

EMEC 1 ∞

CHEMISTRY TOWARDS AN INFINITE ENVIRONMENT

18th European Meeting on Environmental Chemistry

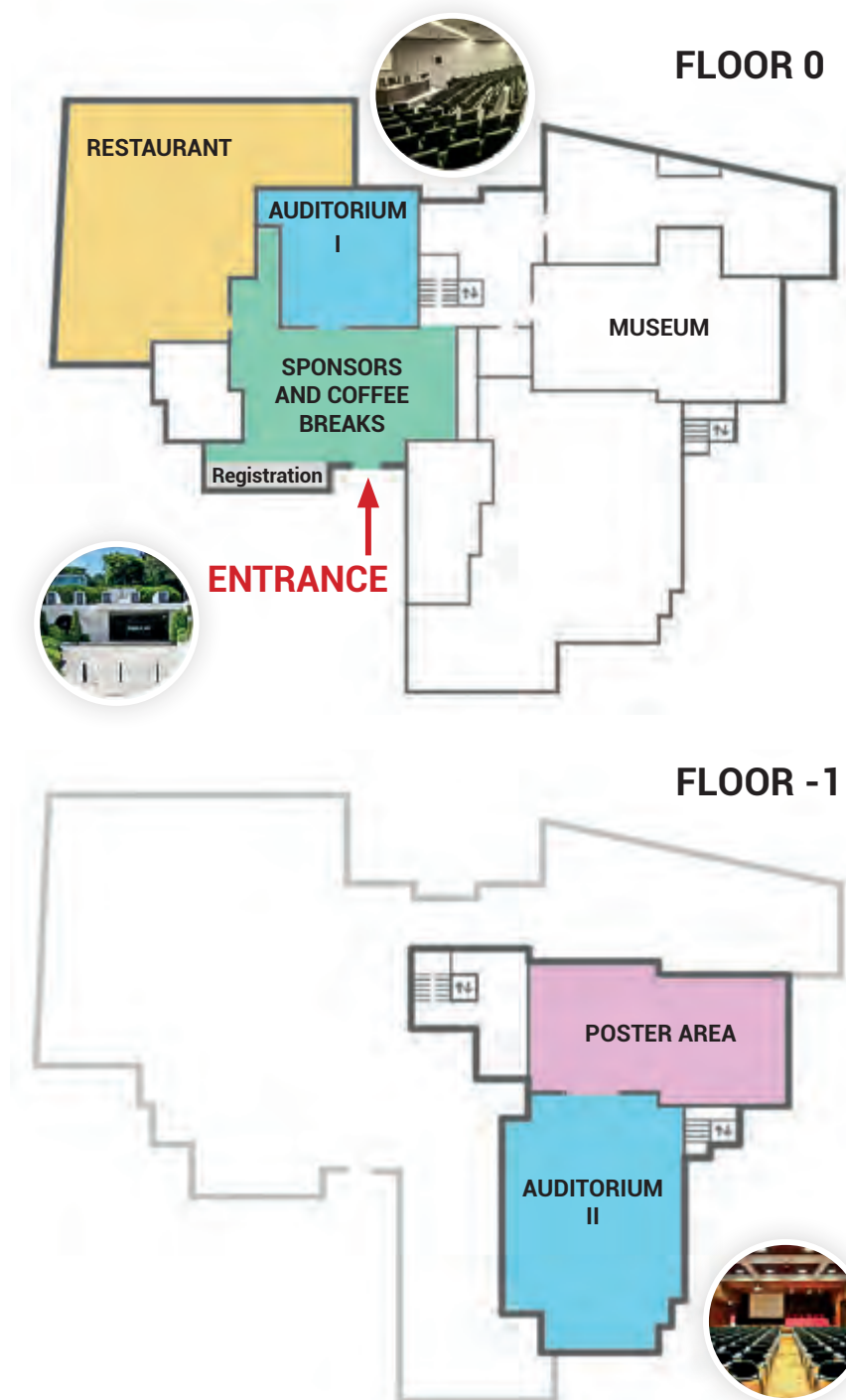
Porto 26-29th November 2017

BOOK OF ABSTRACTS



Venue – Fundação Dr. António Cupertino de Miranda

Avenida da Boavista, 4245, 4150 – 639 Porto; GPS: N 41°9'54" | W 8° 40' 19"



November 26th	November 27th		November 28th		November 29th			
08:30 – 09:00	Participants Registration		Participants Registration		Participants Registration			
09:00 – 09:30	Opening ceremony		PL #2 Despo Fatta-Kassinos		PL #3 Kevin Jones			
09:30 – 09:45	Diamond Sponsor – Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW)		Considerations Related to Contaminants of Emerging Concern and Wastewater Reuse		Passive Sampling the Environment: Why, How and a Vision of the Future			
09:45 – 10:00	PL #1 Damià Barceló		KN #3 Maria Llompart		KN #5 Kurunthachalam Kannan			
10:00 – 10:15	Climate Changes, Water Scarcity, Emergent Contaminants and Other Stressors		Recycled Tire Rubber in Playgrounds for Children and Football Fields: Health and Environmental Concern		Biomonitoring of Human Exposure to Environmental Chemicals			
10:15 – 10:30			OP Env Tech #12 Jianan Li	OP Env Monit #18 Silvia Lacorte	OP Env Safe #3 Marta Silva	OP Env Tech #20 Susana Ortega		
			The Use of Spirodela Polyrhiza in Batch Scale Constructed Wetlands to Remove PPCPs from Synthetic Wastewater	Pharmaceuticals Released from Health Care Facilities: New Control Procedures	Synthesis and Environmental Fate Evaluation of New Nature-Inspired Antifouling Compounds	Ammonium Removal as Struvite from Biologically Treated Human Urine		
10:30 – 10:45	KN #1 Elia Psillakis		OP Env Tech #13 Maria Celeiro	OP Env Monit #19 Triantafyllos Albanis	OP Env Safe #4 Inês Bezerra	OP Env Tech #21 Paula Guedes		
	Microextraction: An Ideal Platform to Analyse and Simulate the Environment		Assessment of Different Photodegradation Strategies To Remove Multiclass UV Filters From The Aquatic Environment	Determination of Pharmaceuticals in Hospital and Municipal Wastewaters by Using LC-LTQ Orbitrap Mass Spectrometry	Effects of Emerging Contaminants Detected in Drinking Water on Bacteria Tolerance to Antimicrobials	Removal of PPCPs from Effluent Based on Electrochemical Process – Possibility of Further Use in Agriculture		
10:45 – 1:00			OP Env Tech #14 Carmen Mazón	OP Env Monit #20 Mónica Santos	OP Env Safe #5 Anne-Marie Delort	OP Env Tech #22 Paulo Augusto		
			Effect of Sunlight and UV-C Disinfection Dose Irradiation on the Degradation of Organophosphorous Pesticide Dichlorvos	Development of an Analytical Methodology for the Analysis of Priority Cytostatics in Water	H ₂ O ₂ Modulates the Energetic Metabolism of the Cloud Microbiome	Exploring Magnetism as a Way to Decontaminate Wastewater and Leachates		
11:00 – 1:30	Coffee-Break & Exhibition		Coffee-Break & Exhibition		Coffee-Break & Exhibition			
11:30 – 11:45	Platinum Sponsor		Platinum Sponsor		Platinum Sponsor			
	Euan Ross (Waters Corporation) – The Analysis of Natural and Synthetic Estrogens at Low ppq Levels in Surface Water and Final Effluent Water by LC-ESI-MS/MS		Peter Abrahamsson (Agilent Technologies) – Using a Novel Accurate Mass MS/MS Library for the Qualitative Analysis of Environmental Samples		Juergen Wendt (LECO) – The Usage of Time-of-Flight Mass Spectrometry for Environmental Analysis			
11:45 – 12:00	OP Env Monit #1 Juan Francisco Facetti	OP Env Tech #1 Amina Khaled	OP Env Tech #15 Joana Vilas Boas	OP Env Monit #21 Patrícia Peixoto	OP Env Safe #6 Rui Santos	OP Env Tech #23 Abuzar Kabir		
	Preliminary Characterization of MTBE in the Aquifer Patiño, Metropolitan Region of Asuncion, Paraguay	Photodegradation of Brominated Flame Retardants in Textiles from End of Life Vehicles (ELVs): Kinetic and Photoproducts Characterization	Single Chamber Microbial Fuel Cell (SCMFC) using Lactobacillus pentosus biofilms	Fast Methods for Screening Fluoroquinolones in Environmental Water	PLASMAQUANT™ MS a new potential tool for Iron Isotope Ratios determination in Biological Samples	Encapsulation of High Surface Area Carbonaceous Particles into Sol-gel Matrix and Their Use in Environmental Pollution Mitigation		
12:00 – 12:15	OP Env Monit #2 Eleonora Conca	OP Env Tech #2 Rajae Chahboune	OP Env Tech #16 Paula Figueira	OP Env Monit #22 Manuela Correia	OP Env Safe #7 Paulo Reis	OP Env Tech #24 Luísa Maia		
	Characterization and Temporal Evolution of the Inorganic Component of PM10 Collected at Ny-Ålesund (Arctica)	Photochemical Processes for the Elimination of Nitrosomorpholine During Water treatment: Kinetic and Analytical studies	Nutshells as Very Low Cost Sorbents for Contaminated Waters Treatment	Assessment of 83 Pharmaceuticals in Wastewater Samples by UHPLC-MS/MS	RIBE Assessed At An Inter-organismic Level In Daphnia magna Exposed To Low Doses Of Uranium Mine Effluent And Waterborne Uranium	Formate Dehydrogenase-catalysed Carbon Dioxide Reduction: Aiming to Develop a Catalyst for Carbon Dioxide Utilisation		
12:15 – 12:30	OP Env Monit #3 Francisco Cereceda-Balic	OP Env Tech #3 João Gomes	OP Env Tech #17 Benigno Nóvoa	OP Env Monit #23 Belen González-Gaya	OP Env Safe #8 Patrícia Palma	OP Env Tech #25 Maria Laura Tummino		
	Vehicle Emissions Impact on Snow Albedo Reduction in Los Andes Mountains. Study Case: Portillo, Chile	Operating Conditions Optimization for Photocatalytic Ozonation of Parabens Using Ag-TiO ₂	Kinetics, Transformation and Toxicity of 1,3-di-o-tolylguanidine and 1,3-diphenylguanidine During Disinfection with Chlorine	Optimizing a Clean Method for Environmental Samples: Antibiotics and Matrix Interferences in Marine Sediments, Water and Biota	Ecotoxicological Tools Used in the Assessment of the Ecological Status of Freshwater Systems: a Case-study of the Temporary River Brejo do Cagarão (South of Portugal)	Green Waste Derived Substances Immobilized on SBA Silica: Adsorbing and Photosensitizing Properties Towards Metals and Organics		
12:30 – 12:45	OP Env Monit #4 Miguel Velázquez Gómez	OP Env Tech #4 Eneliis Kattel	OP Env Tech #18 Elisabete Geraldés	OP Env Monit #24 Liliana Silva	OP Env Safe #9 Joana Lourenço	OP Env Tech #26 Cláudia Neves		
	Organic Contaminants in Indoor Dust: An Approach Through a GC-MS/MS method	Degradation of Ceftriaxone in Aqueous Solution by Heterogeneous Photo-Activated Persulfate System	Eco-Friendly Non-Biocide-Release Coatings for Biofouling Prevention on Submerged Surfaces	SSRIs Antidepressants in Marine Mussels from Atlantic Coastal Areas and Human Risk Assessment	Uranium Mining Legacy Sites: Genetic Effects of Metals and Low-Dose Radiation in Farm Animals Exposed to Contaminated Water and Foodstuffs	Immobilized Porphyrins as Photocatalysts for the Degradation of Metoprolol		
12:45 – 13:00	OP Env Monit #5 Eran Tas	OP Env Tech #5 Maria Conceição Amado	OP Env Tech #19 Djilali Tassalit	OP Env Monit #25 Tamara Gorena	OP Env Safe #10 Pavel Fojt	OP Env Tech #27 Alaæddine Elhalile		
	Ozone Deposition Over Vegetation in the Eastern Mediterranean	Photocatalytic Reactor for Pharmaceutical Drugs and Pesticides Removal From Water, Using Thin Film CVD-Technology	Photocatalysis And Adsorption Synergy For Simultaneous Removal Of Phenol And Acétamiprid Pollutants In Water	Evaluation of the Environmental Impact of High Pollution Load from an Industrial Complex using Cupressus macrocarpa biomonitoring	Ecotoxicity Assessment of Cadmium Using Different Life Stages of the Terrestrial Gastropod Helix aspersa aspersa	Synthesis, Characterization and Photocatalytic Performance of Mg-ZnO-Al ₂ O ₃ Nanocomposite for Degradation of Pharmaceutical Pollutants		
13:15 – 14:15	Lunch		Lunch		Lunch			
14:15 – 14:45	KN #2 Pedro Jiménez-Guerrero		KN #4 Cristina Branquinho		ACE General Assembly (Aud. II)			
	Using Chemistry Transport Models to Evaluate the Fate of Atmospheric Pollutants		Evaluating the Role of Urban Green Spaces in Improving Urban Sustainability: The case of Air Purification and of Climate Regulation					
14:45 – 15:00	OP Env Monit #6 Olga V. Polyakova	OP Env Model #1 Gerhard Lammel	OP Sust Devel #1 André Pereira	OP Env Monit #26 João Sousa	OP Env Safe #11 Helena Soares	OP AgroFood #1 Ana Martínez Piernas		
	Novel Methods for Comprehensive Analysis of Environmental Samples: GCxGC-HR-TOFMS	Monsoon Air Triggers Re-volatilization of Persistent Pollutants Stored in Soils in India	Human Pharmaceuticals in Portuguese Rivers: the Impact of Water Scarcity in the Environmental Risk	Spatiotemporal Monitoring Campaign of the Watch List Compounds in Ave and Sousa Rivers	Additive Inhibitory Free Metal Ion Concentration Index: a New Method for Assessing Multi-Metal Contamination Risk on Freshwaters	Suspect-screening Strategy Applied To The Identification Of Transformation Products Of Carbamazepine In Lettuce And Soil Commodities		
15:00 – 15:15	OP Env Monit #7 Regina Duarte	OP Env Model #2 Noelia Domínguez-Morueco	OP Sust Devel #2 Klara Slezakova	OP Env Monit #27 Gabriela Varela	OP Env Safe #12 Marilyne Pflieger	OP AgroFood #2 Anabela Cachada		
	A Primer on – Omics Strategy for Untargeted Profiling of Organic Aerosols: Lessons Learned and Future Challenges	Combining Monitoring and Modelling Approaches for BaP Characterization Over a Petrochemical Area	Ultrafine Particles in Ambient Air of Metropolitan Area of Porto: Levels and Risk Assessment	Determination of Cardiac Drugs in Sludge by Ultra Performance Liquid Chromatography Followed by Tandem Mass Spectrometry	Ecotoxicity of Biomass Burning Pollutants and Their Nitro Derivatives	Soil interactions of azotochelin and DPH and determination of iron induced chlorosis mending potential in soybean (glycine max)		
15:15 – 15:30	OP Env Monit #8 Isabel Brás	OP Env Model #3 Luís Silva	OP Sust Devel #3 Mirco Volanti	OP Env Monit #28 Polonca Trebse	OP Env Safe #13 Ruth Pereira	OP AgroFood #3 Carlos Ferreira		
	Validation of ICP-MS Methodology for Quantification of 22 Elements in Wastewaters	DFT Calculations on Climate Forcing and on Sustainable CO ₂ Conversion	LCA Methodology: A Case Study Of The Industrial Production Of Terephthalic Acid From Renewable Sources	Identification of disinfection by-products formed within aquatic bromination of avobenzone	Ecosystem Services Provided by Soils Under Different Land Uses: Implications to Water Quality	Soil interactions of azotochelin and DPH and determination of iron induced chlorosis mending potential in soybean (glycine max)		
15:30 – 15:45	OP Env Monit #9 Priscilla Rocío-Bautista	OP Env Model #4 Lotfi Belkhiri	OP Sust Devel #4 José Virgílio Prata	OP Env Monit #29 Jan Schwarzbauer	OP Env Safe #14 Verónica Nogueira	OP AgroFood #4 Filipa Paulo		
	Metal-Organic Frameworks: A New Generation of Sorbents for Solid-Phase Extraction	The DFT Modeling As A Partner Of Reprocessing Nuclear Waste. Rich Interplay Between Theory And Experience	How an Environmental Issue Could Turn Into Useful High-valued Products: The Olive Mill Wastewater Case	Molecular Indicators for Dockyard Works in Coastal Sediments of a Large Industrialized Port Area in Hainan Island, China	The Impact On Soil Biota of Leather From The Footwear Industry Treated With ZnO Nanomaterial: A Microcosm Study	How and Why Incorporation of Microencapsulated Bioactive Ingredients in Foods?		
15:45 – 16:00	OP Env Monit #10 Claudia Fontàs	OP Env Model #5 Davide Vione	OP Env Safe #1 Anabela Francisco	OP Env Monit #30 Filipe Rocha	Scholarship Ceremony & EMEC19 Presentation & Closing Ceremony (Aud. II)			
	Can Polymer Inclusion Membranes be Used as an Integral Tool to Facilitate Environmental Monitoring? The Case of Hg	Photodegradation of Sulfadiazine Under Conditions Significant for Surface Waters, and Inhibition by Organic Compounds	The Predicted Concentrations of Antibiotics in STPs in Portugal – A tool for the Microbial Community Resistance Research	Seaweed Analysis for the Determination of Volatile Methylsiloxanes in Coastal Areas in North of Portugal				
16:00 – 16:15	OP Env Monit #11 Sónia Lopes	OP Env Model #6 Luca Carena	OP Env Safe #2 Elena Bessonova	OP Env Monit #31 Irene Aparicio				
	Evaluation Of The Effect Of Organic Matter On The Dissolution Of Cu From CuO And Cu(OH) ₂ Nanomaterials In Agricultural Soils	Photoinduced Reactions in Sunlit Paddy-Field Water	LC/MS Determination of Anti-TB Drugs and Their Metabolites in Human Plasma for Optimization Therapeutic Treatment of Tuberculosis	Occurrence of Parabens and Bisphenol A in Sludge Stabilization Treatments: Anaerobic Digestion and Composting				
16:15 – 16:45	Coffee-Break & Exhibition		Coffee-Break & Poster Session					
16:45 – 17:00	OP Env Monit #12 Javier Castro-Jiménez	OP Env Tech #6 Yael Mishael						
	Atmospheric Particle-Bound Organophosphate Esters (OPEs) in a North African Mediterranean Coastal Environment (Bizerte, Tunisia)	Efficient Removal of Pharmaceuticlas from Treated Wastwater by Tailored Polycation-Clay Sorbents	Departure for Porto Wine Cellars and Conference Dinner					
17:00 – 17:15	OP Env Monit #13 Sofia Augusto	OP Env Tech #7 Yuan Li						
	Source Apportionment of PAHs in a Petrochemical and Chemical Industrial Area Using Lichens as Biomonitorers	Removal of the Pharmaceuticals Diclofenac and Trimethoprim from Aqueous Media Using Low-Cost Biosorbents						
17:15 – 17:30	OP Env Monit #14 Karen Yáñez	OP Env Tech #8 Elaine Fabre						
	Concentration Ratios for Polycyclic Aromatic Hydrocarbons from Wood Combustion: Comparison of Laboratory Results and Sampling in Temuco City (Chile)	Agricultural Wastes for Mercury (II) Removal in Wastewater Treatment						
17:30 – 17:45	OP Env Monit #15 Albert Lebedev	OP Env Tech #9 Ariana Pintor	Departure for Porto Wine Cellars and Conference Dinner					
	Organic Pollutants in Moscow Rain	Arsenate and Arsenite Adsorption onto Iron-Coated Cork Granulates						
17:45 – 18:00	OP Env Monit #16 Mária Mörtl	OP Env Tech #10 Anna Bogush						
	Determination of Surfactants Used in Agrochemicals	Potential Utilisation of Air Pollution Control Residue from Municipal Solid Waste Incineration Facility in the Cement Industry						
18:00 – 18:15	OP Env Monit #17 Dmitry Mazur	OP Env Tech #11 Nuno Cruz	Poster Session & Porto D'Honra					
	Organic Pollutants in the Snow of Russian Arctic Islands	Waste Management From Pulp and Paper Industry: Recycling to Soil as a Viable Management Option						
18:15 – 19:30	Poster Session & Porto D'Honra							

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Titulo

Book of Abstracts of the 18th European Meeting on Environmental Chemistry - EMEC18:
Chemistry Towards an Infinite Environment

Editor(es)

M.S.F. Santos, A.M.T. Silva, L. Santos, N. Ratola, A.M.F.R. Pinto,
M.F.R. Pereira, V. Homem, N.F. Azevedo, A. Alves

ISBN. 978-972-752-228-6

ISBN: 978-972-752-228-6



Welcome

It is my pleasure to welcome you to the 18th European Meeting on Environmental Chemistry (EMEC18), and to the city of Porto! After Inverness, in Scotland, EMEC will be held for the first time in Portugal, at Fundação Doutor António Cupertino de Miranda, organized by the Department of Chemical Engineering of the Faculty of Engineering of the University of Porto (FEUP) and its three research units (LEPABE, LSRE-LCM and CEFT), on behalf of the Association of Chemistry and the Environment (ACE) and with the collaboration of the Portuguese Chemical Society (SPQ).

The program of this year's conference is tailored to meet the needs and insights of a large variety of topics in the environmental field. Under the motto "Chemistry towards an Infinite Environment", the 18th edition of this meeting will continue the tradition of previous meetings, hoping to contribute to a lasting sustainability of our planet's environment. It will provide a wide forum for the exchange of ideas on recent advances in research and development in environmental chemistry and technology, presented by delegates from academia, research institutes and industry. EMEC18 will present the latest developments in Environmental Monitoring, Environmental Technologies, Environmental Modelling, Sustainable Development, Environmental Safety and Agro-environmental Friendly Processes and Food Chemistry.

The Organizing Committee received more than 260 communications from 31 countries. A total of 97 oral presentations and about 170 posters were selected after the abstracts review by the Scientific Committee. Included are 3 Plenary and 5 Keynote Invited Lectures from worldwide recognized scientists and stakeholders, considering fundamental and applied science, as well as market-oriented sessions.

In order to allow the presence of young scientists and acknowledge the best studies presented, three types of awards will be attributed:

- *ACE Scholarships – Aimed at MSc and PhD students and covering the conference fees as well as travel and accommodation costs.*
- *Best Oral and Best Poster Presentations – The organization of EMEC18 will grant two awards to outstanding contributions (one Oral and one Poster) of young scientists, sponsored by Springer.*
- *Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW) Scholarship – PSIPW will offer in partnership with the organization of the Conference, a scholarship for a MSc, PhD student or young scientist, who has developed an innovative work in the field of water research.*

We acknowledge all the authors for their contributions, the colleagues for reviewing and helping to build this scientific program and the sponsors for their support.

We are confident that the combination of the scientific and social program, the conference venue and the amazing city of Porto will bring all the necessary ingredients to make EMEC18 an exceptional experience!

We look forward to meet you all during the event!

Porto, November 2017

Arminda Alves
Chair of the Organizing Committee

Scientific Committee

Arminda Alves, Faculdade de Engenharia da Universidade do Porto, Portugal
Albert Lebedev, Lomonosov Moscow State University, Russia
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Mónica Santos, LEPABE
Nuno Azevedo, LEPABE
Nuno Ratola, LEPABE
Vera Homem, LEPABE

LEPABE Laboratory of Process Engineering, Environment, Biotechnology and Energy
LSRE-LCM Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials
CEFT Transport Phenomena Research Center

are Research Units at the Department of Chemical Engineering,
Faculdade de Engenharia da Universidade do Porto (FEUP).



The Association of Chemistry and the Environment (ACE) is a European non-profit-making scientific association founded in October 2000 by a group of European scientists. Aiming at the protection of the Environment, it will favour contacts between academics, education, private firms, and social representatives, working in the fields of chemistry, toxicology, agronomy, water science, sociology, among others.

ACE wishes to promote in a balanced way the collaboration of scientists from all scientific fields aiming at the protection of the environment. Therefore, **we strongly welcome scientists from diverse fields such as atmosphere science, biology, geology, industrial chemistry, medicine, sociology, soil science, toxicology and water science to play an active role within the organisation.**

The European Meeting on Environmental Chemistry (EMEC) is organised annually on behalf of the ACE.

BOARD MEMBERS

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Awards & Scholarships

One of the goals of the EMEC conferences is to bring together scientists from diverse fields and expertises. In this spirit, the EMEC meeting scholarships aim to motivate young scientists to fully participate in the conference, thus facilitating an international scientific exchange of PhD candidates, junior scientists with more experienced researchers during the meeting.



The organisation of the 18th European Meeting on Environmental Chemistry (EMEC18) will grant two awards to outstanding contributions of young scientists, sponsored by Springer. One award for the best Oral Presentation (200 EUR book voucher) and another for the best Poster (100 EUR book voucher) will be announced during the Closing Ceremony of EMEC18.



Beginning in 2015, the Association for Chemistry and the Environment (ACE) has been offering a number of scholarships for MSc and PhD students to participate in the annual European Meeting on Environmental Chemistry series. The scholarship covers the conference fee and additionally travel as well as accommodation costs of up to 500 EUR.

Regarding the EMEC18 edition, three candidates were selected based on their academic achievements:

- **Eneliis Kattel**, Tallinn University of Technology, Department of Materials and Environmental Technology, Tallinn, Estonia;
- **Jianan Li**, University College London, Department of Civil, Environmental and Geomatic Engineering, London, United Kingdom;
- **Marlene Vila González**, University of Santiago de Compostela, Department of Analytical Chemistry, Nutrition and Food Science, Santiago de Compostela, Spain.



The Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW) is a scientific prize with a focus on innovation. Established in 2002 by HRH Crown Prince Sultan Bin Abdulaziz, it rewards the efforts made by scientists, inventors and research organizations around the world, focusing on water-related scientific innovation. Five prizes are bestowed every two years. PSIPW sponsors a number of international conferences and exhibitions around the world and it have initiated an event participation grant programme.

PSIPW, besides being Diamond Sponsor of the 18th European Meeting on Environmental Chemistry (EMEC18), will offer a 500 EUR scholarship for a MSc, PhD student or young scientist in partnership with the organisation of the Conference. The recipient will be chosen based on three criteria: (i) suitability of the recipient to make a positive contribution to, or benefit from, the event, (ii) need of the recipient, (iii) innovative nature of the recipient's work (water-related studies).

This scholarship will be announced during the Closing Ceremony of EMEC18.



Prince Sultan Bin Abdulaziz
International Prize for Water

Recognizing Innovation

Invitation for Nominations

8th Award
(2018)



Creativity
Prize



Surface Water
Prize



Groundwater
Prize



Alternative Water
Resources Prize



Water Management &
Policy Prize

**Nominations open online
until 31 December 2017**

www.psipw.org e-mail: info@psipw.org



A Virtual Special Issue of the Elsevier Journal "Science of the Total Environment" (STOTEN) (Impact Factor 2016 = 4.900) will be devoted to the EMEC18 conference and will include peer-reviewed articles.

A selection of the most promising studies will be done by the Scientific Committee of EMEC18, and the respective authors invited to submit a full paper for peer-reviewing, following the author guidelines of STOTEN (<https://www.journals.elsevier.com/science-of-the-total-environment/>).

Science of the Total Environment is an international journal for publication of original research on the total environment, which includes the atmosphere, hydrosphere, biosphere, lithosphere, and anthroposphere.

GUEST EDITORS

Arminda Alves

Nuno Ratola

Vera Homem



Plenary Speakers

Damià Barceló



Prof. Damià Barceló obtained a Ph.D. in Analytical Chemistry from the University of Barcelona in 1984 and was a Post-doc at the Vrije Universiteit, Amsterdam, NL between 1985-86. He is a Full Research Professor at the Institute of Environmental Assessment and Water Studies IDAEA-CSIC (Barcelona, Spain) since 1999 and Director of the Catalan Institute of Water Research (ICRA) (Girona, Spain) since May 2008. From 2009-2015 he was a visiting Professor at King Saud University, Riyadh, Saudi Arabia and is has a Full Professor Chair in Biology at the College of Science under Distinguished Scientist Fellowship Programme (DSFP) in the same institution, since October 2016. His scientific focus is on the Fate and Risk of Emerging Pollutants such as Pharmaceuticals and Nanomaterials in the Environment, Multiple Stressors in Rivers and on the Water Pollution Control and Protection under Scarcity. In 2007 he was awarded the King Jaime I Prize for the Protection of Nature from Generalitat of Valencia, Spain, for his outstanding scientific work; in 2011 he received the Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW) on Water Management & Protection, Saudi Arabia; in 2012 the Recipharm Environmental Award, Sweden; and in 2014 a Doctorate Honoris Causa by the University of Ioannina, Greece. He was also the Chairman of the Scientific and Technological Board (STB) of the EU-Joint Programming Initiative on "Water challenges for a changing World" in 2011-2015. From 2013 to 2019 he is the Coordinator of two European Union-funded projects: GLOBAQUA and SEA-on-a-CHIP and of JPI WATER-FACCE project AWARE. His expertise is documented by the number of original publications (> 1100), an H index of 101, over 48000 ISI citations and supervision of 52 PhD thesis (October 2017).

Despo Fatta-Kassinos

Dr. Despo Fatta-Kassinos is currently an Associate Professor in the Department of Civil and Environmental Engineering, and the Director of Nireas - International Water Research Center, of the University of Cyprus. She received her PhD from the School of Chemical Engineering of the National Technical University of Athens, Greece. Her research centers on the understanding of the fate and behavior of contaminants of emerging concern during advanced wastewater treatment and during their release into the environment. In specific, the activities of her group include the identification of xenobiotic compounds and their transformation products in environmental samples, the assessment of their biological potency, the development of new technological processes for their removal, the evaluation of their transmission to soil and their potential uptake by crops through wastewater reuse, and the spread of antibiotic resistance. She has over 126 peer-reviewed scientific publications in SCI journals and 160 conference papers. She has co-edited various books published by Springer, and she has participated in more than 50 research projects (EU/national). In 2012, she received the distinguished national research award 'Nikos Symeonides' by the Cyprus Research Promotion Foundation for her work on wastewater treatment and xenobiotics. She is the Chair of the NEREUS COST Action ES1403, the Coordinator of the ANSWER project [H2020-MSCA-ITN-2015/675530], and the Chair of the Scientific and Technological Advisory Board of the European JPI 'Water Challenges for a Changing World'.

Kevin Jones

Prof. Kevin Jones has pioneered world leading research into the environmental sources, fate, behaviour and effects of persistent organic pollutants (POPs) over the last three decades. A state-of-the-art 'chemical mass balance and inventory approach' has been used to develop a quantitative understanding of the contribution of particular sources, practices, pathways, policies or actions on environmental levels and the exposure to organisms, including people. Complex chemical fate models continue to be developed and refined to protect human and environmental health around the world. Global waste disposal strategies and chemical regulations have been transformed as a result of his world-leading research. He is one of the most highly cited scientists in Environment and Ecology and has published nearly 600 peer-reviewed journal articles. His long-standing collaboration with the Chinese Academy of Sciences (CAS) has resulted in the formation of the International Research and Innovation Centre for the Environment (IRICE) – a joint initiative between the Chinese Academy of Sciences (CAS) and Lancaster University (LU), and the Joint Institute for the Environment (JIE) with the South China Agriculture University. He is also developing new partnerships with the Chinese Research Academy of Environmental Sciences (CRAES). Kevin has served as Director of the Lancaster Environment Centre, Lancaster University, for the past 5 years.

Keynote Speakers

Elia Psillakis



Dr. Elia Psillakis is a Water Chemistry Professor at the School of Environmental Engineering of the Technical University of Crete, Greece. She received her degree in Chemistry from the Université Montpellier II Sciences et Techniques du Languedoc, France (summa cum laude) and her PhD from the University of Bristol, U.K., working on the synthesis and characterization of supramolecular structures, with Professor Jon A. McCleverty as advisor. Her research activities after obtaining the PhD were shifted to environmental organic and analytical chemistry and ever since she focuses on understanding and developing novel sample preparation methods used for monitoring and studying the fate of organic contaminants in natural and engineered environments. In 2007, she was selected for a Fulbright Research Fellowship and used it at CALTECH, USA at the laboratories of Professor M. Hoffmann.

Pedro Jiménez-Guerrero



Dr. Pedro Jiménez-Guerrero works in the field of atmospheric and climate modeling, where his main contributions are related to the analysis of dynamics and levels of air pollution and atmospheric composition. His interests focus on the study of the feedbacks of future climatic changes on the magnitude and extension of the levels of atmospheric pollutants (especially at regional scales). After several international residencies including the Max Planck Institute for Chemistry (Mainz, Germany) and the Goddard Institute for Space Studies, NASA (New York, USA), his work has been recognized with the prestigious Ramón y Cajal Contract and the Research Award by the Royal Academy of Engineering (Spain), among others. He has participated and managed several national and international research projects, and is currently a Professor and researcher at the University of Murcia (Spain).

María Llompart

Dr. Maria Llompart is a Professor of Analytical Chemistry at the University of Santiago de Compostela (Spain). She was chair of international conferences of excellence in the field of micro-contaminants and extraction technologies such as ExTech 2017 and PESTICIDES 2016, and member of the scientific boards. She is an expert in extraction, chromatography and mass spectrometry and her main research topics include: sample preparation techniques based on Green Chemistry; determination of organic pollutants, pharmaceuticals, personal care products, etc, in environmental and biological matrices; analysis of pesticides and mycotoxins in agri-food matrices; and photodegradation studies of classic and emerging environmental pollutants. She authored over 130 scientific publications and supervised 13 PhD theses. From 2017, she is a member of the Editorial Board of *Analytica Chimica Acta*.

Cristina Branquinho

Dr. Cristina Branquinho received a Ph.D. in Biology, Ecology from the University of Lisbon in 1997 and is currently an Associate Professor with habilitation of the Centre of Ecology and Environmental Sciences at the Faculty of Sciences, Univ. of Lisbon and the leader of the Ecology of Environmental Change group of cE3c. Her research focuses on understanding ecological patterns at the ecosystem level in response to environmental changes. For many years she has been studying the impact of anthropogenic activity in the structure and functioning of ecosystems. She is the National Deputy of IUFRO for: Impacts of air pollution and climate change on forest ecosystems, was the leader of the WG 3 of COST action ES1104 and is a member of MedECC, a network of scientists aiming a regional science-policy interface for climatic and other environmental changes across the Mediterranean.

Kurunthachalam Kannan

Dr. Kurunthachalam Kannan is a Professor in the School of Public Health, Environmental Health Sciences of the Wadsworth Center, New York Department of Health (USA). His research interests involve understanding environmental sources, pathways, distribution, dynamics and fate of chemical pollutants is crucial, if we are to devise solutions to current and future environmental problems. His current studies include biomonitoring of organic pollutants, phenolic endocrine disruptors, and other emerging environmental contaminants for characterizing human and wildlife exposure pathways, and to allow evaluation of sources, pathways and risks. He is also developing techniques to identify and quantify novel organic pollutants (in indoor air, water, foodstuffs and biological tissues) and relating contaminant exposures to health outcomes and effect biomarkers in the general population.

Scientific Program

Sunday, November 26th

17:00-19:30	Registration
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Monday, November 27th

08:30	Registration
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Conference Hall: Auditorium II

09:00	Opening Ceremony
09:30	<i>Diamond Sponsor</i> Prince Sultan Bin Abdulaziz International Prize for Water (PSIPW)
09:45	<i>Plenary</i> Damià Barceló (IDAEA-CSIC and ICRA, Spain) Climate Changes, Water Scarcity, Emergent Contaminants and Other Stressors
10:30	<i>Keynote</i> Elia Psillakis (Tech. Univ. of Crete, Greece) Microextraction: An Ideal Platform to Analyse and Simulate the Environment
11:00	Coffee-break & Exhibition
11:30	<i>Platinum Sponsor</i> Euan Ross (Waters Corporation) The Analysis of Natural and Synthetic Estrogens at Low ppq Levels in Surface Water and Final Effluent Water by LC-ESI-MS/MS

Monday, November 27th

	Session Environmental Monitoring Conference Hall: Auditorium II	Session Environmental Technologies Conference Hall: Auditorium I
11:45	#1 Juan Francisco Facetti (National Univ. Asuncion, Paraguay) Preliminary Characterization of MTBE in the Aquifer Patiño, Metropolitan Region of Asuncion, Paraguay	#1 Amina Khaled (ICCF UMR6296, France) Photodegradation of Brominated Flame Retardants in Textiles from End of Life Vehicles (ELVs): Kinetic and Photoproducts Characterization
12:00	#2 Eleonora Conca (Univ. Torino, Italy) Characterization and Temporal Evolution of the Inorganic Component of PM10 Collected at Ny-Ålesund (Arctica)	#2 Rajae Chahboune (Institut de Chimie de Clermont-Ferrand, France) Photochemical Processes for the Elimination of Nitrosomorpholine During Water treatment: Kinetic and Analytical studies
12:15	#3 Francisco Cereceda-Balic (Tech. Univ. Federico Santa María, Chile) Vehicle Emissions Impact on Snow Albedo Reduction in Los Andes Mountains. Study Case: Portillo, Chile	#3 João Gomes (Univ. Coimbra, Portugal) Operating Conditions Optimization for Photocatalytic Ozonation of Parabens Using Ag-TiO ₂
12:30	#4 Miguel Velázquez Gómez (IDAEA-CSIC, Spain) Organic Contaminants in Indoor Dust: An Approach Through a GC-MS/MS method	#4 Eneliis Kattel (Tallinn Univ. Technol., Estonia) Degradation of Ceftriaxone in Aqueous Solution by Heterogeneous Photo-Activated Persulfate System
12:45	#5 Eran Tas (Hebrew Univ. Jerusalem, Israel) Ozone Deposition Over Vegetation in the Eastern Mediterranean	#5 Maria Conceição Amado (Univ. Algarve, Portugal) Photocatalytic Reactor for Pharmaceutical Drugs and Pesticides Removal From Water, Using Thin Film CVD-Technology
13:00	Lunch	

Conference Hall: Auditorium I

14:15	Keynote Pedro Jiménez-Guerrero (University of Murcia, Spain) Using Chemistry Transport Models to Evaluate the Fate of Atmospheric Pollutants
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Monday, November 27th

	Session Environmental Monitoring Conference Hall: Auditorium II	Session Environmental Modelling Conference Hall: Auditorium I
14:45	#6 Olga V. Polyakova (Lomonosov Moscow State U., Russian Federation) Novel Methods for Comprehensive Analysis of Environmental Samples: GCxGC-HR-TOFMS	#1 Gerhard Lammel (Masaryk Univ., Czech Republic) Monsoon Air Triggers Re-volatilization of Persistent Pollutants Stored in Soils in India
15:00	#7 Regina Duarte (Univ. Aveiro, Portugal) A Primer on -Omics Strategy for Untargeted Profiling of Organic Aerosols: Lessons Learned and Future Challenges	#2 Noelia Domínguez-Morueco (Univ. Rovira i Virgili, Spain) Combining Monitoring and Modelling Approaches for BaP Characterization Over a Petrochemical Area
15:15	#8 Isabel Brás (ESTGV/IPV, Portugal) Validation of ICP-MS Methodology for Quantification of 22 Elements in Wastewaters	#3 Luís Silva (CIQUP/FCUP - Univ. Porto, Portugal) DFT Calculations on Climate Forcing and on Sustainable CO ₂ Conversion
15:30	#9 Priscilla Rocío-Bautista (Univ. La Laguna, Spain) Metal-Organic Frameworks: A New Generation of Sorbents for Solid-Phase Extraction	#4 Lotfi Belkhiri (Mentouri Univ. Constantine, Algeria) The DFT Modeling As A Partner Of Reprocessing Nuclear Waste. Rich Interplay Between Theory And Experience
15:45	#10 Clàudia Fontàs (Univ. Girona, Spain) Can Polymer Inclusion Membranes be Used as an Integral Tool to Facilitate Environmental Monitoring? The Case of Hg	#5 Davide Vione (Univ. Torino, Italy) Photodegradation of Sulfadiazine Under Conditions Significant for Surface Waters, and Inhibition by Organic Compounds
16:00	#11 Sónia Lopes (Univ. Aveiro, Portugal) Evaluation Of The Effect Of Organic Matter On The Dissolution Of Cu From CuO And Cu(OH) ₂ Nanomaterials In Agricultural Soils	#6 Luca Carena (Univ. Torino, Italy) Photoinduced Reactions in Sunlit Paddy-Field Water
16:15	Coffee-break & Exhibition	

Monday, November 27th

	Session Environmental Monitoring Conference Hall: Auditorium II	Session Environmental Technologies Conference Hall: Auditorium I
16:45	#12 Javier Castro-Jiménez <i>(MIO, France)</i> Atmospheric Particle-Bound Organophosphate Esters (OPEs) in a North African Mediterranean Coastal Environment (Bizerte, Tunisia)	#6 Yael Mishael <i>(Hebrew Univ., Israel)</i> Efficient Removal of Pharmaceuticals from Treated Wastewater by Tailored Polycation-Clay Sorbents
17:00	#13 Sofia Augusto <i>(EPIUnit-ISPUP - Univ. Porto, Portugal)</i> Source Apportionment of PAHs in a Petrochemical and Chemical Industrial Area Using Lichens as Biomonitorers	#7 Yuan Li <i>(Univ. Highlands and Islands, UK)</i> Removal of the Pharmaceuticals Diclofenac and Trimethoprim from Aqueous Media Using Low-Cost Biosorbents
17:15	#14 Karen Yáñez <i>(Tech. Univ. Federico Sta María, Chile)</i> Concentration Ratios for PAHs from Wood Combustion: Comparison of Laboratory Results and Sampling in Temuco City (Chile)	#8 Elaine Fabre <i>(Univ. Aveiro, Portugal)</i> Agricultural Wastes for Mercury (II) Removal in Wastewater Treatment
17:30	#15 Albert Lebedev <i>(Lomonosov Moscow State U., Russian Federation)</i> Organic Pollutants in Moscow Rain	#9 Ariana Pintor <i>(FEUP - Univ. Porto, Portugal)</i> Arsenate and Arsenite Adsorption onto Iron-Coated Cork Granulates
17:45	#16 Mária Mörtl <i>(Agroenvironmental Research Institute, Hungary)</i> Determination of Surfactants Used in Agrochemicals	#10 Anna Bogush <i>(Univ. College London, UK)</i> Potential Utilisation of Air Pollution Control Residue from Municipal Solid Waste Incineration Facility in the Cement Industry
18:00	#17 Dmitry Mazur <i>(Lomonosov Moscow State U., Russian Federation)</i> Organic Pollutants in the Snow of Russian Arctic Islands	#11 Nuno Cruz <i>(Univ. Aveiro, Portugal)</i> Waste Management From Pulp and Paper Industry: Recycling to Soil as a Viable Management Option
18:15	Poster Session & Porto D'Honra	

Tuesday, November 28th

08:30	Registration
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Conference Hall: Auditorium II

09:00	<i>Plenary</i> Despo Fatta-Kassinou (<i>Univ. of Cyprus, Cyprus</i>) Considerations Related to Contaminants of Emerging Concern and Wastewater Reuse
09:45	<i>Keynote</i> Maria Llompart (<i>Univ. of Santiago de Compostela, Spain</i>) Recycled Tire Rubber in Playgrounds for Children and Football Fields: Health and Environmental Concern

	Session Environmental Technologies Conference Hall: Auditorium II	Session Environmental Monitoring Conference Hall: Auditorium I
10:15	#12 Jianan Li <i>(Univ. College London, UK)</i> The Use of Spirodela Polyrrhiza in Batch Scale Constructed Wetlands to Remove PPCPs from Synthetic Wastewater	#18 Silvia Lacorte <i>(IDAEA-CSIC, Spain)</i> Pharmaceuticals Released from Health Care Facilities: New Control Procedures
10:30	#13 Maria Celeiro <i>(Univ. of Santiago de Compostela, Spain)</i> Assessment of Different Photodegradation Strategies To Remove Multiclass UV Filters From The Aquatic Environment	#19 Triantafyllos Albanis <i>(Univ. Ioannina, Greece)</i> Determination of Pharmaceuticals in Hospital and Municipal Wastewaters by Using LC-LTQ Orbitrap Mass Spectrometry
10:45	#14 Carmen Mazón <i>(Univ. Barcelona, Spain)</i> Effect of Sunlight and UV-C Disinfection Dose Irradiation on the Degradation of Organophosphorous Pesticide Dichlorvos	#20 Mónica Santos <i>(FEUP - Univ. Porto, Portugal)</i> Development of an Analytical Methodology for the Analysis of Priority Cytostatics in Water
11:00	Coffee-break & Exhibition	

Conference Hall: Auditorium II

11:30	Platinum Sponsor Peter Abrahamsson (<i>Agilent Technologies</i>) Using a Novel Accurate Mass MS/MS Library for the Qualitative Analysis of Environmental Samples
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Tuesday, November 28th

