (lw) and 2.02 ng g^{-1} lw at locations S1 and S2, respectively. BDE-47 was a dominant congener in the samples in which it was detected, accounting for more than 50% to the ∑PBDE in 75% of all eel samples, followed by BDE-100.

A relatively wide range of total PCB concentrations was detected, with a median of 29.3 ng g^{-1} lw and 46.2 ng g^{-1} lw at S1 and S2, respectively. PCB-138 and -153 were the predominant congeners in analysed eel samples, followed by PCB-180. Hexachlorobiphenyls mainly contribute the most to PCB levels in eels, but the same is also typical for different marine organisms in the Adriatic Sea [3,4].

The analysed DDT-type compounds were present in all eel samples from the Raša River. The median of their total concentration was 37.3 ng g^{-1} lw and 53.8 ng g^{-1} lw, at locations S1 and S2, respectively. DDE was the predominant compound among all of the targeted analytes.

Concentrations of targeted organic contaminants were significantly positively correlated with length, weight and the relative condition factor of eels, and even to a greater extent with the lipid content of eels. Since all of the analysed eels were in the yellow stage, such results were expected, because in this life stage, they strongly accumulate lipophilic contaminants due to their high lipid content and sedentary lifestyle. Although the OC compounds included in this study were banned decades before PBDEs were, they were still detected in higher concentrations in eels from the Raša River, confirming their persistence in biota. Generally, the levels of organic contaminants in eels measured in our study were at the lower end of levels reported for eels across Europe.

Acknowledgements

This work was supported in part by the Croatian Science Foundation under project HrZZ-UIP-2017-05-6713.

References

[1] G. Malarvannan, C. Belpaire, C. Geeraerts, …, A. Covaci (2014) *Science of the Total Environment*, 482–483.

[2] M. Couderc, L. Poirier, A. Zalouk-Vergnoux, …, B. Le Bizec (2015*) Science of the Total Environment*, 505, 199-215.

[3] Z. Kljaković-Gašpić, S. Herceg Romanić, D. Klinčić, V. Tičina (2015) *Arhiv za higijenu rada i toksikologiju*, 66, 299-308.

[4] D. Klinčić, S. Herceg Romanić, Z. Kljaković-Gašpić, V. Tičina (2020) *Marine Pollution Bulletin*, 155, 111086.

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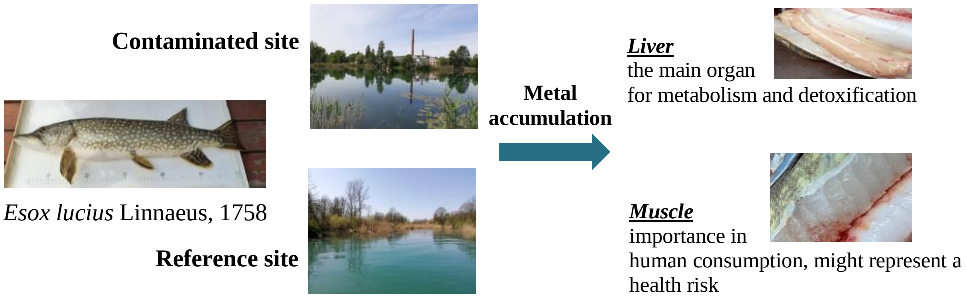
(#5)

Comparative Analysis of Metal Accumulation in Liver and Muscle of Northern Pike from the Mrežnica River: Spatial and Tissue-Specific Differences

T. Mijošek[1,*], *Z. Kiralj*[1], *D. Ivanković*[1], *V. Filipović Marijić*[1], *S. Šariri*[1], *I. Karamatić*[1], *D. Valić*[1], *T. Kralj*[1], *Z. Dragun*[1]

(1) Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia
[*]tmijosek@irb.hr



Contaminated site

Esox lucius Linnaeus, 1758

Reference site

Metal accumulation

Liver
the main organ
for metabolism and detoxification

Muscle
importance in
human consumption, might represent a
health risk

The lower part of the Mrežnica River has long been exposed to industrial pollution from the cotton industry near the Town of Duga Resa.

To assess the level of metal pollution of the Mrežnica River affected by anthropogenic activities, total metal concentrations were measured in liver and muscle of northern pike (*Esox lucius*), as a representative fish species. The liver was selected as the main metabolic site in organism, while the muscle, as the edible part, could pose a health risk to humans in case of elevated metal levels. Fish were caught in autumn 2021 at two sites: upstream of the known pollution source as the reference site (REF) and downstream of the Town of Duga Resa (DRT) as the contaminated site. Tissue samples were digested with mixture of HNO_3 and H_2O_2, and metal concentrations (As, Bi, Cd, Co, Cs, Cu, Fe, K, Mg, Mn, Na, Pb, Rb, Se, Tl and Zn) were measured using HR ICP-MS. The concentrations of Pb were below detection limits in both organs, and of Cd only in the muscle.