	Session Environmental Technologies Conference Hall: Auditorium II	Session Environmental Monitoring Conference Hall: Auditorium I
11:45	#15 Joana Vilas Boas (FEUP - Univ. Porto, Portugal) Single Chamber Microbial Fuel Cell (SCMFC) using <i>Lactobacillus pentosus</i> biofilms	#21 Patrícia Peixoto (FFUP - Univ. Porto, Portugal) Fast Methods for Screening Fluoroquinolones in Environmental Water
12:00	#16 Paula Figueira (Univ. Aveiro, Portugal) Nutshells as Very Low Cost Sorbents for Contaminated Waters Treatment	#22 Manuela Correia (REQUIMTE, LAQV/FOTOCAT, Portugal) Assessment of 83 Pharmaceuticals in Wastewater Samples by UHPLC-MS/MS
12:15	#17 Benigno Nóvoa (Univ. Santiago Compostela, Spain) Kinetics, Transformation and Toxicity of 1,3-di-o- tolylguanidine and 1,3-diphenylguanidine During Disinfection with Chlorine	#23 Belen González-Gaya (IMDEA Water, Spain) Optimizing a Clean Method for Environmental Samples: Antibiotics and Matrix Interferences in Marine Sediments, Water and Biota
12:30	#18 Elisabete Geraldes (Univ. Tech. Lisboa, Portugal) Eco-Friendly Non-Biocide-Release Coatings for Biofouling Prevention on Submerged Surfaces	#24 Liliana Silva (LAQV-REQUIMTE, FFUC - Univ. Coimbra) SSRIs Antidepressants in Marine Mussels from Atlantic Coastal Areas and Human Risk Assessment
12:45	#19 Djilali Tassalit (UDES/EPST, Algeria) Photocatalysis And Adsorption Synergy For Simultaneous Removal Of Phenol And Acetamiprid Pollutants In Water	#25 Tamara Gorena (CETAM, Chile) Evaluation of the Environmental Impact of High Pollution Load from an Industrial Complex using <i>Cupressus macrocarpa</i> biomonitoring
13:00	Lunch	

Conference Hall: Auditorium II

14:15	Keynote Cristina Branquinho (University of Lisbon, Portugal) Evaluating the Role of Urban Green Spaces in Improving Urban Sustainability: The case of Air Purification and of Climate Regulation
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Tuesday, November 28th

	Session Sustainable Development Conference Hall: Auditorium II	Session Environmental Monitoring Conference Hall: Auditorium I
14:45	#1 André Pereira (FFUC - Univ. Coimbra, Portugal) Human Pharmaceuticals in Portuguese Rivers: the Impact of Water Scarcity in the Environmental Risk	#26 João Sousa (FEUP - Univ. Porto, Portugal) Spatiotemporal Monitoring Campaign of the Watch List Compounds in Ave and Sousa Rivers
15:00	#2 Klara Slezakova (FEUP - Univ. Porto, Portugal) Ultrafine Particles in Ambient Air of Metropolitan Area of Porto: Levels and Risk Assessment	#27 Gabriela Varela (Univ. Santiago Compostela, Spain) Determination of Cardiac Drugs in Sludge by Ultra Performance Liquid Chromatography Followed by Tandem Mass Spectrometry
15:15	#3 Mirco Volanti (Univ. Bologna, Italy) LCA Methodology: A Case Study Of The Industrial Production Of Terephthalic Acid From Renewable Sources	#28 Polonca Trebse (Univ. Ljubljana, Slovenia) Identification of disinfection by-products formed within aquatic bromination of avobenzene
15:30	#4 José Virgílio Prata (ISEL - Inst. Politécnico Lisboa, Portugal) How an Environmental Issue Could Turn Into Useful High-valued Products: The Olive Mill Wastewater Case	#29 Jan Schwarzbauer (RWTH Aachen Univ., Germany) Molecular Indicators for Dockyard Works in Coastal Sediments of a Large Industrialized Port Area in Hainan Island, China
	Session Environmental Safety Conference Hall: Auditorium II	
15:45	#1 Anabela Francisco (Escola Universitária Vasco da Gama, Portugal) The Predicted Concentrations of Antibiotics in STPs in Portugal - A tool for the Microbial Community Resistance Research	#30 Filipe Rocha (FEUP - Univ. Porto) Seaweed Analysis for the Determination of Volatile Methylsiloxanes in Coastal Areas in North of Portugal
16:00	#2 Elena Bessonova (Saint-Petersburg Univ., Russian Federation) LC/MS Determination of Anti-TB Drugs and Their Metabolites in Human Plasma for Optimization Therapeutic Treatment of Tuberculosis	#31 Irene Aparicio (Univ. Seville, Spain) Occurrence of Parabens and Bisphenol A in Sludge Stabilization Treatments: Anaerobic Digestion and Composting
16:15	Poster Session & Coffee-break	
17:15	Departure for Porto Wine Cellars and Conference Dinner	

Wednesday, November 29th

08:30	Registration
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Conference Hall: Auditorium II

09:00	<i>Plenary</i> Kevin Jones (Lancaster University, UK) Passive Sampling the Wnvironment: Why, How and a Vision of the Future
09:45	<i>Keynote</i> Kurunthachalam Kannan (Wadsworth Center, New York Department of Health, USA) Biomonitoring of Human Exposure to Environmental Chemicals

	Session Environmental Safety Conference Hall: Auditorium II	Session Environmental Technologies Conference Hall: Auditorium I
10:15	#3 Marta Silva (FFUP - Univ. Porto, Portugal) Synthesis and Environmental Fate Evaluation of New Nature-Inspired Antifouling Compounds	#20 Susana Ortega (Univ. del Mar, Mexico) Ammonium Removal as Struvite from Biologically Treated Human Urine
10:30	#4 Inês Bezerra (FEUP - Univ. Porto, Portugal) Effects of Emerging Contaminants Detected in Drinking Water on Bacteria Tolerance to Antimicrobials	#21 Paula Guedes (FCT-UNL, Portugal) Removal of PPCPs from Effluent Based on Electrochemical Process - Possibility of Further Use in Agriculture
10:45	#5 Anne-Marie Delort (Univ. Clermont Auvergne, France) H ₂ O ₂ Modulates the Energetic Metabolism of the Cloud Microbiome	#22 Paulo Augusto (Univ. Salamanca, Spain) Exploring Magnetism as a Way to Decontaminate Wastewater and Leachates
11:00	Coffee-break & Exhibition	

Conference Hall: Auditorium II

11:30	Platinum Sponsor Juergen Wendt (LECO) The Usage of Time-of-Flight Mass Spectrometry for Environmental Analysis
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Wednesday, November 29th

	Session Environmental Safety Conference Hall: Auditorium II	Session Environmental Technologies Conference Hall: Auditorium I
11:45	<p>#6 Rui Santos (Specanalitica Lda)</p> <p>PLASMAQUANT® MS a new potential tool for Iron Isotope Ratios determination in Biological Samples</p>	<p>#23 Abuzar Kabir (Florida Int. Univ., USA)</p> <p>Encapsulation of High Surface Area Carbonaceous Particles into Sol-gel Matrix and Their Use in Environmental Pollution Mitigation</p>
12:00	<p>#7 Paulo Reis (FCUP - Univ. Porto, Portugal)</p> <p>RIBE Assessed At An Inter-organismic Level In <i>Daphnia magna</i> Exposed To Low Doses Of Uranium Mine Effluent And Waterborne Uranium</p>	<p>#24 Luísa Maia (UCIBIO, REQUIMTE, FCT-UNL, Portugal)</p> <p>Formate Dehydrogenase-catalysed Carbon Dioxide Reduction: Aiming to Develop a Catalyst for Carbon Dioxide Utilisation</p>
12:15	<p>#8 Patrícia Palma (Inst. Polit. Beja, Portugal)</p> <p>Ecotoxicological Tools Used in the Assessment of the Ecological Status of Freshwater Systems: a Case-study of the Temporary River Brejo do Cagarrão (South of Portugal)</p>	<p>#25 Maria Laura Tummino (Univ. Torino, Italy)</p> <p>Green Waste Derived Substances Immobilized on SBA Silica: Adsorbing and Photosensitizing Properties Towards Metals and Organics</p>
12:30	<p>#9 Joana Lourenço (Univ. Aveiro, Portugal)</p> <p>Uranium Mining Legacy Sites: Genetic Effects of Metals and Low-Dose Radiation in Farm Animals Exposed to Contaminated Water and Foodstuffs</p>	<p>#26 Cláudia Neves (Univ. Aveiro, Portugal)</p> <p>Immobilized Porphyrins as Photocatalysts for the Degradation of Metoprolol</p>
12:45	<p>#10 Pavel Fojt (VUT Brno, Czech Republic)</p> <p>Ecotoxicity Assessment of Cadmium Using Different Life Stages of the Terrestrial Gastropod <i>Helix aspersa aspersa</i></p>	<p>#27 Alaâeddine Elhalile (LS3M - Univ. Hassan I, Morocco)</p> <p>Synthesis, Characterization and Photocatalytic Performance of Mg-ZnO-Al2O3 Nanocomposite for Degradation of Pharmaceutical Pollutants</p>
13:00	Lunch	
Conference Hall: Auditorium II		
14:15	ACE General Assembly	

Wednesday, November 29th

	Session Environmental Safety Conference Hall: Auditorium II	Session Agro-environmental friendly processes and food chemistry Conference Hall: Auditorium I
14:45	#11 Helena Soares (FEUP - Univ. Porto, Portugal) Additive Inhibitory Free Metal Ion Concentration Index: a New Method for Assessing Multi-Metal Contamination Risk on Freshwaters	#1 Ana Martínez Piernas (Univ. Almería, Spain) Suspect-screening Strategy Applied To The Identification Of Transformation Products Of Carbamazepine In Lettuce And Soil Commodities
15:00	#12 Marilyne Pflieger (Univ. Ljubljana, Slovenia) Ecotoxicity of Biomass Burning Pollutants and Their Nitro Derivatives	#2 Anabela Cachada (CIIMAR - Univ. Porto, Portugal) Chemical and Biological Methods for the Evaluation of Cu Availability in Soils of the Douro Region
15:15	#13 Ruth Pereira (FCUP - Univ. Porto, Portugal) Ecosystem Services Provided by Soils Under Different Land Uses: Implications to Water Quality	#3 Carlos Ferreira (FEUP - Univ. Porto, Portugal) Soil interactions of azotochelin and DPH and determination of iron induced chlorosis mending potential in soybean (glycine max)
15:30	#14 Verónica Nogueira (FCUP - Univ. Porto, Portugal) The Impact On Soil Biota of Leather From The Footwear Industry Treated With ZnO Nanomaterial: A Microcosm Study	#4 Filipa Paulo (FEUP - Univ. Porto, Portugal) How and Why Incorporation of Microencapsulated Bioactive Ingredients in Foods?

Conference Hall: Auditorium II

15:45	Scholarship Ceremony & EMEC19 Presentation & Closing Ceremony
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Plenary Lectures

Climate changes, water scarcity, emerging contaminants and other stressors

PL #1

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Most ecosystems are exposed simultaneously to several stressors, in the so-called multiple-stress situations. Some stressors such as water scarcity can limit biodiversity and economic activities in entire regions. In addition of being a stressor on its own, water scarcity can drive the effects of other stressors acting upon river ecosystems. It leads to intermittency in water flow, and therefore has implications for hydrologic connectivity, negative side-effects on biodiversity, water quality, and river ecosystem functioning. Water scarcity can amplify the effects of water pollution by reducing the natural diluting capacity of rivers. Interactions between stressors may be exacerbated by climate change. For instance, warmer temperatures and reduced river flows will likely increase the physiological burden of pollution on the aquatic biota, and biological feedback between stressors (e.g. climate change and nutrient pollution) may produce unexpected outcomes. Degradation of drainage basins, destruction of natural habitats, over-exploitation of fish populations and other natural resources, or the establishment of invasive species, are factors whose impacts combine and may give rise to synergistic effects, especially during periods of water shortage. The effects of these stressors are very relevant for the chemical and ecological status of water bodies as well as for the sustainability of ecosystem services they provide.

Water scarcity is a key stressor with direct and indirect effects. The relevance of water scarcity as a stressor is most important in semi-arid regions such as the Mediterranean basin, characterized by highly variable river flows and the periodic occurrence of low flows and even no-flows. Climate change previsions forecast an increase in the frequency and

magnitude of extreme events. Although extremes are part of the normal hydrologic behaviour in Mediterranean-type rivers, many already show a consistent trend towards decreased discharge.

This presentation will show different examples on the risk of emerging contaminants and nanomaterials in Mediterranean river catchments affected by water scarcity. For example, the relevance of environmental factors (light, temperature, water flow) and chemical stressors (nutrients, pharmaceuticals, endocrine disruptors, pesticides, perfluorinated compounds and heavy metals) in the structure and functioning of epilithic biofilms in four Mediterranean watersheds, Ebro, Gualdalquivir, Jucar, Llobregat and Evrotas will be shown. Relevant data Emerging Contaminants and Nanomaterials on three other European river catchments; Adige, Sava and Evrotas will be reported too. Stressors co-occur and interact in specific manners, and the respective relevance of one or another in the response of the biota may be altered also by the flow regime.

Finally, new tools like MALDI-TOF MS were used to better understand the river functioning. The experiments start using standard polymeric materials exposed to natural aquatic environments. Afterwards structural changes related to degradation process of the polymeric surface are monitored by MALDI TOF IMAGING.

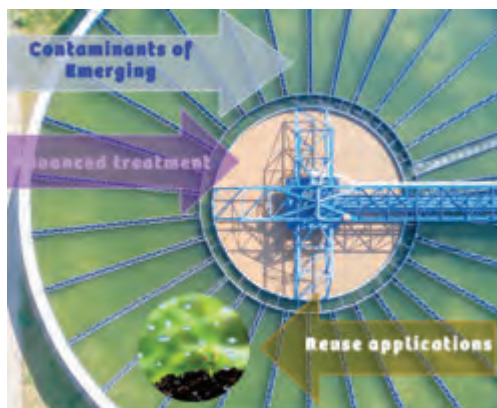
Acknowledgements

The studies covered by this talk have been financially supported by the EU through the FP7 project GLOBAQUA (Grant Agreement No 603629).

Considerations Related To Contaminants Of Emerging Concern And Wastewater Reuse

PL #2

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Despite the fact that wastewater reuse is a strategy that is gaining wider acceptance and is rapidly expanding, there are still a number of issues to be tackled with respect to the presence of contaminants of emerging concern (CEC) in treated wastewater and their potential to induce adverse effects. The need to look beyond the conventional contaminants when assessing the potential risks of wastewater reuse with respect to ecosystems and human health is now recognised as a priority issue in all policy areas at the EU level and beyond. CEC include pharmaceuticals and personal care products' compounds, disinfection by-products (DBPs), etc., as well as their transformation products (TPs) originating during treatment through biotic/abiotic processes. Moreover, the presence of antimicrobial-resistant bacteria and resistance genes (ARB&ARGs) in wastewater should not be overlooked during wastewater reuse.

Conventional activated sludge (CAS) currently applied in urban wastewater treatment plants (UWTPs) is inefficient in eliminating CEC, with their removal being highly variable. Membrane bioreactors have been shown to be more effective than CAS in removing better CEC that are susceptible to biodegradation. In recent years, considerable efforts have been made regarding the application of advanced treatment technologies, such as membrane filtration, adsorption on activated carbon and advanced chemical oxidation processes (AOPs), capable of improving the effluent quality with respect to the presence of CEC. Concerning filtration and separation processes, while the pores in micro- and ultra-filtration are too large to reject CEC, the lower pore sizes used in nanofiltration

and also reverse osmosis, have been shown to effectively reject significant amounts of CEC. However, the membrane technologies generate a residual stream, thereby creating a need for further proper management. Adsorption using activated carbon (AC) has been effectively used for the removal of various CEC, which after reaching its maximum adsorption capacity, should be regenerated and further reused. AOPs (e.g. UV-C/H₂O₂, solar photo-Fenton, ozonation) have experienced popularity over the past few decades in pilot-scale applications for their high efficiency in removing CEC, while also providing disinfection of the wastewater. Noteworthy is that a number of TPs may be formed during the application of AOPs, which may exhibit their own biological effects. Soluble microbial products in wastewater constitute the main precursors to the formation of DBPs which often are biologically potent. Also, the extent to which AOPs inactivate ARB and remove ARGs is driven by the oxidative damage mechanisms, the operating conditions, the target bacterial cell structure and their molecular characteristics.

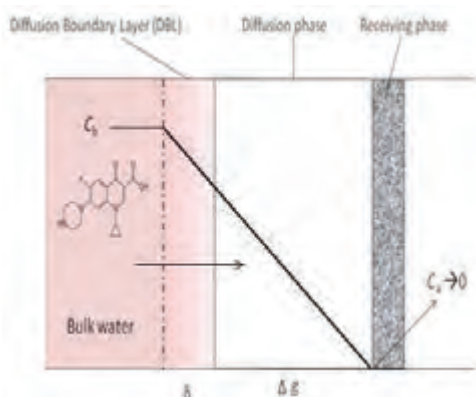
Recent scientific evidence revealed that the extent of crops' uptake of CEC is mainly influenced by the physicochemical properties of the compounds, the physiological properties of the crop and the soil properties. To date, it is difficult to draw concrete conclusions on the effects of soil and wastewater properties on the uptake of CEC, since data in the literature are available for different plant-growth methods and for different plants and CEC in each study. Moreover, there is lack of data on the health risks associated with the consumption of wastewater-irrigated crops, while predictive models to accurately estimate the concentration of CEC in crops grown in different environmental/agronomic practices would be useful for risk assessment.

Summarizing, there is a number of knowledge gaps and open questions related to the potential effects that the wastewater discharges and reuse practice might induce with regard to the CEC. It has become clear that new strategies consistent with the precautionary principle and the "One Health" approach are needed to assess the overall quality of wastewater intended for reuse. Knowledge with regard to risks that relate to low-dose exposure of CEC to non-target organisms, the additive/synergistic behaviour of various CEC in mixtures, crops' uptake, and antibiotic resistance is only now starting to shape. This talk aims at addressing the important issues discussed in this abstract.

Passive sampling the environment: why, how and a vision of the future

PL #3

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There has been interest in the development and application of passive sampling techniques for environmental applications for several decades now. However, the momentum seems to have increased in recent years and there is now a sense that the value and applications of passive

sampling has come of age. There is a demand from researchers with interesting questions; from agencies with responsibilities for monitoring our environment; a greater appreciation of passive sampling tools from industry and drivers from regulators, who increasingly recognise the value of passive sampling in yielding useful and defensible information.

This presentation will address the following topics:

- a brief history and summary of the types of passive samplers (with examples from air, water, soil/sediment);
- current motivations and drivers;
- designs, strengths and weaknesses;
- applications to research and real-world problems;
- challenges and opportunities;
- a vision for future developments and applications.

Acknowledgements

Examples will be drawn from our research groups – for whom funding from UK and Chinese research council sources is gratefully acknowledged.

Keynote Presentations

Microextraction: An Ideal Platform to Analyze and Simulate the Environment

KN #1

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Microextraction techniques represent an important development in the field of environmental analytical chemistry as they result in the selective, fast and sensitive isolation of target pollutants from the sample matrix prior to separation and detection. The methods are defined as nonexhaustive sample preparation with a very small volume of solid or liquid extracting phase relative to the sample volume. In a broad sense, microextraction methods can be viewed as bodies of technology built around discoveries of phenomena like diffusion, sorption or evaporation and can therefore simulate, in a small-scale, the processes found in natural and engineered environmental systems.

This contribution aims bridging two unexpectedly far disciplines such as environmental analytical chemistry and environmental engineering. Several of our new and past investigations will be presented and used as a platform to present the interplay between microextraction and environmental processes next to explore in simple terms the theoretical complexity inherent to these systems. In particular, analyte transfer of fullerenes and perfluorinated compounds during vortex-assisted liquid-liquid microextraction will be viewed at a molecular level. The “simple” data obtained for these compounds whilst adjusting typical experimental parameters (e.g. pH and salt) will be used to discuss the overarching environmental issues and challenges of inter-phase analyte transfer during microextraction [1,2]. Moreover, a new experimental setup will be presented that was used

to study and demonstrate the positive effect of vacuum on headspace single drop microextraction sampling of analytes with a low affinity for the headspace (i.e. polycyclic aromatic hydrocarbons). The experimental data obtained during method optimization will be discussed in terms of pollutants evaporation from natural water bodies as well as analyte uptake from micron-size droplets. Comparison with our previous results on vacuum-assisted headspace solid phase microextraction (Vac-HSSPME) will be presented and applications will include semi volatile contaminants with Henry’s Law constants below the threshold value where gas-phase resistance controls evaporation rates [3].

Looking at the bigger picture, the small-scale simulation feature of microextraction is a platform that can be used to tackle problems in other disciplines. For example, microextraction technologies when overexploited played the leading role in our ice photodegradation simulation studies of brominated diphenyl ethers (BDE-100) [4]. The versatile character of Vac-HSSPME will be demonstrated by adopting the photo-SPME approach whereby the SPME fiber coating is used as photoreaction support. Using this approach, PCBs were exposed to UV irradiation under vacuum conditions after being extracted (i.e. sorbed) on the SPME coating. Photolysis of the parent compounds and by-products formation proceeded onto the same SPME fiber, which was subsequently used for analysis. Interestingly, in the absence of oxygen a marked increase in photolysis rates was recorded. The environmental implications of the results obtained from all these studies will be discussed.

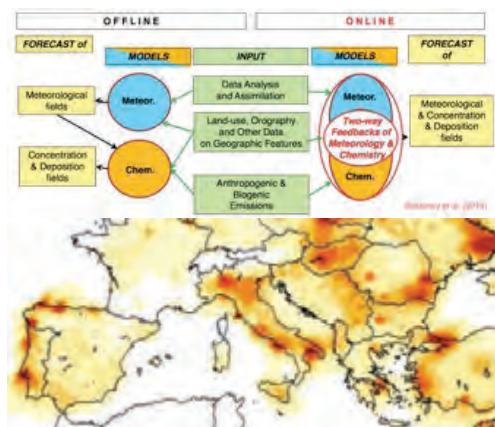
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Using Chemistry Transport Models to Evaluate the Fate of Atmospheric Pollutants

KN #2

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Atmospheric pollution is a major environmental and health problem affecting industrialised and developing countries around the world, especially over highly populated areas. The results of the APHEIS study and CAFE program indicated that atmospheric pollution (mainly by tropospheric ozone or particulate matter with diameters under 10 microns, PM₁₀) causes the premature death of over 310.000 inhabitants in the European Union each year. In this sense, models can give a complete deterministic description of the air quality problem, including an analysis of factors and causes. Within the variety of air quality models, Chemistry Transport Models (CTMs) are the only ones that quantify the deterministic relationship between emissions and concentrations/depositions [1]. Realistic simulations of air pollution, including gas-phase chemicals and particles/aerosols and the corresponding interactions with the climatic system, require, beyond the target contaminants themselves, meteorology/climatology, radiation, clouds and chemistry to be dealt in a fully interactive manner, in so-called coupled CTMs [2]. Therefore, this contribution presents the results of a number of studies, coordinated through collaborative European projects from FP7 and Horizon 2020 (e.g. MACC), International programmes such as AQMEII or COST Actions (e.g. ES1004, EuMetChem), where CTMs have been used to evaluate the fate of atmospheric pollutants (e.g. [3-5]). The most common use of CTMs covers the assessment of air quality and the guidance on the implementation

of mitigation measures. CTMs results over Europe (e.g. [3]) indicate that the objectives proposed by the EU directives for air quality are not as well accomplished in the Mediterranean area of the Iberian Peninsula as in other European areas (e.g. northern countries), partly due to different meteorological situations (e.g., dispersion, radiation), partly due to their particular emission distribution. Therefore, reliable estimations of air pollution for present-day conditions and a better understanding of the physical-chemical processes behind them become essential, not only for the information and alert of the population, but also to understand when and why episodes of air pollution arise and how they can be abated.

Another application of CTMs is to complement and support the use of monitoring or biomonitoring campaigns [4]. Focusing on the Iberian Peninsula, the WRF+CHIMERE modelling system was used to reproduce the levels of benzo[a]pyrene (BaP) in air and vegetation, with deviations below 0.4 ng g⁻¹ (biases lower than 30 % for all stations and seasons). For the same pollutant, these authors used the aforementioned model to assess the future health impacts of BaP on lung cancer under an extreme scenario of climate change. Thus, the use of coupled CTMs is not only important to portray air pollution. The inclusion of particles in an interactive manner in air quality models improve their skills to represent meteorological/climatic variables such as temperature or precipitation [5].

Acknowledgements

This research has been carried out under the support of the Project REPAIR (CGL2014-59677-R, MINECO and FEDER European program).

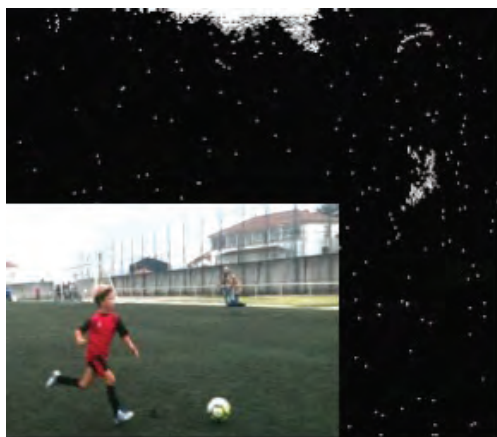
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Recycled Tire Rubber in Playgrounds for Children and Football Fields: Health and Environmental Concern

KN #3

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Disposal of used tires has been a major problem in soil waste management. The indestructible nature of discarded tires makes them to persist in the environment indefinitely, creating long-lasting piles of toxic, synthetic waste. One of the most valuable applications of used tires is the transformation in recycling products used in sidewalks, animal flooring, fitness centre flooring, playground surface and sport fields.

The tires are crumbled and transformed in rubber mulch that is a product consisting of granular rubber particles. This product can be used directly, such as the case in rubber artificial turf sport fields, or after an agglutination process, as it is the case of the rubber flooring for playgrounds (tire rubber mats and tire rubber tiles). These flooring surfaces have a durability of several years, but in the case of artificial turf, the rubber infill is continuously lost with the use, and it is necessary to add *new* rubber mulch regularly. It is very common to find granular rubber particles in the houses of people that practice sport on artificial rubber turf. In Spain, football is the “king” sport and a high percentage of children, mainly very young boys, practice football on these kind of surfaces several times per week.

Recently, concern about the safety of recycled tire rubber used in playgrounds and recreational sports surfaces, mainly football fields, has been raised.

In this presentation, several studies aiming at evaluating the presence of organic toxic (hazardous) compounds in outdoor playgrounds and football

fields of synthetic turf, will be shown [1-3]. Real samples were directly taken *in situ* by hand at the playgrounds and football fields or from the shoes and clothes of some players. Some samples of an indoor playground were also included as a case study. Additionally, commercial samples were also bought and analysed (rubber tiles and rubber mulch).

The samples were solvent extracted using ultrasounds energy and analyzed by GC-MS.

Some studies were conducted to evaluate the transfer of the hazardous organic chemicals to the the runoff water and the air in contact with these surfaces, and some real rain water samples were analyzed. The environmental risk arising from the burning of rubber crumb tires has been assessed, as well.

These studies revealed the presence of a high number of hazardous substances, including PAHs and other toxic chemicals in the tire rubber play and sport surfaces. Some of these compounds could easily reach the environment directly (soil, sediments), or indirectly through water leachates (water systems) and volatilization (air). Therefore, the use of recycled rubber tires, especially those intended for play and sport areas and other facilities for children, should be a matter of concern for health and the environment.

Acknowledgements

This research was supported by European Regional Development Fund 2007-2013 (FEDER) and projects GPC2014/035, R2014/013 (Consolidated Research Units Program), CRETUS (AGRUP2015/02) (Xunta de Galicia), and UNST13-IE-2152 and CTQ2013-46545-P (Ministry of Economy and Competitiveness, Spain). M.C. acknowledges CRETUS (Centre for Research in Environmental Technologies) for her contract.

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Evaluating the Role of Urban Green Spaces in Improving Urban Sustainability: The case of Air Purification and of Climate Regulation

KN #4

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Urban green spaces provide numerous ecosystem services in urban areas, such as air purification and microclimate regulation. Detailed information on the provision of ecosystem services and its integration with social-demographic data is an important tool to improve citizens quality of life.

Studying the provision of ecosystem services by green spaces requires data with high spatial resolution. However, as air quality stations have high operating costs, they are just a few in cities and seldom associated to green infrastructure. A solution to overcome this problem is to use ecological indicators, in this case we selected lichens.

Lichens have been used since the 19th century as ecological indicators. They lack roots or cuticle, and for that reason they take up water and nutrients directly from the atmosphere. Different lichen species have distinct sensitivities to atmospheric conditions (to water available in the atmosphere, or to nutrients or pollutants in the atmosphere). The number of species present in one place is one of the most common metrics used.

The main aim was to study the effect that green spaces in providing the ecosystem services: air purification and climate regulation.

Forty parks existing in the UGI in Lisbon were selected in a randomly stratified way with the following criteria: location within the city, type of surrounding land cover and green space size (area). In each UGI epiphytic lichen diversity was surveyed in the four suitable trees closest to the centroid of the green infrastructure, adapting the sampling procedure of the standard European protocol. Environmental variables in each UGI were

calculated, such as vegetation density and total park area. The information on Lisbon population at the parish level was retrieved from the last Census in the city (2011). Spearman correlations were determined between the environmental variables and lichen richness. Demographic population data for each Lisbon parish was related to the estimated average lichen species richness of UGI in the same parishes. These results of lichen sensitivity to air pollution and microclimate showed us that parks with a higher abundance of species, including the most sensitive ones, have a higher capacity to provide the ecosystem services of air purification and microclimate regulation, than those where they are less abundant and less sensitive species are present. We observed that, parks where lichen diversity was lower were in the city center where we have simultaneously the highest percentage of elderly population. This may result in an increased risk, as this population age group has a high susceptibility to respiratory infections and other diseases related to air pollution. We observed also that the smaller green spaces were those with lower capacity to mitigate the urban heat island effect. Projections forecast an increase of heat wave episodes for the future, which may lead to a future increase in social and health problems in city centers.

We built a model to understand how much we could gain in ecosystem services if we increased a green infrastructure area or vegetation density. The results indicate that the largest improvement in the ecosystem services provided would result by increasing the area and/or vegetation density of small green areas and/or areas with low vegetation density.

This work shows very clearly that parks vegetation density and area are very important features to improve local microclimate and air quality, highlighting the importance of green infrastructure as a nature-based solution to mitigate the urban heat island effect and air pollution and improve human well-being.

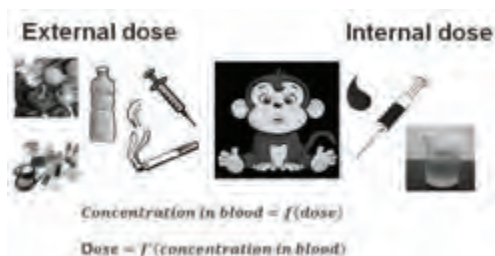
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The authors acknowledge the European projects: GreenSurge-FP7 and BioVeins-BiodivERsA32015104;

Biomonitoring of human exposure to emerging environmental contaminants

KN #5

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Long term, low-level exposure to a variety of toxic environmental chemicals present in consumer products and foodstuffs can interfere with hormone function and contribute to the development of a variety of diseases and health problems. To address the exposure to toxic chemicals to which people are exposed, and the amounts of chemicals in people's bodies, many developed nations have implemented nation-wide biomonitoring programs. The biomonitoring programs have been successful in informing the regulatory agencies on the health and nutritional status of populations along with a variety of toxic chemical exposures. This presentation is focused on how the biomonitoring programs can help make decisions in protecting the public health.

Biomonitoring studies focused on endocrine disrupting chemicals such as phthalate esters, parabens and bisphenol A (BPA) are discussed. Phthalates, parabens and BPA are reproductive toxicants and endocrine disruptors. Although human exposure to these chemicals is inevitable, owing to their use in several consumer products, the daily exposure dose is still not well known. A biomonitoring approach, that involves measurement of concentrations of target chemicals in human urine and by use of a simple pharmacokinetic model, we estimated total daily exposure doses of these toxic

chemicals. To complement the results obtained in biomonitoring studies, we also measured contaminants in various exposure sources including dust, indoor air, cosmetics, and food samples for the calculation of daily exposure doses using the direct measurements, which is termed as external dose. A comparison was made between the exposure doses calculated using the biomonitoring approach and the direct measurement of contaminants in food and dust. This approach helped in the identification of novel metabolites of toxic chemicals in human specimens.

Biomonitoring and environmental monitoring studies on human exposure assessment to toxic chemicals were applied for a wide range of contaminants in populations. Several multinational studies were conducted to elucidate global exposure patterns of emerging environmental contaminants. It was found that the chemical exposures in populations in various countries are similar, although the profiles (i.e., patterns of various chemicals) of exposure varied. Age, gender, ethnicity, occupation and other life style factors affect chemical exposures, depending on the type of chemical in question. The sources of exposures varied among chemical classes.

Current research is focused on elucidating the association between chemical exposures and health outcomes in populations. Furthermore, the chemical exposure biomarkers are concurrently measured with various effect markers (such as oxidative stress markers) in human specimens to enable association between chemical exposures and effects as well as pathways/mechanisms of such effects. The exposure assessment studies are further advanced to the concept of exposome which includes biomonitoring and metabolomic analyses of human specimens.

Platinum Sponsors Presentations

The Analysis of Natural and Synthetic Estrogens at Low ppq Levels in Surface Water and Final Effluent Water by LC-ESI-MS/MS

PtS #1

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Estrogens are routinely used either as contraceptive medicines or in hormone replacement therapy and can enter aquatic environments via the discharge of final effluent waters. Estrogens are believed to have a negative effect on aquatic environments by disrupting the hormonal systems of fish. In EU directive 2013/39/EU fifteen additional priority substances were added to the water framework directive (2000/60/EC). In this update, 17 α -ethinylestradiol and 17 β -estradiol were not included in this list but instead added to a watch list in order to gather further data regarding the presence of these compounds in aquatic environments and the risks they pose. In this presentation we highlight a method for the analysis of synthetic estrogens in surface and final effluent waters at low ppq levels using LC-MS/MS.

Spiked surface water and final effluent samples were extracted and concentrated using an off-line solid phase extraction (SPE) method. After evaporation and reconstitution in LCMS grade water, the samples were then analysed by LC-MS/MS using a large volume injection (100 μ l). The method's performance was evaluated by assessing linearity, repeatability, sensitivity and recovery. Satisfactory

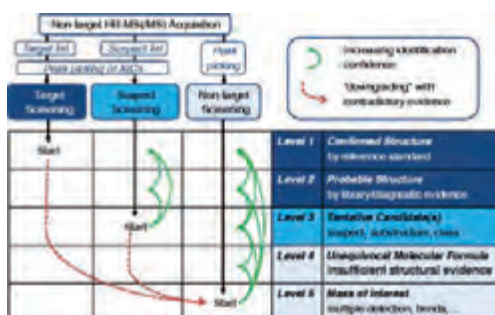
linearity was achieved for all compounds in matrix matched (spiked post extraction) calibration curves over appropriate ranges. In surface water, a range of 10 to 320 ng/L for 17 α -ethinylestradiol and 62.5 to 2000 ng/L for 17 β -estradiol and estrone ($R^2 > 0.998$, residuals < 15%) provided good linearity. For final effluent, the matrix matched calibration curves ranged from 120 to 2000 ng/L for all three compounds, also giving acceptable linearity ($R^2 > 0.997$, residuals < 10%).

The method's extraction efficiency was evaluated in surface water by comparing low level (pg/L) matrix extracted samples (sample spiked prior to extraction), against matrix matched calibration curves, where all recoveries were $\geq 70\%$, with %RSD < 13% (n=3). The robustness of the method was assessed using spiked water samples (n=8 for each sample type) where %RSD values below 6% were obtained. The method showed high sensitivity, achieving the required European (2015/495/EU) LLOQ (PtP s/n=10) levels for each compound in matrix. Low level concentrations of 17 α -ethinylestradiol were detected in the final effluent matrix and a standard addition method was used to quantify the concentration (16.9 pg/L).

Using a novel accurate mass MS/MS library for the qualitative analysis of environmental samples

PtS #2

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Clean water is a pre-requisite for wildlife, humans, agriculture and for food manufacturing and processing. Pollutants, as a result of anthropogenic activities, have a direct effect on water quality. Consequently, several different water regulations have been put in place, both to monitor the presence of the regulated compounds but also quantify them. A compounds class of particular interest is the so called PPCP's, i.e. pharmaceuticals and personal care products. This class of compounds span from over the counter prescriptions, veterinary drugs, cosmetics, sunscreen products, diagnostic agents etc. Including the transformations products and metabolites, there are thousands of compounds. To screen for such a large and diverse suite of compounds, it requires non-discriminating sample preparation techniques and, ideally, universal detection techniques. Liquid chromatography in combination with accurate mass high resolution mass spectrometry techniques (LC-HRMS/MS), has proven to be both universal, sensitive and offers excellent confirmation capabilities [1]. In addition, when using internal standards, it offers the possibility to quantify, even over a wide concentration range (3-5 orders of magnitude) [1]. In this work we have utilized a new accurate mass MS/MS library, the Agilent water screening PCDL, containing some 1400 compounds for the analysis of contaminants in various types of water. The use of curated accurate mass libraries has been proven to be an effective tool for the confirmation of compounds also in difficult matrices [2].

Samples were collected from 4 waste water treatment plants in central Europe. Effluent samples were collected over a 14 day period and the collection was repeated 9 times. The samples were stored dark at 3-8°C until sample preparation. The samples were prepared by adjusting the pH value, addition of internal standard followed by a simple filtering through a glass filter. Samples were injected (injection volume of 100µL) directly on to an analytical column (Zorbax) and separated through a gradient followed by detection on a 6550 LCQToF system (Agilent). Data was acquired in MS and MS/MS mode and the results were evaluated using MassHunter software and the Agilent water screening PCDL library.

The results showed seasonal variation of various pesticides. For the pharmaceuticals, diclofenac showed an even distribution over both seasons and various water treatment plants. The concentration levels were up to above 1000ppt. The investigation highlighted the effectiveness of the waters screening solution based on accurate mass MS/MS libraries.

Acknowledgements

We would like to thank Jean-Daniel Berset at the water and soil protection laboratory in Bern, Switzerland for the generous help with the selection and collection of samples. In addition Cristian Zwiener at the University of Tübingen, Germany for the sample measurements and valuable input on the accurate mass MS/MS libraries.

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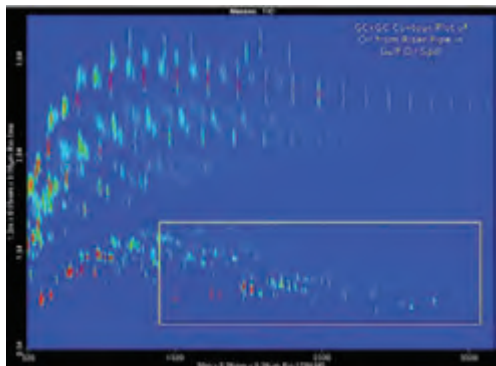
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The Usage of Time-of-flight Mass spectrometry for Environmental Analysis

PtS #3

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GCxGC-TOF Environmental Analysis



The growing concern about the quality and safety of the environment has led regulatory authorities to compile lists of priority pollutants and to establish rules and regulations for their control [1]. Consequently there has been a rapid increase in demand for the determination of a variety of micropollutants in water, air and soil. These challenges call for sophisticated analytical techniques, which are sensitive robust, fast and cost-effective. Chromatography and mass spectrometry are two techniques which can help. Mass Spectrometry (MS) is a popular technique for environmental analysis because of its ability to carry out sensitive qualitative and quantitative analysis [2]. A number of mass analyzers can be used to separate ions based on their mass-to-charge ratio. Analyzers vary depending on their mass measurement accuracy, resolving power, acquisition speed and linearity. Recent progress in instrumentation design as well as the use of fast

recording electronics together with improvements in signal-processing techniques has led to the renaissance of time-of-flight (TOF) mass analyzers for the determination of a wide range of both target and non-target organic components occurring in environmental matrices [3]. This presentation focuses on three applications using TOF mass analyzers with unit and high resolution. The systems were hyphenated to one- and two-dimensional gas chromatography [4].

Acknowledgements

Thomas M. Groeger

Cooperations Group „Comprehensive Molecular Analytics“, Helmholtz Zentrum Muenchen, German Research Center for Environmental Health GmbH, Muenchen, Germany
Tomáš Kovalczuk
LECO Instrumente, Plzeň, Česká republika

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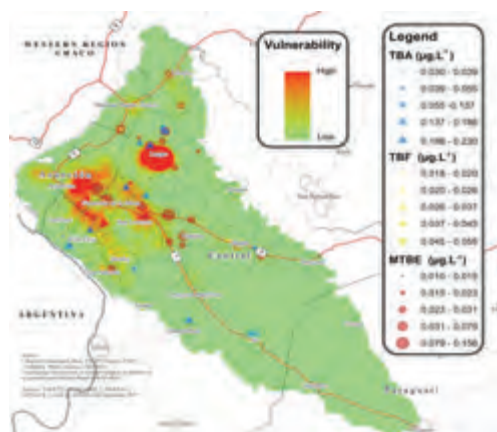
Oral Presentations

Environmental Monitoring

Preliminary Characterization of MTBE in the Patiño Aquifer, Metropolitan Region of Asuncion, Paraguay

OP Env Monit #1

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The Patiño Aquifer supplies water to the largest and most populous urban area in Paraguay with near 2 million inhabitants. Given its geographic position and its geological conditions (aeolian and fluvial cretaceous sands deposited in a NW-SE trending graben, of some 20 to 30 km wide [1], it is expected to be contaminated from landfills, insufficient sewage system access [2], as well as problems in the welding of gasoline tanks and spilling of fuel in gas stations. Other pressure is the over-exploitation rates [3].

Due to its physicochemical properties as high solubility, easy mobility and limited degradation, and potential release into the environment during the manipulation of fuels, the methyl tertiary-butyl ether (MTBE) has become one of the most frequent pollutants in groundwater around the world [4]. In 2013 imports of MTBE in Paraguay reached a pick [5]. The aim of this work is to characterize the pollution by MTBE and its degradation products (TBA, TBF) in the Patiño Aquifer and its presence in the vulnerability zones. Samples were taken from 90 water wells ranging from 30-100 m. deep selected by vulnerability criteria, e.g. maximum distance of 650 m. to a gas station. The sampling campaign was performed at the end of the rainy season. MTBE, TBA and TBF were analyzed by solid phase microextraction (SPME) and gas chromatography coupled with mass spectrometry (GC/MS). Validation of this method was performed with the fiber temperature between 21 to 25°C. Lower Detection Limits obtained were 0.009 µg.L⁻¹ for MTBE; 0.029 µg.L⁻¹ for TBA and 0.010 µg.L⁻¹ for TBF [6].

MTBE was detected in 44%; TBA in 21%; and TBF in 13% of the monitored wells. Average and maximum concentration of MTBE (0.033 µg.L⁻¹ and 0.156 µg.L⁻¹), are lower than the values found elsewhere [7]. Taking into account that 52% of all sampling points with presence of MTBE are close to gas stations, it can be inferred that the presence of MTBE is related to the spills of gasoline or not well welded tanks. These results are consistent with other authors [4,7] who report that detection of MBTE in groundwater might be associated with recharge rate of the aquifer and use of MTBE in gasoline.

Therefore the presence of MTBE and its degradation products may indicate pollution by hydrocarbons, either from point sources (leakage of underground gasoline tanks) or diffuse (infiltration after rain). The low concentrations found could be influenced by MTBE low density, meteorological conditions of the study period, regulations applied since 2015 to the import of fuel oxygenates, and the enforcement of regulations for tanks containments. More studies on water wells should be done near surface in order to detect gradient concentrations.

Acknowledgements

This results presented were part of the PROCENCIA Program, FIUNA-14-INV-284.

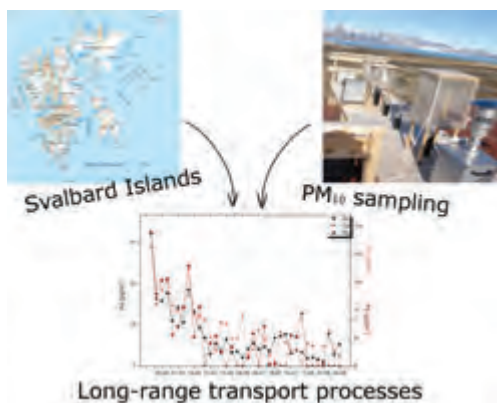
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Characterization and Temporal Evolution of the Inorganic Component of PM₁₀ Collected at Ny-Ålesund (Arctica)

OP Env Monit #2

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The chemical composition of atmospheric particulate matter (PM) has a strong variability, as it is heavily influenced by environmental conditions (season, weather and geographical area) and human activities [1]. Conversely, PM composition is able to strongly influence the climate changes, by altering cloud formation and the radiative balance of the atmosphere. This is particularly true for the polar regions, as they play a key role in regulating the global climate systems, by means of complex feedback mechanisms [2]. For this reason, the identification of local and global sources and the understanding of transport mechanisms and deposition processes of polar PM has a great importance [3].

This study investigated the inorganic composition of PM₁₀ collected in a polar environment (Ny-Ålesund, Arctica), with the purpose to identify its sources and to understand the short- and long-range transport processes, their possible future evolution and their effects on the radiative balance of the atmosphere.

The results obtained so far on samples collected over four subsequent summer seasons (2010-2013) evidence a remarkable seasonal trend for most of the investigated elements. For both geogenic and anthropogenic elements, concentrations are generally higher in March and April, period during which the ground is almost entirely covered by snow and ice, suggesting that long-range transport processes might be taking place. On the other hand, the concentration of elements typically deriving

from the marine aerosol (i.e. K, Mg, Na) present a peak in late spring and summer, together with Co, Ni and V, typical anthropogenic analytes related to ship emissions. A peak in the concentration of K (typical marker of biomass burning) was registered in correspondence to the occurrence of a large fire in North America, in good agreement with the direction of the air currents.

By comparing data obtained for Ny-Ålesund with data registered by other researchers on PM₁₀ collected in industrial, urban, and rural areas all over the world, it emerges that the concentrations obtained in this study are, for most of the analytes, the lowest; this is true not only for anthropogenic elements but also for geogenic ones, as the snow and ice covering the ground for most of the year prevent the local soil dust resuspension. As expected, the concentrations registered for PM₁₀ collected in Terra Nova Bay (Antarctica) are generally similar to the ones obtained in this study.

Enrichment factors have been calculated with respect to the mean values for the Earth's crust reported by Turekian and Wedepohl [4], in order to distinguish elements having natural, anthropic or mixed origin. Principal Component Analysis, Hierarchical Cluster Analysis and Factor Analysis have been executed for identifying correlations among variables and similarities among samples.

Acknowledgements

This research was supported by the National "Dirigibile Italia" and "ARCTICA" Research Programs (PRIN07 and PRIN09). We are grateful to the Italian participants to the 2010-2013 expeditions for carrying out the samplings.

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Vehicle Emissions Impact on Snow Albedo Reduction in Los Andes Mountains. Study Case: Portillo, Chile

OP Env Monit #3

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There is numerous studies about the reduction of snow albedo by ambient black carbon aerosol deposition [1, 2], however, in studies made in remote areas, black carbon concentrations are generally too low to quantify their influence on snow albedo. Otherwise, some studies conducted in laboratory conditions, have examined the effect of soot deposition on artificial snowpacks[3, 4], but these studies were made far from real-world conditions, may not include realistic sources, deposition mechanisms, or realistic snow characteristics. That's why there is little amount of literature about the effect of direct deposition of vehicle particulate matter emissions onto snow surfaces with well-quantified sources and atmospheric conditions. Portillo is a sky resort located in central Andes (Chile) very close of "Los Libertadores" border crossing between Chile and Argentina at more than 2800 m altitude, across the border pass has a very high traffic density (approx. 2,000 vehicle's/day), with a large number of passenger cars and trucks travelling in both directions. However, during heavy snowfalls in winter, the access for vehicles is often restricted. In this area road traffic is the main source of contamination and relative contributions of other sources are negligible. Given those characteristics, Portillo is an ideal place to study vehicle emissions impact on snow albedo reduction and the results can also be extrapolated to other vehicle-contaminated snowy areas, thereby helping to quantify their contribution to radiative forcing and climate change impact.

The main objective of this work is to analyse the relation between contamination source, atmospheric

conditions, and reduction of the snow albedo over a one-week period. Albedo was determined by measuring incident and reflected solar radiation using a portable radiometer Kipp&Zonen CNR4, weather conditions (T° , %HR, wind speed and direction) were measured using a HOBO portable weather station, and traffic information was obtained from Chilean Customs. As quality control of the obtained data, daily trends for the snow albedo were confirmed by comparison with the snow albedo modelled with the SNICAR code, for which the albedo of the underlying surface, the snowpack density and thickness, and the grain size, were measured and introduced as inputs.

The changes in albedo observed at Portillo, in the Chilean Andes, were a mean increase of around 8% every 10 cm of fresh snow accumulation, and a mean decrease of around 8% per day with heavy traffic. This implies that the increase in albedo derived from a light snowfall event (~10 cm) would be compensated within one day by the decrease in albedo derived from intense traffic conditions, and the increase in albedo derived from a heavy snowfall event (~20 cm) would be compensated within two days by the intense traffic-induced albedo decrease. Other parameters such as wind velocity and direction did not greatly affect the snow albedo during this study because the wind direction was fairly constant due to the terrain restriction. Moreover, it is difficult to estimate how much the snow metamorphism and melting contributed to the observed decrease.

Acknowledgements

Authors acknowledge to FPA-Environmental Ministry-Chilean Government for their financial support, and Chilean Army for their logistic support.

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Organic Contaminants in Indoor Dust: An Approach Through a GC-MS/MS method

OP Env Monit #4

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Dust is a well-known matrix and one of the most employed to carry out human exposure studies. It is defined as the solid particles with a diameter smaller than 500 μm , whose origin is the lifted-by-wind dust from the ground, volcanic eruptions and pollution [1]. In particular, indoor dust has a higher complexity by adding organic micromatter such as pollen or dead skin cells. These organic components are the main food for house dust mites, which secrete enzymes and feces that can cause allergic reactions in humans, such as respiratory and dermatological inflammations [2-3]. In addition, dust is considered a component of the particulated matter and it is directly related to potential health concerns such as cardiovascular disease, adverse birth outcomes as well as neurological and psychiatric disorders [4]. Finally, dust is a sink for organic pollutants and thus becomes an important exposure route of contaminants to humans.

The main objective of this study was to develop an efficient multiresidue analytical method for the determination of 59 compounds in indoor dust coming from different environments. To achieve this purpose, a simple, reliable and sensitive gas chromatography-electron impact-mass spectrometry in tandem (GC-EI-QqQ MS/MS) methodology was carefully optimized and validated. Compound selection was performed according to their expected presence in indoor environment and include legacy compounds (DDTs, PCBs), compounds used in recent times (organophosphorus flame retardants and organophosphorus pesticides, bisphenol A, phthalates and alkylphenols) and compounds originated from combustion processes

(PAHs), as well as nicotine. An experimental design was developed to optimize the extraction conditions for the selected analytes, which ended up being a solid phase extraction (SPE) by using florisil cartridges and a mix of hexane:acetone (1:1, v/v) as extraction solvent. In general, good method performance was obtained to determine low concentrations (ng/g) of the contaminants, although care had to be taken in the analysis of phthalates due to blank contribution. All the analyzed samples were contaminated, and the compounds detected at the highest concentration were phthalates, alkylphenols, organophosphorus flame retardants and bisphenol A, followed by PAHs. However, organochlorinated compounds, mainly dominated by DDE, and PCBs were detected at lower concentrations. The total amount was up to 10 $\mu\text{g/g}$, highlighting the importance of dust as a source of contaminants to humans [5].

Acknowledgements

The authors are grateful to the Spanish Government for the financial assistance. Specifically, they want to thank to the “Ministerio de Empleo y Seguridad Social” for the training contract (within the frame of the Sistema Nacional de Garantía Juvenil), as well as to the “Ministerio de Economía y Competitividad” for the Juan de la Cierva postdoctoral contract. Likewise, they also want to thank to Maria Ribas, *Biblioteques de Barcelona*, *Biblioteca Nacional de Catalunya*, *Arxiu Nacional de Catalunya* and *Equipaments Educatius* for their facilitation and provision for samples.

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Ozone Deposition Over Vegetation in the Eastern Mediterranean

OP Env Monit #5

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During the industrial age, anthropogenic emissions of fossil fuel have acted to approximately double the global mean tropospheric ozone (O_3) concentration. Studying the deposition of O_3 over vegetation, and particularly its uptake by stomata is of special interest for several reasons: a) O_3 is an air-pollutant and a greenhouse gas, while its deposition over vegetation tends to enhance its removal from the atmosphere. b) stomatal closure by O_3 uptake tends to mitigate the carbon sink strength of vegetation, thereby also leading to an increase in atmospheric CO_2 and an increase in global warming. c) O_3 adversely affects natural and agricultural plants functioning and growth. Currently O_3 reduces vegetation production rate of major food crops, with associated economic losses of several billion dollars per year in the US, EU and East Asia. The damaging effect of O_3 in both crops and natural plants is strongly related to its integrated uptake by plant stomata, associated with stomatal closure, reduced CO_2 uptake and photosynthesis. O_3 deposition over vegetation under Mediterranean climatic conditions is of special interest, considering that high irradiance and temperature tend to enhance photochemical O_3 formation. On the other hand warm and dry conditions tend to a) enhance

O_3 deposition over vegetation by increasing the release rate of biogenic volatile organic compounds (BVOCs) from the vegetation, thereby enhancing their reaction rate with O_3 [1] b) limit O_3 uptake by vegetation by reducing stomatal conductance. In the present study we applied the eddy covariance technique to study O_3 deposition over a mixed Eastern Mediterranean shrubbery in Ramat Hanadiv (Israel; $32^{\circ}33'19.87''N$, $34^{\circ}56'50.23''E$) [2]. Measurements of air-pollutants, including nitrogen oxides ($NO_x = [NO] + [NO_2]$), sulfur dioxide and carbon monoxide were used to study the impact of nearby air-pollution emission sources on O_3 deposition flux. The measurements were performed for two consecutive years and were compared with O_3 deposition over several other sites under different climatic conditions and vegetation in the Eastern Mediterranean. The results indicate high O_3 removal rate over the vegetation and strong limitation on stomatal O_3 uptake. Our findings further point out to significant influence of NO_x emitted from anthropogenic sources on O_3 deposition flux and large contribution of BVOCs emission from the vegetation to local O_3 removal, under the studied conditions at Ramat Hanadiv.

Acknowledgements

This study was supported by the Israel Science Foundation, Grant No. 1787/15. E.T. holds the Joseph H. and Belle R. Braun Senior Lectureship in Agriculture.

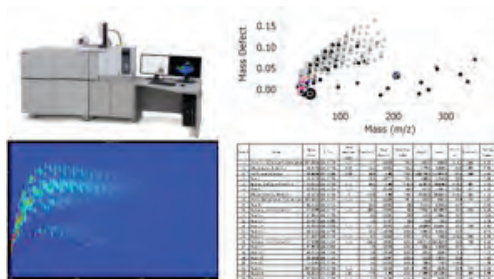
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Novel Methods for Comprehensive Analysis of Environmental Samples: GCxGC-HR-TOFMS

OP Env Monit #6

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The analytical methods for comprehensive environmental analysis have to address a variety of challenges. One of such challenges is humongous number of chemical compounds and their large chemical diversity. There are more than 109 million organic and inorganic substances in the CAS data base; almost 45 million compounds listed in the ChemSpider, over 750 thousand MS spectra in the Wiley library and more than 240 thousand in the NIST library. Development of analytical methods, capable of dealing with complexity of environmental samples is a very daunting task. Gas chromatography coupled with mass spectrometry provides one of the best analytical tools which combine selectivity, sensitivity, reliability, and information capacity for both targeted and non-targeted methods of environmental analysis. GC-MS identification of known compounds of interest and structural elucidation of unknown compounds becomes considerably more reliable if accompanied by accurate mass measurements while using High Resolution Mass Spectrometry (HRMS) [1, 2]. When analyzing real-life samples in a complex matrix, a high number of analytes of interest with a wide range of concentrations are likely present. Consequently, a significant increase in chromatographic peak capacity is required

which can be realized by the use of comprehensive GCxGC [3].

An ultrahigh resolution time-of-flight (TOF) mass spectrometer with a Folded Flight Path[®] Mass Analyzer was used in this study. This instrument has resolving power up to 50,000 and is capable of acquiring up to 200 full spectra per second, which matches the requirements for optimal GCxGC analysis. The novel data acquisition technique, Encoded Frequent Pushing (EFP[™]), was implemented to significantly increase sensitivity of the instrument [4].

Several environmental sample sets were analyzed, as extracts from various water sources, including rain, ice and snow. The samples were prepared according to EPA Method 8270. The analysis was performed using 1D GC and GCxGC methods, and the data were processed using ChromaTOF[®] software which includes novel features such as High Resolution Deconvolution, enhanced library matching, Advanced Spectra Analysis Tool and others which significantly improve accuracy of the results. Several examples of addressing the complex samples challenges, using novel analytical techniques and methods will be presented.

Acknowledgements

Authors thank Scientific Centre *Arctica* for providing samples for analysis.

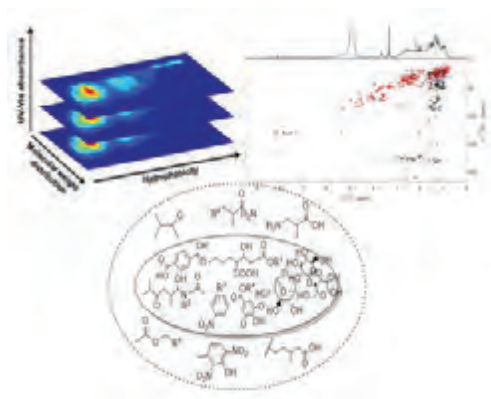
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A Primer on -Omics Strategy for Untargeted Profiling of Organic Aerosols: Lessons Learned and Future Challenges

OP Env Monit #7

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Organic aerosols (OA) is an important component of air particles and one of the key drivers that impacts the Earth's radiative budget, ecosystems, and health. Understanding the processes involving OA in the atmosphere depends on how well the chemical composition of this component is decoded. Yet, obtaining this information for atmospheric OA faces a number of challenges, such as their collection, extraction, and chemical complexity. To overcome these challenges, we pioneered a multidimensional non-targeted analytical strategy that allows for detailed structural characterization and source attribution of OA from contrasting environments. This integrated approach includes state-of-the-art analytical techniques and data processing tools for assemble useful and usable information for the identification of chemical patterns. Excitation-emission matrix (EEM) fluorescence data [1], comprehensive 2D liquid chromatography (LC²LC) coupled to different detectors [2,3], and 1D and 2D nuclear magnetic resonance (NMR) with compound identification by spectral database matching [4–7] constitute the core of avant-garde analytical tools that have allowed us to perceive and resolve the chemical and size continuum of atmospheric OA.

The combination of those techniques provided complementary datasets of primary (anthropogenic and biogenic) and secondary OA. The obtained dataset showed the existence of an “annual background” profile of the structural composition

of OA, featuring a core with heteroatom-rich branched aliphatics from both primary and secondary origin, aromatic secondary organics originated from anthropogenic aromatic precursors, as well as primary saccharides and amino sugar derivatives from biogenic emissions. Lignin-derived structures, nitroaromatics, and saccharide-derived signatures were also identified in smoke impacted OA, reflecting the influence of biomass-burning sources.

This novel integrated strategy has been providing unique insights into the composition and persistence of OA in the atmosphere, and has paved the way into a future where we can, indeed, learn to read the wealth of molecular information within the OA pool in order to achieve a much clearer picture of their impact in a changing climate scenario.

Acknowledgements

Centre for Environmental and Marine Studies (CESAM, UID/AMB/50017/2013); FEDER under the PT2020 Partnership Agreement; and, Portuguese Science and Technology Foundation (FCT), through the European Social Fund (ESF), Portuguese NMR network, and “Programa Operacional Potencial Humano – POPH”. FCT is also acknowledged for an Investigator FCT Contract (IF/00798/2015) and a PhD grant (SFRH/BD/84247/2012).

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Validation of ICP-MS Methodology for Quantification of 22 Elements in Wastewaters

OP Env Monit #8

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique used for elemental determinations having the capacity of simultaneously evaluate metals and metalloids from samples. The analysis of metals in wastewaters is an important step in the monitoring of environmental health and evaluation of potential risks to natural ecosystems. With the goal of minimize the pollution introduced into natural waterways wastewaters are regulated differently in different countries and thereby lower attention is given to elements with no maximum permissible levels established. This work included the validation of a multi-element methodology able to determine low levels of 22 elements. A problem that usually arises from ICP-MS technique is the interferences even from the carrier gas (argon) or environmental oxygen but also from major elements of environmental samples like chlorine, carbon or phosphorous [1]. In this study the configuration of parameters of the collision cell was optimized and a reaction gas flow (helium) of 5mL/min was established as the condition for the method. The efficiency of this configuration was tested with solutions of potential interferences (100 and 500 ppm of Cl, P, C, Mg, Ca and Na).

The analytical procedures were done in a ICP-MS 7900 (Agilent) controlled by MassHunter software. Wastewater samples were digested with nitric acid prior to analysis. The elements under study are: Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, V and Zn.

The parameters evaluated in the validation were the linearity, analytical limits, blanks, working range, sensitivity, precision (intermediate precision and repeatability), accuracy (with proficiency tests) and uncertainty.

The quantification limits (LOQ, established as the mean of blanks results plus 10 times its standard deviation) varied between 0.5ppb (Cd) and 2 ppm (Na). The majority of the elements have LOQ of 1 ppb. The specificity and selectivity were evaluated by recovery tests by spiking a known concentration of major and trace elements, showing good results once the recovery was around 100% \pm 20%.

Analytical precision is concerned with the variability between repeated measurements of the same analyte, irrespective of the presence or absence of bias. For the study of the repeatability of the method for validation purposes, ten independent tests were carried out on the same day on the same wastewater sample. The intermediate precision was estimated using range charts. For the repeatability, the relative standard deviation was below 10%, which is acceptable [2]. For all the elements the average amplitude of duplicate in wastewaters was below 10%, showing a good agreement. Proficiency tests (PTs) were performed to evaluate the accuracy through the determination of the Z-score. In PTs organized by BIPEA, LGC and Relacre a satisfactory performance was observed for 95% of the determinations and 5% were evaluated as questionable.

The uncertainty is an important parameter to estimate the errors in the final results. Uncertainties were calculated from the intermediate precision of a control standard in the range of the quantification limit of each element and from recoveries (accuracy). The uncertainties varied between 10 and 25%.

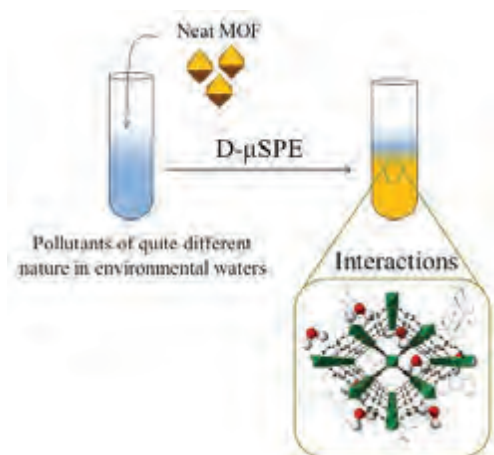
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Metal-Organic Frameworks: A New Generation of Sorbents for Solid-Phase Extraction

OP Env Monit #9

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Recent efforts in Analytical Chemistry are devoted to the employment of environmental-friendly methods, being particularly successful those based on microextraction approaches with novel sorbents. Among microextraction methods, it is worth mentioning the miniaturized version of solid-phase extraction (μ SPE), in which solid sorbents amounts lower than 500 mg are required [1], particularly when performed in its dispersive version (D- μ SPE). Several materials have been reported in the literature as promising sorbents in D- μ SPE, such as molecular imprinted polymers, carbonaceous materials (carbon nanotubes and graphene), surface confined ionic liquids, and recently, metal-organic frameworks (MOFs). MOFs are porous hybrid materials composed by metal ions and organic linkers, presenting the highest surface areas known. They have a crystal structure, and high thermal and chemical stability. Considering their chemical and physical properties, and using rational design,

MOFs can be prepared with very high surface areas (from ~ 200 to ~ 7000 m² g). MOFs can be used as neat materials, being then the unique extraction material responsible of the microextraction efficiency. However, despite its increasing use in extractive techniques, the type of interactions that have taken place during extraction has not been completely established. [2].

In present study, several MOFs have been properly synthesized, characterized and tested as sorbent materials in D- μ SPE followed by liquid chromatography. The analytical application has been shifted to the determination of a variety of environmental water contaminants [3,4], while trying to give insights into the mechanisms involved in the extraction process.

Acknowledgements

V.P. and C.R.-P. thank the Spanish Ministry of Economy and Competitiveness (MINECO) for the Project Ref. MAT2014-57465-R. P.R.-B. thanks her FPI PhD research contract associated to the Project Ref. MAT2014-57465-R. J.P. thanks funds from the Cabildo de Tenerife under the 'Agustín de Betancourt' Program.

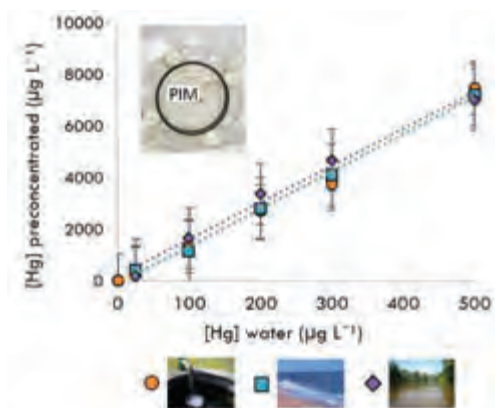
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Can Polymer Inclusion Membranes be Used as an Integral Tool to Facilitate Environmental Monitoring? The Case of Hg

OP Env Monit #10

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There is a need for simple and efficient techniques to improve the analysis of pollutants in complex matrices, such as the environmental ones. Moreover, the design of devices to facilitate the monitoring of the pollutants is also necessary to obtain reliable and significant data concerning contamination in aquatic environments.

In this context, chemically functionalized membranes can play an important role, and polymer inclusion membranes (PIMs) are one of the most promising functionalized membranes existing nowadays. PIMs consist of a polymer, which provides mechanical strength, the carrier, which is the responsible of the extraction process, and sometimes also a plasticizer can be used to provide elasticity. Hence, PIMs can be tailor-made depending on the characteristics of the analyte, incorporating either commercial extractants or specifically synthesized ligands. The stability, versatility and easy manufacturing show PIMs as a useful separation technique to be taken into account.

In this work we have studied how PIMs can solve different analytical difficulties in the analysis and/or monitoring of mercury (Hg). For that, PIMs have been prepared fixing cellulose triacetate as polymer and the ionic liquid trioctylmethylammonium thiosalicylate (TOMATS) as extractant. This PIM

was successfully used to collect Hg from a polluted river when incorporated in a diffusive gradients in thin films (DGT) device [1]. Moreover, it has effectively been used as a solid sorbent to extract Hg from different natural waters as well as from agricultural soils. Once the metal is collected, different analytical instrumentation can be used to quantify the metal without the need of an elution step, such as an advanced mercury analyser AMA-254, atomic absorption spectroscopy) or an X-ray fluorescence spectrometer.

From our studies, it has been seen that the addition of the plasticizer nitrophenyloctyl ether (NPOE) to the PIM, and with an optimized composition of 50%CTA+30%TOMATS+20NPOE (% mass) this membrane allowed the selective transport and pre-concentration of Hg at low µg L⁻¹ levels in several natural waters such as well water, river water and seawater, without any previous treatment (pH adjustment or salinity control). A special device has been designed to incorporate the PIM and to contain a small reservoir of a 10⁻³ M cysteine solution where Hg is released after membrane transport. An effective transport efficiency of the PIM-system has been obtained in the different water samples, with no effect of water characteristics. This important result shows this new PIMs-based device as a promising tool to perform Hg monitoring.

Hence, we have demonstrated that PIMs can be used as collectors to facilitate Hg determination from both natural waters and soils, and that can act as sensors for metal monitoring in different environments when incorporated in a special device.

Acknowledgements

The financial support of the research project CTM2016-78798-C2-2-P (AEI/FEDER/UE) and the scholarship IFUG2016-2018 from University of Girona are acknowledged.

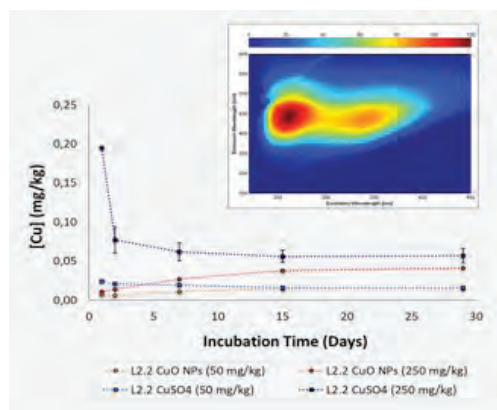
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Evaluation of the Effect of Organic Matter on the Dissolution of Cu from CuO and Cu(OH)₂ Nanomaterials in Agricultural Soils

OP Env Monit #11

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Copper-based nanoparticles (NPs), such as copper oxide (CuO) and copper hydroxide (Cu(OH)₂), can be used as fungicides due to their antimicrobial properties, and as fertilizers due to their ability to deliver micronutrient-Cu to plants [1]. The use of nanomaterials in agrochemicals can offer targeted delivery, controlled release, enhanced solubility and increased efficacy of active ingredients, and considerably reduce the amounts of agrochemical products applied to crops and soils when compared to conventional formulations. The increasing interest on these agro-enabled agrochemicals raised however numerous questions regarding potential environmental risks arising from their application. In this study, we evaluate how natural organic matter (NOM), and most particularly properties of dissolved organic matter (DOM), affect the temporal variability of the dissolution and extractability of Cu from soils amended with Cu-based NPs. Pots containing Lufa 2.1 or 2.2 standard soils were amended with a suspension of CuO NPs (Sigma, 50 nm), Cu(OH)₂ NPs (synthesized following the method described by Lu *et al.* [2]), or bulk CuSO₄; two concentrations levels of Cu in soils were tested ([Cu]=50 or 250 mg/kg, dry weight) and incubated for 30 days at constant moisture content (50% of WHC). Soil pore water samples were collected in selected days throughout the experiment using two different methods: low-pressure method using Rhizon samplers and soil extraction by 0.01M CaCl₂. Levels of dissolved organic carbon (DOC) in pore water were determined by using a Shimadzu

TOC analyzer, and DOM composition was characterized by UV-Vis, molecular fluorescence, and ¹H NMR.

Results showed that DOC concentrations in pore water samples or soil extracts collected from Lufa 2.2 soil along 30 days (38.1-127 mg/L) were higher than those in Lufa 2.1 soil (30.0-43.6 mg/L). Differences in DOM composition between the two soils were also observed.

After 30 days, the levels of dissolved Cu in pore water samples or soil extracts from Lufa 2.2 soil amended with CuO or Cu(OH)₂ NPs were similar to those in soils amended with ion control CuSO₄. By contrary, in soil Lufa 2.1, Cu concentrations in pore water or soil extracts amended with CuO or Cu(OH)₂ NPs (250 mg/kg) were always below levels of dissolved Cu in soils amended with CuSO₄. These results suggest that the dissolution of Cu from CuO or Cu(OH)₂ NPs was higher in Lufa 2.2 soil compared to Lufa 2.1 soil, and that both Cu nanomaterials were fully dissolved in soil Lufa 2.2 after 30 days. Differences in Cu dissolution in the two soils were related to both DOC levels and soil DOM composition.

The effect of the variation of DOM composition on Cu-based nanomaterials' dissolution in soils as well as potential implications for the use of nano-enabled agrochemicals will be discussed in detail in this presentation.

Acknowledgements

This work was supported by the Centre for Environmental and Marine Studies (CESAM, UID/AMB/50017/2013), and the Portuguese Science and Technology Foundation (FCT). This work was also funded by FEDER under the Operational Program for Competitiveness Factors and by National funds via FCT within the framework of the research project *NanoFertil* (POCI-01-0145-FEDER-016749 e PTDC/AGR-PRO/6262/2014).

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Atmospheric Particle-Bound Organophosphate Esters (OPEs) in a North African Mediterranean Coastal Environment (Bizerte, Tunisia)

OP Env Monit #12

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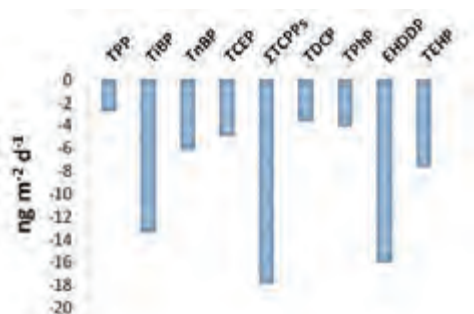


Figure 1. Median atmospheric dry deposition fluxes of the nine OPEs studied in Bizerte coastal area (TCCP is the sum of the two major isomers)

Last scientific reports confirm the multi-media global distribution of organophosphate esters (OPEs) flame retardants and plasticizers [1-3]. Evidence of their environmental persistency, bioaccumulation and adverse effects in aquatic organisms and humans have also been reported for some OPEs [1, 4]. The marine environments, and in particular coastal areas, are important sources/receptors of these “emerging” contaminants. However, still very little or no information exists on current base line levels, stocks and atmospheric loading for many marine areas, like the NW Mediterranean African coast. The aim of this study was to assess -for the first time- the occurrence and loading of atmospheric particle-bound OPEs in a coastal area at the Mediterranean Sea African edge. Sampling was conducted in the Bizerte city, which is a medium-size city (~127 000 inhabitants), located in the north of Tunisia, between the Mediterranean Sea and the Bizerte lagoon. Agriculture and fishery activities are important in the area but a considerable number of light and heavy industries are present too. Air (total suspended particles, TSP) samples were collected from March 2015 to January 2016 on pre-combusted quartz fiber filters (QFFs) using a high volume air sampler. OPEs were extracted for the QFFs by accelerated solvent extraction (ASE) and quantified by gas chromatography coupled with mass spectrometry (GC/MS). Overall, 60 samples were collected and analysed for the most

widely distributed OPEs. Σ_9 OPE concentrations varied from 85 to ~2000 pgm⁻³. Tris-(1-chloro-2-propyl) phosphate (TCCP), 2-Ethylhexyl diphenyl phosphate (EHDDP) and Tri-iso-butyl phosphate (TiBP) were the most abundant OPEs over the study area. The seasonality of these atmospheric concentrations is currently under evaluation. The atmospheric dry deposition fluxes (F_{DD} , ng m⁻² d⁻¹) of OPEs were calculated as $F_{DD} = v_d C_A$, where C_A is the OPE volumetric concentration in the aerosol (ng m⁻³) and v_d (cm s⁻¹) is the particle deposition velocity. A reference value of 0.2 cm s⁻¹ for v_d was adopted in this study. The dry position fluxes (Σ_9 OPE) ranged from 15 to 340 ng m⁻² d⁻¹. Individual values are presented in Figure 1. According to our estimations, the sensitive environment of Bizerte coastal lagoon (1.28 x 10⁸ m²) could receive up to ~15 kg of OPEs yearly. This atmospheric loading of “emerging” toxic chemicals may have, yet unknown, implications for the water quality status.

Acknowledgements

Thanks to the financial support from the IRD French-Tunisian International Joint Laboratory (LMI) “COSYS-Med”. This work was also funded by the Labex OT-Med (no. ANR-11-LABX-0061) – MEDPOP, funded by the French Government “Investissements d’Avenir” (ANR) through the A*MIDEX project (no ANR-11-IDEX-0001-02), the MIO-IRD Action Sud project “AEROBIZ” and the PACA region project “Particule”.

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Source Apportionment of PAHs in a Petrochemical and Chemical Industrial Area Using Lichens as Biomonitors

OP Env Monit #13

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Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that consist of two or more fused aromatic rings with some of them being carcinogenic and mutagenic [1]. Main sources of PAHs include urban (e.g., traffic) and many industrial activities (e.g., coke production, waste incineration, petrochemical industry, crude oil refineries) [2]. Identifying the contribution of each source for the PAH burden in a region is a difficult task.

In this study PAH profiles in lichens were used to track different pollution sources in the largest petrochemical and chemical complex of Southern Europe. Lichens are symbioses of fungi and algae and/or cyanobacteria, which have been used to monitor gas phase and particle-bound PAHs [3-5]. Lichens were collected from a background area and transplanted to 15 sites in the industrial and urban areas of Tarragona County, Spain (Fig.1). After two months of exposure (from November 2014 to January 2015), lichen transplants were collected, the concentrations of the 16 priority US EPA PAHs were quantified, and PAH profiles (relative contribution of each compound for the sum of the 16 PAHs) were derived for each sample.

A cluster analysis revealed differences between PAH

profiles in lichens deployed in the petrochemical area and the ones deployed in chemical and urban areas. The contribution of the 3-ringed compound anthracene for the profile of lichens deployed in the petrochemical area was 6-fold the remaining ones. Not accounting with anthracene, the profile in lichens was dominated by phenanthrene, fluoranthene and pyrene in both industrial areas. The increased contribution of anthracene in the petrochemical area in relation to chemical and urban areas was also found previously in the same area in vegetation and soil samples (3- and 2-fold, respectively), but not in air.

By observing the variation of PAH profiles in lichens after exposure across the study area in comparison with the ones in lichens before exposure, it was possible to identify the areas where PAH profile has changed the most.

This method has revealed to be effective to disclose fugitive and unexpected PAH pollution sources, and to assess their spatial impact.

Acknowledgements

Sofia Augusto acknowledges the European Union Seventh Framework Programme for the Marie Curie Intra-European Fellowship for Career Development (FP7-PEOPLE-2013-IEF-624022) and FCT (SFRH/BPD/109382/2015).

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Concentration Ratios for Polycyclic Aromatic Hydrocarbons from Wood Combustion: Comparison of Laboratory Results and Sampling in Temuco City (Chile)

OP Env Monit #14

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In Chile there are serious problems due to pollution by particulate matter (PM) smaller than $2.5\mu\text{m}$ ($\text{PM}_{2.5}$) and PM_{10} . The atmospheric pollution problem extends from northern, central and southern cities in Chile, where the cities of south have showed the most serious problems related to air quality. In Chile, fuel wood consumption accounts for 20% of total primary energy demands, besides being the main fuel used in residential sector [1]. Wood combustion is the emissions source of a variety of different air pollutants, where highlight fine particles $\text{PM}_{2.5}$ and Polycyclic Aromatic Hydrocarbons (PAHs) adsorbed on their surface. Although they arise from natural sources, their principal sources are anthropogenic emissions such as the combustion of fossil fuels and biomass (wood) [2]. PAHs, in the form of both gases and particulate matter, may be discharged into the atmosphere and transported over long distances. The ratio values of individual PAHs species in ambient samples are frequently employed as diagnosis tools to identify the impact of different sources of PAHs in ambient air [3].

In this research, an analytical methodology was optimized using Accelerated Solvent Extraction (ASE) and GC-MS for determination of Emission Factor (EFs) of priority 16 EPA-PAHs adsorbed in $\text{PM}_{2.5}$ (particulate phase) generated by the combustion of the most common woods used in the south central zone of Chile: *Eucalyptus globulus* (EG), *Nothofagus obliqua* (NO) and *Pinus radiata* (PR) using the Controlled Combustion Chamber for Emissions (3CE, CETAM patent application No. 843-2008, 2010 in Chile and International Patent Application No. PCT / CL 00058, 2010, pending) [4].

The objective of the present work is to evaluate the variation of PAHs Concentration Ratios (CRs)

for combustion of EG, NO and PR at 0% and 25% humidity (H) in 3CE and to compare with results from air sampling taken in Temuco city, during winter time, using a speciation sampler (partisol 2300, Thermo, USA) with $\text{PM}_{2.5}$ impactor.

In this studied, all CRs from NO, EG and PR present similar values at two different humidities, so we can conclude that there is not effect of wood humidity in the CRs.

If we compare the CRs for PAHs from Temuco city and from 3CE, exist concordance between CRs of BAA/ (BAA + CRY) in the range 0.4–0.6 and CRs obtaining in 3CE for combustion of NO with CR of 0.48 (0%H) and CR of 0.53 (25%H), but not for EG and PR (both ≤ 0.4). Respect FLT/ (FLT + PYR) ratio for Temuco city was 0.5 and the CRs in 3CE for wood species EG and PR, to both humidities was 0.5 in all cases, except NO was 0.3 (0%H). About FLT/PYR to Temuco city, the calculated value is between of 0.9 and 1.0, showing only concordance with EG (0.99) and PR (1.0) both species at two humidities studied. CRs for NO was 0.4 for 0 and 25%H. Respect CRs obtained in 3CE (NO, EG and PR) in general was not concordance with CRs associated to vehicular pollutions of another authors (results not showing in this studied). Of the results it can be concluded that the CRs from NO, EG and PR obtained in the 3CE have similar interpretation like the CRs from Temuco city showing that wood combustion is predominant in the Temuco city.

Acknowledgements

Authors thank to CONICYT-PAI/Concurso nacional tesis de doctorado en la empresa 2014-78141103; FONDEF IDEA en 2 Etapas N° ID15110580, Proyecto CONICYT-FONDECYT/postdoctorado 3150685, FONDECYT 1161793. DGIP-UTFSM-PICC- 2015.

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Organic Pollutants in Moscow Rain

OP Env Monit #15

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Rain and snow are rather valuable matrixes to estimate atmospheric pollution. For several years we were studying pollution of the air in Moscow (Russia) analyzing the snow samples [1-3]. However snow sampling may be achieved only in winter period. To estimate the atmospheric pollution in a warm period and to check the usefulness of the approach based on precipitates analysis eight samples of rain were collected in two districts of Moscow in April-May 2017. Semi volatile pollutants were the target of the research.

The volume of the rain samples, collected using wide glass funnel was 250-1000 ml. Ultrapure water was used as a laboratory blank. USEPA 8270 Method was used for the sample preparation. Pegasus® GC-HRT (LECO Corporation, Saint Joseph, MI, USA) coupled to an Agilent 7890A Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) was used for the analysis. The data were acquired using 10 full (10-800 m/z range) spectra per second in high resolution mode (25000), with high mass accuracy (<1 ppm), reliably determining elemental composition of all ions of interest in mass spectra.

Chromatographic separation of the samples was performed using an Rxi-5SiMS 30 m x 0.25 mm (id) x 0.25 μm (df) (Restek Corporation, Bellefonte, PA) column with a constant helium flow of 1 mL/min. All injection volumes were 1 μL , splitless for 60 s. The injector and the transfer line temperature were set at 270 °C and 320 °C, respectively. The GC oven program was as follows: 0.5 min isothermal at 50 °C, then 10 °C min^{-1} ramping to 320 °C and 8 min isothermal hold at 320 °C.

Since sample preparation was carried out immediately after sample collection the losses of semi volatile compounds due to biological or physico-chemical degradation were minimal.

More than 500 semi volatile organic compounds were identified in the samples. They were divided into three groups according to the reliability of identification. The first group (56 compounds) represented priority pollutants (USEPA list). In addition to the most reliable identification quantification of these analytes was carried out as well. Polycyclic aromatic hydrocarbons, phenols, phthalates, organochlorines, including PCB were the main classes inside the first group. Detection of various nitrophenols and oxydized PAH reflects the chemical processes in clouds.

The second group (over 250 compounds) represents reliably identified chemicals with high scores, correct accurate masses of all ions and correct fragmentation pattern (checked manually). Aldehydes, ketones, alkanes, fatty acids, aromatic hydrocarbons and their numerous derivatives, halogen containing compounds, furanes, amides, organophosphates, glycols, N and O-containing heterocycles including pyridines, quinolines, indols, were the constituents of this group.

The third group consists of partially identified chemicals, when only elemental composition, affiliation to a certain class, or the presence of certain functional groups was established.

The obtained results are very useful for the reliable estimation of the environmental pollution of the Moscow air and selection of the candidates for the priority pollutants for the city. Besides they were very useful addition to the previous results obtained with the snow samples. The importance of the accurate mass measurements was nicely demonstrated in several structural elucidation cases. Besides, library search applying exact masses of the ions appeared to be much more reliable.

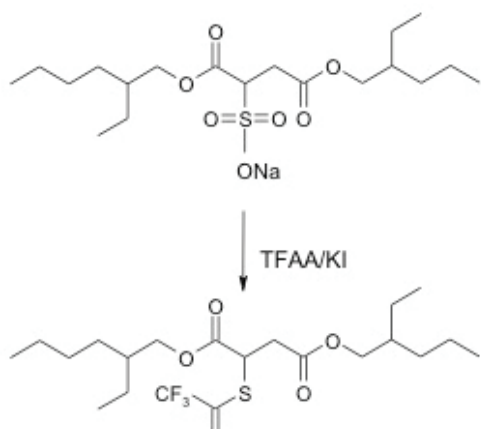
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Determination of Surfactants Used in Agrochemicals

OP Env Monit #16

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Additives in formulated pesticides are regarded as inert components, but have been proven in many cases to exert detrimental side-effects or modify the toxicity of the active ingredient. Thus, authorisation and use of these agricultural additives should be regulated more strictly.

Environmental assessment, i.e. identification of toxic hazards, as well as determination of maximum residue levels require reliable analytical methods. Analysis is often challenging as surfactants are usually complex mixtures, their composition is not exactly known or not well defined, and reliable information and certified reference materials are not available. In addition, they represent a wide range of chemicals in a broad range of polarity, which should be monitored in the environment as pollutants. Surfactants are determined mainly by liquid chromatography coupled to mass spectrometry (LC-MS), as gas chromatography (GC) can be applied only to smaller groups and often rely on derivatisation. An advantage of the GC method is that due to better separation it allows more detailed information about the composition of the mixtures analysed.

To facilitate our ecotoxicological studies of the components in formulated pesticides containing neonicotinoid insecticides (clothianidin, CLO; acetamiprid, ACE) and herbicide glyphosate (GLY) as active ingredients, methods for analytical determination of these ingredients and their surfactant additives were assessed. We have developed an LC-MS method for characterisation of sulfonic acid surfactants in CLO-based insecticide formulation, found to be 46.5 times more toxic

than CLO itself on *Daphnia magna* [1]. Linear alkylbenzene sulfonates (LASs) were determined in an ACE-based insecticide, and the decomposition of these substances was characterised in surface water. Dissipation of LAS was determined alone and in the presence of ACE by using an HPLC-UV method. DT_{50} values were 67 ± 9 hrs and 21.7 ± 4.5 days for LAS alone and in formulation, respectively. Dissipation of GLY was monitored in the presence and absence of formulant polyethoxylated tallowamine (POEA) [2]. EC_{50} values on *D. magna* were 84.07 ± 3.11 , 4.01 ± 1.00 and 11.17 ± 2.79 mg/l for GLY, POEA and Roundup, respectively.

Investigation of derivatisation reactions for GC focussed on different sulfonates and on a trisiloxane surfactant. Measurements were carried out by using GC coupled to MS (GC-MS), and the results were compared to those obtained by GC with electron capture detection mode or by HPLC-UV. Among sulfonates conversion of LASs and alkylsulfonates (e.g. Nonit, dioctyl sulfosuccinate salt) were investigated by using derivatisation. Reaction with potassium iodide and trifluoroacetic acid were studied, but the stability of these derivatives is poor. Therefore, other reagents (e.g., *in port* derivatisation with tetrabutyl-ammonium-hydrogensulfate) resulting in more stable derivatives were also studied. Silvet Star (Trisil, heptamethyl-trisiloxane modified with polyalkene oxide) together with related compounds (Triton X, Genamin and Sapogenate) were silylated by using silylcarbamates that were used earlier. Based on their mass spectra and chromatographic properties, oligomers of Silvet Star and other investigated surfactants were identified, and their distribution pattern was determined. Stability of the silyl derivatives was ensured by using the appropriate reagent excess or can be further improved by formation of corresponding *tert*-butyldimethylsilyl esters.

Acknowledgements

The work was funded by the Hungarian Scientific Research Fund (OTKA K109865 and K112978).

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Organic Pollutants in the Snow of Russian Arctic Islands

OP Env Monit #17

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Arctic environment previously has been shown to be very sensitive to changes in the chemical composition of the air–snow interface and climate changing in general [1,2]. Snow has been used as an efficient indicator of air pollution in cold climate regions due to “cold finger” effect [3]. Regular monitoring of the Arctic environment can give insight in the understanding of the global air transfer processes and identify pollution sources.

This study represents results obtained during research program of Northern (Arctic) Federal University “Arctic Floating University”. Snow samples were taken within the expedition carried out by “Prof. Molchanov” ship. The main sampling points are marked in the graphical abstract. All snow samples were stored freezed during the sailing. The sample preparation procedure involved melting of the snow samples under room temperature and further classical liquid-liquid extraction with dichloromethane according to US EPA 8270 method. Distilled water subjected to the same procedures was used as a blank. The extracts were combined and analysed using gas chromatography – high resolution mass spectrometry (GC-HRMS) with electron ionization (EI). All experiments were carried out using Pegasus GC-HRT instrument (LECO, USA). The identification of organic compounds was made using mass spectral library

NIST14. Besides, all identification results were checked manually for avoiding the false-positive results.

Hydrocarbons (alkanes, naphthenes and PAH), phthalates, fatty acids and some natural organic compounds (terpenes and terpenoids) were the main organic constituents of all 18 samples. Only several US EPA priority pollutants were identified and quantified (phenol, pyridine, phthalates, some PAH). Large number of identified fatty acids signifies the intensive photo-oxidation processes in the atmosphere or on the snow surface involving hydrocarbons. Hydrocarbons by themselves could appear in the Arctic due to long distance air transfer or due to increased number of cargo ships using Northern sea route. Unexpectedly rather high levels of non-ionic surfactants (polyethylene and polypropylene glycol derivatives) were observed. The blanks were carefully checked for the presence of these compounds. On the contrary persistent organic pollutants (POP) like chlorinated hydrocarbons, pesticides, fire retardants etc., which are usually used as environmental indicators, were poorly presented only by several phosphates (for example tri(2-chloroethyl) phosphate).

The obtained results represent the unique peace of information on the organic pollutants in Arctic snow obtained by reliable GC-HRMS non targeted analysis.

Acknowledgements

The research was done in terms of RSF 17-13-01112 project.