Obtained results confirmed liver as metabolically more active organ than muscle, as accumulation of most elements was 2-250 times higher in liver. The most prominent difference was observed for Fe, Cu, Co and Zn at both investigated sites, with concentrations in the liver higher 10-250 times compared to the muscle. However, Cs, K, Mg and Rb showed higher bioaccumulation in the muscle.

Despite different roles and structures of the two organs, they reflected environmental conditions in a similar manner. Significant differences between REF and DRT sites were evident for Bi, Rb and Se in both organs, and for Cd, Mn and Zn only in liver. Bismuth and Zn showed higher levels at DRT, whereas enhanced accumulation of Cd, Mn, Se and Rb was observed at REF. These results can be partially explained by differences of metal exposure from water and sediments. Namely, patterns of Bi, Cd, Mn, and Zn are consistent with their exposure levels in sediments or water [1], while the causes of increased Se and Rb accumulation at REF should be further investigated. Some spatial variability in both organs were also observed for As, Co, Fe, K, Mg and Na, but were not shown significant.

Comparison to literature revealed that metal(loid) concentrations in analyzed organs of northern pike indicate certain increase of bioaccumulation due to anthropogenic pressure. The concentrations in the fish muscle, however, were acceptable at both sites based on the national and European legislations [2,3], which provide permissible levels for As, Cd and Pb.

Therefore, moderate impact of the historical contamination was observed in the Mrežnica River, and further monitoring of the environment and biota is still recommended.

Acknowledgements

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

References

[1] Z. Dragun, D. Stipaničev, Ž. Fiket, M. Lučić, N. Udiković Kolić, A. Puljko, S. Repec, Z. Šoštarić Vulić, D. Ivanković, F. Barac, Z. Kiralj, T. Kralj, D. Valić (2022) *Science of the Total Environment*, X, 537.

[2] European Commission Regulation (2006) Setting maximum levels for certain contaminants in foodstuffs. No. 1881/2006 of 19 December 2006. *Official Journal of the European Union* 364, 5-24.

[3] Official Gazette of the Republic of Croatia NN 146/2012. Pravilnik o najvećim dopuštenim količinama određenih kontaminanata u hrani, in Croatian.

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(#5)

Heavy Metals in the River Water and Sediment - an Impact to Human Health

A. Šapčanin[1,], Ž. Jaćimović[2], G. Jančan[3]*

(1) Faculty of Pharmacy, Department of Natural Sciences, University of Sarajevo, Zmaja od Bosne 8, 71 000, Sarajevo, Bosnia and Herzegovina, (2) Faculty of Metallurgy and Technology, University of Montenegro, Dzordza Vasingtona bb, 81 000, Podgorica, Montenegro, (3) Chemilab d.o.o., Dunajska cesta 238E, 1000, Ljubljana, Slovenia
[*]aida.sapcanin@ffsa.unsa.ba

River Željeznica

River Bosna

This study was aimed to assess risks posed to human health based on contents of heavy metals found in water and sediment of the rivers Bosna and Željeznica. The water and sediment samples were analysed for the total content of heavy metals by using an inductively coupled plasma-mass spectrometer (ICP-MS) Agilent 7700 Series. The total contents of heavy metals in the water and sediment samples were found to be in the ranges (µg/L): 0.60 – 2,16 for Pb, 0,14 for Cd, 1.60 for Cu, 18,0 – 32,0 for Zn, 3,11 – 4,80 for As, 1,80 – 3,64 for Ni, and 0,59 – 1,91 for Cr. The hazard coefficient (HQ), non-carcinogenic hazard index (HI) and carcinogenic risk (RI) have been calculated [1-4]. Overall, HQ and HI were lower than the safe limit of 1, indicating that there is no direct risk to human health from heavy metals in the investigated area; however, these levels should be monitored in a long-term perspective.