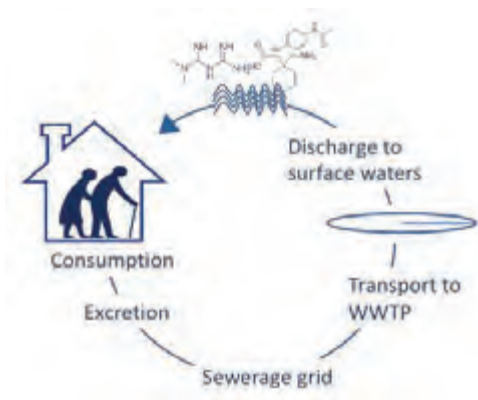
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Pharmaceuticals Released from Health Care Facilities: New Control Procedures

OP Env Monit #18

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Health care facilities have been identified as an important source of pharmaceuticals to the environment [1, 2]. The aim of this study is to determine the amount and type of pharmaceuticals released from 2 health care facilities located in Barcelona. Selected establishments included a senior residence oriented to housing or day care (i.e. for independent individuals that do not require help or assistance) and a sociosanitary center devoted to general impairment (individuals with general loss of daily function activities and with specific types of psychologic or physical diseases). Both establishments host 130 people and up to 164 different types of pharmaceuticals are administered daily. The water consumption is of 20 m³/day and wastewaters are discharged untreated to the sewerage system.

In a first step, we have calculated the predicted concentrations discharged based on consumption data [3]. This information revealed that more than 600 g of pharmaceuticals are consumed on a daily basis in each establishment, and thus, are discharged to the sewerage grid via wastewaters. In a second step, we have prioritized compounds more likely to be detected in water and have developed an analytical method based in solid-phase extraction and liquid chromatography coupled to tandem mass

spectrometry to be used for the characterization of wastewaters from health institutions. In a third step, we have monitored the levels of the 52 pharmaceuticals prioritized in effluents from the health establishments to determine their occurrence. Based on this information, we have estimated the loads to WWTP and surface waters according to dilution factors and degradability of target compounds. For compounds likely to be discharged to receiving waters at concentrations higher than 0.01 µg/L, which is the European Medicines Agency threshold for risk evaluation of pharmaceuticals in surface waters [4], we have evaluated the impact based on aquatic toxicity using *Daphnia magna*. Among the studied substances, macrogol, amoxilin, glucosamide, ibuprofen, metformin, paracetamol and megestrol were the compounds bearing the highest environmental hazards. For these compounds, elimination treatments based on advanced oxidation processes are envisaged for their *in situ* removal, at the outlet of the effluent of the health care facilities.

Acknowledgements

This study has been financed by the SUDOE program with the project Innovec'Eau (2016-2019)/Project SOE1/P1/F0173 Interreg SUDOE funded by FEDER: 1.177.875,64 €; <http://innovec-eau.univ-perp.fr>. We would like to acknowledge the associated partners of project: Sant Joan de Deu (SJD) and Llars d'Avis de Catalunya (L'Onada).

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Determination of Pharmaceuticals in Hospital and Municipal Wastewaters by Using LC-LTQ Orbitrap Mass Spectrometry

OP Env Monit #19

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In this study, the occurrence of eleven pharmaceutical compounds in wastewaters was investigated. The compounds investigated include frequently used pharmaceuticals belonging to various therapeutic categories, i.e., the non-steroidal anti-inflammatory, NSAID's drugs salicylic acid, ibuprofen, paracetamol, naproxen and diclofenac, the antihyperlipidemics gemfibrozil and fenofibrate, the psychomotor stimulant caffeine, the anti-epileptical carbamazepine, the analgesic/antipyretic phenazone and the disinfectant triclosan. A monitoring program was carried out for the four seasons of the year 2006. The selected areas of the study were the municipal and hospital wastewater treatment plants (WWTP) of Ioannina city, located in Western Greece.

Hybrid LTQ Orbitrap mass spectrometry was employed for the ultra-trace detection and quantification of target pesticides and finally was successfully applied to the analysis.

The results of the monitoring study, showed the occurrence of all target compounds in the wastewater samples. Mean concentrations in the influent ranged between 86.34 and 0.85 µg/L and in the effluent ranged between 6.69 and 0.30 µg/L. Removal efficiencies ranged between 13.8% and 98.0% for the WWTP of the city, and between 20.0% and 92.2% for the WWTP of the hospital. Removal efficiencies were higher in the WWTP of the city than in the WWTP of the hospital.

Development of an Analytical Methodology for the Analysis of Priority Cytostatics in Water

OP Env Monit #20

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Cancer is one of the leading causes of morbidity and mortality worldwide and its incidence in the population is gradually increasing, being expected to rise by about 70% over the next 2 decades [1]. The increasing consumption of anticancer drugs in chemotherapy and their relatively low degradation rates at conventional wastewater treatment plants (WWTPs) have contributed to their continuous input and accumulation in the environment [2]. Anticancer drugs are being found in influents/effluents of WWTPs and in river/receiving waters [3]. Predicted environmental concentrations (PECs) based on the total national consumption of cytostatics have been determined and values higher than the trigger for further environmental risk assessment (10 ng/L, according to EMA [4]) have been obtained for some of them. Based on the studies of Catalonia and Portugal, eight cytostatics were identified as priority compounds [5, 6]: mycophenolic acid (MPA), hydroxyurea (HYD), cyclophosphamide (CYC), prednisone (PRED), capecitabine (CAP), imatinib (IMA), bicalutamide (BICA) and 5-fluorouracil (5FU). Therefore, the main objective of the present study was to develop an analytical method to identify and quantify such priority cytostatics in water.

Solid phase extraction and liquid-liquid extraction procedures were tested at different conditions and optimized towards the maximum recovery of the target analytes. The mass spectral characterization,

the optimization of the chromatographic separation and the study of the quality parameters were also included. The final analytical methodology was successfully applied for the analysis of real water samples.

Acknowledgements

This work was the result of the project: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (ii) NORTE-01-0145-FEDER-000005 - LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Mónica S. F. Santos is grateful to the Portuguese Foundation for Science and Technology (FCT) for her postdoctoral grant (ref. SFRH/BPD/104039/2014).

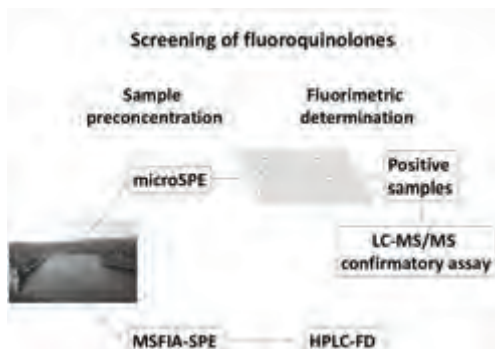
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Fast Methods for Screening Fluoroquinolones in Environmental Water

OP Env Monit #21

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Environmental monitoring of antimicrobial agents is currently an important issue, due to the increasing prevalence of antimicrobial resistance and the toxic effects of antibiotics on natural ecosystems. Fluoroquinolones (FQs) are widely used in human and veterinary medicine. These compounds are mainly degraded by photolysis. However, photolytic degradation of FQs results in toxic photoproducts, which present additional inhibitory effect on microbiota metabolism, particularly when the products are in presence of their parent compounds [1]. As these compounds are frequently found in the environment, development of screening methods for determination of FQs in water is required.

The aim of this report is the discussion of features, advantages and limitations of recently proposed methodologies for screening FQs in environmental water. Fluorescent intrinsic properties of FQs were applied for their determination with the implemented methods. First, a method based on automatic solid-phase extraction coupled with chromatographic fluorimetric detection of FQs at ng levels was developed. The selective retention of FQs was attained through a lab-made extraction

column containing molecularly imprinted polymers targeting FQs, which was automatically operated using a multisyringe flow injection system. System optimization was performed, including physical and chemical variables. A second method was also developed, based on microsolid-phase extraction associated with fluorimetric determination of FQs under high-throughput microplate format. Norfloxacin, ciprofloxacin and enrofloxacin were selected as model analytes and determination was attained at μg levels after studying physico-chemical variables for analyte retention in membrane-based solid-phase sorbent. Using the same eluate tested in the microplate, LC-MS/MS was applied as confirmatory method for positive samples. Real samples were analysed using both methodologies and the application of each method to environmental monitoring will be critically addressed.

Acknowledgements

This work received financial support from the European Union (FEDER funds POCI/01/0145 / FEDER/007728 and POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e a Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreements PT2020 UID/MULTI/ 04378/2013 and PT2020 UID/QUI/50006/2013. L. Barreiros thanks FCT and POPH (Programa Operacional Potencial Humano/ Human Potential Operational Program) for her post-doc grant (SFRH/BPD/89668/2012). P.S. Peixoto thanks funding from CAPES, Ciência sem Fronteiras program under grant BEX 9532/13-7.

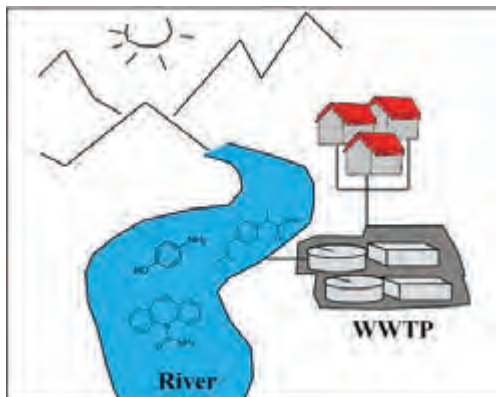
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Assessment of 83 Pharmaceuticals in Wastewater Samples by UHPLC-MS/MS

OP Env Monit #22

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Modern societies have benefited from the introduction of thousands of synthetic chemicals in the last century. However, the importance of their environmental fate has only been recognized in the last few decades, particularly in the case of micropollutants, such as pharmaceutical compounds [1]. The assessment of their presence in the aquatic environment, at very low levels (ng/L), has been possible due to the developments in analytical determination, such as the use of ultra-high performance liquid chromatography coupled to tandem mass spectrometry detection (UHPLC-MS/MS) [2].

The massive use of pharmaceuticals for both human and veterinary purposes leads to the introduction of tons of these compounds in wastewaters. After treatment in wastewater treatment plants (WWTP), considerable amounts can be transferred to surface waters either due to insufficient removal efficiencies or, if high removals are attained, concentrations up to ng/L and mg/L can still be found, depending on the compounds' mass loadings. This may affect water quality and potentially impact drinking water supplies, ecosystems and human health [1, 3].

In a previous study, the occurrence of 33 pharmaceuticals and metabolites was evaluated along the Lis river (Leiria, Portugal) and in influents and effluents of two WWTPs located along the river [3]. In samples collected from August 2013 to June 2014, pharmaceuticals, such as ibuprofen, ketoprofen, carbamazepine and fluoxetine, and the

metabolite salicylic acid showed 100% of detection frequency, at levels up to $1.3 \mu\text{g L}^{-1}$ for ibuprofen [3]. The purpose of this study is to extend the number of pharmaceutical compounds analysed, using a new sampling campaign that took place in June 2017. Samples of Norte WWTP (Leiria, Portugal) effluent and influent were collected hourly, for 24 hours. Effluent samples were collected taking into account the WWTP hydraulic retention time. Flow proportional 24-h composite samples of the influent and the effluent were also collected.

A set of 83 pharmaceutical compounds belonging to different therapeutic classes, including non-steroidal anti-inflammatory drugs, analgesics, anorexics, stimulants, anxiolytics, antidepressants, antibiotics, beta-blockers, and laxatives was assessed.

Pharmaceuticals were extracted using Strata-X cartridges (200 mg, 3 mL) from Phenomenex and analysed by liquid chromatography coupled to tandem mass spectrometry (LCMS-8030, Shimadzu Corporation) with an electrospray ionization source (ESI).

The presence of more pharmaceutical compounds could be confirmed when compared to the previous study.

Acknowledgements

The authors would like to thank the EU and FCT / UEFISCDI/FORMAS for funding, in the frame of the collaborative international consortium REWATER financed under the ERA-NET Cofund WaterWorks2015 Call. This ERA-NET is an integral part of the 2016 Joint Activities developed by the Water Challenges for a Changing World Joint Programme Initiative (Water JPI).

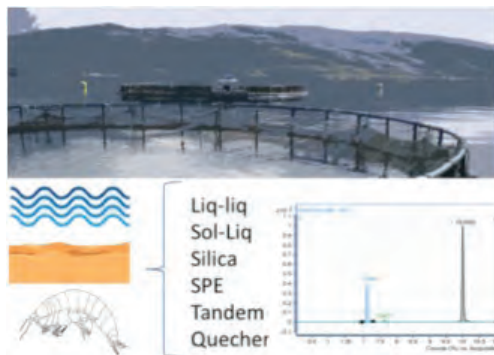
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Optimizing a Clean Method for Environmental Samples: Antibiotics and Matrix Interferences in Marine Sediments, Water and Biota

OP Env Monit #23

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The presence of anthropogenic organic pollutants in aquatic ecosystems has been a key topic in environmental studies during the last decades. The more persistent, accumulative and toxic contaminants are frequently regulated [1, 2], whereas the more degradable polar compounds (i.e. personal care or pharmaceutical products) are normally less controlled in the open environment [3]. Only recently, particular efforts have been put towards the development of appropriate techniques to assess their environmental occurrence, fate and risks. The extremely wide range of chemical characteristics, their low stability and the general lack of reported lethal effects at environmentally relevant concentrations makes the determination of these chemicals a big challenge, out of the scope of many environmental considerations [3]. Moreover, most of the environmental monitoring studies do not show analytically adequate methods due to the complexity of the matrices where they are analysed (sewage waters, sediments, biological tissues), and their particular physicochemical properties (ionic, susceptible to chelation and degradable) [4]. It is common to find articles using matrix matched calibration curves, very large injection volumes with reported matrix effects, or qualitative assessments [5, 6] leading to misguided real concentrations and very high detection limits, leading to inaccurate environmental assessments. Intensive aquaculture is considered to be an important source of antibiotics, leached out from food sources intended for the caged fish, but also by the spread of fish faeces into riverine and marine aquatic ecosystems. The objective of this work was to develop and validate an analytical method for

the determination of some of the most commonly used antibiotics in aquaculture (oxytetracycline, flumequine and florfenicol) in several marine environmental matrices, including seawater, sediments and biota (biofilm and two species of invertebrates). Special attention was paid on the optimization of the extraction and purification steps (i.e. liquid-liquid and solid-liquid extractions, the use of silica and other commercial sorbents' clean-up, single and tandem solid phase extraction, etc.). Samples were analyzed by high pressure liquid chromatography coupled with a time-of-flight mass spectrometer (LC-TOF-MS). Instrumental optimization included chromatographic and spectrometry parameters selection (i.e. LC column, mobile phases and gradients, flow, ionization, voltages, etc.). Finally, the chromatographic separation was carried out with a Luna Omega Polar C18 column (100 mm x 2.1 mm x 5 µm) (supplied by Phenomenex). The mobile phase used was a mixture of 0.1% formic acid in water (A) and methanol (B) in gradient elution mode at a flow rate of 0.4 mL/min. Mass spectrometry with an electrospray ionization mode (ESI) was performed in positive mode. The good resolution and mass accurate measurement provided by the TOF-MS allowed reaching quantification limits (1 ppb for oxytetracycline and flumequine and 5 ppb for florfenicol) with satisfactory precision (RSD (relative standard deviation) <10%). The recovery percentages ranged 90-100% for seawater and sediment samples (low organic matter) and near 70-80% for biological samples. These represent extraordinary advances in the analysis of antibiotics in environmental samples and should be taken into account for a proper assessment of aquaculture environmental side effects like antibiotics' accumulation in marine ecosystems and through the food chain.

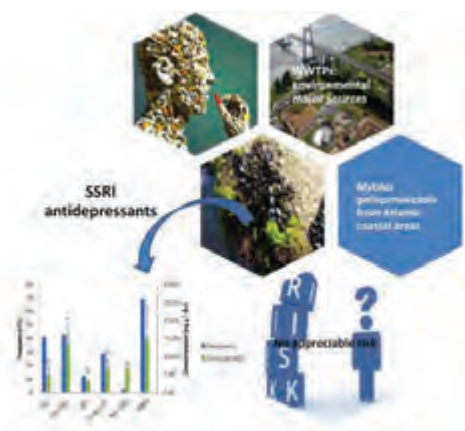
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SSRIs Antidepressants in Marine Mussels from Atlantic Coastal Areas and Human Risk Assessment

OP Env Monit #24

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Selective serotonin reuptake inhibitors (SSRIs) are among the most prescribed antidepressants nation and worldwide requiring chronic administration to elicit the desired therapeutic effects [1]. In Portugal the prevalence of use (15%) of antidepressants, doubles the European Union (EU) average presenting the highest use when compared to every other member-state [2]. Here between 2003 and 2011, an increase of around 100% in SSRIs consumption was observed [3]. Their presence in the aquatic environment is known, and most likely to occur from wastewater treatment plants (WWTPs), causing growing environmental pressures in heavily populated coastal areas. Disruption of invertebrate endocrine systems has been described, causing reproduction reduction, abnormalities in embryos development and sexual maturation delay. Discrete seawater sampling may not be suitable to evaluate such environmental risk; however, filter-feeders mussels bioconcentrate chemicals [4] allowing evaluating a much longer time frame.

Therefore, we aimed to assess SSRIs and metabolites in wild *Mytilus galloprovincialis*, and assess risk to human health [5].

A total of 1225 mussels were sampled during one year along the Portuguese Atlantic coast. Each freeze-dried pool of 25 specimens was analyzed, in duplicate, by solid phase extraction (SPE) and liquid chromatography with tandem mass spectrometry (LC-MSn) [5].

Approximately 70% of the samples were contaminated with at least one, and up to 4 from the 7 targeted compounds. The cumulative SSRIs and metabolites content in mussels ranged between 3.17 and 33.93 ng g⁻¹ dry weight, in a mean level of 14.68±9.69 ng g⁻¹. Norfluoxetine was the most recurring SSRI and the one with the highest mean concentration, 13.52 ng g⁻¹. Although some differences were found between different sampling periods and locations, those were not statistically significant ($p > 0.05$) and no correlation was found between wet weight and mean contamination levels [5].

Regarding risk to human health following consumption of these filter-feeders, when considering the average sample contamination of positive samples and the average Portuguese and European consumption, the ratio between the estimated daily intake (EDI) and the acceptable daily intake (ADI) ranged from 0.45 to 5.50% and from 1.60 to 19.41%, respectively. Therefore, although the resultant risk is lower for the Portuguese consumer than for the average EU consumer, apparently, no appreciable risk to human health is expected. However, one should note that these compounds occur in mixtures with other pharmacologically active compounds and with other chemical contaminants that share similar modes of action, resulting in possible additive or synergistic effects [5].

Acknowledgements

The authors are grateful to the POCI/01/0145/FEDER/007265 and to FCT under PT2020 UID/QUI/50006/2013 and the post-PhD fellowship SFRH/BPD/62877/2009. We are also grateful to the Laboratory of Mass Spectrometry of the Node UC integrated in RNEM, and to IPMA (Instituto Português do Mar e da Atmosfera).

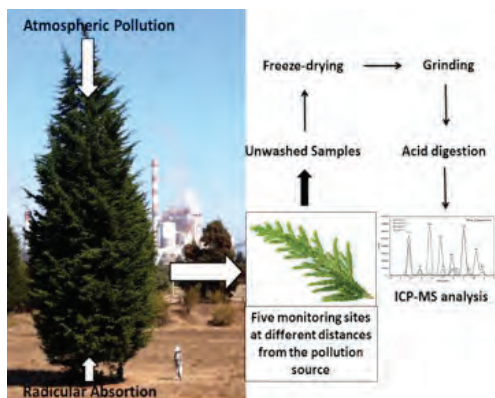
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Evaluation of the Environmental Impact of High Pollution Load from an Industrial Complex using *Cupressus macrocarpa* Biomonitoring

OP Env Monit #25

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Anthropogenic contamination by trace elements and heavy metals degrades water, soil and air, affecting the ecology of diverse populations, both natural and human. In central Chile (V Region) is located the Puchuncaví valley. In this area there is an important industrial complex which main activities are copper smelting and coal-fired power plants (thermoelectric), but also including a terminal for liquefied petroleum gas (LPG), chemical industries and cement companies, among others. Due to the type of activity developed in the area, the environment is strongly affected by the anthropogenic pollution, such as discharged of atmospheric deposition, gaseous pollutants and deposition of metal-rich particles [1,2].

Plants tend to accumulate pollutant elements in leaves due to their great ability to adapt to the chemical variabilities of the environment. In this way, plants become reservoirs of trace elements of soil, water and air [3]. Trace pollutants get into the plant tissues mainly through two pathways, stomatal and root, and also can be deposited in the cuticle of the leaves [4,5].

The goal of this study was to determine the profile and concentration of trace elements in *Cupressus macrocarpa* leaves at different areas in the Puchuncaví Valley.

Leaves of 1 year old were sampled during the fall (April, 2016) in 5 areas located at different distance from the industrial complex (between 0.8 to 15 km). For the trace element analysis the leaves were

first frozen, then lyophilized, milled in an agate mill, digested with acid and subsequently analyzed by ICP-MS. Ca, Al, K, Ti, Cr, Mn, Fe, Cu, Zn, As, Sr, Cd, Sb, Hg, Pb and S were analyzed.

In *C. macrocarpa* leaves, a clear tendency to increase the concentration of Cu, Sb and S with the proximity to the industrial complex was observed, because their high correlation when adjusted to a lineal regression ($r^2 > 0.8$), follow by As, Cd ($r^2 > 0.6$) and Pb ($r^2 > 0.5$). The elements such as Al, Ti, Fe, Ca, Mn, Zn, Sr, Cr and Hg a low lineal regression ($r^2 < 0.4$) was observed. Besides, cluster analysis was performed in order to identify the sources of this elements, were 3 clusters were observed. The first cluster groups Al, Fe, K, Ti which most likely source is geogenic. The second cluster, groups Ca, Mn, Zn, As, Pb, Sr, Cr and Hg. Finally, the third cluster groups Cu, Sb, S and Cd. The elements coming from the second and third cluster, have in common their origin in anthropogenic sources. While the second group is conformed by elements from diverse sources such as traffic and copper smelting, the most probable origin of the elements of the third group is direct pollutants from copper smelting [1,2]. The *C. macrocarpa* leaves are good biomonitor to evaluate the high pollution load of elements.

Acknowledgements

CONICYT+PAI/ Concurso Nacional Inserción en el Sector Productivo, Convocatoria 2014 + Folio (781301007), AES-GENER, Chile.

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Spatiotemporal Monitoring Campaign of the Watch List Compounds in Ave and Sousa Rivers

OP Env Monit #26

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Natural and synthetic organic compounds are constantly released into the environment, accumulating in aquatic compartments. Their presence in water bodies originates the deterioration of water quality [1]. Even when present at trace levels (ng L^{-1}), these compounds may cause adverse ecological and human health effects. In this sense, some regulations have been published and a Watch List of substances for European Union monitoring of surface water was launched in Decision 2015/495, including estrone (E1), 17- β -estradiol (E2), 17- α -ethinylestradiol (EE2), diclofenac, azithromycin, clarithromycin, erythromycin, 2,6-ditert-butyl-4-methylphenol (BHT), 2-ethylhexyl 4-methoxycinnamate (EHMC), methiocarb, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid, oxadiazon and triallat [2]. In the present study, a one year spatiotemporal monitoring campaign of these Watch List compounds was performed in Ave and Sousa Rivers (Northern Portugal). Analytical methods based on solid phase extraction (SPE) followed by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) and gas chromatography coupled to mass spectrometry (GC-MS) were used. Conventional physicochemical

parameters were also analysed to evaluate water quality at each sampling site. Eight contaminants of emerging concern (CECs) were quantified in Ave River: diclofenac, azithromycin, clarithromycin, erythromycin, EHMC, imidacloprid, thiamethoxam and clothianidin. Thirteen CECs were detected in Sousa River, namely E1, diclofenac, azithromycin, clarithromycin, erythromycin, EHMC, BHT, imidacloprid, thiacloprid, thiamethoxam, methiocarb, oxadiazon and triallat. Risk assessment was also evaluated for the pharmaceuticals quantified in each sampling point. This study provides the first spatiotemporal monitoring of all Watch List compounds in surface water collected from two different rivers of Northern Portugal.

Acknowledgements

Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. Co-financed by QREN, ON2 and FEDER, under Programme COMPETE (Projects NORTE-07-0124-FEDER-000015 and NORTE-07-0162-FEDER-000050). ARR, MOB, AMTS acknowledge FCT (SFRH/BPD/101703/2014, SFRH/BD/115568/2016 and IF/01501/2013, respectively). CR and MET acknowledge the financial support from CESPU (Project Chiral Drugs CESPU 2017) and from European Regional Development Fund (ERDF) through the COMPETE – Programa Operacional Factores de Competitividade (POFC), under the Strategic Funding UID/Multi/04423/2013.

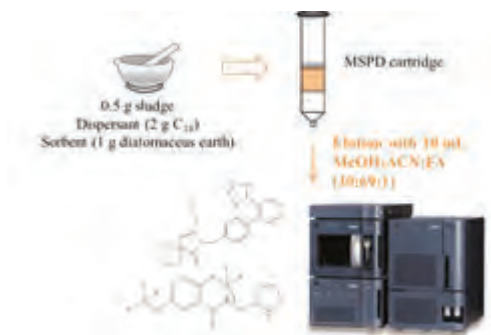
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Determination of Cardiac Drugs in Sludge by Ultra Performance Liquid Chromatography followed by Tandem Mass Spectrometry

OP Env Monit #27

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Cardiovascular diseases are the most common cause of death in the world. Thus, medical prescription of cardiovascular pharmaceuticals has increased to treat the different heart and blood vessel diseases, such as coronary artery diseases, strokes, hypertension, arrhythmias or heart failures [1].

In the same way as many other pharmaceuticals, the cardiovascular drugs, and their human metabolites, enter wastewater treatment plants (WWTP) through urban sewers [2,3]. Depending on their lipophilicity and/or resistance to biodegradation, these compounds might be concentrated in sewage sludge [4,5], which is usually used as fertilizer in agriculture. In this scenario, compounds are introduced in the terrestrial environment. Thus, the determination of potential residues of this kind of pharmaceuticals in sludge is of interest to fully understand their environmental risks. Although the determination of different kinds of pharmaceutical residues in sludge is matter of current research [6], to the best of our knowledge, for the moment, amiodarone, and its main metabolite, are the only cardiovascular drugs determined in sludge [4].

The aim of this presentation is to show an analytical procedure for the determination of nine cardiovascular drugs, with moderate to low polarities from different chemical families, in sludge from urban WWTPs. Matrix solid-phase dispersion is employed as sample preparation technique,

attending to its operational simplicity and low solvent consumption. Compounds are determined by ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS) using electrospray ionization (ESI).

Effects of sample preparation conditions in the efficiency and selectivity (evaluated through matrix effects) of the developed method are described. Under optimized conditions, limits of quantification below 3 ng g^{-1} and overall recoveries above 80% were attained for all the compounds. Analytes are investigated in samples from 14 WWTPs, located in areas with elderly population and a traditional high incidence of cardiovascular diseases. Seven out of nine compounds were ubiquitous in the processed samples, with valsartan showing the highest average concentration.

Acknowledgements

This study has been financially supported by the Spanish Government (project CTQ2015-68660-P). I.C. acknowledges her postdoctoral grant to Xunta de Galicia. We also thank Indrops laboratories for providing the sludge samples used in this research.

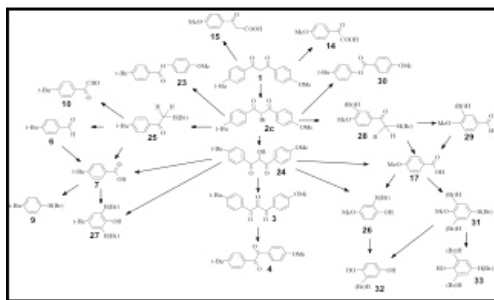
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Identification of Disinfection By-products Formed Within Aquatic Bromination of Avobenzone

OP Env Monit #28

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Transformation of avobenzone in aquatic bromination reaction

Disinfection of swimming pool water is essential to deactivate pathogenic microorganisms. Many swimming pools apply chlorine or bromine base disinfectants to prevent microbial growth. While disinfectants inactivate pathogens in swimming pools, unintended reactions between disinfectants (e.g., chlorine, ozone, etc.) and natural organic matter (NOM), bromide/iodide and human inputs (e.g., constituents of sweat and urine, skin particles, hair, microorganisms, cosmetics, and other personal care products) form disinfection by-products (DBPs). [1]

UV filters represent an important group of anthropogenic organic compounds often appearing in swimming pool and natural bath waters. Quite often they are treated as emerging contaminants. Avobenzone (4-*tert*-butyl-4'-methoxydibenzoyl-methane) is an UV filter, belonging to dibenzoyl methanes. It is the most common UV-A filter present in the formulations of sunscreens and sold under the various trade names. Our previous study under the combined influence of active chlorine and UV-irradiation has shown the formation of twenty five compounds identified by GC/MS as transformation products of avobenzone in reactions of aquatic UV-irradiation and chlorination with sodium hypochlorite. [2]

The present study involves GC/HRMS analysis of bromination reactions of avobenzone with sodium hypobromite conducted in distilled and sea water in the dark with samples collection after 1 and 24 hours. To understand the effect of inorganic salts

the reactions were also carried out with addition of KI, KBr, and CuSO₄.

Pegasus® GC-HRT¹ (LECO Corporation, Saint Joseph, MI, USA) coupled to an Agilent 7890A Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) was used for the analysis. The data were acquired using 10 full (10-800 *m/z* range) spectra per second in high resolution mode (25000), with high mass accuracy (<1 ppm), reliably determining elemental composition of all ions of interest in the mass spectra.

Chromatographic separation of the samples was performed using an Rxi-5SilMS 30 m x 0.25 mm (id) x 0.25 µm (df) (Restek Corporation, Bellefonte, PA) column with a constant helium flow of 1 mL/min. All injection volumes were 1 µL, splitless. The injector and the transfer line temperatures were set at 270 °C and 320 °C, respectively. The GC oven program was as follows: 0.5 min isothermal at 50 °C, then 10 °C min⁻¹ ramping to 320 °C and 8 min isothermal hold at 320 °C.

Aquatic bromination of avobenzone resulted in detection of 33 identified DBPs. Many of them contain bromine in the molecular structure. The results allow for conclusion that aquatic bromination proceeds less actively than chlorination (conversion rate is lower), however toxicity of the corresponding products is much higher. Addition of copper salt significantly decreases conversion rate simultaneously increasing the levels of the vast majority of the detected semi volatile products. Special attention requires 65-fold increase of the toxic bromoform level. After 24 hours of bromination bromoform becomes the major product of the reaction.

Acknowledgements

»The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. **P3-0388**«.

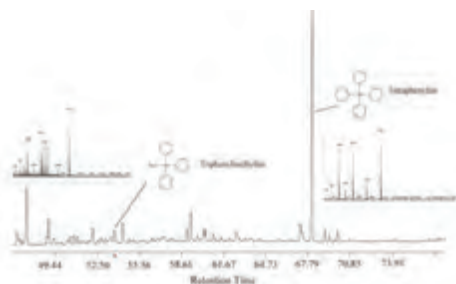
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Molecular Indicators for Dockyard Works in Coastal Sediments of a Large Industrialized Port Area in Hainan Island, China

OP Env Monit #29

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With the long history of global industrial activities, the pollution of industrially influenced coastal areas caused much concern. For these ecosystems industrial wastes were reported as a major source of contamination to the environment, such as heavy metal and persistent organic pollutant, which caused the decrease of biodiversity or had direct toxic effects or indirect effects on habitat quality and food webs.

This study characterized the chemical contamination of particulate matter in the heavily modified coastal waters of Yangpu Bay, a large industrialized port and dockyard area located in Hainan Island, China. It is based on the identification of a wide range of lipophilic organic pollutants by applying a GC-MS non-target screening approach. The focus was to recognize molecular organic indicators reflecting the intensive shipping traffic and dockyard works in this coastal area. For this purpose, sediment samples were collected from 17 stations in 2015, which covered the main docks, the dockyards as well as the major industrial wastewater outlets.

The applied screening approach allowed for the identification of around 70 organic pollutants. As highly specific indicators, butyltin and phenyltin compounds have been identified as typical constituents of antifouling paints used to prevent aquatic organisms from settling and growing on the ships hull. Noteworthy, also tributylmethyltin and triphenylmethyltin were identified, probably

resulting from microbial assisted biomethylation of synthetic organotin compounds in the sediments. Noteworthy, the pesticide bis(chlorophenyl) trichloroethane (DDT) and its metabolites were found in the same samples as the organotin derivatives pointing to similar emission sources. Lastly, high concentrations of polycyclic aromatic compounds were detected in the samples from the central dockyard and industrial area, likely originating from industrial wastewater discharges and shipping transportation. These compounds can act as indicators of minor specificity.

The concurrent presence of organotin derivatives and DDT-metabolites in the dockyard samples suggest a combined usage of organotin compounds and DDT as active ingredients in antifouling paints in China. Moreover, our results indicate that among the organotin species, tetraphenyltin seems to be a prominent ingredient of the paints. It can therefore be a useful molecular indicator for dockyard and shipping activities in China. Due to the high acute toxicity of organotin compounds [1], the specific composition of the contamination resulting from the use of antifouling products is highly relevant with respect to the effects on the coastal ecosystems.

Acknowledgements

This study is part of the Sino-German cooperative ECOLOC project (Environmental change affecting COastal ecosystems of tropical China during the Anthropocene: Landward vs. Oceanic influence). It was funded by the German Federal Ministry of Education and Research (BMBF, Grant No. 03F0721D) and supported by the Chinese State Oceanic Administration (SOA) and Midwest University Project (MWECSP-RT08, ZXBHJH-XK004 and ZXBHJH-XK005).

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Seaweed Analysis for the Determination of Volatile Methylsiloxanes in Coastal Areas in North of Portugal

OP Env Monit #30

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Volatile methyl siloxanes (VMSs) are massively produced chemicals that find a role in a wide range of industrial applications, with its common use in personal care products being referred as one of the main sources of their ubiquitous environmental distribution [1]. Several studies determined the presence of cyclic and linear VMSs in air, water, soil and living organisms [2], whereby its persistence in the environment with associated potential of bioaccumulation and biomagnification in trophic chains with possible toxicological effects is raising concerns [3,4].

Since marine and coastal areas are potential hotspots for the presence of such pollutants due to the high anthropogenic pressure in its vicinities, monitoring the distribution levels of siloxanes in such areas is an important task. Seaweed matrices can provide important information on the distribution levels of these pollutants in such environments, enhancing our knowledge about its possible contamination sources and their seasonal or geographical trends.

In this study, several species of seaweed, collected in 12 different locations in the seashore of North of Portugal between May and December of 2016, were analysed for the determination of 4 cyclic (D3-D6) and 3 linear (L3-L5) VMSs. An analytical method based on a QuEChERS extraction (Quick, Easy, Cheap, Effective, Rugged, and Safe), followed by gas chromatography/mass spectrometry (GC/MS)

analysis, was employed, with limits of detection and quantification on pg.g^{-1} levels. A global mean of recoveries of $93 \pm 7\%$ was obtained, and good intraday and interday precision values were achieved (RSD values lower than 10 and 15%, respectively, for most of the target compounds).

Sampling marine vegetation proved to be a suitable approach for the analysis of VMSs in coastal environments, with cyclic ones, mostly D5 and D6, being predominantly detected when compared to linear VMSs. However, seasonal trends were not clear in all the locations, despite higher concentrations of VMSs being identified in summer months in some cases.

Acknowledgements

This work was financially supported by projects: (i) POCI-01-0145-FEDER-006939 (LEPABE UID /EQU/00511/2013), funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (ii) NORTE-01-0145-FEDER-000005 - LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the ERDF; (iii) Investigator FCT contract IF/01101/2014 (Nuno Ratola); (iv) Post-Doctoral grant SFRH/BPD/76974/2011 (Vera Homem).

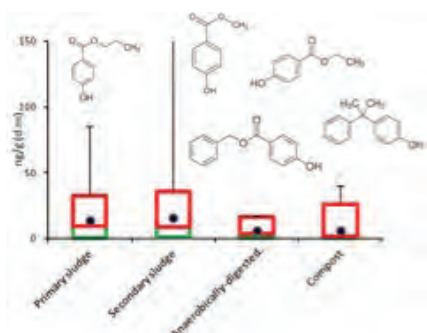
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Occurrence of Parabens and Bisphenol A in Sludge Stabilization Treatments: Anaerobic Digestion and Composting

OP Env Monit #31

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Sewage sludge generated in urban WWTPs is of great interest as soil fertilizer because of its nitrogen, phosphorous and organic matter content. That application is promoted in the European Union by the sewage sludge Directive 86/278/EEC. Nevertheless, as a product of wastewater treatment, pollutants present in wastewater can be accumulated in sewage sludge and can affect soils and crops when applied onto agricultural lands. To prevent such harmful effects, concentration limits are fixed for seven heavy metals but no concentration limits are fixed for other compounds.

In the last years, an increasing concern about the presence other pollutants widely described in wastewater, has been arisen [1]. That interest has been initially focused on pharmaceutical compounds for which their occurrence in sludge stabilization treatments has been reported [2] but not much information about other compounds is available.

The aim of this work was to evaluate the occurrence of five endocrine disrupting compounds (four parabens and bisphenol A), widely present in daily-use products, in anaerobic digestion and composting stabilization

treatments. Parabens are used as preservatives in cosmetics and pharmaceuticals. Bisphenol A is widely used as plasticizer in polycarbonate plastics. Parabens monitored were methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP) and benzylparaben (BzP). Primary, secondary and digested sludge were sampled from four WWTPs based on activated sludge technology, in their water line, and in anaerobic digestion, in their sludge line. Compost sludge was sampled from a composting plant where anaerobically-digested sludge from the above mentioned WWTPs is composted in dynamic batteries thermally controlled with aeration facilitated by turning. Nine samples of each type of sludge were sampled from each WWTP and from the composting plant.

Samples treatment was based on ultrasonic-assisted extraction and extract clean-up by dispersive solid-phase extraction. Analytical determination was carried out by liquid-chromatography-tandem mass spectrometry based on a previous reported method [3]. EtP and BzP were not detected in any of the analyzed samples. MeP was detected in primary, secondary, digested and compost sludge, at mean concentrations of 13.4, 15, 5.6 and 5.8 ng/g dry matter (d.m.), respectively. PrP was detected in primary and secondary sludge at mean concentrations of 0.09 and 0.07 ng/g d.m, but not in digested neither in compost sludge. BPA was detected in primary, digested and compost sludge at mean concentrations of 5.1, 2.6 and 126 ng/g d.m, respectively. Anaerobic digestion and composting treatment resulted in a decrease of MeP and PrP concentrations. A different behaviour was observed for BPA. It was detected in primary sludge, but not in secondary sludge, and its concentration increased after composting to concentrations up to 249 ng/g d.m.

Acknowledgements

The authors wish to thank the financial support from the Ministerio de Educación y Ciencia, Spain (Project no. CGL2013-44402-R).

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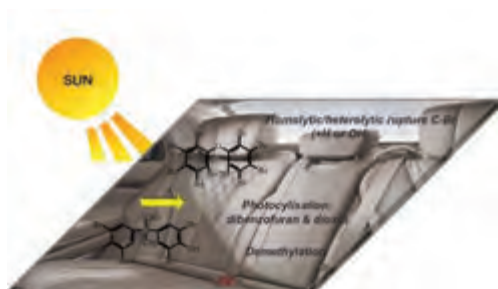
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Environmental Technologies

Photodegradation of Brominated Flame Retardants in Textiles from End of Life Vehicles (ELVs): Kinetic and Photoproducts Characterization

OP Env Tech #1

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Pollution by polybrominated diphenyl ethers (PBDEs), the popular brominated flame retardants (BFRs) incorporated into flammable polymers (electronics and textiles), is now a worldwide problem even in remote areas (Lu Pan, 2013). In recent years, they have attracted special environmental concern because of their potential toxicity to humans and wildlife worldwide (Da Chen, 2015). Due to the detrimental environmental properties of several PBDE congeners, the use of Deca-BDE has been banned in electrical and electronic applications since 2008, and it is currently slated for listing under the Stockholm Convention. Following these bans on PBDEs, new flame retardants have emerged (EFRs) (Fang Tao, 2016) for example: tetrabromobisphenol A (TBBPA) and its derivatives such as TBBPA bis (allyl)ether (TBBPA BAE) and TBBPA bis (2,3-dibromopropyl)ether (TBBPA BDBPE). All these molecules absorb solar light and can potentially undergo photodegradation. The aim of our study was to investigate the photolytic degradation of the molecules cited above in natural and spiked textiles samples (car seats of the 1990s). Some samples have been directly analysed for identifying photoproducts. Others

were spiked, irradiated and analysed.

In the case of decaBDE, similar photodegradation rates and oxidation products were found in all textile samples. This tends to prove (i) that irradiation of our artificial samples reproduces natural phenomena and (ii) that photolysis can occur even inside vehicles. Many photoproducts have been identified: molecules less brominated, brominated and hydroxylated products brominated and hydroxylated dibenzofurans and brominated dioxins. In the case of EFRs, photolysis also takes place leading to new photoproducts.

The starting molecules are apolar showing $\log k_{ow} > 8$ (Harbison et al., 2015). However, the replacement of Br by OH is expected to make photoproducts more polar than the starting molecule. Therefore, ongoing work is conducted to determine if some of most polar photoproducts could be leached into aquatic media. The main results will be presented and discussed.

Acknowledgements

The authors gratefully acknowledge the financial support from LASER (Libanese Association for Scientific Research) for Amina Khaled to study in France.

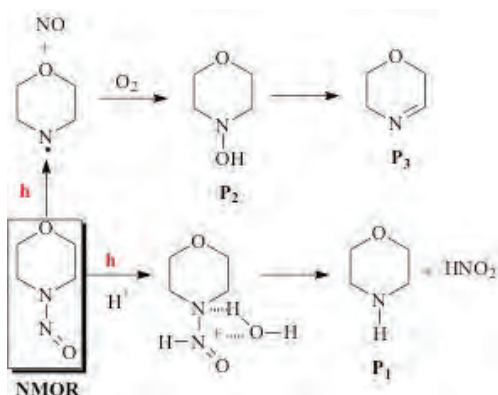
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Photochemical Processes for the Elimination of Nitrosomorpholine During Water Treatment : Kinetic and Analytical Studies

OP Env Tech #2

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N-nitrosamines are a class of some emerging nitrogenous drinking water disinfection by-products (1,2). Such compounds are considered carcinogenic and may seriously affect the safety of drinking water. These nitrosamines are generated from precursors that involve primary and secondary amines that could be present in industrial waste waters. Their formation proceeds through reaction with nitrosant agents such as nitrites. Among these N-nitrosamines, nitroso-morpholine represents a product of great importance since the risk on human health is real (3). It is formed from the nitrosation of morpholine which is, for example, largely used in pharmaceutical industry. It is also generated via disinfection processes such as chloramination and ozonation/chlorination. The present work is devoted to the photochemical behavior of nitrosomorpholine upon solar light excitation and also to its photoinduced degradation using hydrogen peroxide/UV; Ozone and Ozone/UV.

The direct excitation of nitrosomorpholine using solar simulator (SUNTEST) permitted its efficient degradation. The quantum yield was evaluated to 0.32 at pH = 5.5. It is highly pH dependent since it is equal to 0.10 at pH=7. Such process leads to the formation of morpholine and 4-hydroxymorpholine as the main products. It is worth noting that no products arising from the opening of the

chemical structure was observed. A photohydrolysis process and a homolytic scission of the N-N bond are then proposed (Figure 1). In order to eliminate nitrosomorpholine from water, we undertook studies using H₂O₂/UV; O₃ and O₃/UV processes.

The UV excitation of hydrogen peroxide in the presence of Nitrosomorpholine permits its efficient degradation leading, in the first stages of the irradiation to the formation of morpholine that represents 25% of the conversion. When the excitation is prolonged, the total degradation was observed leading to the formation of several products arising from the scission of the chemical structure. All the products were clearly identified using HPLC/MS and GC/MS techniques. The formation of the products was explained by the hydroxylation of nitrosomorpholine at the a and b positions. Moreover, the Ionic chromatography analyses permitted us to conclude for the formation of small molecules such as acetic acid and formic acid. This clearly demonstrates the efficient oxidation of the intermediate products till the mineralization of the solution. Such aspect was clearly demonstrated using the TOC analyses.

In the presence of ozone, the degradation of nitrosomorpholine was effective without a sign for the mineralization of the solution. However, the combination of O₃ with UV appears to be more efficient for the elimination of nitrosomorpholine and also its mineralization. A complete mechanism of degradation will be proposed.

Acknowledgements

The authors acknowledge ANSES for the financial support through the CRD program 2016-CRD-01.

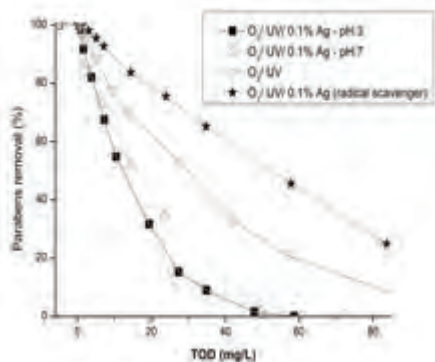
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Operating Conditions Optimization for Photocatalytic Ozonation of Parabens Using Ag-TiO₂

OP Env Tech #3

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The conventional wastewater treatments are inefficient for the removal of microcontaminants [1]. So the challenge of this century is finding a solution for their abatement from wastewater. As an example, parabens are endocrine disruptor compounds widely used as antimicrobial and preservative in pharmaceutical and personal care products and were detected on natural courses. Advanced oxidation processes (AOP's) can be suitable solutions for this problem [2]. Particularly, ozone is a powerful oxidant widely used to treat effluents. However, O₃ can be a source of refractory compounds [3]. Its oxidant activity can be enhanced by the presence of heterogeneous catalysts. Moreover, the usage of photosensitive materials coupled to a source of radiation enough to activate them may improve the process. TiO₂ is the most used photocatalyst, due to easy handling, chemical stability and low cost. The main drawback is its high bandgap. To reduce the bandgap this catalyst can be doped with noble metal (Pt, Ag, Pd). In a previous work 0.1%wt. Ag-TiO₂ revealed the best performance during the photocatalytic ozonation of parabens among a group of doped catalysts. In this context, the aim of the present research is the optimization of the operating conditions of this process.

Thus, photocatalytic ozonation of a mixture of five parabens degradation (Methyl, Ethyl, Propyl, Butyl and Benzyl) was analysed using 0.1%wt. Ag-TiO₂. The toxicity of the test mixture was assessed after treatment, using three species *Corbicula fluminea*,

Lepidium sativum and *Vibrio fischeri*. The effect of pH and of the amount of catalyst was also analysed. Moreover, the process mechanism was still discussed. The best conditions were applied to a secondary effluent spiked with the mixture of parabens.

The experiments were carried out in a 2-L glass photoreactor equipped with 3 lamps (UV-A main emission 365nm). The photon flux (5.75×10^{-7} Einstein/L.s) was obtained using ferrioxalate actinometer. The ozone concentration entering and leaving the reactor was measured by gas ozone analysers, with gas flow rate of 0.2 L/min. The results were expressed as a function of transferred ozone dose (TOD). The parabens concentration along reaction was determined by HPLC. Chemical oxygen demand (COD) and total organic carbon (TOC) analyses were also performed. The presence of Iso-propanol, used as hydroxyl radical scavenger, reveals that the hydroxyl radicals are the main responsible for the mixture of parabens degradation with the photocatalytic ozonation. In fact, the curves of parabens degradation with radical scavenger were slightly different to the photolytic ozonation curves. Which means that photolytic ozonation also produces hydroxyl radical.

The effect of pH was almost negligible. This can be due to the presence of high amount of hydroxyl radical.

The toxicity reduction verified for all the tested species reveal the efficiency of this process on leading to safe water for reuse from wastewater. Photocatalytic ozonation proved to be efficient for the removal of organic matter and parabens from a secondary wastewater coming from a municipal effluent treatment plant.

Acknowledgements

FCT is gratefully acknowledged by the financial support under the contract IF/00215/2014.

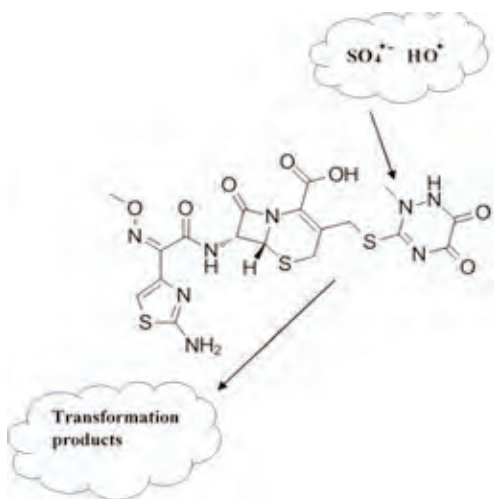
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Degradation of Ceftriaxone in Aqueous Solution by Heterogeneous Photo-Activated Persulfate System

OP Env Tech #4

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Ceftriaxone (CTA) is a relatively new antibiotic that was first synthesized in the beginning of the 1980s. However, it has already been listed as an essential medicine by WHO [1]. This subsequently causes its long-term existence in the environment and affects various environmental compartments. In the past decade, a combination of persulfate and UV-light has shown effective results in the degradation of different pharmaceuticals [2,3].

In the present study, the degradation of CTA in aqueous solutions by heterogeneous UV-induced persulfate systems was studied. The heterogeneous persulfate oxidation was carried out by the addition of goethite, a ferric iron containing iron oxyhydroxide. The treatment was conducted in buffered solutions (pH 7.4) to simulate the inhibitory properties of environmental and processed water matrices. The process efficacy

was assessed by the CTA concentration and total organic carbon (TOC) content decrease during the treatment time (120 min). The influence of CTA (5-100 μM), persulfate (50-2000 μM) and goethite concentrations (0.1-2.5 g/L) was evaluated. The radical species responsible for the target compound oxidation were proposed. In addition, probable by-products of CTA degradation were detected.

Both, UVC- and UVA-light were used as an irradiation source in the treatment systems. Expectedly, the UVC-exposed oxidation systems achieved higher target compound degradation and TOC content decrease efficacies than compared with UVA-exposure. In general, the use of buffers considerably influences the overall treatment efficacies of UV-induced persulfate systems. Thus, this kind of process requires carefully adjusted conditions that could allow resultant CTA removal from aqueous solution.

The use of UVA suggests that these processes have the potential to be used under sunlight contributing to the sustainable water treatment technology.

Acknowledgements

The financial support provided by institutional research funding IUT (1-7) of the Estonian Ministry of Education and Research is gratefully acknowledged.

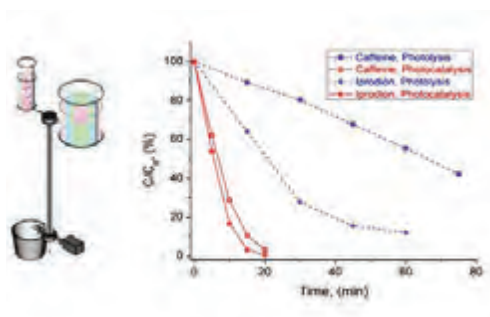
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Photocatalytic Reactor for Pharmaceutical Drugs and Pesticides Removal from Water, Using Thin Film CVD-Technology

OP Env Tech #5

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Photocatalytic technology of water purification from organic pollutants produced by agricultural, textile and pharmaceutical industries has a great potential of application.

There are several methods to improve the efficiency of photocatalytic reactors. Firstly, by of improvement of photocatalysts properties, which can be achieved by different ways, namely, by increasing the effective contact area using suspended TiO₂ particles, extending the light adsorption into visible diapason [1,2], doping to suppress the electron-hole recombination process [3] and so on. Secondly, by addition into reaction system of strong oxidants such as ozone [4], hydrogen peroxide [5, 6], persulfate ions [7] which generate hydroxyl radicals and significantly increase the overall oxidation rates. Thirdly, by improving the constructive properties of the reactor.

A tubular photocatalytic reactor of the immersion type for water purification from organic pollutants was developed using four general principles in simultaneously: 1) Tubular configuration of the reactor with symmetric radial uniform light distribution to a surface area of TiO₂ photocatalyst and with direct incidence of UV radiation onto the photocatalyst surface. 2) Ultraviolet (UV) lamp

without any transparent jackets so that the water was used to cool the UV lamp. 3) High active mixing of contaminated water achieved by air bubbling providing a better contact of the contaminants with the TiO₂ photocatalyst surface and the simultaneous oxygen necessary supply for the photocatalytic reaction. 4) The photocatalytic reactor design allows an easy connection of photoreactors in a successive or in a parallel way in order to increase either the purification level or cleaning productivity. The feasibility of the developed photoreactor was demonstrated for the degradation of recalcitrant organic pollutants, such as pharmaceuticals and pesticides in water [8].

Acknowledgements

This work was supported by Fundação para Ciência e Tecnologia (FCT), Portugal, Centro de Investigação em Química do Algarve (CIQA - Project PEST-OE/QUI/UI4023/2014)) and Centre of Marine Sciences (CCMAR), Portugal.

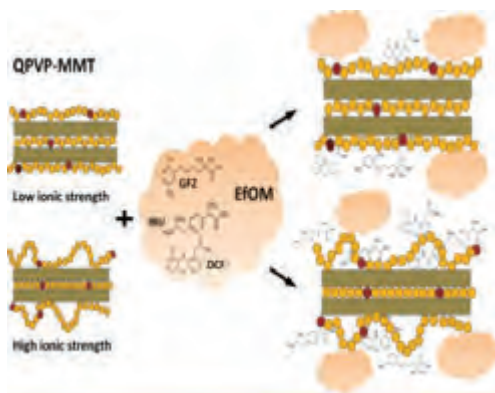
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Efficient Removal of Pharmaceuticals from Treated Wastewater by Tailored Polycation-Clay Sorbents

OP Env Tech #6

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The removal of emerging micro-pollutants, including pharmaceuticals, by different composites sorbents is widely studied in recent years [1]–[5]. Most of the studies examine the removal of a single pollutant by a single composite. The real challenge of treating pharmaceuticals from surface waters and all the more so from treated wastewater, is the variety of pharmaceuticals and the background water solution. More specifically, the pharmaceuticals are present at low concentrations while higher concentrations of dissolved organic matter (DOM) and salts are present. In the current study, novel polymer-clay composite sorbents were developed based on poly-4-vinylpyridine (PVP). Functional groups, methyl (QPVP), ethanol (OHPVP), or proton (HPVP), were synthesized to create unique properties and the new polymer adsorbed to montmorillonite (MMT). The physico-chemical compatibility between the pollutant and the composite determines the affinity of the pollutant towards a specific sorbent. In the first stage we focused on the removal of one anionic pharmaceutical, sulfamethoxazole and one non-ionic, lamotrigine by OHPVP-MMT and PVP-OHPVP-MMT composites, respectively. Higher

affinity of OHPVP-MMT to sulfamethoxazole and of PVP-OHPVP-MMT to lamotrigine was obtained. The higher affinity of the anionic pharmaceutical to the highly positively charged composite and the higher affinity of the non-ionic pharmaceutical to a less charged one, can explain these trends. In the second stage we studied the removal from treated waste water by four different composites and 11 pharmaceuticals (~1 ng/L per pollutant). The pharmaceuticals included anion, non-ionic and one positive molecules. The removal was measured (LC-MS/MS) and compared to the removal by GAC after 10 minutes in order to simulate contact time in filters. The removal of most of the pharmaceuticals by the composites was higher than by GAC. The removal by a composite, of the non-ionic molecules lamotrigine and carbamazepine was twice its removal by GAC. The removal of anionic molecules such as sulfamethoxazole and diclofenac was even better with an advantage of 6–7 folds. Furthermore, the removal of DOM by the composites was substantially higher than by GAC. Metoprolol, the only cation molecule, was completely removed by the composites, while only 10% was removed by GAC. Its strong interaction with DOM which is well removed by the composites may explain its high removal by the positively charged composites. These results suggest that polymer-clay composites can be designed to efficiently remove an array of pollutants from treated waste water.

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Removal of the Pharmaceuticals Diclofenac and Trimethoprim from Aqueous Media using Low-cost Biosorbents

OP Env Tech #7

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With a growing and aging global population, and with improving health care in many regions of the world, the use of human pharmaceuticals is increasing. Conventional treatment of domestic wastewater is often not sufficient to remove all pharmaceuticals and other biologically active compounds (such as steroid hormones) [1]. As a result, these may be discharged into surface waters in effluent and have been widely detected at trace (part per billion/trillion (ppb/ppt)) concentrations in receiving waters [2]. As steroid hormones have been linked to reproductive disturbance and developmental problems in wildlife and humans, regulatory concerns have been raised [3]. The environmental and ecological impacts of pharmaceuticals are poorly characterised, but may include environmentally acquired antibiotic resistance and other biological effects [4].

This study evaluates the potential to use industrial and agricultural by-products as low cost biosorbents for the removal of human pharmaceuticals and hormones from aqueous media. The overall aim of the project is to develop a tertiary treatment step that may be applied to waters that have undergone sewage treatment, i.e., an efficient and cost-effective 'polishing' treatment to remove residual compounds from a simplified matrix in low flow conditions.

Eleven low-cost biosorbents (derived mainly from Scottish industrial and agricultural wastes), including spent grain, crab carapace, coffee waste and marine macro-algae were investigated in batch

studies for their ability to absorb 17 prioritised pharmaceuticals and hormones (using activated carbon as a reference material). The three most efficient materials were biochar, marine macro-algae and wood chippings and these were used to assess kinetics, isotherms, impact factors and sorption mechanisms for two target compounds, diclofenac and trimethoprim. Future work will consider real wastewater effluents and assess the economic feasibility of the approach. This will be done through pilot studies in collaboration with Scottish Water and the Chinese Academy of Sciences. It is anticipated that the resultant treatment system will be applicable in rural or semi-rural (low flow) plants and septic tanks.

Acknowledgements

This project is sponsored by the Scottish Government Hydro Nation Scholarship Scheme. Special thanks to Scottish Water, Scottish Environment Protection Agency and Centre of Expertise for Waters.

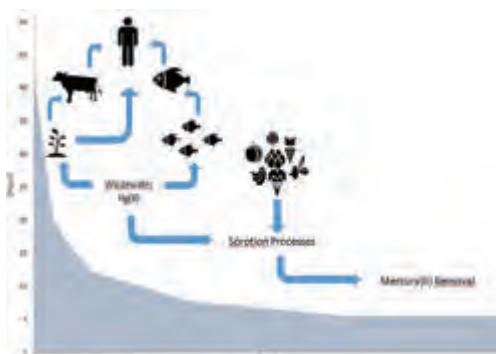
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Agricultural Wastes for Mercury(II) Removal in Wastewater Treatment

OP Env Tech #8

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Water is an essential resource for the survival of human beings and its preservation and reuse is a global concern. Mercury is one of the most hazardous toxic metals even at low concentrations because of its ability to accumulate in the living organisms tissues and be amplified along the food chain [1]. Several industries are responsible for Hg(II) discharges into the aquatic system including metal finishing, welding, alloy manufacturing plants, pulp industries and petroleum refining [2]. The removal of toxic contaminants from aqueous waste streams can be achieved by a variety of processes, such as chemical precipitation, membrane processes, ion exchange and adsorption [3]. However, most of these technologies are expensive, involve high operation costs and are ineffective in low metal concentration systems [4]. On the other hand, sorption processes are considered better alternatives in water treatments since they are eco-friendly, economic and allow to treat wastewater in trace realistic concentrations [5].

Agricultural wastes are mainly composed of lignin and cellulose and may also contain other polar functional groups, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups are able to establish associations with the contaminants through different binding mechanisms [5].

In this work the ability of five agricultural wastes (banana and potato peels, egg shells, *eucalyptus* bark and coffee waste) has been used in order to

determine their removal performance in tap water under a low Hg(II) concentration of 50 µg/L. Two of the biosorbents used (*eucalyptus* bark and coffee waste) are real industrial wastes provided by a paper and coffee industry, respectively, and the other biosorbents were obtained from a local market.

All the sorbents tested exhibited the same trend, the concentration of mercury(II) reduced with the time. Banana peels has showed the best efficiency, removing more than 90% of the Hg(II) in 72 hours until reaching the equilibrium. This biosorbent also presented the faster kinetic, reducing 80% of the metal in the first 10 hours. It is worth mentioning that all the materials have not received any pretreatment and they are wastes or industrial by-products and do not have any cost to be obtained and even more, they occasionally represent disposal costs. The kinetic study has been performed using the pseudo-first order, pseudo-second order and Elovich equations. The pseudo-second order and Elovich models have showed the best fits to the experimental data for the biosorbents tested presenting correlations coefficients between 0.9744 and 0.9986. Finally, it was concluded that the biosorbents studied in this work offer remarkable advantages for wastewaters treatment.

Acknowledgements

The current work has been performed with the support of CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Brazil.

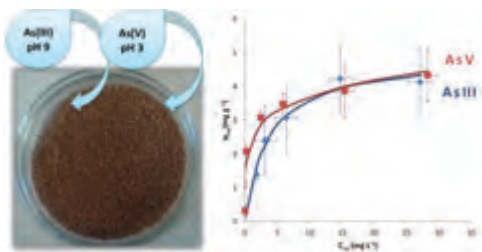
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Arsenate and Arsenite Adsorption on to Iron-coated Cork Granulates

OP Env Tech #9

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Arsenic (As) is a naturally occurring element, a metalloid considered a pollutant of priority interest by both the European Union and the United States [1]. When present in drinking water it can be toxic to human health and therefore it is subject to legal limits ($< 10 \mu\text{g L}^{-1}$ being the WHO guideline [2]). Inorganic As species are the most common in drinking water. Arsenate (As(V)) predominates in oxidizing conditions, while arsenite (As(III)) in reducing ones, such as groundwater [3]. Even though arsenite is more toxic and mobile than arsenate [4], both forms must be treated. Adsorption is one of the most effective removal methods, but it is usually more efficient toward As(V), and previous oxidation of As(III) is sometimes required for complete treatment [3].

Unlike other adsorbents, iron-based materials are highly selective in As adsorption since the uptake mechanism is based on complexation of As with iron(oxy)hydroxides at the surface. This process has been observed for both As(III) and As(V) [5]. Previous work, developed in the research group, has shown that raw cork granulates, byproducts from the processing of cork, the bark of *Quercus suber* L., can be coated with iron (oxy)hydroxides for enhanced As adsorption. This study aimed to optimize the adsorption process by changing the aqueous system conditions.

Iron coating of cork granulates was carried out in 50 mL plastic tubes, in a rotating shaker at 20 rpm and temperature of 20 °C, by contacting cork (20 g L^{-1}) with precipitated iron hydroxides ($\text{pH} = 7$) from a 0.05 M FeCl_3 solution for 24 h. Arsenic adsorption was carried out in similar conditions, but using 2.5 g L^{-1} of iron-coated cork granulates.

The effect of pH on adsorption was studied in the range 2–10. The kinetics of the adsorption process was determined at optimal pH by varying the contact time. Adsorption equilibria were obtained for several As concentrations.

The dependence of As(III) and As(V) adsorption on pH was similar to previous results obtained in ferrihydrite [6], namely high variability but opposite trends – As(III) adsorption increased with pH while As(V) adsorption decreased. At pH below 3, undesired iron leaching was observed.

Kinetics of adsorption were faster for As(III) than As(V), also in accordance with the literature [4]. Equilibrium was reached in 16 h for As(III) but 48 h were required for As(V) uptake.

Adsorption isotherms in optimised conditions, at 20 °C, predicted similar maximum adsorption capacities for both As(III) and As(V). The adsorption of As(III) ($\text{pH} 9$) showed best fit to the Langmuir model ($r^2 = 0.98$) with q_{max} of $4.9 \pm 0.3 \text{ mg g}^{-1}$. As(V) adsorption ($\text{pH} 3$) was higher at lower equilibrium concentrations and presented better fit to the Freundlich model ($r^2 = 0.94$).

Speciation studies showed that As(III) is not oxidized to As(V) in solution before uptake. Therefore, it was demonstrated that iron-coated cork granulates present similar adsorption capacity for both forms of arsenic, when As(III) is present in alkaline pH and As(V) in acid pH.

Acknowledgements

This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT. A. Pintor acknowledges her postdoctoral fellowship by FCT (SFRH/BPD/117680/2016).

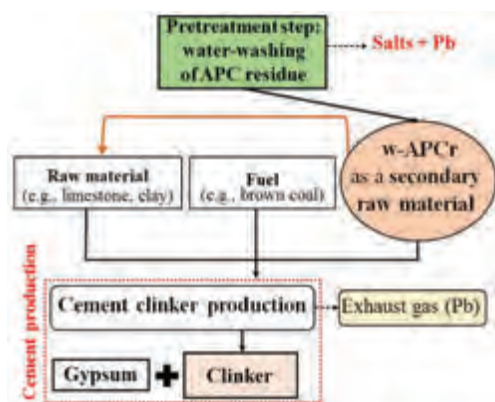
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Potential Utilisation of Air Pollution Control Residue from Municipal Solid Waste Incineration Facility in the Cement Industry

OP Env Tech #10

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Air pollution control residue (APC) from municipal solid waste incineration (MSWI) in energy-from-waste (EfW) plants is classified as hazardous waste under code 19 01 07* in the European Waste Catalogue [1] because it is alkaline, contains high concentrations of heavy metals and soluble salts, and small but measurable concentrations of very toxic organic compounds (e.g., dioxin and furans) [2-4]. APC residue is generally landfilled as hazardous waste in many countries.

Co-processing of mineral wastes as an alternative raw material in cement kilns is situated in the waste hierarchy in between recycling and energy recovery [5]. The potential for co-processing of raw APC residues and APC residues that were washed with water to remove chlorides and other soluble phases were investigated in this work.

The cement mixtures were composed of analytical grade pure chemical compounds (e.g., CaCO_3 , SiO_2 , Al_2O_3 , and Fe_2O_3), and raw and washed APC residues (henceforth denoted as APCR and w-APCR, respectively). Co-processed clinkers containing 5%, 15%, and 35% of APCR; 5%, 15%, and 34% of w-APCR; and a control, were produced in a laboratory kiln at 1450°C.

Co-processed clinkers containing up to 15% APCR or up to 34% w-APCR were found to consist of all mineral phases (C_3S – alite; C_2S – belite;

C_3A – tricalcium aluminate; C_4AF –tetracalcium aluminoferrite) typical of ordinary Portland cement clinker and have higher later compressive strength than a control sample. Chlorine in raw APC residues was found to: 1) reduce the temperatures of CaCO_3 decomposition and clinkering; 2) increase volatilisation of potential pollutants, including Zn and Pb. Zn can be incorporated completely into the washed APC residue-derived clinkers in C_4AF solid solution of variable composition. The incorporation of Pb is also increased by using washed APC residue. Co-processing of APC residue, especially after pre-treatment by water washing can incorporate potential pollutants in stable phases. Remaining issues of environmental concern include the fate of wash water, volatilised pollutants, and demolition wastes enriched in metals.

Acknowledgements

This work was conducted with funding from the UK Engineering and Physical Sciences Research Council Grant number (EP/M00337X /1) and the National Science Foundation of China.

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Waste Management from Pulp and Paper Industry: Recycling to Soil as a Viable Management Option

OP Env Tech #11

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Currently the EU is working towards a transition from a linear economy to a more circular economy where existing resources such as nutrients and organic matter present in materials classified as waste are effectively being recycled.[1] In fact, the re-use of materials that are now classified and disposed of as waste is one of the key principles underlying the launch of the revision of the Fertiliser Regulation by the EC in 2016.[2]

The aims of this study were to prepare mixtures of biomass ashes with biological sludge from wastewater treatment in order to obtain new soil improvers and to test their efficacy in the recovery of degraded soils collected at selected mining sites (correction of acidic pH and input of organic matter and plant nutrients). Two different types of soil improvers (with different proportion of biomass ashes/biological sludge) were produced, and were subjected to a stabilization period prior to their addition to soils.

Pots and columns experiments were conducted, testing two dosages of these new soil improvers (5 and 10%, in weight) in two soils from São Domingos mine (south of Portugal). These soils are acidic (3.55 and 3.92), with a low content of organic matter (0.10 and 0.31%), and are sandy loam in nature.

Soil incubation experiments were conducted during

a period of 30 to 70 days. During that period, pore water samples were collected from pots/columns and analysed (for pH, dissolved organic carbon (DOC), electrical conductivity (EC), chloride content, macro- and micronutrients and potentially toxic elements (PTEs)).

Results showed that the addition of soil improvers led to an increase in the pore water pH relative to control pots (0% of soil improvers added), and had an impact on the solubilisation of both macro- and micronutrients. The main factors determining pore water properties, namely pH and DOC, as well as the solubility of macro- and micronutrients and PTEs in amended soils will be discussed in detail in this work.

These results provided information on adequate dosages of soil improvers to be added to soils for the correction of soil acidity. This study also provided an insight on the potential of the new soil improvers for the recovery/ improvement of soil functions at mining areas.

Acknowledgements

Authors acknowledge the financial support of European Commission, and LIFE programme through the project No_Waste - Management of biomass ash and organic waste in the recovery of degraded soils: a pilot project set in Portugal (LIFE14 ENV/PT/000369) and CESAM (Centre for Environmental and Marine Studies).

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The Use of *Spirodela Polyrrhiza* in Batch Scale Constructed Wetlands to Remove PPCPs from Synthetic Wastewater

OP Env Tech #12

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Test	Light ($\mu\text{mol m}^{-2}\text{s}^{-1}$)	Oxygen (aeration)	<i>E.coli</i> abundance (CFU/100mL)	Plant biomass (kg/m ²) (g)
1	160	Full	None	0.50, 20
2	240	Intermittent	None	1.00, 40
3	240	Full	1.0×10^4	0.25, 10
4	80	Full	1.0×10^6	1.00, 40
5	240	None	1.0×10^6	0.50, 20
6	160	Intermittent	1.0×10^6	0.25, 10
7	80	Intermittent	1.0×10^4	0.50, 20
8	160	None	1.0×10^4	1.00, 40
9	80	None	None	0.25, 10

[adapted from Li et al., 2017]

Pharmaceuticals and personal care products (PPCPs), which are regarded as emerging contaminants, have increased concerns and interests from researchers and public over the last several decades [1]. Conventional wastewater treatment techniques are designed to remove nutrient (e.g. N and P) but not PPCPs. In recent years, constructed wetlands (CWs) have become popular and have been regarded as promising eco- and costly- friendly tertiary treatment techniques for wastewater [1-5]. *Spirodela polyrrhiza* (i.e. greater duckweed) as a floating plant has advantages including ammonia preference uptake, ability to survive in dry conditions and low temperature endurance, but hasn't been tested to remove PPCPs compounds [1].

In our study, *Spirodela polyrrhiza* based lab-scale free water constructed wetland (CW) was tested to remove four selected common PPCPs compounds

at batch scale (i.e. DEET, paracetamol, caffeine and triclosan). In order to test the effect of light intensity, oxygen, *E.coli* abundance and plant biomass on the selected PPCP compounds removal, orthogonal design was used to design the batch test. For the consistency of used wastewater, synthetic wastewater contaminated with the 25 $\mu\text{g/L}$ target compounds was prepared [1].

Paracetamol, caffeine and tricolsan achieved up to 100% removals in batch test. However, the DEET behaved recalcitrant and highest removal for DEET was just 32.2% [1]. Based on orthogonal Duncan analysis result, high light intensity (240 $\mu\text{mol m}^{-2}\text{s}^{-1}$), full aeration, high plant biomass (1.00 kg/m²) and high *E.coli* abundance (1.0×10^6 CFU/100 mL) favoured removal of the selected PPCPs [1]. Batch verification test under the optimal conditions achieved removals of 98.8%, 96.4%, 95.4% and 17.1% for PAR, CAF, TCS and DEET, respectively [1]. *Spirodela polyrrhiza* used under the conditions of this study showed to be a promising plant to be used in constructed wetlands for the removal of PPCPs from wastewater.

Acknowledgements

Mr Jianan Li was supported by the China Scholarship Council (CSC, No. 201406320168) and UCL Dean's Prize. Special thanks to Dr Melisa Canales for assistance with the microbial tests.

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Assessment of Different Photodegradation Strategies To Remove Multiclass UV Filters From The Aquatic Environment

OP Env Tech #13

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UV filters are used in cosmetic and personal care products formulations, mainly in sunscreens, in order to protect consumers against the UV radiation. Their final destination is usually natural waters, by direct discharges from domestic sources and bathing areas. They have been detected at ppb levels or even ppm levels, specially in recreational waters. In last years, their presence in the environment is increasing and one of them, the 2-ethylhexylmethocinnamate (2EHMC), has been recently included in a Watch List with the purpose to limit its presence in aquatic systems [1].

Since UV filters contain chromophore groups able to absorb UV radiation, different photodegradation strategies were assessed in order to obtain the highest degradation efficiency for multiclass organic UV filters. In this way, simple photolysis employing different types of radiation, UVA ($\lambda=365$ nm) and UVC ($\lambda=254$ nm) was carried out. More effective Advanced Oxidation Processes (AOPs),

employing the UV/H₂O₂ system, was employed in order to generate more reactive \bullet OH radicals capable to accelerate the degradation process.

The determination of the target analytes and the monitoring of the degradation kinetic profile was performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) and by gas solid-phase microextraction followed by gas chromatography-tandem mass spectrometry (SPME-GC-MS/MS), depending on the chemical nature of the target UV filters.

Finally, different types of recreational (swimming-pool, spa, aquapark) and natural waters (river, sea) containing UV filters were irradiated. Besides, the tentative identification of possible photodegradation by-products was performed by high resolution.

Acknowledgements

This research was supported by FEDER funds and projects GPC2014/035, and CRETUS (AGRUP2015/02) (Xunta de Galicia) and CTQ2013-46545-P and Infrastructure Program IGDC13-1E-2016 (MINECO, Spain). M. Vila acknowledges Ministry of Education, Culture and Sport for a FPU grant.

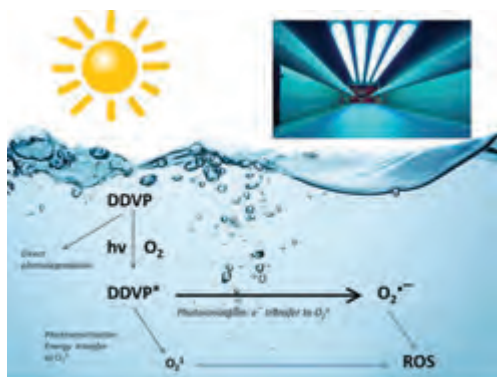
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Effect of Sunlight and UV-C Disinfection Dose Irradiation on the Degradation of Organophosphorous Pesticide Dichlorvos

OP Env Tech #14

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Dichlorvos (2,2-Dichlorovinyl dimethyl phosphate, DDVP) is a chlorinated organophosphorus pesticide, employed as insecticide in agriculture, as well as to treat parasite infections in livestock and domestic animals [1]. The widespread employment of this insecticide has caused its detection in surface waters worldwide. DDVP is classified by the World Health Organization (WHO) as a highly hazardous pesticide [2] and it has been banned in the European Union.

Despite the risks potentially posed by its presence in water compartments, little is known about the behavior and fate of DDVP under natural sunlight and UV-C irradiation, being the latter increasingly adopted as a primary disinfection method for drinking water and wastewater effluent. This study investigated the photodegradation mechanism of DDVP under sunlight and UV-C irradiation and the role that reactive oxygen species (ROS) plays in it. To simulate sunlight effect on DDVP, pesticide water solutions were irradiated by a Xe-OP lamp (Phillips 1kW), in a SOLAR BOX® (Co.fo.me. gra 220 V, 50 Hz). The photonic flow of the Xe-lamp in the 290-400 nm range was $2.98 \mu\text{Einstein s}^{-1}$. The UV-C photoreactor used to simulate disinfection doses irradiations was equipped with one low pressure UV-C (254 nm) lamp (4W, 30% UVC efficiency, Philips TUV G4T5), with a photon flow of $0.17 \mu\text{Einstein s}^{-1}$. The role of oxygen in the phototransformation of DDVP was examined with dissolved oxygen (at a concentration of 6.03

$\pm 0.5 \text{ mg L}^{-1}$) and without oxygen, in N_2 bubbled solutions (O_2 concentration $< 0.3 \pm 0.1 \text{ mg L}^{-1}$). The contribution of ROS was monitored by adding radical scavengers into reaction solutions. Concretely, tert-butanol (3 mmol L^{-1}) and sodium azide (2.5 mg L^{-1}) were used to deplete hydroxyl radical (HO^\bullet) and singlet oxygen ($^1\text{O}_2$) reaction pathways, respectively.

Results showed that photodegradation of DDVP occur under simulated sunlight, providing an alternative degradation mechanism to hydrolysis in water. In N_2 -saturated solution virtually no direct photolysis was produced under simulated sunlight irradiation, and therefore the most relevant contribution to pesticide depletion could be associated with the presence of dissolved oxygen.

The experimental evidence points to a photoionization of DDVP and the scavenging of hydrated electrons by oxygen generating the formation of superoxide radicals ($\text{O}_2^{\bullet-}$). It is not probable that $\text{O}_2^{\bullet-}$ reacts with the pesticide but other oxidant species like hydroxyl radicals (HO^\bullet) resulting from different radical reactions.

The possible contribution of singlet oxygen generation (O_2^1) by photosensitization of excited DDVP could also account to the decomposition of organophosphorous pesticide in aqueous solutions. DDVP degradation rate is significantly increased under UV-C irradiation at disinfection doses ($40\text{--}100 \text{ mJ cm}^{-2}$), due to the contribution of direct photolysis. However, dissolved oxygen still plays an important role in the pesticide degradation.

Acknowledgements

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Programme H2020-MSCA-RISE-2015 under REA grant agreement n° 690618.

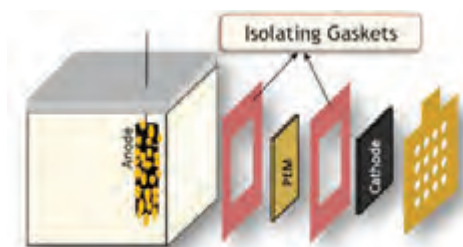
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Single Chamber Microbial Fuel Cell (SCMFC) using *Lactobacillus pentosus* Biofilms

OP Env Tech #15

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Microbial fuel cells (MFCs) are able to produce energy during a biological wastewater treatment [1, 2]. However, to overcome their current limitations, such as electron production and transfer, proton transfer and microbial metabolism, a clearly understanding of the effect of operation and design parameters on its performance is mandatory [2-4]. Towards that, in this work, the effect of the operating time (24, 48 and 72 h), anode electrode area (61 and 30 cm²), yeast extract concentration (5 and 50 mg/L), membrane thickness (Nafion 212 and Nafion 117) and active area (25 and 42 cm²) on the performance of a single chamber MFC (SCMFC) working with *Lactobacillus pentosus* and a synthetic dairy wastewater, was investigated. The performance was evaluated through the cell power output, the chemical oxygen demand (COD) removal rate and the biofilm formed on the anode electrode, through its biomass dry weight, proteins and polysaccharides content. The results show that an operating time of 48 h achieved higher power densities and COD removal rates. A decrease of 52% on the anode electrode size lead to a decrease of the electrochemical performance of the SCMFC and the biofilm dry weight. The yeast extract concentration improved the electrochemical performance cell, however lead to a decrease of the COD removal rate, possible due to an accumulation of fermentation products. A thinner membrane (Nafion 212) with a lower area (25 cm²) lead to a higher power output, COD removal rate and biofilm dry weight.

A maximum power density of 5.04 ± 0.39 mW/m² was achieved for the SCMFC with an anode electrode area of 61 cm², an operating time of 48 h, 50 mg/L of yeast extract and a Nafion 212 membrane with 25 cm² of active area. For these conditions, the COD removal rate was 50 % and the biofilm dry weight 4.89 g/L.

The present work shows that changes on the SCMFC characteristics are effective ways to increase the MFC electrical and wastewater treatment performances, control the biofilm properties and reduce the MFC costs.

Acknowledgements

The authors acknowledge the Master research grant fellowship (SAESCTNPIIC&DT/1/2011 - NORTE-07-0124-FEDER-000026) supported by “Fundo Europeu de Desenvolvimento Regional” (FEDER), inserted in the program “O Novo Norte” (ON.2) and also the national funding of FCT/MEC (PIDDAC), the post-doctoral fellowship (SFRH/BDP/91993/2012) supported by the Portuguese “Fundação para a Ciência e Tecnologia” (FCT), POPH/QREN and European Social Fund (ESF). POCI (FEDER) also supported this work via CEFT and LEPABE.



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Nutshells as Very Low Cost Sorbents for Contaminated Waters Treatment

OP Env Tech #16

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The presence of potentially toxic elements such as arsenic, cadmium, chromium, mercury and lead in waters is a major concern due to their high toxicity and easy bioaccumulation, representing a risk for environment and human health [1]. Though, there is a need to find effective ways to diminish their concentrations in waters, since the available technologies, such as ion exchange or chemical precipitation fail or become extremely expensive when the aim is to achieve low residual levels or to treat large volumes of water [2].

Biosorption has emerged as an area of great potential for water treatment due to the use of environmental friendly and largely available materials, together with their low cost and no commercial value associated. However, the majority of biosorption studies found in literature evaluates the efficiency of the biosorbents using large quantities of material, focusing mainly on single contaminant systems [3]. Since every year large amounts of wastes such as nutshells are generated by agroindustries, in this work we present a valorization proposal for these materials by reusing them as biosorbents to remove several potentially toxic elements from waters.

The efficiency and sorption capacity of peanut, walnut and pistachio nuts (1g, 2.5g and 5g of each one) was tested in multi-contaminant systems of

As, Cd, Cr, Pb and Hg with concentrations equal to 1000, 1500, 700, 2750 and 2700 µg/L, respectively. Hg analysis was performed by cold vapor atomic fluorescence spectroscopy (CV-AFS) and the other elements were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Under the experimental conditions studied the results demonstrated a good capacity of the nutshells for the sorption of the contaminants tested. Overall, the removal efficiencies ranged from 17% for As to 97% for Pb, with peanut shell showing the best performance. For Pb and Cd it was possible to achieve lower concentrations than those allowed for effluents discharge [4].

The proposed solution presents a water treatment method with lower costs than conventional methods, being possible to achieve a considerable improvement in water quality, in an environmental friendly way.

Acknowledgements

Authors thank University of Aveiro and FCT/MEC for the financial support to CICECO, CESAM and CIIMAR (UID/CTM/50011/2013, UID/AMB/50017/2013, UID/Multi/04423/2013, respectively), and the FCT project PTDC/QEQ-EPR/1249/2014, through national funds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement. Bruno Henriques also thanks FCT for his postdoctoral grant (SFRH/BPD/112576/2015).

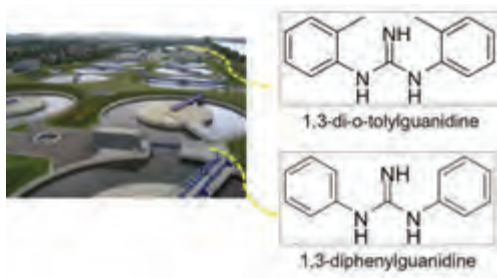
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Kinetics, Transformation and Toxicity of 1,3-di-*o*-tolylguanidine and 1,3-diphenylguanidine During Disinfection with Chlorine

OP Env Tech #17

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1,3-di-*o*-tolylguanidine (DTG) and 1,3-diphenylguanidine (DPG) are used as accelerators in the vulcanization of rubber and other polymer applications, that have only recently been detected as potential Persistent and Mobile Organic Compounds (PMOCs) in a screening study [1]. Furthermore, DTG has been reported in the literature because of its pharmacological effects, thus, being a potential environmental and human threat (if it reaches drinking water) [2].

In this work, a full kinetic study was evaluated for DTG and DPG upon reaction with free chlorine, the most widely used water disinfection agent. Also, bromination experiments were performed. Half-lives and kinetic rate constants were calculated and a kinetic model accounting for the pH was constructed. Subsequently, transformation products (TPs) and conventional disinfection by-products (DBPs) were identified and the toxicity was assessed by the *Microtox* test and *in-silico*.

Competitive kinetics experiments using resorcinol as a reference compound indicated that DTG and DPG react very fast, both with half-lives below 15 s for 1 mg Cl₂ /L at pH 7. Further chlorination experiments were performed in a range of pH from 2.0 to 12.0 by using 1 µM of each compound versus 10 µM of free chlorine in ultra-pure water. The results, in terms of kinetic constant, were compared to a calculated theoretical model, considering the pK_a values of the compounds and hypochlorous acid, showing a good agreement between experimental

and model values, and indicating also that DTG is more reactive than DPG. Faster reaction kinetics were obtained for experiments at pH 7.5-9.5. In bromination experiments, results also fit the model described for this oxidant.

TPs were identified by liquid chromatography coupled to quadrupole-time of flight mass spectrometry (LC-QToF). Most of the TPs consisted on halogenated (chlorinated and brominated) and hydroxylated derivatives. Cleavage or cyclization TPs were also detected. Haloacetonitriles and trihalomethanes were quantified by GC/MS after liquid-liquid extraction. High production yields of 0.38 and 0.15 mol/mol were obtained for chloroform and dichloroacetonitrile, respectively, after 48 hours contact time and Cl₂/DPG molar ratio of 100.

A preliminary estimation of the toxicity was done for the identified TPs by using quantitative structure-activity relationship (QSAR). Many of the TPs of DPG and DTG are predicted to be more toxic than the parent compound, particularly the halogenated ones.

Acknowledgements

This work was financed by Spanish MINECO (JPIW2013-117) and French ONEMA (ref. PROMOTE), in the frame of the collaborative international consortium (WATERJPI2013-PROMOTE) of the Water Challenges for a Changing World Joint Programming Initiative (Water JPI) Pilot Call. Authors also acknowledge the support of Xunta de Galicia (GRC2013-020 & EM2014-004) and FEDER/ERDF.

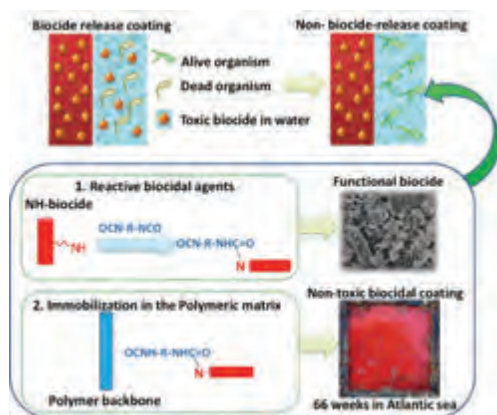
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Eco-Friendly Non-Biocide-Release Coatings for Biofouling Prevention on Submerged Surfaces

OP Env Tech #18

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Water, the primary resource for the growth and sustainability of our society, has ironically become one of the biggest challenges. The spontaneous colonization by aquatic micro/macroorganisms (freshwater/seawater) of submerged surfaces, known as biofouling, is responsible for serious economic and environmental penalties and health risks on several industrial activities (e.g. marine transport, aquaculture, water purification). It can promote premature substrate deterioration (e.g. up to 20%), drag resistance increases (up to 40% in shipping) and subsequent fuel consumption and Greenhouse gas emissions increase. Furthermore, its potential side-effects due to the introduction of waterborne invasive species, is becoming of utmost importance [1, 2].

Conventional antifouling technologies, mostly based on the controlled release of toxic substances into the waters, imply limited life-cycle and significant ecotoxicity subjected to rigid regulations (BPD EU Regulation n° 528/2012).

Eco-friendly and more efficient technologies are sought to combat this waterborne burden. This work proposes a novel approach, based on the development of functional reactive antifouling agents with ability to be chemically-linked through covalent bonds in polymeric systems (coatings). Thus, the antifouling action will be provided by contact, substituting the biocide release into the contaminated area, reducing and/or avoiding the associated side-effects.

Non-biocide-release process [1]: Briefly, the linkage ability of antifouling agents is provided by

their functionalization with bi-functional isocyanate reagent at optimised conditions (e.g. Ecomea, Irgarol). The isocyanate (NCO) function is highly reactive with conventional coating components.

Physical-chemical properties: Biocides structure and NCO functionality was confirmed by FTIR and NMR spectra analysis. Their linkage ability was proved by the binding reaction with conventional marine coatings components (e.g. silicone based) and leaching tests. Uniform polymeric film coatings with minor roughness increases and adhesion performances losses were obtained after biocides immobilisation on marine paints.

Proof-of-concept: Bioactivity of the functional biocides was confirmed against several organisms, such as *Pseudoalteromonas tunicata* D2, *Bacillus cereus* G201 strains, *Staphylococcus aureus* and *Enterococcus faecalis*. Antifouling performances of the developed non-biocide-release coatings at real conditions (static prototype tests in Atlantic sea) showed very promising results, since the protective action remained for more than a year. Auspicious antifouling effects for a field ship trial test in progress were also achieved with one of the most potential coatings containing immobilised Ecomea, after 8 months in open sea.

Aiming to contribute to the safety and sustainability of our aquatic ecosystems, this novel approach is presented as an attractive alternative to the conventional antifouling releasing strategies.

Acknowledgements

Support for this work was provided by the projects FP7 FOUXSPeL (Grant Agreement n°285552) and NOVOMAR (ref. 0687-NOVOMAR-1P), and FCT through UID/MULTI/00612/2013, POCI-01-0145-FEDER-006939 (LEPABE-UID/EQU/00511/2013) and Pest-OE/QUI/UI0612/2013. E. R. Silva also thanks FCT for the Post-Doc fellowship SFRH/BPD/88135/2012.

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Photocatalysis and Adsorption Synergy for Simultaneous Removal of Phenol and Acetamiprid Pollutants in Water

OP Env Tech #19

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Synthesis of activated carbon from Pomegranate bark biomass



Zinc Oxide/Activated carbon hybrid composite exhibit both excellent adsorption capability of pollutants and photocatalytic activity having great potential in organic compounds photodegradation [1, 2]. This paper reports on photocatalytic and adsorption hybrid treatment of a phenol and acetamiprid in wastewater. The photocatalytic degradation was carried out in the presence of the ZnO nanoparticles as catalyst and activated carbon (AC). The effects of pH, concentration of the pollutants, amount of ZnO/AC on the degradation process were observed [3, 4]. It was found that photocatalytic degradation by ZnO is an effective, economical and faster mode of removing phenol and Acetamiprid from aqueous solutions. The use of activated carbon alone in the water solution for the elimination of these two pollutants was tested. The results shown that Activated carbon is a potential adsorbent to remove phenol and Acetamiprid from wastewater.