References

[1] US EPA (2015) United States Environmental Protection Agency, in Quantitative Risk Assessment Calculations 7–9. https://www.epa.gov/risk/risk-assessment-guidance
[2] World Health Organization, Environmental Health Criteria Series, EHC 228. Principles and Methods for the Assessment of Risk from Essential Trace Elements. WHO Geneva, 2002. https://apps.who.int/iris
[3] World Health Organization, International Programme on Chemical Safety, Publications. IPCS/EHC Series. https://apps.who.int/iris/
[4] US EPA (2002) A review of the reference dose and reference concentration processes. EPA/630/P-02. https://www.epa.gov/risk/risk-assessment-guidance.

Heavy Metals in Edible Mushrooms -an Health Risk Assessment

A. Šapčanin[1,], Ž. Jaćimović[2], G. Jančan[3]*

(1) Faculty of Pharmacy, Department of Natural Sciences, University of Sarajevo, Zmaja od Bosne 8, 71 000, Sarajevo, Bosnia and Herzegovina, (2) Faculty of Metallurgy and Technology, University of Montenegro,DzordzaVasingtona bb, 81 000, Podgorica, Montenegro, (3) Chemilab d.o.o., Dunajska cesta 238E, 1000, Ljubljana, Slovenia

**aida.sapcanin@ffsa.unsa.ba*

Macrolepiota procera

The content of lead, cadmium, zinc, copper, cobalt, iron, arsenic, nickel, selenium and chromium were determined in different species of edible mushrooms (*Macrolepiota procera*, *Agaricus campester*, *Amanita caesarea*, *Boletus edulis*, *Lycoperdon pyriforme* and *Agaricus urinascens*. The mushroom samples which traditionally used in diet and some medical purposes, were collected from different rural localities in Bosnia. USEPA deterministic approaches were followed to assess the carcinogenic risk and noncarcinogenic risk which was measured by target hazard quotient (THQ) and hazard index (HI). Obtained results for the heavy metals were compared according to the WHO/FAO standard. The study also assessed potential health risks of heavy metals and the target hazard quotient (THQ) for As, Cd, Pb, Cu, Co, Fe, Zn, Ni, Se, and Cr in the analysed mushrooms was lower than the safe level.

References

[1] M. Tüzen (2003). *Microchem. J.*, 74, 289–297
[2] J. Cibulka, L. Sisak, K. Pulkrab, J. Szakova, and A. Fucikova, *Scintia Agric. Biochem.*, 27, 113–129 (1996).
[3] J. Falandaysz, D. Danisiewicz, H. Bona (1994) *Bromatol. Chem. Toksykol*. 27, 129–134 (in Polish).
[4] P. Kalaˇc, M. Wittingerova, I. Staˇsková, M. Simak, and J. Bastl (1989) *Ceskoslovenska Hygiena* 34, 568–576 (in Czech).

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EMEC22 – 22nd European Meeting on Environmental Chemistry took place in Ljubljana, Slovenia between the 5th and the 8th of December 2022. It was organised by the Faculty of Health Sciences, University of Ljubljana, Slovenia, on behalf of the Association of Chemistry and the Environment (ACE).

This period is traditionally reserved for EMEC conferences – previous conferences took place all over Europe:
2021 Novi Sad, Serbia | 2020 cancelled due to Covid19 | 2019 Lodz, Poland | 2018 Clermont Ferrand, France | 2017 Porto, Portugal | 2016 Inverness, UK | 2015 Torino, Italy | 2014 Brno, Czech Republic | 2013 Budva, Montenegro | 2012 Moscow, Russia | 2011 Clermont Ferrand, France | 2010 Portorož, Slovenia | 2009 Limoges, France | 2008 Girona, Spain | 2007 Inverness, UK | 2006 Brno, Czech Republic | 2005 Belgrade, Serbia | 2004 Bari, Italy | 2003 Plymouth, UK | 2002 Geneva, Switzerland | 2001 Dijon, France | 2000 Nancy, France

The main objectives of EMEC conferences are to bring together scientists, senior and early-career, working in the field of environmental chemistry and related disciplines to report on the latest advances in their fields in the form of oral and poster presentations and rich scientific discussions. Social events between the scientific sessions provide a great opportunity to develop networks among researchers.

EMEC22 included a rich scientific programme, including sessions on Solid matrices, Water, Atmosphere, Sustainable development, and One health. Additionally, social events – Get together, Gala dinner, tours to Bled, Ljubljana and Ljubljana Castle, as well as Early-Career Researcher workshop and social, provided ample opportunity for informal friendly and scientific exchanges, and hopefully long-lasting friendships and collaborations. This Book of Abstracts contains abstracts of works presented in oral and poster presentations at EMEC22, as well as abstracts of renowned plenary speakers and cutting-edge keynote lectures.

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