A combination of activated carbon and photocatalytic semiconductor (ZnO) was used in different mass ratios to increase the rate and kinetics rate constants of phenol and acetamiprid photodegradation, the initial concentration of (CA / ZnO), the initial concentration of the pollutants, The pH of the solution and the addition of H₂O₂ were carried out.

In order to determine the influence of the bulk composition between the activated carbon and the zinc oxide (CA / ZnO) on the efficiency of the adsorption/ photodegradation process, tests were carried out for different CA / ZnO compositions (70/30, 75/25, 80/20 and 85/15%) using an amount of this weight ratio equal to 0.5 gL⁻¹ for each experiment, an initial concentration of 10 mg.L⁻¹ pollutants and a pH free. The system ZnO/AC achieved removal rates between 70 and 98%. This system allows a greater degree of flexibility in the manner the system can be operated.

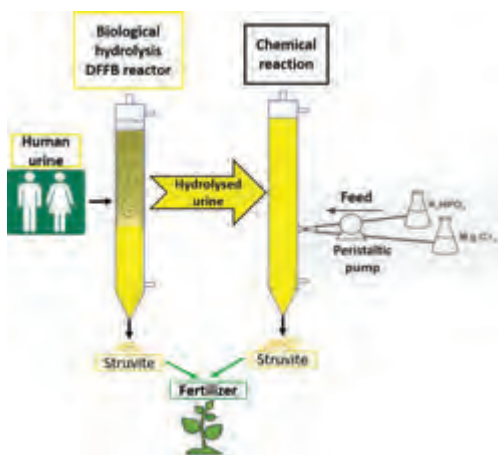
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Ammonium Removal as Struvite from Biologically Treated Human Urine

OP Env Tech #20

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The source separation of household effluents is an alternative way for more efficient treatment of wastes, but also, for nutrient and energy recovery [1]. Human urine has been considered as a potential source of nutrients such as nitrogen and phosphorus [2]. Precipitation of nutrients in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is an alternative for the removal of ammonium in urine. Struvite is a slow release nutrient fertilizer that can be used to preplace other less effective fertilizers such as urea. Also, the removal of N and P from source separated urine reduces the environmental effect over water resources [3].

Struvite precipitation occurs when Mg^{2+} , NH_4^+ and PO_4^{3-} are in equimolar concentrations in alkaline conditions (7.5 – 11.5 pH) [4]. Nonetheless, factors such as pH, saturation and reactor configuration affects the struvite precipitation [5,6]. During biological ureolysis, two molecules of NH_3 are produced, thus, under alkaline conditions the precipitation of struvite is favoured. Additionally, enzymatic ureolysis is a fast occurring process [7,8]. In this work the main objective was to evaluate ammonium removal in the form of struvite from biologically hydrolysed human urine testing three molar ratios of Mg:P (1.0:1.0, 1.5:1.0 and 2.0:1.0), via dosing with magnesium and calcium salts ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and K_2HPO_4 respectively). Human urine was previously biologically hydrolysed in a down-flow fluidized bed (DFFB)

reactor at 7 h HRT. The chemical reaction was done in a cylindrical reactor with a conic bottom, the total working volume was 1.9 L, a glass settler device was attached. The hydrolysed urine (influent) was pumped at 4.6 L/h, the salts solutions were added at 1 L/h and the recirculation flow was 12 L/h. This reactor was run at 1.5 h HRT, at ambient temperature (26–33 °C).

The highest amount of N-NH_4^+ recovered (2228.9 mg/L) was using the 2.0:1.0 Mg:P ratio, the total amount of precipitate characterized mainly as struvite was 104.5 g. The pH during the chemical reaction was >8.0 which was favourable for struvite precipitation. As the molar ratio of Mg:P was increased, also the amount of N-NH_4^+ recovered. The precipitation reaction occurred during the first 30 min. These results shown that struvite can be obtained effectively from hydrolysed human urine after the addition of Mg and P salts in a 2.0:1.0 ratio.

Acknowledgements

The authors thank Universidad del Mar, this work was done in the Environmental Engineering Laboratories, under the project 2IE1603. Also, we thank Programa Nacional de Becas 2016 SEP for the writing up grant to L. J. del Valle Medina. Finally, we thank all the urine donors.

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Removal of PPCPs from Effluent Based on Electrochemical Process - Possibility of Further Use in Agriculture

OP Env Tech #21

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As world demands for water grow, effluent reuse becomes increasingly important as an indispensable component of the integral water resource management, and is widely regarded as a sustainable approach in agricultural irrigation. Effluent reuse in agriculture also contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 20 Critical Raw Materials). However, it has been reported that pharmaceuticals and personal care products (PPCPs) are not completely removed from effluent in wastewater treatment plants (WWTPs).

The potential of the electrokinetic process (EK) for PPCPs removal from effluent is explored in this work. PPCPs with different physical and chemical characteristics between them were studied. The effect of two electrode material (graphite and titanium), “non-active anodes”, were tested. After the EK, effluent parameters (e.g. pH, nitrite, electrical conductivity) were evaluated to guarantee its safe use in agriculture.

The effluent was collected at an urban WWTP located in Portugal (38°34'13" N, 9°2'7" W) belonging to Águas de Lisboa e Vale do Tejo (ALVT)

Group. The plant has the capacity to treat in the project horizon 19 300 m³/day of urban wastewater, corresponding to about 94 000 population equivalents. The preliminary results suggest that EK is a promising technology for PPCPs removal through electrodegradation, promoted by oxidation and reduction reactions at the same time. The nature of the selected electrodes showed to have influence in some PPCPs degradation.

Acknowledgements

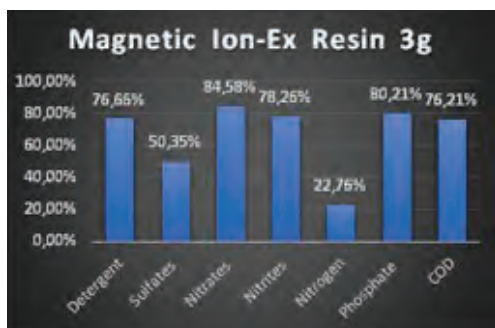
The authors would like to thank AdP, Dr. Cristina Santos for providing the samples, Eng. Olga Paredes, and the Laboratory of Control and Processes for the assistance. Financial support was provided by UID/AMB/04085/2013 and 4KET4Reuse (SOE1/P1/E0253), co-financed by the European Regional Development Fund (FEDER). The Associação Nacional de Farmácias (ANF), Portugal, is also acknowledged for giving the HPLC. N. Couto and P. Guedes acknowledge Fundação para a Ciência e a Tecnologia for their Post-Doc fellowships, respectively, SFRH/BPD/81122/2011 and SFRH/BPD/114660/2016.

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Exploring Magnetism as a Way to Decontaminate Wastewater and Leachates

OP Env Tech #22

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The treatment of leachates as pollutant concentrated wastewaters, is still an open issue, and although several different methods are applied for this goal, we are still far way from obtaining low-cost and at the same time efficient processes. Even for wastewater and water, removal of specific contaminants is far from being economical.

Magnetic particles (nano or micron-sized), namely those based on iron oxides, have shown good sorption capabilities, which may be useful for removal/concentration of pollutants/nutrients. Joining this sorption capabilities with their magnetic properties, and with potential functionalization, makes the application of these particles for wastewater or leachate treatment very interesting, specially as we may use magnetic separation methods to further remove, recover and reuse these particles.

In this work we have tested three different kind of magnetic particles, in order to remove/concentrate organic matter (DQO reduction), Nitrogen (Total Nitrogen) and Phosphorous (Total Phosphorous), during several time periods, being successful in

removing between 4 and 65 % of them, depending on the controlled parameter, sorption time and type of particle.

We have applied the same particles in three different water streams with different degrees of pollution, so we would be able to analyze the pollutant concentration influence: these being water, wastewater and leachate. In Figure 1 we present as example the case of removal for wastewater resultant from sludge centrifugation, by one of the three different magnetic particle systems we have used.

Acknowledgements

This work was supported by the projects:

(i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia.

(ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

(iii) Project MINECO-17-MAT2016-76824-C3-2-R (MINECO, Spain)

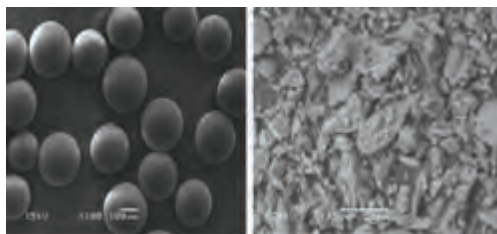
(iv) Project MAGPRO2LIFE (European Union) and supported by Protocols with:

- a) FCC Aqualia
- b) FCC Servicio Ciudadanos

Encapsulation of High Surface Area Carbonaceous Particles into Sol-gel Matrix and Their Use in Environmental Pollution Mitigation

OP Env Tech #23

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Due to the explosive growth of anthropogenic activities during the last couple of decades, fresh water systems across the world have been continuously polluted by thousands of toxic and hazardous synthetic organic compounds produced for industrial, domestic and agricultural usage. Many of these pollutants are known as persistent organic pollutants (POPs). When POPs are released into the environment, they remain unchanged for a long period of time by resisting photocatalytic, chemical and biological degradation. Due to their prolonged presence in the environment, many of these pollutants finally find their way in the food chain, with severe ramifications in the health and well being of human. As such, it is imperative that these compounds be efficiently removed from environmental water through more efficient sewerage treatment processes and other reliable remediation techniques.

Among many classical processes used in removing pollutants from water such as precipitation, coagulation, sedimentation, filtration, adsorption, chemical oxidation, and ion exchange, adsorption is one of the most effective removal technique. A large number of carbonaceous adsorbents including activated carbon, carbon nanotube, biochar, graphene, beta-cyclodextrin, calixarenes, poly(styrene-divinyl benzene), carboxen, fullerene, cation exchange resins, anion exchange resins, zwitterionic resins and many others are used individually or in different combinations as adsorbents in sewerage treatment plants. These adsorbents offer a large variety of intermolecular interactions towards the analytes via μ - μ stacking interactions, cation- μ bonding interactions, electron donor-acceptor interactions,

hydrophobic interactions, hydrogen bonding interaction, cation exchange, anion exchange, dipole-dipole interactions etc. Many of these adsorbents possess extremely high surface area and demonstrate strong tendency to form agglomeration. As such, when they are used in their pristine form, a large portion of their available surface area cannot be readily accessed by the analytes due to their agglomeration and formation of lump. As a result, the adsorption capacities of these adsorbents remain largely unexploited during their applications. The agglomeration of these unique particulate matters can be inhibited by encapsulating them into sol-gel silica network. Sol-gel chemistry provides a convenient and mild reaction pathway to create pure silica or organically modified silica 3-D network. Addition of sol-gel active organic polymer(s) as an additive in the sol solution during the sol-gel synthesis is also a common practice to engineer the selectivity of the resulting sol-gel sorbents. Addition of adsorbent particles into the sol solution during sol-gel synthesis results in a sol-gel composite sorbent system with homogeneously trapped particulate matters. Due to the inherently porous and open architecture of sol-gel silica network, the encapsulated particulate matters maintain their high surface area as well as freely accessible interaction sites. As such, the synergistic combination of silica chemistry, organic polymer chemistry as well as the chemistry of particulate matters result in robust composite material systems capable of exerting intermolecular/ionic interactions towards a wide variety of analytes including polar, medium polar, nonpolar, ionic, and metal species and successfully trap them in the sol-gel composite sorbent matrices.

Analytical data obtained from a number of real-life applications of the sol-gel composite sorbents including endocrine disrupting chemicals (EDCs), Pharmaceuticals and personal care products (PPCPs), polycyclic aromatic hydrocarbon (PAHs) in environmental water will be presented showcasing their advantages, extraction characteristics, performance superiority, and analytical figures of merit.

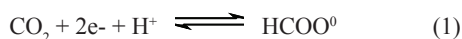
Formate Dehydrogenase-catalysed Carbon Dioxide Reduction: Aiming to Develop a Catalyst for Carbon Dioxide Utilisation

OP Env Tech #24

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Formate dehydrogenases (FDH) are enzymes that catalyse the reversible two-electron oxidation of formate to carbon dioxide (eq. 1) [1]. FDHs can be divided into two major groups, based on their metal content and the consequent chemical strategy followed by the enzyme's active site to catalyse the reaction [2, 3]. The group of metal-dependent FDHs comprises only prokaryotic enzymes that hold different redox-active centres and whose active site harbours one molybdenum or one tungsten atom that mediates the formate oxidation/carbon dioxide reduction [2, 3].



In this communication, the ability of the molybdenum-containing FDH from *Desulfovibrio desulfuricans* (Dd FDH) to reduce carbon dioxide will be discussed. The Dd FDH was found to be one of the most efficient carbon dioxide reducers so far described in the literature, with a k_{cat} of

47s^{-1} and a $K_{\text{m}}^{\text{CO}_2}$ of 16mM [4] and a novel FDH reaction mechanism was proposed [4,5]: formate oxidation and carbon dioxide reduction proceed through hydride transfer, through a mechanism where the sulfo group of the oxidised and reduced molybdenum centre ($\text{Mo}^{6+}=\text{S}$ and $\text{Mo}^{4+}-\text{SH}$, respectively) are suggested to be the direct hydride acceptor and donor, respectively (Fig. 1).

Acknowledgements

LBM thanks to Fundação para a Ciência e a Tecnologia, MCTES, for a fellowship grant (SFRH/BPD/111404/2015, which is financed by national funds and co-financed by FSE). This work was supported by the Unidade de Ciências Biomoleculares Aplicadas-UCIBIO, which is financed by national funds from FCT/MEC (UID/Multi/04378/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER-007728).

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Green Waste Derived Substances Immobilized on SBA Silica: Adsorbing and Photosensitizing Properties Towards Metals and Organics.

OP Env Tech #25

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Over the last years, urban wastes have become a major source of environment contamination, especially when they are not properly disposed. Nowadays, researchers are finding innovative solutions for recycling and reusing of wastes in order to favour a sustainable development of our society in the viewpoint of circular economy. In this context, the recalcitrant lignin-like fraction of biomass derived from urban biowastes is a cost effective source of soluble bio-based substances (BBS). Herein, this acronym indicates a particular kind of substances isolated from urban public park trimming and home gardening residues aged under aerobic conditions.

These complex macromolecules/ supramolecular aggregates bear chemical similarities with humic substances [1], thus they are characterized by adsorbing features (thanks to the variety of functional groups) and photosensitizing properties. In a previous paper [2], it has been already demonstrated that BBS can be effectively immobilized on silica supports maintaining, also in heterogeneous form, their photoactivity for the degradation of phenolic water pollutants under simulated solar light.

In this work, BBS were attached, through a grafting stepwise approach, on SBA silica with ordered porosity and tested in the adsorption of metal ions (Fe, Al, Ni, Mn, As, Hg, Cr) and differently charged dyes (Rhodamine B and Orange II), common indicators of compromised waters near industrial areas and/or dumps. The hybrid SBA-

BBS was able to interact with all the substances tested. These promising results are ascribable to the surface properties of SBA-BBS, which were deeply investigated by ζ -potential measurements, N_2 adsorption at 77K and micro-calorimetric techniques.

Furthermore, in the case of the experiments carried out with Orange II, that was totally adsorbed on the SBA-BBS, the suspension was irradiated in order to exploit the photosensitizing capability of BBS and reach a sort of hybrid self-regeneration. Indeed, beyond the dye adsorption, a partial photoactivated disappearance of the dye (50%) was observed as well. To deepen how this material works as heterogeneous photosensitizer, Reactive Oxygen Species produced by irradiated SBA-BBS were studied by Electron Paramagnetic Resonance in presence of spin-traps, showing the formation of hydroxyl radicals.

In conclusion, SBA-BBS seems to be a promising material for the removal of pollutants from wastewater since the combination of photocatalytic and adsorption properties allows employing this kind of systems for the simultaneous treatment of different substances.

Acknowledgements

This work was realized with the financial support of Mat4Treat project funded by the European Commission H2020-MSCA-RISE-2014. Part of this research is realized with the support of the grant Borsa di Studio- Bando Talenti della Società Civile – edizione 2016, promoted by Fondazione Giovanni Gorla and Fondazione CRT (Italy).



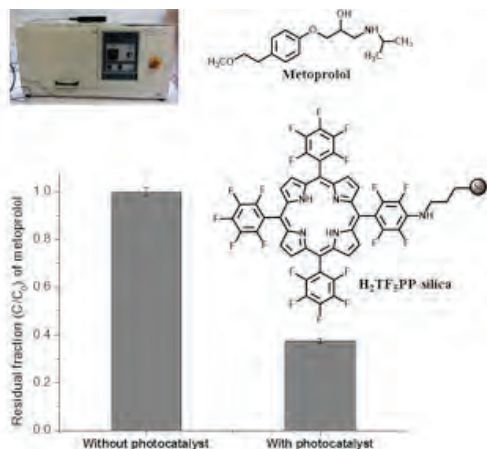
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Immobilized Porphyrins as Photocatalysts for the Degradation of Metoprolol

OP Env Tech #26

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Metoprolol, a highly prescribed b-blocker, does not suffer direct photodegradation [1]. In natural waters, metoprolol can undergo indirect photodegradation under the effect of dissolved organic matter (DOM), which can act as photosensitizer [2]. However, even suffering indirect photodegradation, it is necessary to prevent its introduction into the aquatic environment by removing it from the effluents of sewage treatment plants. The sewage treatment plants are not prepared for the removal of micropollutants and particularly they have a lack of efficiency in the elimination of b-blockers [3]. A possible solution to overcome the existing gaps in the conventional treatment processes is the use of photocatalysts.

Porphyrins possess triplet states of appropriate energy to allow, under light irradiation, an efficient energy transfer to ground state oxygen, producing high yields of oxygen reactive species like ¹O₂ [4]. Such properties are responsible for the application of these compounds in different areas such as in photodynamic therapy (PDT) to treat oncological and non-oncological situations [5,6], in the photodynamic inactivation of microorganisms [7], in the photooxidation of organic compounds [8] or in the degradation of organic pollutants in a water remediation context [9].

In this work, the potential of the *meso*-tetrakis(pentafluorophenyl)porphyrin immobilized on a silica support (H₂TF₅PP-silica) as photosensitizer for the treatment of water contaminated with metoprolol was evaluated. Studies were carried out under simulated solar irradiation and the immobilized porphyrin showed to be effective in the photodegradation of metoprolol.

Acknowledgements

Thanks are due to FCT/MEC (POPH/FSE) for the financial support through national funds and, where applicable, co-financed by FEDER, within the PT2020 Partnership Agreement, to QOPNA (Pest-C/UI0062/2013), CERNAS (UID/AMB/00681/2013), CICECO (UID/CTM/50011/2013), and CESAM (UID/AMB/50017/2013). The authors are also grateful to FCT and POPH/FSE for the PhD Grant to C. M. B. Neves (PD/BD/52531/2014).

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Synthesis, Characterization and Photocatalytic Performance of Mg-ZnO-Al₂O₃ Nanocomposite for Degradation of Pharmaceutical Pollutants

OP Env Tech #27

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In this work, Mg-doped ZnO-Al₂O₃ heterostructure photocatalyst at different content of Mg (1, 3 and 5 wt%) was prepared from Zn-Al-CO₃ layered double hydroxides precursors using ceramic process at 500 °C. The synthesized catalysts were characterized

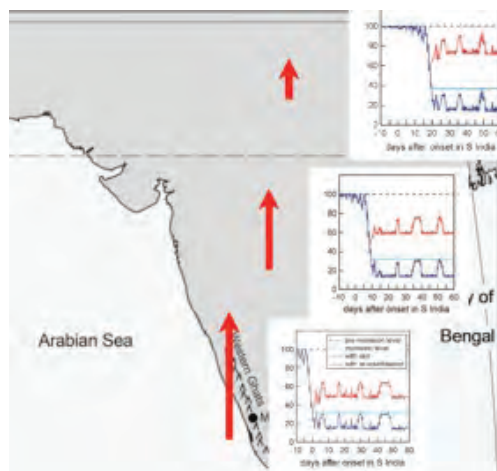
by various physicochemical techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX). The photocatalytic activity of the catalysts was evaluated for the photocatalytic degradation of caffeine as a model of pharmaceutical pollutant in aqueous solutions under UV irradiation. Detailed photocatalytic experiments based on the effects of dopant amount, irradiation time, catalyst dose, initial pH, caffeine concentration and reuse were performed and presented in this study. The enhancement of photocatalytic activity was strongly dependent on the Mg amount and adsorption process. The 1%Mg-ZnO-Al₂O₃ sample with high adsorption capacity showed the highest photocatalytic activity with a degradation efficiency of 98.9% after 70 min of irradiation. It showed a significantly higher rate of degradation compared to undoped, pure ZnO and standard Degussa P-25 titanium dioxide. The photocatalyst showed high stability after three regeneration cycles.

Environmental Modelling

Monsoon Air Triggers Re-volatilization of Persistent Pollutants Stored in Soils in India

OP Env Model #1

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Persistent organic pollutants such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) undergo long-range atmospheric transport, enhanced by multi-hopping (secondary sources, so-called ‘grasshopper effect’) [1,2]. We studied the influence of the onset of the southwest monsoon in southern India (arrival of clean southern hemisphere air) 2014 on POP cycling by field measurements at a mountain background site (Munnar, Kerala) and 3D and 1D modelling.

Air and soil samples were analysed for penta- and hexachlorobenzene, PCBs ($n=7$), HCH (5 isomers), DDT and metabolites (6), endosulfan and other OCPs (10) using GC-MS/MS.

The direction of diffusive air-soil mass exchange was indicated by the ratio of the fugacities in both compartments, assuming that absorption in soil organic matter is the process determining retention. The response of the air-soil cycling to onset of southwest (summer) monsoon was studied by a 1 month regional scale 3D simulation of meteorology, atmospheric and soil chemistry (WRF/Chem-PAH/POP [3] 27 km \times 27 km, nudged with 6-hourly 1 $^{\circ}\times$ 1 $^{\circ}$ NCEP re-analyses, change of boundary conditions with onset) and by a long-term (1965–

2014) 1D model simulation [2,4] (non-steady state multimedia box model chain of 7 double-boxes representing latitudinal zones).

Pollutant concentrations in both air and soil are among the lowest ever reported from India. With the onset of monsoon, near-ground air concentrations in Munnar dropped from 12.6 to 3.1 for Σ HCH, from 7.4 to 1.9 for Σ DDX, and from 21.3 to 9.9 pg m $^{-3}$ for Σ PCB. This triggered enhanced re-volatilisation of PCBs and HCH and suppressed dry deposition of DDX compounds.

The 3D model simulation suggests that while propagating across the subcontinent, air gets increasingly polluted, also due to triggered re-volatilisation. The 1D model simulation indicates that since the ban of HCH and DDT from agriculture in the 1980s, air-surface exchange of these pollutants has been declining, but re-mobilisation of higher chlorinated PCBs may have reached a historical high today, 40 years after peak emission.

Acknowledgements

We thank T.U.Ansari (IIT Madras), C.V.Biju (College of Engineering Munnar) and R.Prokeš (MU) for on-site and logistic support. This research was supported by the Max Planck Society, the Czech Ministry of Education, Youth and Sports (LO1214 and LM2015051) and DST-Max Planck Partner Group on Bioaerosol Research at IIT.

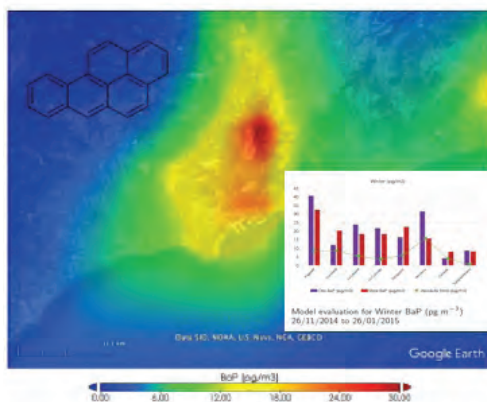
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Combining Monitoring and Modelling Approaches for BaP Characterization Over a Petrochemical Area

OP Env Model #2

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Winter BaP (pg m⁻³) 26/11/2014 to 26/01/2015

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds characterized by their ubiquity in the environment, long-range atmospheric transport capacity (LRAT) and relatively high toxicity [1,2]. Among these compounds, benzo[a]pyrene (BaP) has already been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC). Furthermore, international studies suggest that the toxicity and environmental fate of PAHs can be affected by the variations in the temperature and solar radiation associated with the climatic change [3]. PAHs are mostly emitted by anthropogenic sources, being the oil refineries one of the most important emission points [4]. One of the largest petrochemical complex in Southern Europe is located in Tarragona County (Catalonia, NE of Spain), for this reason to combine the monitoring and modelling approaches for PAHs is a crucial step in order to evaluate the impact of these contaminants in the surrounding environment, as well as to assess the risks for the local population. In this study, air concentrations of BaP from Tarragona County in two different seasons (winter 2015 and summer 2016) were used as control simulations run with the chemistry transport model (CTM) WRF (Weather Research and Forecasting)

+ CHIMERE. The modelling methodology used follows the work developed by Ratola and Jiménez-Guerrero [5]. Once the CTM was validated for the present climatology, the variation of the BaP concentration in air and soil was simulated for the time series 1996-2015 and for the climate change scenario RCP 8.5 (2031-2050). Finally, in order to assess the potential risk of atmospheric BaP for the local population, a quantitative risk assessment (QRA) method was conducted, concerning the risk of lung cancer associated to BaP.

Acknowledgements

This study was financially supported by the Spanish Ministry of Economy and Competitiveness, through the project CTM2012-33079. Noelia Domínguez Morueco received a PhD fellowship (FPI Pre-doctoral Contracts for the Formation of Doctors 2013) and a visiting research grant (EEBB-I-17-12509) from the same institution. Further support was provided under projects: (i) project CGL2014-59677-R also partially funded by FEDER; (ii) POCI-01-0145-FEDER-006939 (LEPABE -UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (iii) NORTE-01-0145-FEDER-000005-LEPABE-2-ECO-NNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the ERDF; (iv) Investigador FCT contract IF/01101/2014 (Nuno Ratola).

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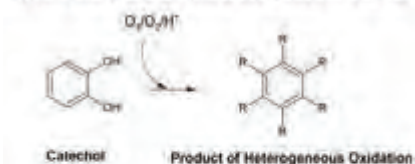
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DFT Calculations on Climate Forcing and on Sustainable CO₂ Conversion

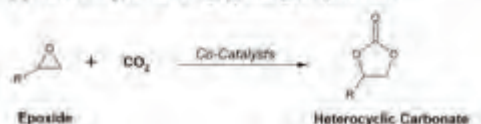
OP Env Model #3

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(1) DFT Study of the Optical Properties of Organic Aerosols



(2) DFT Study of the Ring-Opening of Epoxides



Density Functional Theory (DFT) calculations have become a reliable and essential tool in environmental chemistry, providing detailed information regarding reaction mechanisms, energetics, transition states and absorption properties [1-3]. This is achieved with efficiency gains regarding experimental approaches, as there is no need for a high number of steps such as chemical synthesis, separation and purification, and characterization processes.

Here we present two case studies for the application of DFT calculations on environmental chemistry:

(1) Recent reports have shown that optical absorption by organic aerosol components also occurs, and so, should be included in radiative forcing models. However, little is known regarding the relationship between optical properties and aerosol chemical compositions, as their optical properties and chemical composition evolve in the atmosphere. Thus, we have characterized with a DFT approach the optical properties of catechol (a common organic aerosol) and known heterogeneous oxidation products (under humid tropospheric conditions) [4]. This approach allowed us to obtain

information useful for radiative forcing modelling.

(2) The ring-opening of epoxides is one of the steps in the conversion of CO₂ into value-added heterocyclic carbonates. Thus, controlling its activation energy is essential for the development of methods in which CO₂ can be recycled under mild conditions. We have used a DFT approach to obtain insight into the ring-opening reaction of epoxides, when co-catalysed by different organocatalysts (phenylboronic acids and pyridinic bases) [5]. The presence of both catalysts decreases the activation energy of this process from ~60 to ~20 kcal mol⁻¹. Moreover, pyridinic bases present similar results to those provided by halide nucleophiles. Thus, two-component systems composed by phenylboronic acids and pyridinic bases appear to be a good choice for catalysing the ring-opening reaction of epoxides under mild, metal-free and nonhalogenated conditions.

Acknowledgements

Acknowledgements to projects NORTE-01-00145-FEDER-000028 and POCI-01-0145-FEDER-006980.

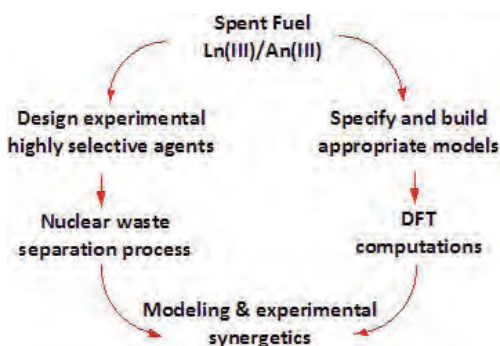
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The DFT Modeling as a Partner of Reprocessing Nuclear Waste. Rich Interplay between Theory and Experience

OP Env Model #4

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The chemistry of lanthanides (Ln) and actinides (An) species has experienced an extensive growth during the past two decades [1]. However, the use of f-elements, e.g. actinides as a nuclear fuel for energy needs, has resulted in an accumulation of contamination issues, including reprocessing and nuclear waste storage. This later requires $\text{Ln}^{\text{III}}/\text{An}^{\text{III}}$ partitioning to reduce long-term radiological risks to the environment by transmutation of the minor actinides. This originates from the long-lived ($>10^3$ years) radioactive elements such as americium (Am) and curium (Cm) present in spent nuclear fuel. The main remediation issue is the removal of these minor actinides (Am, Cm) by their partitioning from lanthanide elements (fission products) using selective reagents. Polydentate aromatic amines ligands or polyazines, have emerged as highly selective ligands towards actinides over lanthanides ions, and considerable efforts have been thus devoted at both experimental and theoretical levels, to the design, synthesis and developing of these polyazines in order to carry out the challenging $\text{Ln}^{\text{III}}/\text{An}^{\text{III}}$ separation. Indeed, the better affinity of these molecules for An^{III} rather than Ln^{III} ions is generally explained by the stronger interaction between the softer (or less hard) 5f ion and the nitrogen atom, which is less likely in the lanthanide 4f counterpart [2].

The relative scarcity and the difficult experimental handling of such complexes, make of the theoretical studies essential to understanding the different

factors, electronic, steric or energetic which can account in favor of $\text{Ln}^{\text{III}}/\text{An}^{\text{III}}$ separation. In this context, a relativistic DFT/ZORA computational study, was carried out with the aim to correlate the electronic structure properties of some $\text{M}(\text{polyazine})\text{L}_3$ ($\text{M}^{\text{III}} = \text{Ce}, \text{U}, \text{Eu}, \text{Am}$; L co-ligand) complexes to the observed polyazines selectivity towards actinide ions.

The ZORA/DFT approach using ADF program [3], was found to properly reproduce the higher selectivity of the polyazines towards actinides ions, particularly for $\text{Eu}^{\text{III}}/\text{Am}^{\text{III}}$ pair operating in spent nuclear fuel, using computed energetic factors as criterion. Moreover, the more covalent $\text{An}^{\text{III}}-\text{N}$ bonds than $\text{Ln}^{\text{III}}-\text{N}$ appear also to rationalize well the observed selectivity.

Our works are likely to show a way for future predictive design of highly selective ligands.

Keywords: f-complexes, separation, polyazine, Modeling, DFT/ZORA.

Acknowledgements

The authors are grateful to Algerian CNEPRU (Project Grant 2015-2018: E00920140093), for financial support.

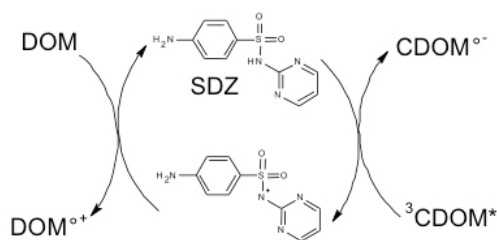
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Photodegradation of Sulfadiazine Under Conditions Significant for Surface Waters, and Inhibition by Organic Compounds

OP Env Model #5

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Sulfadiazine (SDZ) is a sulfonamide antibiotic that is found in surface waters due to incomplete degradation by wastewater treatment plants. Because of its partially biorecalcitrant nature, SDZ undergoes important photoinduced degradation in sunlit surface waters by direct photolysis, reaction with photogenerated hydroxyl radicals (OH^\bullet), and with the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$). The latter process is potentially very important and it takes place upon one-electron oxidation of SDZ by $^3\text{CDOM}^*$ to yield SDZ^+ and CDOM^- . The oxidised species SDZ^+ can evolve into transformation intermediates, but it is also efficiently reduced back to SDZ by antioxidant compounds occurring within the organic matter that is dissolved in surface waters [1]. The back-reduction might play a potentially important role in inhibiting the photodegradation of SDZ, but its importance in surface-water conditions is still poorly understood.

In this work we have addressed the topic of SDZ photodegradation in surface water samples and the effect of antioxidants on its $^3\text{CDOM}^*$ -sensitised transformation. The antioxidant effect was studied by using phenol as model reductant and 4-carboxybenzophenone as CDOM proxy. Different effects of phenol were detected for the acidic and basic forms of SDZ ($\text{pK}_a \sim 6.5$), with much higher inhibition by phenol in the case of the basic form. The photochemical behaviour of SDZ in surface water samples was compared with that of 2,4,6-trimethylphenol (TMP), which is well known

to undergo phototransformation predominantly by reaction with $^3\text{CDOM}^*$ but does not undergo back-reduction processes [2].

Interestingly, while the photodegradation rate of TMP increased with increasing the organic content of the water, which enhances the $^3\text{CDOM}^*$ -induced processes, that of SDZ soon reached a plateau that is consistent with the back-reduction phenomenon. Coherently, the expected extent of SDZ back-reduction was directly proportional to the measured electron-donating capacity of the water samples [3]. The experimental data allowed the photodegradation of SDZ to be modelled by photochemical software [4] under conditions that are significant for surface waters. Results suggested that an increase in pH would enhance the SDZ direct photolysis at the expense of the $^3\text{CDOM}^*$ process, but the pH change would not necessarily modify the overall phototransformation kinetics. Despite the back-reduction phenomenon that is favoured by a high organic matter content, the relative importance of SDZ degradation by $^3\text{CDOM}^*$ would still increase with increasing organic matter. This is an important finding with implications for the photodegradation of compounds that undergo the back-reduction phenomenon like SDZ.

Acknowledgements

DV and SC acknowledge SNSF (grant number IZK0Z2 173662 / 1) that supported a one-month stay of DV in Dübendorf. DV also acknowledges support from MIUR-PNRA and from Compagnia di San Paolo (project CSTO168282 ABATEPHARM).

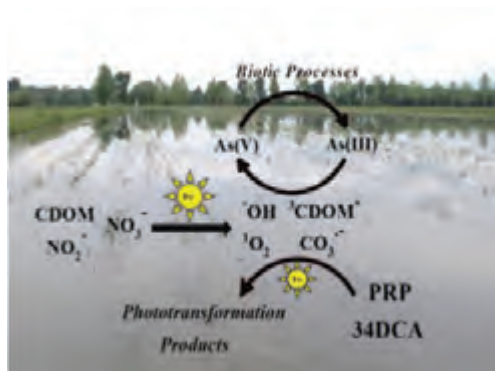
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Photoinduced Reactions in Sunlit Paddy-Field Water

OP Env Model #6

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Photochemical reactions occurring in sunlit surface waters (e.g., lakes and rivers) play a key role in the transformation of dissolved compounds. These compounds could be either autochthonous, like the organic material formed in the water bodies, or allochthonous, such as xenobiotics. Photochemical processes can be divided into direct photolysis and indirect photochemistry. Direct photolysis occurs when a compound, such as a xenobiotic, absorbs sunlight and undergoes transformation as a consequence. Instead, the degradation of compounds via indirect photochemical reactions is triggered by *Photochemically Produced Reactive Intermediates* (PPRIs). The main PPRIs are hydroxyl radicals (HO·), the excited triplet states of Chromophoric Dissolved Organic Matter (³CDOM*), carbonate radicals (CO₃·⁻) and singlet oxygen (¹O₂). PPRIs are formed upon absorption of sunlight by compounds called photosensitizers that occur naturally in surface waters. Usually, the Dissolved Organic Matter (DOM) plays a major role in the formation of the different PPRIs thanks to its chromophoric moieties, but nitrate and nitrite are also important photosensitizers that produce hydroxyl radicals. Moreover, DOM act as the major scavenger of HO· and CO₃·⁻.

The photochemical processes taking place in surface waters can be modelled by knowing the relevant kinetic parameters of the photoreactions (formation quantum yields of PPRIs, direct photolysis quantum yields of xenobiotics and reaction rate constants with PPRIs) and by using a suitable photochemistry-modelling software.

Therefore, the photochemical fate of a xenobiotic and its phototransformation pathways can be foreseen.

Lakes (and at a lesser extent rivers) are the main inland aquatic environments that have been photochemically characterized [1]. In this work, we studied the photochemistry of paddy-field water, assessing the formation quantum yields of PPRIs by using suitable probe compounds. The considered paddies were located in the province of Vercelli (Piedmont region, NW Italy), an important agricultural area in which over 90% of the total Italian rice is grown.

The photochemical parameters of paddy water were used as input data for the APEX software (*Aqueous Photochemistry of Environmentally-occurring Xenobiotics*), previously developed by one of us [2]. By using photoreactivity data available in the literature or measured by us, we studied the photochemistry in paddy floodwater of: (i) propanil (PRP) [3], a post-emergence contact herbicide widely used in rice cultivation; (ii) its main biotic degradation product 3,4-dichloroaniline (34DCA), and (iii) As(III) species that undergo photoinduced oxidation into less bioavailable As(V) [4]. It is interesting to compare the relative importance of photochemistry with respect to biotic degradation processes for the three species. Biodegradation would dominate in the case of As(III) and PRP, but, as far as 34DCA is concerned, photochemical reactions could play an important role in the fate of this compound in paddy water.

Acknowledgements

We acknowledge financial support from Compagnia di San Paolo (project CSTO168282 ABATEPHARM).

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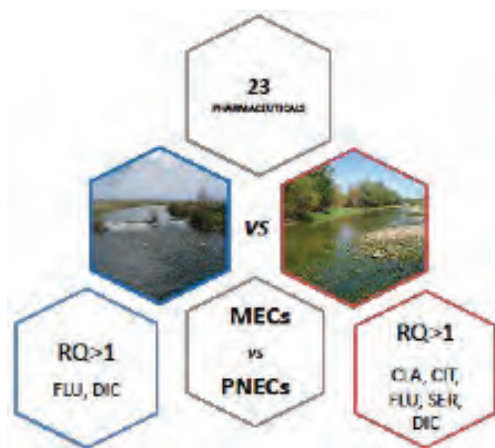
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Sustainable Development

Human Pharmaceuticals in Portuguese Rivers: The Impact of Water Scarcity in the Environmental Risk

OP Sust Devel #1

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Human pharmaceuticals represent a group of widely used chemicals that contaminate the aquatic environment [1]. Although they are found at ng L^{-1} levels, their environmental impact is of concern due to the ecotoxicological effects that these low concentrations can promote in the aquatic environment [2]. Nonetheless, all the ecotoxicological risks associated to the ubiquitous occurrence of pharmaceuticals in aquatic ecosystems are still far from known [2].

Therefore, pharmaceuticals occurrence and environmental risk assessment were assessed in Portuguese surface waters, evaluating the impact of wastewater treatment plants (WWTPs) and river flow rates. Twenty three pharmaceuticals from 6 therapeutic groups, including metabolites and 1 transformation product, were analysed in 72 samples collected from 20 different sites, upstream and downstream the selected WWTPs, in two different seasons. Analysis was performed by solid phase extraction followed by liquid chromatography coupled to tandem mass spectroscopy.

Pharmaceuticals were detected in 27.8% of the samples. Selective serotonin reuptake inhibitors (SSRIs), anti-inflammatories and antibiotics presented the highest detection frequencies (27.8, 23.6 and 23.6%, respectively) and average concentrations (37.9, 36.1 and 33.5 ng L^{-1} , respectively). When assessing the impact of WWTPs, an increase of 21.4% in the average

concentrations was observed in the samples located downstream these facilities, when compared with the upstream samples [3].

Increased detection frequencies and concentrations were observed at lower flow rates, both when comparing summer and winter campaigns and by evaluating the different rivers.

Risk quotients (RQs) higher than one were found for two pharmaceuticals, concerning two trophic levels. However, since Iberian rivers are highly influenced by water scarcity, in drought periods, the flow rates in these rivers can decrease at least ten times from the lowest value observed in the sampling campaigns. In these conditions, RQs higher than 1 would be observed for 5 pharmaceuticals, additionally, all the detected pharmaceuticals (11) would present RQs higher than 0.1.

These results emphasize that the river flow rate represents an important parameter influencing pharmaceuticals concentrations, highlighting the ecotoxicological pressure, especially due to water scarcity in drought periods. This should be a priority issue in the environmental policies for minimizing its impact in the aquatic environment.

Acknowledgements

This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013 and through the post-PhD fellowship granted to L.J.G. Silva (SFRH/BPD/62877/2009). The authors are also grateful to the Laboratory of Mass Spectrometry (LEM) of the Node UC integrated in the National Mass Spectrometry Network (RNEM) of Portugal, for the MS analysis, and to Fátima Nunes for all the assistanceP.

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Ultrafine Particles in Ambient Air of Metropolitan Area of Porto: Levels and Risk Assessment

OP Sust Devel #2

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Overwhelming scientific evidence has shown that exposure to ambient particulate matter (such as PM_{10} or $PM_{2.5}$) is associated with increased mortality rates, in particular from cardiovascular and respiratory disease [1]. In the last years the focus has shifted towards ultrafine particles (UFP; i.e. particles <100 nm). Unlike larger particles, UFP can cause adverse health effects even at low mass concentrations because of their high number concentrations, high specific surface area, and ability to penetrate into the interstitial spaces of the lungs [2]. UFP originate from both natural and anthropogenic sources; emissions from vehicular traffic are the most significant source in urban areas [2], though the existent data is far from comprehensive. The regulatory aspect of UFP has not been addressed yet, with the ongoing discussion over the most suitable metric; however, the need to establish network of monitoring stations has been emphasized [1, 2]. Thus this work aimed to assess UFP levels in ambient air of urban zones and to estimate the risks for the respective population.

Sampling was conducted during three weeks of May-June 2015 at 4 sites situated in Metropolitan area of Porto: road site (US1), and background urban (US2-US4). UFP number concentrations in size range $0.02-1 \mu m$ were measured by condensation particle counters – TSI P-Trak™ using an intake flow of $0.7 L min^{-1}$ and UFP logging interval of 60 s. Meteorological parameters and outdoor pollutants (PM_{10} , $PM_{2.5}$, O_3 , and NO_2) were also registered; traffic density in streets surrounding

each site was recorded. UFP dose rates (from inhalation exposure) were estimated according to previous methodology [3].

Over the sampling period levels of all pollutants (PM_{10} , $PM_{2.5}$, O_3 , NO_2) were in compliance with European legislation [4]. UFP (range $1.6 \times 10^3 - 51.4 \times 10^3 \# cm^{-3}$ across all sites) were the highest (2–4 times) at US1 (median of $20.0 \times 10^3 \# cm^{-3}$), which exhibited the highest traffic density (906–1842 vehicles h^{-1}); vehicular traffic and local emissions were the main identified the main sources of UFP. Inhalation dose rates of UFP due to outdoor activities were estimated for 6 different age categories of adults (16 to <21 yrs. up to <70 yrs). Overall, dose rates ranged $1.12-5.03 \times 10^5 \# kg^{-1}$, at US1 being up to 4 times higher than at other sites (mostly due to higher UFP levels). The respective dose rates increased (3.8–4.2 times) if people conducted exercising (running, biking). It is though necessary to remark that the respective UFP inhalation doses were estimated for outdoor exposure only, which represents up to 15% of the total daily time. Therefore, characterization of the indoor exposures to UFP is of utmost importance.

Acknowledgements

This work was supported by European Union (FEDER funds through COMPETE) and National Funds (Fundação para a Ciência e Tecnologia) through projects UID/EQU/00511/2013-LEPABE UID/QUI/50006/2013, POCI-01-0145-FEDER-007265 and POCI-01-0145-FEDER-006939, by the FCT/MEC with national funds and co-funded by FEDER in the scope of the P2020 Partnership Agreement. Additional support was provided by FCT through fellowship SFRH/BPD/105100/2014.

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LCA Methodology: A Case Study of the Industrial Production of Terephthalic Acid from Renewable Sources

OP Sust Devel #3

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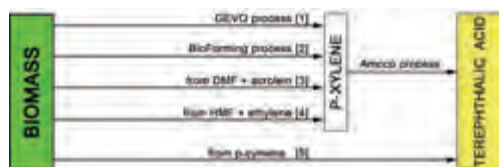


Figure 1 - Representation of alternative routes for the production of bio-TA

The scope of the present study is to investigate the environmental sustainability of different routes of terephthalic acid (TA) production from renewable sources in order to identify which of the selected pathways has the lowest environmental load. The comparison is between five different production processes illustrated in Figure 1, and described below:

- GEVO's process: isobutanol from the fermentation of biomass is converted into hydrocarbons, iso-octene and p-xylene [1];
- BioForming's process: it is able to convert sugars derived from biomass into a product similar to that obtained through the typical petroleum reforming [2];
- TA from DMF and acrolein: it consists in a Diels-Alder reaction between the DMF (2,5-dimethylfuran) and the acrolein to obtain p-xylene [3];
- TA from HMF and ethylene: it involves the production of HMF (5-hydroxymethylfurfural) from starch, its conversion to DMF and the Diels-Alder reaction with ethylene to obtain p-xylene [4];
- Alternative pathway from p-cymene: it is given the possibility of obtaining bio-TA from p-cymene using O₂ as an oxidizing agent in the presence of a catalyst [5].

The first two routes are already set at industrial level, while the others are still in the development phase. In order to estimate the energy requirements of the scenarios, a simulation of the chemical processes was carried out using ChemCad software. Among those investigated, four ways provide for the formation of p-xylene, subsequently oxidized to terephthalic acid through the Amoco's process,

while the last is proposed as an alternative because it uses p-cymene as a precursor to obtain the molecule of interest.

In order to conduct the comparison the methodology LCA (Life Cycle Assessment) has been used as a scientific tool of analysis and evaluation of the potential impacts of each scenarios. LCA is a method of analysis which allows the evaluation of the environmental weights associated with the entire life cycle of a product or a process. The LCA is standardized by ISO 14040 and 14044 and is divided into four conceptual stages: goal and scope definition, life cycle inventory, impact assessment and interpretation of results. In the first phase the objectives of the study must be defined, identifying the boundaries of the system and the functional unit. In the second phase data are collected and a model of the system is built using materials and energy balances in input and output from the system under consideration. Once defined balances and built the model, through the software SimaPro (v. 8.0.5.13) and the database Ecoinvent (v. 3.1) we proceed with the evaluation of the potential environmental impact of emissions and consumption of resources. The last phase, interpretation of results, is transversal respect to the others, because it could be necessary to suggest changes and improvements at every level of the study, from the design stage to that of calculations: LCA methodology is an iterative process and the results must be interpreted at the end of each step.

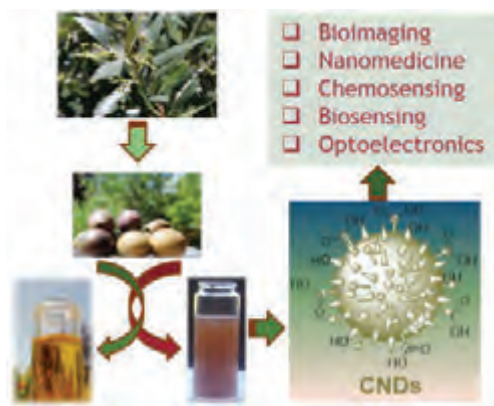
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How an Environmental Issue Could Turn Into Useful High-valued Products: The Olive Mill Wastewater Case

OP Sust Devel #4

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Olive oil production is a tremendously important agro-industrial activity in the Mediterranean region. Portugal is a significant contributor, with an average production of 76 kton/year of olive oil (2010-2015 period) and exports exceeding 350 million euros in 2014 [1]. Olive oil is typically extracted from olive paste by two main processes: batch press and continuous centrifugation. Both processes generate considerable amounts of aqueous waste. Depending on the particular process used, 200-1600 L of olive mill wastewater (OMWW) is produced per ton of processed olives [2]. The OMWW exhibits very low biodegradability parameters which pose serious issues for its treatment. The effluent toxicity/phytotoxicity and its poor biodegradability are normally attributed to the presence of high levels of phenol- and polyphenol-type compounds which are toxic to most microorganisms. Over the last 70 years, several isolated or combined treatment methodologies, including physicochemical treatment (e.g. membrane filtration, coagulation-flocculation), aerobic and anaerobic digestion, co-digestion, combined physicochemical and biological methods and oxidation/advanced oxidation processes (e.g. ozone/H₂O₂, UV/H₂O₂, Fenton and photo-Fenton) have been proposed [2,3]. Apparently, however, none of the researched methods or technological processes developed so far has found a widespread application, probably due to unaffordable economical costs.

In this communication, we will address our proposal to deal with this complex effluent. It will be shown that highly fluorescent carbon nanodots (CNDs) can be obtained directly from OMWW in

excellent yields following expedite and sustainable hydrothermal processes with minimum post-processing.

CNDs are a very recent class of spherical-shaped nanosized carbon materials that have found widespread application in fluorescent bioimaging and nanomedicine, chemo/biosensing, photocatalysis and optoelectronics, owing to their unique properties, which include tunable photoluminescence, outstanding photostability and negligible cytotoxicity [4].

The carbon nanoparticles were obtained under a variety of conditions from OMWW collected in a mill operating by a two-phase centrifugation system. Several operation variables (*viz.* reaction temperature, reactor dwell time and amount/nature of additives) were investigated, allowing the establishment of certain processing-structure-property correlations. The as-prepared CNDs display a remarkable quantum yield ($F_F = 0.3-0.4$), a pH-responsive luminescence (pH 1-12), and an extremely high photostability. Preliminary results on the synthesis of chiral CNDs will also be presented.

The structural characteristics and luminescent properties of CNDs, allied to their easy synthesis, carbon source affordability and excellent dispersion in aqueous solutions, render them with unique capabilities to be used in several current and emerging technological applications.

Acknowledgements

We thank Instituto Politécnico de Lisboa (Projects IPL/2016/NANOLIVE/ISEL and IPL/2017/NANOCHIRAL/ISEL) and FCT/MCTES (UID/QUI/00616/2013) for financial support.

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Environmental Safety

The Predicted Concentrations of Antibiotics in STPs in Portugal- A Tool for the Microbial Community Resistance Research

OP Env Safe #1

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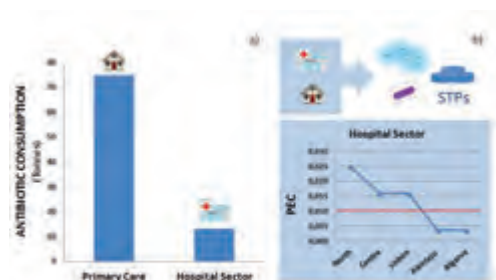


Figure 1. Antibiotic use in Portugal in 2015: a) Consumption in primary care and hospital sector (amount in tonnes); b) Predicted Environmental Concentrations (PEC, µg/L/day) in STPs in different regions of Portugal.

Human antibiotic medicines can accelerate the evolution and spread of antibiotic-resistant bacteria in the microbial community of sewage treatment plans (STPs). Nonetheless, no regulatory system considers such risk. Several studies have demonstrated that antibiotic concentrations below the Minimal Inhibitory Concentrations (MICs) can select for resistant bacteria [1]. Therefore, knowledge about antibiotics used in primary health care and hospital sectors, which may reach the STPs, is essential.

Main objective

Considering the use of different antibiotic molecules in the two main health sectors - primary care and hospitals, the antibiotic exposure in the STPs in different regions of Portugal were assessed.

Material and methods

The most recent official Portuguese antibiotic data available (2015) in health sectors, primary care and hospitals, was used. Data from the 46 public Portuguese hospital centres considered were categorized according to the mainland Portuguese regions: North, Centre, Lisbon, Alentejo and Algarve regions.

Environmental exposures were estimated by Predicted Environmental Concentrations (PEC), in primary care [2] and in hospital [3] sectors.

Results

The total amount of crude antibiotics used in 2015, in primary care and hospital sectors, was 88 tonnes.

Only 15% (about 13 tonnes) corresponded to hospital consumption, across all regions (Figure 1a). In this sector, antibiotic consumption ranged from 0.6 to 4 tonnes in the five regions of Portugal analysed.

The predicted environmental exposure was accentuated in STPs at North, Centre and Lisbon regions, with PEC values above the threshold (0.01 mg/L/day) (Figure 1b).

Considering both sectors, antibiotics that presented values above the threshold (ranging from 1.1 to 55.8 mg/L/day) are listed in descending order: 1) amoxicillin; 2) ciprofloxacin; 3) flucloxacillin; 4) clarithromycin; 5) sulfametoxazol; 6) fosfomycin; 7) cefuroxime; 8) azithromycin; 9) cefradine; and 10) levofloxacin.

In the hospital sector, the ten most consumed antibiotics were: 1) piperacillin 2) cefazoline 3) ceftriaxone, 4) meropenem, 5) vancomycin, 6) sulfametoxazol, 7) ampicillin, 8) cefoxitin 9) flucloxacillin and 10) cefuroxime. Piperacillin presented the higher PEC value (0.029 mg/L/day), followed by amoxicillin (0.011 mg/L/day), both exceeding the threshold considered by regulatory entities in the scope of medicines environmental risk assessment.

Conclusion

STPs exposure must be assessed in different regions of Portugal in order to understand the potential risk of antibiotic amounts reaching this compartment. Hospital sector represent a specific risk by adding *hospital-specific compounds* (e.g. piperacillin). In this context the hospital sector should be pointed out as a hotspot for some of these STPs which in our predicted assessed concentrations, are more accentuated in the North Centre and Lisbon regions.

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LC/MS Determination of Anti-TB Drugs and Their Metabolites in Human Plasma for Optimization Therapeutic Treatment of Tuberculosis

OP Env Safe #2

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Therapeutic drug monitoring (TDM) is the process of obtaining the serum concentration of a medication and modifying the dose based on the results, with the intention of optimizing therapeutic benefits, while minimizing the risk of side effects or toxicity. Today tuberculosis remains a major global public health problem. According to World Health Organization's typical initial treatment for tuberculosis includes a combination four antitubercular (anti-TB) drugs – isoniazid, rifampicin, pyrazinamide and ethambutol. Treatment for these diseases are long-term and the individual pharmacokinetic variation, drug–drug interactions or non-adherence may introduce sub-therapeutic exposure or toxicity. The application of TDM for patients with MDR-TB can be used to ensure efficiency and avoid toxicity. So, the development of sensitive, reliable and facile analytical method for determination of these drugs in plasma samples becomes necessary.

In this study a rapid and sensitive liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the simultaneous determination of four anti-TB drugs (isoniazid, pyrazinamide, ethambutol and rifampicin) and their active metabolites in human plasma was developed. The drugs were separated by using reversed-phase HPLC and a hydrophilic interaction LC (HILIC). Detection was carried out in multiple reaction-monitoring (MRM) mode. The conditions for

human plasma preparation for HPLC/MS analysis, including the protein precipitation with ACN were chosen allowing for high sample throughput. The matrix effects on the separation and ionization anti-TB were estimated by post-extraction additives method. The method was validated by evaluating its selectivity, sensitivity, linearity, accuracy and precision. The stability of anti-TB drugs during the analysis (in autosampler at 1 and 12 hours) and at storage conditions (3 cycles of freeze-thaw) was studied. The developed method was successfully applied to the identification and quantitation of anti-TB drugs in patients with TB treatment.

To identify potential biomarkers for diagnosis of TB, we applied state-of-the-art technology for metabolomics profiling of plasma samples from TB patients using developed LC/MS/MS method followed by multi- and univariate statistical analyses. Multiple logistic regression analysis of metabolites was calculated to determine the suitable biomarker group that allows the efficient differentiation of patients with TB active from the control subjects.

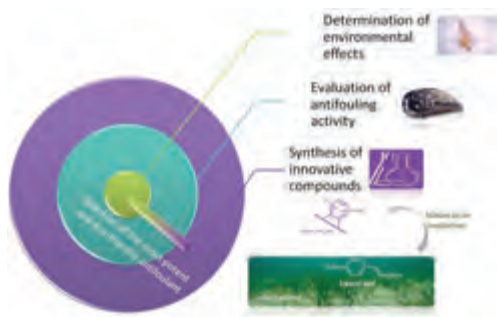
Acknowledgements

This work was supported financially by grant of Russian foundation for basic research no [a. 16-03-00791-a](#). Authors thank Research Centre “Chemical Analysis and Materials” of Research Park Saint-Petersburg State University for technical support.

Synthesis and Environmental Fate Evaluation of New Nature-inspired Antifouling Compounds

OP Env Safe #3

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The continued release of antifouling substances to the environment, is leading to harmful side effects on ecosystems. Developing alternative environmentally friendly and non-toxic antifouling substances is an urgent demand.

Natural products have emerged as antifouling agents with low or nontoxic effects to the environment [1]. However, natural products are often structurally too complex to be synthesized on a large scale. Besides, the yields are generally poor, which hampers their further development as antifouling agents.

In our group Nature-inspired compounds have been synthesized and some were recently shown to have promising antifouling activity against the settlement of *Mytilus galloprovincialis* plantigrades [2]. However, only biocides that show low ecotoxicity and rapid degradation in seawater will survive the close regulatory scrutiny to which they are being increasingly subjected.

Nine promising compounds were selected for ecotoxicity studies on *Artemia salina* and five compounds showed no toxicity to this nontarget species (< 10% mortality at 50 and 250 μ M). In addition, the luminescent *Vibrio fischeri* bacteria test (ISO 11348-2), one of the three basic level tests proposed and included in the EU hazard assessment of substances and European Eco-label, was performed for these five compounds and again no toxicity was found.

Following, KOWWINTM v1.68 developed by Syracuse Research Cooperation jointly with the Environmental Protection Agency (EPA) was used for *in silico* calculation of log Kow (octanol-water partition coefficient) in order to evaluate the bioaccumulation potential of the most promising compounds and biomagnification through the food chain. In contrast to commercial AF agents, namely the toxic agent tributyltin oxide (TBTO), Sea-nine and ECONEA, four of the synthesized compounds showed a log Kow lower than 3, indicating their low bioaccumulation potential.

The evaluation of toxicological and environmental fate parameters allowed to assess early into the antifouling discovery process the potential of our nature-inspired synthetic compounds as new eco-friendly antifouling alternatives.

Acknowledgements

Support for this work was provided by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT – Foundation for Science and Technology and European Regional Development Fund (ERDF), in the framework of the programme PT2020 and under the project PTDC/AAG-TEC/0739/2014 supported through national funds provided by Fundação da Ciência e Tecnologia (FCT/MCTES, PIDDAC) and European Regional Development Fund (ERDF) through the COMPETE – Programa Operacional Factores de Competitividade (POFC) programme (POCI-01-0145-FEDER-016793) and Reforçar a Investigação, o Desenvolvimento Tecnológico e a Inovação (RIDTI, Project 9471). JRA also acknowledges FCT for the postdoctoral scholarship (SFRH/BPD/87416/2012).

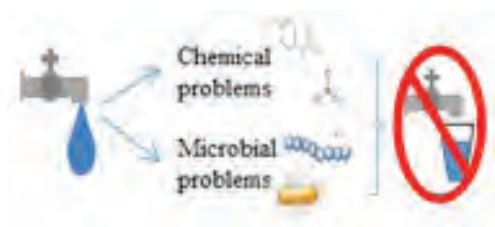
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Effects of Emerging Contaminants Detected in Drinking Water on Bacteria Tolerance to Antimicrobials

OP Env Safe #4

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The access to safe drinking water (DW) is a major concern worldwide. The consumption of contaminated water has been responsible for some waterborne diseases and may constitute a risk for human health. Therefore, several barriers are used in drinking water distribution systems (DWDS) to avoid chemical and biological water contamination and protect the consumer's health. Nevertheless, some emerging contaminants such as pharmaceuticals and personal care products (PPCPs) have been detected in DW [1]. Also, the presence of biofilms in the pipe walls is unavoidable, despite of the use of disinfection particularly with chlorine. Biofilms can harbour pathogenic organisms that if released to the bulk water may constitute a public health risk. Due to environmental pollution problems biofilms in DWDS can be continuously exposed to trace concentrations of different PPCPs. Nevertheless there is scarcity of information about the consequences of the presence of PPCPs in DW microorganisms. It is known that the presence of antibiotics and antimicrobial agents in the environment may be responsible for the selection and spread of antibiotic resistance [2]. However, to our knowledge, there is no information on the effects of the continuous exposure to non-antibiotics contaminants. Therefore, the aim of this study was to understand the effects of the continuous exposure to trace levels of PPCPs on bacterial tolerance to antibiotics and sodium hypochlorite (NaOCl).

Stenotrophomonas maltophilia, an emerging pathogen previously isolated from a DWDS in Braga (Portugal) [3], was used in this work. Eight PPCPs were selected: 3 non-steroidal anti-inflammatory drugs (antipyrine-ANTP, diclofenac - DCF and ibuprofen - IBP), 2 musks fragrances (galaxolide - GAL and tonalide - TON), 1 neuro-active drug

(carbamazepine - CBZ), 1 lipid regulator (clofibrilic acid - CA) and 1 veterinary antibiotic (tylosin - TY). *S. maltophilia* was exposed to PPCPs at levels detected in DWDS [1] for 26 d. Afterwards, bacterial and biofilm tolerance to antibiotics and NaOCl was evaluated.

The presence of PPCPs did not cause significant changes in bacterial tolerance to antibiotics independently of the compound tested. Nevertheless, the prolonged exposure to CBZ slightly increased *S. maltophilia* tolerance to NaOCl, as after exposure to CBZ a higher concentrations of NaOCl (4.5-6 mg/L) was needed to completely inactivate bacterial growth. The ability of *S. maltophilia* to form biofilms increased after the exposure to the mixture of the 8 PPCPs. These biofilms were also more resistant to removal by NaOCl.

In conclusion, the exposure to PPCPs can alter bacteria and biofilm tolerance to NaOCl. However, a threatening impact on bacterial resistance was not observed.

Acknowledgements

This work was the result of the project: POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the ERDF and grants attributed by FCT to Inês Gomes (SFRH/BD/103810/2014) and Lúcia Simões (SFRH/BPD/81982/2011).

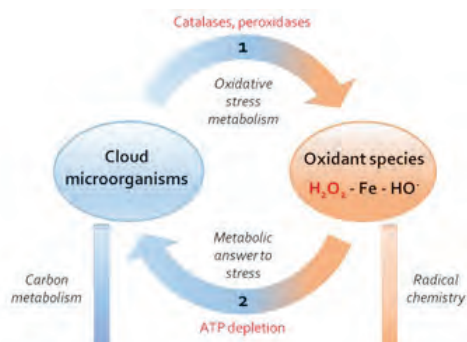
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H₂O₂ Modulates the Energetic Metabolism of the Cloud Microbiome

OP Env Safe #5

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Chemical reactions in clouds lead to oxidation processes driven by radicals (mainly HO[•], NO₃[•] or HO₂[•]) or strong oxidants such as H₂O₂, O₃, nitrate and nitrite. Among those species, hydrogen peroxide plays a central role in the cloud chemistry by driving its oxidant capacity. In cloud droplets, H₂O₂ is transformed by microorganisms which are metabolically active [1]. Biological activity can therefore impact the cloud oxidant capacity. The present article aims at highlighting the interactions between H₂O₂ and microorganisms within the cloud system.

First, experiments were performed with selected strains studied as reference isolated from clouds in microcosms designed to mimic the cloud chemical composition, including the presence of light and iron. Biotic and abiotic degradation rates of H₂O₂ were measured and results showed that biodegradation was the most efficient process together with photo-Fenton process. H₂O₂ strongly impacted the microbial energetic state as shown by adenosine triphosphate (ATP) measurements

in the presence and absence of H₂O₂. This ATP depletion was not due to the loss of cell viability. Secondly, correlation studies were performed based on real cloud measurements from 37 clouds samples collected at the puy de Dôme station (1465 m a.s.l., France) [2]. The results supported a strong correlation between ATP and H₂O₂ concentrations and confirmed that H₂O₂ modulates the energetic metabolism of the cloud microbiome. The modulation of microbial metabolism by H₂O₂ concentration could thus impact cloud chemistry, in particular the biotransformation rates of carbon compounds and consequently can perturb the way the cloud system is modifying the global atmospheric chemistry [3].

Acknowledgements

N. Wirgot is a recipient of a PhD fellowship from the MESR (French government).

Part of this work was supported by the french ANR program BIOCAP. The authors are very grateful to the OPGC/LaMP staff for collecting the cloud samples at the puy de Dôme station, see the database of cloud biological and chemical composition www.obs.univ-bpclermont.fr/SO/beam/index.php.

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PLASMAQUANT® MS a new potential tool for Iron Isotope Ratios determination in Biological Samples

OP Env Safe #6

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To assess iron bioavailability, iron isotopes ratios were conducted in biological samples using the PlasmaQuant® MS. Optimization factors related to precision and accuracy of iron isotope ratios were optimized. Polyatomic ions (e.g., ArN^+ , ArO^+ , ArOH^+) and matrix polyatomic interferences (e.g., CaO and CaOH) were identified and significantly reduced using a “cool plasma” and hydrogen as a reactive gas in the integrated Collision Reaction Cell (iCRC) [1]. Isobaric interferences (e.g., $^{54}\text{Cr}^+$ on $^{54}\text{Fe}^+$ and $^{58}\text{Ni}^+$ on $^{58}\text{Fe}^+$) were minimized by

equation correction and platinum sampler cones. Fe isotopic compositions of the samples were corrected for instrumental mass bias by the standard-sample bracketing method using the certified reference standard IRMM-014, after mineralization of the biological samples by microwave digestion. Precisions on the order of 0.05–0.20 (% RSD), 0.09–0.25 (% RSD), 0.30–0.40 (% RSD) and 0.12–0.26 (% RSD) were obtained for $^{54}\text{Fe}/^{56}\text{Fe}$, $^{57}\text{Fe}/^{56}\text{Fe}$, $^{58}\text{Fe}/^{56}\text{Fe}$ and $^{54}\text{Fe}/^{57}\text{Fe}$, respectively, in biological samples for ten replicates measurements. Such precision demonstrated that PlasmaQuant® MS, with its superior sensitivity, half argon-consumption, and its innovative interference management system, iCRC, it was able to eliminate or drastically reduce interferences, without the need of chemical samples purification. Such achievements allow iron isotope ratios determination in biological samples with precision between 0.05–0.40 (%RSD) for a low resolution collision/reaction ICP-MS system.

Acknowledgements

The authors would like to thank Professor Doutor Agostinho Almeida from FFUP to provide Human Whole Blood Samples for posterior analysis (aalmeida@ff.up.pt).

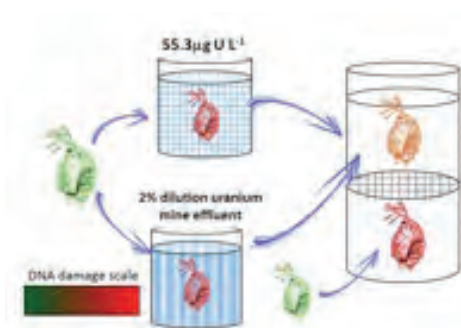
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RIBE Assessed at an Inter-organismic Level in *Daphnia magna* Exposed to Low Doses of Uranium Mine Effluent and Waterborne Uranium

OP Env Safe #7

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RIBE (radiation induced bystander effect) is a one-way stress communication, in which non-exposed cells/organisms display responses (usually injuries) that result from the exposure of others to ionizing radiation. In the last decade several studies verified this phenomenon at an inter-organismic level in fish and small mammals [1–4] as well. However, there is still a knowledge gap regarding invertebrates and exposures to environmental samples rich in radionuclides. As so, aimed in perceiving if this phenomenon has impacts in the field of environmental risk assessment (ERA) concerning radionuclide's rich-wastewaters [5], we designed this study, in which *Daphnia magna* (<24h and 5d old) were exposed for 48h to a 2% dilution of a uranium mine effluent (UME) and a matching dose of waterborne uranium (WU) (55.3mgL⁻¹). Then organisms cohabitated (24 and 48h) in a clean medium with non-exposed neonates. Our

data clearly revealed the occurrence of RIBE at an interorganismic-level in *D. magna*, which in the ecological relevant UME exposure were less pronounced. Different rates of DNA damage recovery of exposed daphnids were also observed as well as an age and time-dependent variability in the induction of RIBE. The data gathered bring some valuable new worthwhile points for the not unanimous discussion of RIBE relevance for ERA.

Acknowledgements

FCT, through National Funds, provided financial support to Joana Lourenço through Post-Doc grant (SFRH/BPD/92554/2013). This research was also partially supported by the Strategic Funding UID/Multi/04423/2013 and UID/AMB/50017/2013 through COMPETE and national funds provided by FCT and ERDF (PT2020). The authors would like to thanks to EDM for the collaboration given for this work.

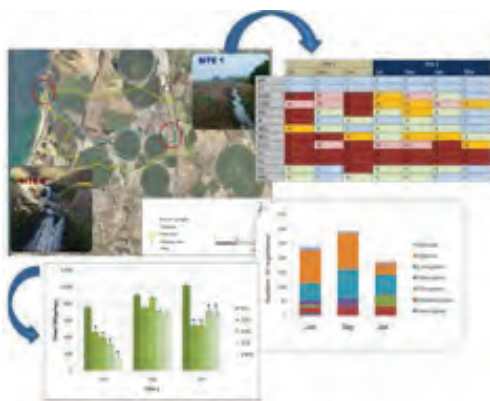
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Ecotoxicological Tools Used in the Assessment of the Ecological Status of Freshwater Systems: a Case-study of the Temporary River Brejo do Cagarrão (South of Portugal)

OP Env Safe #8

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At the present time, the global change scenario, which entails with the appearance of new stressors, namely changes of climatic patterns (including drought and temperature increase) or of economic, social, and demographic pressures, may influence negatively the quality of freshwater systems incrementing its scarcity and degradability [1]. All these new stressors and deviations impose new challenges for water management, which remain one of the key for the next decades. Consequently, the implementation of appropriate management actions for each type of freshwater ecosystem requires periodic reviews of water policies and of monitoring strategies. Moreover, at the present, some of these freshwater ecosystems, namely temporary water streams, remain among the least studied worldwide [2], with no parameters and standard values to use as reference for their good chemical and ecological status. In order to manage this kind of water body appropriately, increment its quality status and stop the strong decrease of its biodiversity, it is essential to understand its specific dynamic, and determine whose parameters are most sensitive to pollution in different scenarios. The aim of this study was to evaluate the biological responses to water pollution induced by agricultural activities in a temporary river, Brejo de Cagarrão (located in Mira River Basin, South of Portugal, a semi-arid region where the agricultural is one of the main activities), at two locations, Site 1 (source) and 2 (mouth of the river),

considering: (i) physical and chemical characterization of the water column; (ii) quantification of pesticides; (iii) evaluation of benthic macroinvertebrates communities; and (iv) ecotoxicological assessment. Considering the physicochemical analysis, the results showed high levels of organic matter and nutrients, mainly in the dry period. Site 1 was classified as ‘extremely contaminated’ being the nutrients and the organic matter parameters the responsible for this classification. The water from Site 2 was classified as ‘very contaminated’ to ‘extremely contaminated’, due to phosphorus and organic matter indicators. Arsenic and chlorides achieved concentrations characteristic of ‘extremely contaminated’ freshwaters, during all the period of the study. In general, the amounts of pesticides were low, with the exception of July (Site 2), with a total amount of $17712.88 \text{ ng L}^{-1}$ ($> 500 \text{ ng L}^{-1}$; ECC, 1998). The main pesticides detected were terbuthylazine, 2-methyl-chlorophenoxyacetic (MCPA), bentazone, mecoprop and metolachlor. The benthic macroinvertebrates analysis showed low levels of communities’ diversity, with populations dominated by groups resistant to high organic matter load, mainly the Chironomidae family. On the other hand, results from the ecotoxicological assessment showed that there was a marked decrease of the *D. magna* reproduction when exposed to the samples. This fact may be correlated to the amounts of pesticides quantified. The source of the river was more contaminated than its mouth, which was highlighted by the biological assessment. This integrative approach evidence the importance of a biological evaluation, that covers the interactions between the ecosystem’s species and the different types of pollutants.

Acknowledgements

This work was supported by the Portuguese Science Foundation (FCT) through the grant UID/MAR/00350/2013 attributed to CIMA of the University of Algarve.

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Uranium Mining Legacy Sites: Genetic Effects of Metals and Low-dose Radiation in Farm Animals Exposed to Contaminated Water and Foodstuffs

OP Env Safe #9

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Many uranium mines were left abandoned with no remediation after a severe drop of uranium prices worldwide, creating the so called “legacy” sites that are very difficult to remediate [1]. In the Cunha Baixa uranium mine (Viseu, Portugal), acidic waters re-emerge in wells downstream, and can expose the population, breeding cattle and other domestic animals to radiation and also to chemical toxicity from the dissolved metals [2]. Also, the clandestine use of these waters for irrigation may facilitate the transfer of contaminants throughout the food chain [2].

This study aimed at evaluating genetic effects caused by the exposure to contaminated water and foodstuffs, in rabbits raised in the Cunha Baixa village. To do so, we evaluated the expression profile of oncogenes and genes known to be involved in response DNA damage in 3 different organs. A significant induction of some genes was observed right after 1 month of exposure, in the liver (CDKN1A and RB) and kidneys (FGF2 and RB) of exposed rabbits. After 3 months of exposure, it was possible to observe an overexpression of ATM, GADD45A and SET genes

in the lungs and FGF2, RB and SET in the kidney. Problems in the analysis of the liver after 3 months of exposure have been encountered, probably due to the presence of contaminants in this organ. The results obtained so far indicate that: 1) genetic effects can be seen right after 1 month of exposure; 2) there are differences in the gene expression profile between organs, probably due to different susceptibilities and bioaccumulation patterns; 3) for short term exposures the kidney is probably the best organ to analyze due to a higher fraction of responding genes; 4) the tumour suppressor gene RB is the best gene for short term exposures and the oncogene SET is for now the best gene for long term exposures, since their induction was observed for both liver and kidneys and lungs and kidneys, respectively; 6) rabbits seem to be a good bioindicator species; 5) data suggest potential risks for the local population of suffering genetic alterations. The bioaccumulation of metals and radionuclides in organs and also in vegetables is still being analyzed.

Acknowledgements

This work was supported by UID/AMB/50017/2013 project, through COMPETE and National Funds awarded by FCT. FCT, through National Funds, provided financial support to Joana Lourenço and Sérgio Marques through Post-Doc grants (SFRH/BPD/92554/2013 and SFRH/BPD/112803/2015). This research was also partially supported by the Strategic Funding UID/ Multi/04423/2013 through national funds provided by FCT and ERDF (PT2020). The authors would like to thank EDM for the collaboration given for this work.

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Ecotoxicity Assessment of Cadmium Using Different Life Stages of the Terrestrial Gastropod *Helix aspersa aspersa*

OP Env Safe #10

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The main aim of this work is to present the possibility of using a cosmopolitan terrestrial organism and its two different life stages for evaluating possible effect of environmental contaminants. The organism used in this study is a pulmonate gastropod *Helix aspersa aspersa* (syn. *Cantareus aspersus* or *Cornu aspersum*), or the brown garden snail in common. For this study, we have chosen two different life stages of this snail: eggs and juvenile individuals. The evaluated substance was cadmium chloride (CdCl_2). There were three main parts of the study: standard growth inhibition test with juvenile snails, hatching success test with the eggs [1], embryotoxicity test. In the first case, the juvenile snails were exposed to different concentrations of cadmium (0 – 500 mg/l) and the toxicant was spiked onto a filter paper on the bottom of the breeding boxes. This test lasted for 28 days and the monitored endpoints were: mass and shell diameter. Second part of study - the exposition of eggs was performed in small Petri dishes with a filter paper on the bottom and the concentrations of cadmium were the same as in the first case. In this case test lasted for 14 days and the endpoint was the percentage of successfully hatched snails. In the last case, we observed the effect of cadmium in a low concentration (6 mg/l) on the embryos in

different time periods from the start of the test. This test lasted also for 14 days and the endpoints were: size and state of the embryo, morphological and physiological changes.

The results showed significant differences between the sensitivity of eggs and juvenile snails and also negative effects of cadmium chloride on the development of the snail embryos. The present study summarizes a scale of different endpoints, which could help for better understanding the effects of environmental toxicants.

The present study summarizes a scale of different endpoints, which could help for better understanding the effects of toxicants on environment.

Acknowledgements

This study was supported by project No. FCH-S-17-4766 from the Ministry of Education, Youth and Sports of the Czech.

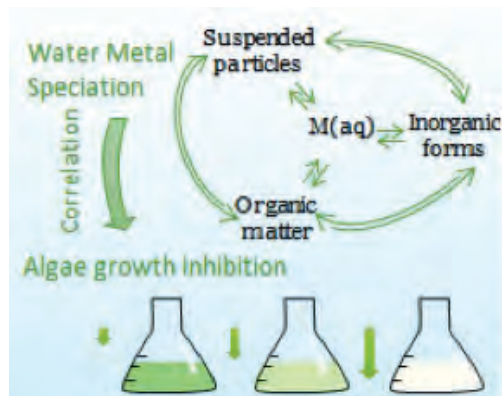
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Additive Inhibitory Free Metal Ion Concentration Index: A New Method for Assessing Multi-metal Contamination Risk on Freshwaters

OP Env Safe #11

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In regulatory applications, metal mixture toxicity has generally been modelled by toxic unit or other additive approaches that are based on water-exposure concentrations [1]. Data reviews [2, 3] have shown that additive approaches based on dissolved-metal concentrations are not always sufficient in predicting mixture toxicity. Thus, the main aim of the present work was to develop a multi-metal model framework that consider chemical and physiological interactions when multiple metals are present. For this purpose, the impact of freshwaters containing multiple metals (Cd, Cr, Cu, Ni, Pb and Zn) on the chronic toxicity (72h) to the alga *Pseudokirchneriella subcapitata* was evaluated and the observed toxicity results were compared to the total and free metal concentration of each sample. Water and pore waters were collected in two zones of abandoned mines of northern Portugal, wherein metals were the sole or dominant contaminants. To characterize the stream samples, the pH, redox potential (Eh), total metal (Cd, Cr, Cu, Fe, Pb, Ni and Zn), total inorganic (chlorides, sulphates, ammonium and nitrates) ligands and total organic and inorganic carbon concentrations were determined. The toxicity of samples was evaluated using the standard 72-h chronic alga test [4]. To evaluate the metal speciation, specific software

was used (Visual MINTEQ; Stockholm humic acid model was used). Multivariate analyses were conducted using Principal Component Analyses in MatLab software coupled with the PLS Toolbox for MatLab from Eigenvector Research Inc.

With this work, it was possible to demonstrate that the toxic effects of the metals on the alga *P. subcapitata* are better related to the free metal concentration than to the total metal concentration. The results demonstrated that the toxicity of fresh water containing multiple metals (Cd and/or Cu and/or Pb and/or Zn) to *P. subcapitata* was additive when expressed as the free metal ion concentration, especially when different toxicity parameters (such as, 72h-IC₁₀, 72h-IC₂₅, 72h-IC₅₀ and 72h-IC₇₅) were employed. These data support the idea that concentration addition based on the free metal ion can be a reliable tool for evaluating the ecological risk of natural waters containing multiple metals and can be leveraged to influence the development of future regulatory targets.

Acknowledgements

This work was performed in the framework of the financing with references LAQV (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265) and UID/BIO/04469/2013-POCI-01-0145FEDER006684 with financial support from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020 and Project RECI/BBB-EBI/0179/2012 (FCOMP-01-0124FEDER-027462).

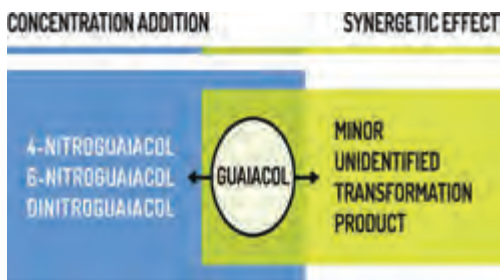
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Ecotoxicity of Biomass Burning Pollutants and Their Nitro Derivatives

OP Env Safe #12

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Guaiacol (2-methoxyphenol, GUA) is the main component of wood lignin and is essentially emitted to the atmosphere during biomass burning [1]. It is estimated that several hundred tons of GUA are annually released into the troposphere, where the compound partitions between the atmospheric gaseous and aqueous phases and undergoes various aging processes. GUA and its degradation products are then deposited onto the Earth's surface by dry deposition or precipitation. They can potentially accumulate on surface and reach high concentration locally. The transformation products of GUA are believed to be particularly toxic for living organisms, especially when nitrogen-containing reactive species are involved in the chemistry [2], resulting in the formation of nitroguaiacols (NG). However, no ecotoxicological data for GUA or NG have been reported to date.

This study presents the first ecotoxicological study of GUA and its nitrated derivatives, namely 4-nitroguaiacol (4NG), 6-nitroguaiacol (6NG) and dinitroguaiacol (DNG), and reveals their harmful potential for the ecosystem [3]. Aquatic toxicities of individual compounds, as well as of their environmentally relevant mixtures, were determined applying *Vibrio fischeri* bioluminescence acute toxicity test. Individual EC50 values range from 16.7 to 103 mg L⁻¹ after

a 30-min incubation period, which classifies all investigated compounds as "harmful" according to the European legislation. No joint actions between the four studied compounds have been observed therefore their concentration addition can be considered for ecotoxicological purposes. However, a synergistic effect between GUA and a minor unidentified first-generation product of its aqueous-phase degradation was observed and should be taken into account when assessing the reaction mixture toxicity.

These results highlight the need for further toxicological testing, including organisms of different trophic levels. Thus, besides the bioluminescent bacterium assay, the following tests have been selected: i) immobilization of *Daphnia magna*; ii) seed germination inhibition of *Trifolium repens* and *Triticum aestivum*, iii) inhibition of *Saccharomyces cerevisiae* viability, and iv) embryotoxicity of zebrafish. This ongoing investigation will allow to better evaluate the environmental hazard of guaiacol and its nitro derivatives. In addition, other compounds emitted by biomass burning such as catechol and syringol, as well as their main nitration products, will be studied.

Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0034, research core funding No. P3-0388).

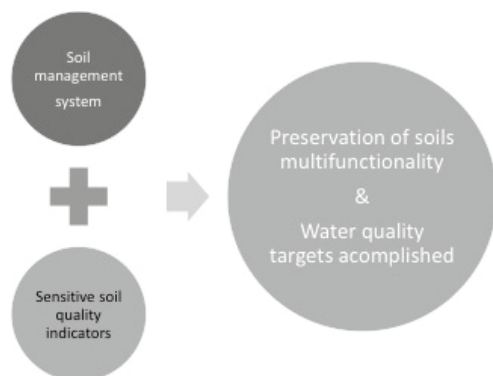
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Ecosystem Services Provided by Soils Under Different Land Uses: Implications to Water Quality

OP Env Safe #13

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Land use significantly affects key aspects of land system functioning (e.g. evapotranspiration, canopy water storage, infiltration and runoff) and the ability of biological systems to support human needs [1]. However, if properly managed, different land use types may help to support ecosystem services and to contribute for maintaining biodiversity while using local resources [2].

Agricultural activity can affect soil functions, due to point/diffuse contamination, loss of biodiversity, and soil erosion. Moreover, the quality of adjacent water bodies may be compromised. In this context, the evaluation of soil quality, by using different chemical, physical, and biological indicators is of paramount importance as part of River Basin management processes. Thus, aiming at defining a set of parameters for this evaluation, several indicators were measured in agriculture soils and compared with soils under preserved riparian vegetation in the banks of two Portuguese rivers (the Sousa River, an affluent of Douro River, and the Minho River).

Since soil is a complex system where microorganisms, invertebrates, and plant interactions determine their chemical and physical environment, biological indicators are of upmost importance when assessing soil quality, as a complement of soil physico-chemical properties. Considering this, several biological indicators were tested, such as: enzymatic activity (dehydrogenase, cellulase, and phosphatase), and nitrification and

mineralization potential [3]; OM decomposition evaluation through the litter bags test [4]; evaluation of the ability of soils to sustain an active community of soil invertebrates, through the bait-lamina test [5]. In addition, ecotoxicological endpoints were also selected, due to their importance in monitoring the effects of different management practices and assure the multifunctionality of the ecosystem. For example, tests with aquatic organisms (*V. fischeri*, algae growth inhibition test) allow to assess the retention function of soil.

Differences between agricultural and non-agricultural soils were observed in this study, considering both physical-chemical and biological indicators. Thus, data obtained allowed to understand how different management practices compromise soil quality, with possible subsequent impacts on the quality of water bodies.

Acknowledgements

This work was supported by the structural project INNOVMAR (NORTE-01-0145-FEDER-000035) within the research line (NOVELMAR/INSEAFood/ECOSERVICES), and by the Strategic Funding UID/Multi/04423/2013 (CIIMAR) and UID/AMB/50017/2013 (CESAM RU), through national funds provided by FCT (Foundation for Science and Technology) and European Regional Development Fund (ERDF), in the framework of the PT2020 Partnership Agreement. FCT, also supported the work through an individual research grant attributed to A. Cachada (SFRH/BPD/100429/2014).

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The Impact on Soil Biota of Leather from the Footwear Industry Treated with ZnO Nanomaterial: A Microcosm Study

OP Env Safe #14

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In the beginning of the century, it was forecasted that about 65 million tons of wet salted hides and skins were processed worldwide annually and 3.5 million tons of chemicals were used in leather processing (Ramasami et al. in [1]). More recently, innovation in leather treatments was brought by the use of nanomaterials. Some metal-oxide nanomaterials (NM) (e.g. nano-ZnO, nano-AgO, nano-TiO₂) are presently being used in the footwear industry mainly due to their antimicrobial properties, but also due to other enhanced properties that increase the resistance and quality of leather. At the end of its life cycle, footwear may end up in the environment, where it will be degraded. Thus, in parallel with the evaluation of risks to human health of these NM, that will be in contact with the skin, it is of utmost importance to evaluate the risks to soil biota, of both the NMs and of the NMs-treated leather. We hypothesize that during the degradation of NM-treated leather nano-oxides as well as other chemical compounds used to produce leather will be released to soil affecting the soil biota and the overall functions of this compartment. To test this hypothesis, an experiment was carried out in microcosms. A natural reference soil was used and four treatments were tested each one with three

replicates. Thus in all the treatments the microcosms contained: (1) natural soil in both sides of the boxes (CTL-CTL); (2) natural soil with non-treated leather in one side, and natural soil only in the other side (Leather-CTL); (3) natural soil with leather treated with ZnO NM in one side and with natural soil only in the other side (ZnO_NM-Leather-CTL) and, (4) natural soil contaminated with ZnO NM (200ppm) in one side and with natural soil only in the other side (ZnO-NM-CTL). The microcosms were maintained in greenhouse conditions for three months. During this period, and at the end of the experiment the following endpoints were measured: a) earthworms (*Eisenia andrei*) survival, growth and reproduction (number of juveniles); b) colonization behaviour of earthworms (percentage of adult individual found in the side of the boxes with Leather, ZnO_NM-Leather or with ZnO_NM); c) *Brassica oleraceae* seeds germination and seedlings growth (fresh and dry biomass above soil, root length); d) feeding activity of earthworms in each side of the microcosm boxes, evaluated by the *Bait Lamina* assay; e) soil microbial activity: acid phosphatase and arylsulphatase enzymes and N-mineralization. Data from different endpoints suggest that no meaningful impacts on soil biota are caused by both leather and ZnO-NM treated-leather. In opposition, these materials can stimulate the activity of the soil microbial activity, and their ability to perform their functions in the soil.

Acknowledgements

This work was carried out under the project NANOFOOT – (contract 606570) funded under FP7-SME; Project New Walk (13850) ADI-QREN COMPETE.

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Agro-environmental friendly processes and food chemistry

Suspect-screening Strategy Applied to the Identification of Transformation Products of Carbamazepine in Lettuce and Soil Commodities

OP AgroFood #1

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Currently, treatment processes applied in municipal wastewater treatment plants (WWTPs) do not remove completely a large variety of contaminants of emerging concern (CECs) [1]. Consequently, due to the increasing use of treated wastewater for crop irrigation, it is important to evaluate the impact that CECs could produce in the environment. Some of these compounds have the potential to be taken up from the soil via plant roots. Once the CEC has entered the plant, a subsequent translocation toward the edible parts of the plants can take place [2]. Among the CECs reported in soils and crops, carbamazepine (CBZ) is the most frequently detected compound. It is resistant to degradation and can be discharged to the soil through various ways. In addition, the formation of several of its transformation products (TPs) has been reported under different wastewater treatments [3]. CBZ undergoes transformation to various aldehydes, ketones and hydroxylderivatives. However, there is

no knowledge about the presence and behaviour of these compounds in edible crops.

This work presents a qualitative screening workflow based on data-independent acquisition on LC-QTOF/MS for the detection and identification of TPs of CBZ in lettuce and soil. The workflow is based on a suspect analysis searching a list of potential candidates present in the samples. The list is built according to those TPs found in literature after application of different tertiary treatments to WWTP effluents and some biotransformation products found in soil. Application in a lettuce crop cultivated under controlled conditions and irrigated with i) simulated tap water spiked with CBZ and ii) simulated tap water spiked with CBZ after UV treatment, showed the potential of the suspect screening approach.

Acknowledgements

The authors acknowledge Nereus COST Action “ES1403: New and emerging challenges and opportunities in wastewater reuse” for the Short Term Scientific Mission support.

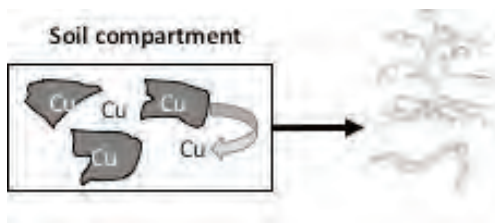
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Chemical and Biological Methods for the Evaluation of Cu Availability in Soils of the Douro Region

OP AgroFood #2

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The century-old practice of pesticides use for control of grapevine diseases, insect damages, and weed competition in vineyards has led to long-term accumulation of chemical substances in soils and other environmental compartments [1]. Among the most used pesticides in viticulture are the Cu-based fungicides such as: $\text{Cu}(\text{OH})_2$, $3\text{Cu}(\text{OH})_2$, CuCl_2 , CuSO_4 , and Cu_2O . Recently, Cu-based nanopesticides have been produced and their use is increasing. The use of these fungicides in viticulture for centuries, resulted in the long-term accumulation of Cu in soils [1-3]. Indeed, this was observed in a previous study conducted in the Douro vineyards, where high levels of Cu were related to the age of vineyards [1]. Considering the economic and ecological importance of the Douro landscapes, it is of utmost importance to study the behavior of this contaminant in these soils. Thus, this study aims to evaluate the mobility of Cu in vineyard soils using chemical and biological methods.

Three different vineyards with different ages were studied. Soil physical-chemical parameters were determined (pH, organic matter, total carbon and sulfur, and potentially toxic element concentrations) to characterize the different vineyards [1]. Further, a sequential selective extraction (SSE) was carried out to study the association of Cu with the different soil phases [2]. Two bioaccumulation experiments were carried out, one with plants (*Luzerna dimitri*) and another with invertebrates (*Enseia andreii*). In parallel, the soil porewaters of the plant bioaccumulation assay were collected.

Soils studied can be classified as acidic ($\text{pH}_w < 5$) and

with a medium to poor content in organic matter ($< 4\%$). Older vineyards showed higher levels of Cu, reaching 180 mg/kg, followed by the youngest vineyard (71 mg/kg). The fraction of Cu associated with the most labile fractions of the SSE was as high as 26%, with the highest value observed in the older vineyard. Indeed, the behavior of Cu was different for the three studied areas.

Considering the bioaccumulation assays, levels found in organisms reflected the total content of Cu in soils, reaching 50 mg/kg in plants and 65 mg/kg in earthworms. Nevertheless, levels found in organisms were better correlated with labile fractions than with total Cu levels.

Although levels found in Douro's vineyard soils are not particularly high [1, 3], there is a risk of transfer to trophic chains and of leaching to the water compartment. Thus, it is important to setup monitoring programs in these areas, and especially to evaluate possible environmental changes, which may affect the mobility of Cu.

Acknowledgements

This work was supported by the Strategic Funding UID/Multi/04423/2013 (CIIMAR), UID/GEO/04035/2013 (GEOBIOTEC), and UID/AMB/50017/2013 (CESAM RU), through national funds provided by FCT (Foundation for Science and Technology) and European Regional Development Fund (ERDF), in the framework of the PT2020 Partnership Agreement. FCT, also supported the work through an individual research grant attributed to A. Cachada (SFRH/BPD/100429/2014) and N. Durães (SFRH/BPD/81059/2011).

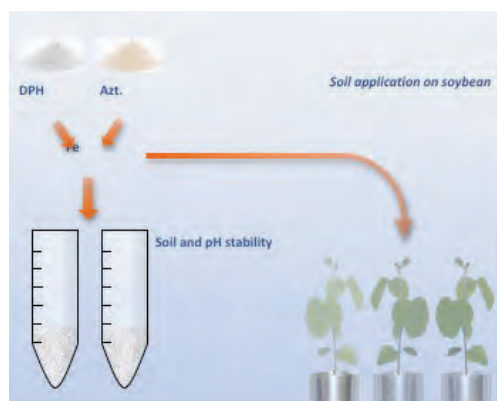
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Soil Interactions of Azotochelin and DPH and Determination of Iron Induced Chlorosis Mending Potential in Soybean (glycine max).

OP AgroFood #3

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The use of amino polycarboxylic acids, such as ethylenediamine tetraacetic acid (EDTA) or ethylenediaminedi-(2-hydroxyphenylacetic) acid (EDDHA), is currently the main method to reduce iron induced chlorosis in agriculture. Despite their effectiveness, environmental concerns rise from the fact that these compounds are not readily biodegradable [1]. Given their persistence, environmental issues may rise, such as metal leaching and mobilization into water sources [2]. In this work, more environmentally suitable alternatives were sought. For this matter, two chelates were tested; one siderophore and one analogue, synthesized in laboratory, namely azotochelin and N,N-Dihydroxy-N,N'-diisopropylhexanediamide (DPH), respectively.

Firstly, the interaction of the Fe-chelate complexes with soil components and soils was studied, as well as the chelate stability *versus* pH in the presence of calcium. Secondly, ⁵⁷Fe-chelates were applied to the soil of chlorotic soybean plants in pots, and their growth and SPAD index was monitored, as well the iron isotope levels on plants (leaves, stem and roots) after 7 and 21 days.

Results have shown that azotochelin interacts slightly with soils and its main constituents, such as

calcium carbonate, organic matter, montmorillonite-Ca and iron oxides, whereas DPH suffers more adsorption, namely in montmorillonite-Ca and organic matter. Fe-chelate soybean application results evidenced an increase of the SPAD index levels in comparison to the control plants in both tested chelates, followed by a significant increase of Fe determined in leaves and roots. However, isotope deconvolution [3] results suggest that most iron did not come from the chelates themselves but from iron oxides present in the soil, possibly via dissolution of Fe oxides present in the soil (shuttle effect).

These results show that azotochelin and DPH are good alternative environmental friendly chelating agents for application in iron chlorosis mend in calcareous soils due to its stability and effectiveness.

Acknowledgements

This work has been supported under the financing with the references PTDC-AAC-AMB-111206-2009 and UID/QUI/50006/2013 with financial support from European Union (FEDER funds) under the framework of QREN and FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020, respectively, and also supported under the financing with the reference AGL2013-44474-R from the Spanish Ministerio de Economía y Competitividad. Carlos M.H. Ferreira acknowledges his grant scholarship (SFRH/BD/95490/2013) financed by FCT.

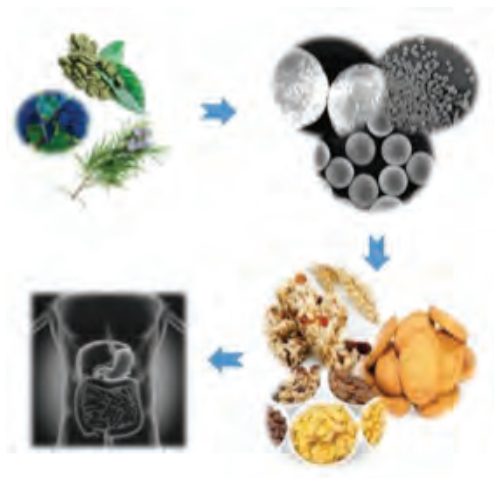
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How and Why Incorporation of Microencapsulated Bioactive Ingredients in Foods?

OP AgroFood #4

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The present study aimed to microencapsulate and perform the sustained release studies of selected antioxidants to improve the effectiveness of these bioactive compounds intended to be incorporated in food matrices.

Nowadays, the consumption of foods natural rich in antioxidants is considered highly important to prevent the appearance of neurodegenerative pathologies as the Alzheimer and the Parkinson diseases and even cardiovascular diseases, diabetes and cancer. Therefore, an increasing concern on antioxidant supplementation has been widely reported as antioxidants may prevent cells oxidative stress [1]. Notwithstanding, antioxidants are highly sensitive bioactive compounds mainly to pH, temperature and light. Consequently, microencapsulation methods may allow the protection of this type of bioactives from natural oxidation [2].

Microencapsulation methods effectively protect bioactive compounds from the external environment, allowing a controlled release of them [1,2].

The selected antioxidants (resveratrol, rosmarinic, caffeic and chlorogenic acids) were microencapsulated

in a matrix of ethyl cellulose, a biocompatible polymer that may act as an intestinal fibre. The microparticles were produced by the double emulsion solvent evaporation method. Additionally, was intended to study the release of the selected antioxidants from simulated salivary, gastric and intestinal fluids at human body temperature (37 °C).

The w/o/w solvent evaporation technique allowed to successfully entrap the selected antioxidants.

The preliminary results regarding the product yield, loading, encapsulation efficiency, antioxidant capacity, particle size distribution and microparticles morphology prove that the selected microencapsulation method is suitable for the microencapsulation of these antioxidants.

A natural delivery of resveratrol, rosmarinic, chlorogenic and caffeic acids may be achieved in the gastrointestinal fluids and therefore these antioxidants may be from now on incorporated in foods to improve foods nutritional value.

Acknowledgements

This work was financially supported by the projects POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia and NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

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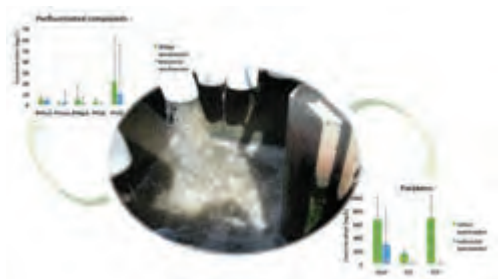
Poster Presentations

Environmental Monitoring

Discharge Patterns of Perfluorinated Compounds and Parabens from Urban and Industrial Areas

PP Env Monit #1

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In recent years, research in the field of environmental pollution has extended beyond the study of classical contaminants, pesticides, biocides, PAH, PCB and dioxins, to other families of compounds, which are being considered as “emerging contaminants”. Among them, perfluorinated compounds, which are used to make fluoropolymer coatings and resistant products [1], and parabens, widely used as preservatives [2], constitute one of the most relevant categories [3].

In spite of several studies reporting their presence in wastewater treatment plants, only a reduce number of studies have been focused on their sources [4]. In this work, the distribution of five perfluorinated compounds, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) and three parabens, methyl (MeP), ethyl (EtP) and propyl (PrP) parabens in urban and industrial wastewater collection systems has been studied and their discharge patterns have been evaluated.

A method, based on solid-phase extraction prior to high-performance liquid chromatography–triple

quadrupole mass spectrometry determination, was used for the simultaneous determination of selected pollutants in wastewater. All compounds were quantified in both, urban and industrial wastewater, reaching concentration levels up to 1023 ng L⁻¹ and 64 ng L⁻¹, for parabens and perfluorinated compounds, respectively.

A major contribution of all these compounds was observed from urban areas in comparison with industrial discharges, pointing out the wide use of the studied compounds on dairy products such as personal care products or food.

Daily discharge patterns of the studied compounds, measured during 24-h, showed a similar behavior for most of the compounds reaching their highest concentrations in the morning and late in the evening.

Acknowledgements

This work has been carried out in collaboration with Empresa Metropolitana de Abastecimiento y Saneamiento de Aguas de Sevilla (EMASESA), financed by Corporación Tecnológica de Andalucía (CTA) and Agencia de Innovación de Andalucía (IDEA) and supported by the ERDF.

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Organic Micropollutants from the EU Watch List: Their Occurrence in Drinking Waters

PP Env Monit #2

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In recent years, a growing interest has been raised about the fate and effects of organic micropollutants on the aquatic environment, in particular those known as contaminants of emerging concern (CECs) that are found at residual concentrations (ng L^{-1} to $\mu\text{g L}^{-1}$) [1]. These pollutants are generally not completely removed during conventional wastewater treatment, reaching other water matrices such as surface and groundwater, which might be sources for drinking water production and, thus, jeopardizing the human health safety [2]. Recently, the Commission published the Decision 2015/495 on the establishment of a Watch List of substances for Union-wide monitoring in water bodies. The list includes three estrogens (estrone, E1; 17- β -estradiol, E2; and 17- α -ethinylestradiol, EE2), eight pesticides (methiocarb and the neonicotinoids imidacloprid, thiacloprid, thiamethoxam, clothianidin and acetamiprid), two herbicides (oxadiazon and triallat), four pharmaceuticals (macrolide antibiotics azithromycin, clarithromycin and erythromycin and the anti-inflammatory diclofenac), an UV filter (2-ethylhexyl 4-methoxycinnamate, EHMC) and an anti-oxidant (2,6-ditert-butyl-4-methylphenol, BHT) [3].

Until now, most of the studies reported in the literature deal with the occurrence of these compounds in surface, ground and wastewater [3], and only a few of them are focused on drinking water [4].

Since little is known about the occurrence of most of the above referred Watch List compounds in drinking water, the present study aimed at the optimization of an analytical method based on offline solid phase extraction (SPE) followed by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) and the respective application of this method to determine these Watch List compounds in drinking water samples from different sources (such as tap, fountain and well water).

Acknowledgements

Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds through FCT. MOB, ARR and AMTS acknowledge FCT for SFRH/BD/115568/2016, SFRH/BPD/101703/2014 and IF/01501/2013, respectively.

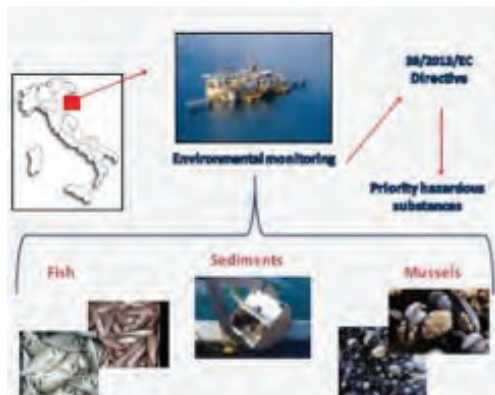
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Trace Metals in Biota and Sediment Samples Near to Regasification Platform (Northern Adriatic Sea)

PP Env Monit #3

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The Adriatic Sea is a semi-enclosed basin containing ecosystems that are subject to intensive anthropic pressures, such as unsustainable fishing and inputs of environmental contaminants. The major sources of contaminants have been related to coastal industrial activities as well as riverine discharges. In the Northern Adriatic, it was placed a Liquefied Natural Gas (LNG) regasification platform.

Natural gas, produced by the anaerobic decomposition of organic material and retrieved from underground, is used primarily for the production of electricity and for residential use. Italy does not extract a sufficient amount of natural gas to meet domestic demand, consequently Italy import by other countries and to make less dependent on individual countries has developed an offshore LNG regasification Terminal located approximately 12 km away from nearest coast, in Porto Viro (RO) [1, 2].

However, this structure could create a variety of impact on the environment. Monitoring of chemical-physical characteristics of sediment together with bioaccumulation analyses both in the mussel and in the fish, let to provide the necessary information for assessing the spatial and temporal perturbations occurring in the marine ecosystem.

A radial sampling design was performed for

sediment, allocating stations around the platform according to fixed distance from it. Two stations near the platform structure and a control site were selected for biota monitoring [1, 2].

Between 2005 and 2015 data related to ante operam phase (2005-2006), before construction of platform, to construction phase (2006-2010), during the building of platform, and to post operam phase, during LNG platform is in activity, were collected [3-5].

The aim of this work was to assess the concentrations of trace metals in sediment and biota (mussel and fish) of the area near to the structure. Concentrations data of arsenic, cadmium, lead, mercury, chromium and nikel were compared with Environmental Quality Standards (Directive 39/2013/EC and Legislative Decree 219/2010) and threshold levels for human health (Reg. 1881/2006 and further updates). Results enabled to assess spatial and temporal trend of contaminants in sediment and biota samples of area study and whether their concentrations had significantly increased in these matrices, as well to verify impacts concerning to presence of this structure.

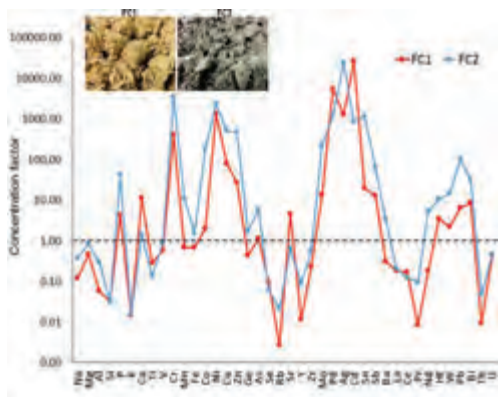
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Filter Cakes from UK Metal Treatment Plants: Element and Mineralogical Composition, Metal Speciation

PP Env Monit #4

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Two metal treatment filter cakes (FC1 and FC2) were obtained from UK metal finishing companies that provide services to industrial sectors including aerospace, defence, automotive, electrical and general engineering. Metal finishing processes applied in these sectors include electroplating (silver, copper, nickel, diffused nickel/cadmium, chrome, tin, zinc/nickel, zinc), anodizing (chromic and sulphuric), conversion coating (manganese phosphate, zinc phosphate, chromate, stainless steel passivation). Metal treatment sludges are generally generated by neutralisation of effluents from these industries containing dissolved metals (such as rinse waters and depleted baths from metal plating, and effluents from mineral preparation and centralised waste treatment facilities) with NaOH or Ca(OH)₂ to a pH of ~9-10, followed by dewatering to a moisture content of ~40-80% (wet mass basis) [1]. Metal treatment sludge is categorized as hazardous waste under European Waste Catalogue Code [2] and usually stockpiled in an area open to the atmosphere so that carbonation to a pH of ~8-9 rapidly occurs.

The main goal of this work was comprehensive characterisation including physical characteristics, element and mineralogical composition, and metal speciation, of UK metal treatment sludges. This investigation can help to in decision-making regarding appropriate environmentally friendly treatment, utilization and/or potential application for recovery of valuable metals.

Powder x-ray diffraction analysis showed that filter cake FC2 is completely amorphous material, and only calcite (CaCO₃) was identified as a crystalline phase in filter cake FC1, which was consistent with previous work with filter cakes from the same sources [3].

Major elements in both filter cakes are Ca, Cr, Fe, and Ni. The main difference between the two filter cakes was that FC1 contained 10x more Ca (up to 37%) than FC2, whereas FC2 had higher concentration of the other major elements, and also Al, Mg, Cu, Zn, and P. The concentrations of following elements, including potential pollutants and strategically important metals, Cr, Ni, Sn, P, Ca, Cu, Zn, Cd, Pb, Co, Ag, Mo, Pd, Sb, Hf, W, As, and Bi are enriched in both filter cakes comparing to the average upper crustal abundances of these elements [4]. Additionally, the concentrations of Mn, Fe, Ge, Ba, and Nd are enriched in FC2. The concentrations of Na, Mg, Al, Si, K, Se, Rb, Sr, Zr, Th, U and almost all rare earth elements are depleted in the filter cakes.

Metal speciation in the filter cakes were examined using X-ray absorption near-edge structure (XANES) spectroscopy. Preliminary results compliment previous work to examine speciation of Ni [3] and suggest that PbO (42%), PbCO₃ (46%), and PbSO₄ (12%) were the main Pb species in FC1, and Pb₃(PO₄)Cl (36%), PbO (31%), PbCO₃ (17%), and PbSO₄ (16%) were present in FC2.

Acknowledgements

This work was conducted with funding from the UK Engineering and Physical Sciences Research Council Grant number (EP/M00337X /1) and the National Science Foundation of China.

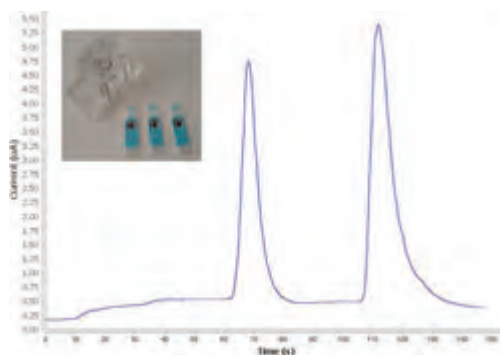
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Study of the Voltammetric Behavior of Dithiothreitol (DTT) on Screen-printed Carbon Electrodes Modified with Cobalt Phthalocyanine for the Measurement of Aerosol Oxidative Activity

PP Env Monit #5

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Airborne Particulate Matter (PM) is the cause of significant adverse health effects, like premature deaths, respiratory and cardiovascular diseases. A leading hypothesis is that particles present high oxidative activity due to different components of PM (e.g. redox-active quinones). These components have been shown to catalyze the generation of reactive oxygen species ROS in pulmonary fluid, which then react with tissues [1].

Analytical methodologies for measuring oxidative potential have been described in the literature including chromatography, spectrometry, fluorescence and absorption spectroscopy. One of the reference techniques is the dithiothreitol (DTT)-based chemical activity assay, where DTT reacts with oxidant species present in the aerosol sample [2]. Unfortunately, these methods require relatively large sample mass, sample preparation and expensive laboratory-based instruments which increases analysis time and difficult integration in portable systems.

As a result, new researches are focused on developing smaller, less expensive and portables systems. A microfluidic electrochemical sensor was recently developed for on-line monitoring of aerosol oxidative activity based on DTT assay. The sensor consists of an electrochemical platform using a homemade cobalt (II)-phthalocyanine modified carbon paste as working electrode and amperometric detection [3].

In the present work, we have studied the electrochemical behavior of dithiothreitol (DTT) using a commercial screen-printed carbon electrode modified with Cobalt (II) phthalocyanine (410 Dropsens) and flow injection analysis with amperometric detection (AM) for monitoring atmospheric aerosol oxidative activity with high sensitivity and easy operation using portable devices.

The hydrodynamic voltammogram of DTT was first explored by amperometric detection in 0.1 M phosphate buffer (pH 7.4) solution containing 10^{-3} M DTT when a potential scan varied from -200 mV to 200 mV (± 50 mV), using a flow rate of 2.3 mL/min and 20 μ L injection ($n = 2$). The medium and variables were selected based on previous voltammetric research of detection DTT with fabricated modified CoPC carbon paste electrodes [3]. The highest signal was observed at +100 mV.

The flow rate was optimized in the range from 0.4 mL/min to 2.50 mL/min. Optimal flow rate was 0.5 mL/min, because the highest and best defined signal peaks were obtained.

Under these optimized conditions, work is in progress to exploit the signal in the concentration range of 1 μ M to 100 μ M DTT, and explore applicability to determine the oxidative potential of real samples of PM collected on filters or generated in combustion chambers.

Acknowledgements

We acknowledge Junta de Extremadura, Spain (projects PRI IB16114 and GR15087), and the air quality surveillance network of Extremadura (REPICA), all partially financed by European Union Funds for Regional Development (FEDER).

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Annual Variation of Hg in Soils of Puchuncaví-ventanas Valley

PP Env Monit #6

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In 2014, 41% of the electric energy produced in Chile came from thermoelectric generation based on coal as fuel [1]. Among the environmental problems derived from the combustion of coal is the emission of elements of recognized toxicity such as Hg [2]. Emissions from coal-fired power plants may increase Hg content in soil [3] by deposition of particulate matter containing trace elements [4]. Puchuncaví-Ventanas valley, located in the Valparaíso Region, Chile, has an important industrial complex, which includes a copper smelter, a coal-fired thermoelectric plant which began its activities in 1964, among other industries. Therefore, the soils of Puchuncaví-Ventanas valley have been impacted by trace elements (including Hg) due to the emission of contaminants from the industrial complex [5, 6]. Pollutants that subsequently reach the soil via dry deposition and/or wet deposition.

Due to the above mentioned, the main objective of the present work is to study the historical evolution (2007 – 2015) of Hg concentration in the soils of Puchuncaví – Ventanas valley. In order to fulfill the main objective, our research group has been carrying out annual monitoring soil campaigns in Puchuncaví-Ventanas valley, where samples were taken at different locations, La Greda (LG), Los Maitenes (LM), Puchuncaví (PU), Valle Alegre (VA), Maitencillo (MA), Zapallar (ZA) and Papudo (PA). Distances and location of monitoring stations respect of the industrial complex are LG 1.7 km north, LM 2.4 km east, PU 8.3 km north-east, VA 6.5 km south-east, MA 11 km north, ZA 22 km and PA, 33 km north. Surface soil samples (1m², 5 cm deep) were taken monthly on each location, then transported to the laboratory where they were sieved (2 mm mech), digested and analyzed by

ICP-MS according to the procedure described in literature [7].

The results shown that the average annual concentration of mercury in LG (monitoring station nearest to the industrial complex) soils increased 7 times between 2007 and 2010, then in 2011, Hg concentration decreases 15 times probably due to the promulgation of the thermoelectric emission standard (Decree 13/11, Ministry of the Environment) and partial detention of 65 days of the thermoelectric plant due to maintenance. From 2011 to 2015, average annual concentration of mercury in LG presents a sustained increasing (2015, 13 times higher than 2011) with a maximum observer in 2013 (2013, 21 times higher than 2011) probably due to the entry into operation of a new generating unit in the thermoelectric plant.

LM (second station nearest to the industrial complex) presents similar trend than LG, being average annual concentration of mercury in 2015, 8 times higher than 2011. The rest of the monitoring stations present high variability between years.

A dependence was observed between the average annual concentration of Hg in soil and the distance to the industrial complex. The nearest station, LG, had the highest concentration while at the furthest station from the industrial complex, PA, presents the minimum concentration of the valley.

Acknowledgements

Authors acknowledge AES-Gener for their financial support.

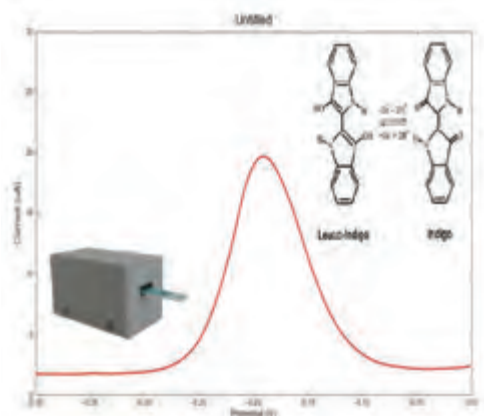
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Study of the Voltammetric Behavior of Indigotrisulfonate as a Potential Electrochemical Indicator for Tropospheric Ozone Levels in Ambient Air

PP Env Monit #7

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Tropospheric ozone is an atmospheric secondary pollutant formed by photochemical reactions of volatile organic compounds and nitrogen oxides activated by solar radiation and temperature. In Southern Europe, summer ozone levels are of great concern due to a mix of natural (high temperature and solar irradiation) and anthropogenic factors [1]. Periodic episodes of high ozone concentrations, are related with negative effects to public health and damage to vegetation [2].

Several analytical techniques for detecting ozone have been described in the literature, including UV-Vis spectrophotometry, chemiluminescence and fluorescence. Although these methods enable accurate determination of ozone concentrations in real time, the instruments employed tend to be bulky and expensive.

Chemical methods are an alternative for low-cost monitoring, and normally involve a chemical reaction of ozone with a reagent and measurement of the product formed or the remaining reagent. A chemical method was recently developed for the determination of ozone based on its reaction with indigotrisulfonate (ITS) [3].

In this work, we explore the electrochemical behavior of ITS as a means to determine of ozone in the ambient air. A screen-printed carbon electrode was employed for the oxidative determination of indigo using square wave voltammetry (SWV)

as the analytical signal. Electrochemical methods have the advantages of low cost, high sensitivity, easy operation, miniaturization and automation potential, allowing the construction of simple portable devices for fast screening purposes and in-field/ on-site monitoring [4].

The overall voltammetric response of ITS was explored by cyclic voltammetry on a screen printed carbon electrode in a 0.1 M HClO₄ solution [5] containing 10⁻³ M indigo, applying a potential scan ranging from -0.5 V to +1.0 V. ITS showed two oxidation processes during the anodic potential scan, attributed to the oxidation of leuco-indigo/ indigo (generated by means of the application of the initial potential for 45s) followed by the oxidation of indigo/dehydro-indigo.

The instrumental variables (frequency, amplitude, and potential increment) affecting SWV were optimized. Selecting the best experimental conditions, the optimized values were: 10 Hz, 70 mV, and 2 mV, respectively. Finally, a valid calibration plot for ITS was obtained. We have also observed the degradation kinetics of 10⁻³ M indigo by reaction with ozone, measuring the oxidation signal of ITS.

Acknowledgements

We acknowledge Junta de Extremadura, Spain (projects PRI IB16114 and GR15087), and the air quality surveillance network of Extremadura (REPICA), all partially financed by European Union Funds for Regional Development (FEDER).

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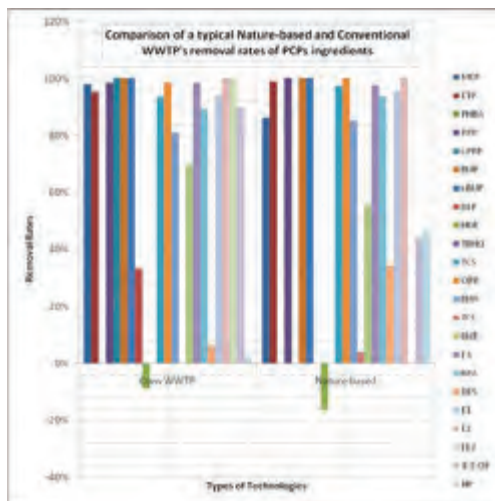
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An Investigation Into The Effectiveness Of Nature-based Technologies For The Removal Of Pharmaceutical And Personal /Household Products Ingredients.

PP Env Monit #8

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Introduction

Waste Water Treatment Plants (WWTPs) are designed for pre-processing of wastewaters before discharge into the receiving water bodies. However, the occasional upsurge in hydraulic loads can exceed the design capacities of the plants, which can lead to direct discharge into receiving water bodies without or only minimal treatment. Conventional WWTPs are expensive to run. However, nature-based technologies or Integrated Constructed Wetlands (ICW) have been proven to be a solution to these problems by improving water quality through interactions between a range of plants species and the constructed ponds where wastewaters are processed.

Chemicals and Treatment Technologies

This study investigated removal rates of antibiotics, antioxidants, preservatives and endocrine disruptive compounds [1] in six constructed nature-based treatment technologies and three conventional WWTPs. They were of various sizes with influent loads ranging from 7.5 to 55,300 m³/day across the constructed/nature-based technologies covering 60-60,000 population equivalents. The Conventional WWTPs serve an average of 115,000 population equivalent with an average daily loads 30,350 m³/day.

Sampling & Analysis

Sampling campaigns were carried out using DGT [2] based passive samplers with XAD Amberlite 18 and Hydrophilic-Lipophilic Balance resins as binding gels for antibiotics and PCPs, respectively. Agarose Gel was used for the diffusive layer. In total 220 DGT passive samplers were deployed for seven days. Methanol and acetonitrile HPLC were used as extraction solvents and analysis was carried out using LCMS QqQ.

Results and Discussions

Data from the conventional WWTPs for antibiotics revealed removal rates ranging from -272% (AMX) to 100% (OTC, LIM, STX etc) and for PCPs, -1174% (NP) to 100% (E3, i-PRP etc). However, removal of antibiotics by nature-based treatments ranged from -318% (CLM) to 100% (TMP, STX etc) and -877% (NP) to 100% (OPP, i-BUP etc) for PCPs. It is suggested that degradation of related substances could result increasing concentrations of the analytes resulting in net 'production'. In summary, nature-based systems depict aggregated removal rates of 54% for preservatives, 12% for antioxidants, 32% for EDCs and 88% for antibiotics, while for conventional WWTPs removal rates were 67% for preservatives, 72% antioxidants, -30% EDCs and 51% for antibiotics

Conclusion

Significant variation of removal rates was found between treatment technologies as well as between study compounds that require further investigation.

Acknowledgements

NERC and TellLab Ireland for sponsorship, Lancaster University and University of Florence for laboratory support. For research update, please contact (e.babalola@lancaster.ac.uk).

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Ave Estuary (Portugal) Water, Soil and Plant Assessment: Focus On Trace Element And Main Physicochemical Parameters

PP Env Monit #9

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All compartments of the biosphere are polluted by a variety of inorganic and organic pollutants as a result of anthropogenic activities altering the normal biogeochemical cycling [1]. In order to manage these pollutants, it is necessary to understand the relationship between the sources and their environmental levels, namely in river waters, aquatic sediments and plants [2].

The Ave estuary (water, soil and plants) was studied. Soils and plants were digested by a microwave assisted acid digestion procedure. Water, and soil and plant tissues digests were analysed by ICP-MS for their trace elements concentration (Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb and U). Other physicochemical parameters, such as pH, conductivity, dissolved oxygen, temperature, nutritive elements (nitrates, nitrites, ammonium, orthophosphates) and chlorophyll a were also determined in waters; and pH, electrical conductivity and salinity in soils.

To take into account the expected spatial changes and to look for anthropogenic influences on trace element and physicochemical parameters values, samples (water and soil) were collected at 4 sampling sites in Ave river in four sampling campaigns (May, July, November and March). Plants were collected in May.

According to widely accepted water quality guidelines for the protection of aquatic life [3], the Ave river water quality was found out of safe limits regarding several parameters. Nitrate levels were consistently high (> 50 mg/L in a significant

number of samples). Trace elements mean values were found high for Al (1932 ppb), Cu (22 ppb), Se (33 ppb), Ag (0.64 ppb), Cd (0.62 ppb), Pb (11 ppb) and Zn (49 ppb) in Ave water samples [3]. Significant spatial differences were found, with a noticeable increasing trend from upstream to downstream for values of several elements. Sampling site 1 showed considerably higher levels for all trace elements and significantly higher levels of nutrients (e.g., nitrates and phosphates). This site forms a lagoon with high residence time and has an important natural ornithological reserve, the oldest one in Portugal.

Superior mean values were found for Li, Cr, Co, Ni, Cu, Zn, Ba, Tl, Pb and U in soils. Sampling site 4 soil showed significantly higher levels of the majority of trace elements analysed.

For the different plant tissues (root, stem, leaf, flower and fruit) higher trace elements levels were generally presented in roots. *Lagurus ovatus* L. root tissue collected at sampling site 1 presented the highest values for most trace elements analysed.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Ministério da Ciência, Tecnologia e Ensino Superior (MCTES), under Project PTDC/SAU-ESA/108871/2008, and CESPU, through Projects MYCO-CESPU-2016 and ChiralDrugs-CESPU-2017.

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Chemometric Assessment of the Heavy Metals Content in Soil and Cabbage Leaves

PP Env Monit #10

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Sixteen soil samples collected at different locations in Poland were characterized by specific physicochemical parameters and content of four toxic metals. The data set was completed by additional data for the same toxic metals content in the cabbage leaves samples grown on the same soils. The major goal of the chemometric interpretation (hierarchical and non-hierarchical cluster analysis, principal components analysis) was to reveal patterns of similarity between the soil locations, on one hand, and, on the other to study correlations

and dependencies between all parameters involved in the study. Significant step in the chemometric expertise was to select the optimal number of indicators able to determine the structure of the large data set. The results from the intelligent data analysis could be used for proving the remediation ability of cabbage in treating polluted soils.

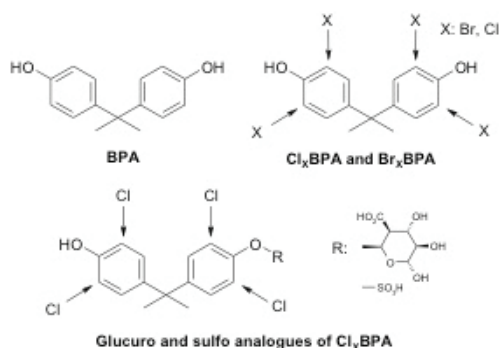
Acknowledgements

Authors are grateful to National Science Fund (NSF), project DCOST 01/6 - 2017.

Synthesis of Chloro and/or Bromo Analogues of Bisphenol A and their Conjugated Analogues

PP Env Monit #11

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For decades, studies of endocrine-disrupting chemicals (EDCs) have challenged traditional concepts in toxicology, in particular the dogma of “the dose makes the poison,” because EDCs can have effects at low doses that are not predicted by effects at higher doses. BPA is an endocrine disrupting chemical, specifically a selective estrogen receptor modulator. Numerous studies suggested that prenatal BPA exposure was correlated with preterm delivery [1], low birth weight [2] and reduced head circumference [3] but also induced adult disease with reproductive disorders (infertility, endometriosis) [4-5], neurobehavioral development and metabolic diseases (obesity, diabetes, heart disease, thyroid and liver function).

We focused our research on the determination of BPA but also its chlorinated derivatives (Cl_xBPA) which were formed during the water chlorination. The formation of brominated derivatives of BPA (Br_xBPA) was also expected in presence of bromine, which was formed by oxidation of bromide during the chlorination step. Therefore, mixed compounds Br_xCl_xBPA were also detected. *In vivo*, these compounds could be oxydated, reduced or metabolized in glucuro or sulfo conjugated derivatives.

Herein, in a first time, we described the synthesis of halogeno BPA. It is important to emphasize that these compounds were not commercially available. They were used as analytical standards in LC/MS/MS to quantify them in human biological fluids (urine, colostrum) and drinking water. They were

also evaluated toward their biological profile. Indeed, some derivatives like Cl_xBPA have more estrogenic effect than BPA. Starting from Cl_xBPA, their conjugated analogues, as glucuro and sulfo derivatives, were synthesized. They could serve as analytical standards to study the metabolism of these Cl_xBPA, but also to quantify them in biological samples (urine).

For this proposal, a cohort of pregnant women was set up (EDDS cohort) by our team and human biological fluids were collected like urine, colostrum but also drinking water [7-8].

In a second time, we analyzed urine and colostrum through online solid-phase extraction coupled to ultra high-performance liquid chromatography tandem mass spectrometry (Xevo® TQS) to quantify BPA, Cl_xBPA. The detection frequency of BPA in colostrum and urine ranged from 45 to 71% and at least one Cl_xBPA was detected (57-93%). For both biological samples concentration ranged from 0.30 to 52.10 ng/mL and from 0.03 to 1.71 ng/mL for BPA and Cl_xBPA derivatives, respectively. First results were described.

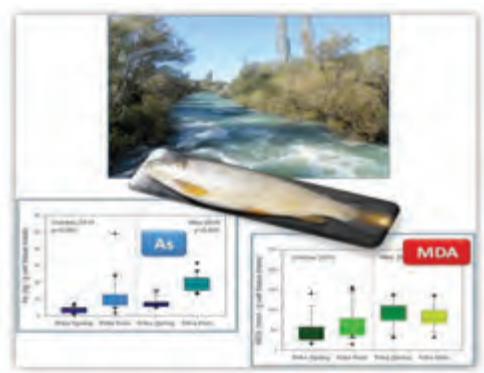
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Multibiomarker Approach on the Gills of Brown Trout (*Salmo Trutta*) as a Tool for the Assessment of the Krka River Metal Pollution

PP Env Monit #12

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The Krka River is a karst Croatian watercourse, which is considered as one of the most beautiful pristine environments in the region. However, recently, an increase in the concentrations of several trace elements was observed downstream of Knin town, as a consequence of direct discharge of untreated municipal and industrial wastewaters into the river [1,2]. A part of the Krka River, starting 2 km downstream of Knin town, was proclaimed a National park, and reported contamination could present a potential threat for its conservation.

With an aim to evaluate the current pollution status of the Krka River we have applied multibiomarker approach, which encompassed the assessment of trace element bioaccumulation and analyses of several biomarkers in the gill cytosol of brown trout (*Salmo trutta* Linnaeus, 1758), as a representative fish species in this river.

Trace element concentrations in the gill cytosol were determined by high resolution inductively coupled plasma mass spectrometry (HR ICP-MS), and the analyses included thirteen elements, seven essential (Co, Cu, Fe, Mn, Se, V, and Zn) and six nonessential (As, Cd, Cs, Rb, Sr, and Tl). Analyzed biomarkers included the activity of enzymes catalase (CAT) and acetylcholinesterase (AChE), and concentrations of malondialdehyde (MDA), glutathione (GSH), total cytosolic proteins (TP) and metallothioneins (MTs). All biomarkers were analyzed spectrophotometrically, except for MTs, which were determined electrochemically.

The study was performed in two sampling campaigns (October 2015 and May 2016) at two sampling sites, the Krka River spring as a reference site, and the location downstream of Knin, as a contaminated site, which was confirmed by analyses of dissolved trace element concentrations in the river water. The concentrations of As, Co, Fe, Mn, Rb, Se, Sr, V, and Zn were higher downstream of Knin in comparison to the reference site, whereas the concentrations of Cd, Cs, Cu, and Tl were comparable at both sites [2].

Higher cytosolic concentrations of As, Co, Mn, Se, and Sr in brown trout gills downstream of Knin town in both seasons confirmed the influence of water contamination on trace element bioaccumulation. However, higher concentrations of Cd, Cs, Tl and Fe in brown trout gills were observed at the reference site, which could not be associated to the exposure from the water, and thus association with food and sediment should be considered. The activities and concentrations of biomarkers were generally comparable at both sites in both campaigns, with the exception of higher GSH (biomarker of oxidative stress) and TP (biomarker of general stress) downstream of Knin town in the October sampling. The obtained results confirmed the contamination of the Krka River water with trace elements and consequently higher trace element bioaccumulation in the gills of brown trout downstream of Knin town. However, general absence of the changes in biomarker levels was an indication that observed contamination level was still not high enough to cause observable effects in fish.

Acknowledgements

This study was carried out in the scope of a project "Accumulation, subcellular mapping and effects of trace metals in aquatic organisms" (Project no: IP-2014-09-4255), funded by the Croatian Science Foundation.

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Application of Strong Basic Nano-sized Anionite for the Capillary Electrophoresis Separation and On-line Concentration of Inorganic Anions and Carboxylic Acids

PP Env Monit #13

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Capillary electrophoresis methods provide combine advantageous features of on-line detection, high separation efficiency, low sample consumption and require low amounts of sample and reagents. Nevertheless, CE techniques have also some pitfalls. One critical issue in CE of basic analytes is their adsorption on the capillary wall. Therefore, a great deal of studies is devoted to the development and application of novel effective capillary coating materials. The sensitivity of CE methods can be substantially improved by application of various preconcentration techniques. Nanomaterials have great potential in capillary coating preparations based on their advantageous properties such as large surface-to-volume ratios and a wide variety of chemistry options.

In the present study, the possibilities of strong basic nano-sized anionite based on anionite AB-17 as a modifier of background electrolyte (BGE) in CE were discovered. This approach has been successfully used for the analysis of inorganic anions and simultaneous electrophoretic determination of 8 carboxylic acids. It was established that the additive of strong basic nano-sized anionite to the BGE provides reversed EOF. The influence of the concentration of nano-sized anionite in BGE on the velocity and direction

of EOF as well as on the efficiency and peaks resolution of analytes was determined. It indicates the dynamic modification of the silica capillary walls by the particles of nano-sized anionites and leads to better separation efficiency (up to $1\ 200 \times 10^3$ t.p./ m) and the peaks resolution of inorganic anions compared to BGE containing conventional cationic surfactant – CTAB.

The various on-line concentration techniques were applied to decrease the LODs of analytes. The LODs of inorganic anions with UV detection and nano-sized anionite as a modifier of BGE were 8–30 ng/ml in case of field amplified sample stacking and 1 pg/ml – 7 µg/ml for electrostacking. These values in case of carboxylic acids were 9–34 ng/ml and 1–2 ng/ml. The developed approaches for the fruit acids determination were applied for the red and white wine analysis, which is important for the control of wines quality.

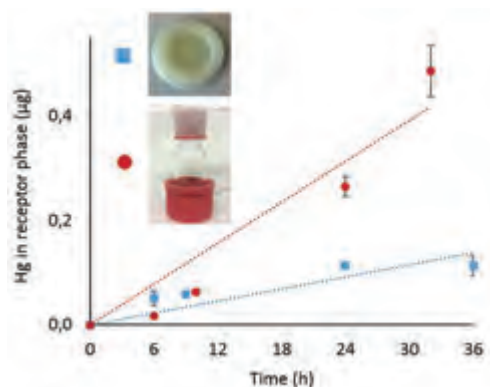
Acknowledgements

This work was carried out with equipments of Chemistry Educational Centre of Research Park, Saint-Petersburg State University and supported by the Russian Foundation for Basic Research (project no. 14-03-00735-a and no. 16-03-00791-a).

Design and Evaluation of a Novel Passive Sampler Based on a Polymer Inclusion Membrane for Hg Monitoring

PP Env Monit #14

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Mercury (Hg) is considered a priority hazardous substance because of its toxicity and widespread occurrence (UNEP 2013). The development of methodologies to control and determine its concentration in the environment has become necessary.

Discrete grab sampling provides results that are only representative of the concentration of metal at the physical location and time of sampling and it is not suitable for detecting episodic emissions of Hg in the environment [1]. To overcome these issues, techniques providing time-weighted average (TWA) concentrations of the target analyte are recommended, such as diffusive gradient in thin films (DGT).

DGT is a passive sampling technique that has been successfully used as a mean to monitor the concentration of Hg species in natural waters, using selective resins including thiol groups as a binding phase [1].

Another approach that has been investigated lately is the use of devices with functionalized membranes, which contains a carrier that allows the transport and preconcentration of metal species or organic compounds [2, 3]. Polymer inclusion membranes (PIMs) are a kind of functionalized membrane composed of an extracting agent (carrier), a base polymer (such cellulose triacetate (CTA)), and it can also include a plasticizer (like nitrophenyl octyl ether (NPOE)). The ionic liquid trioctylmethylammoniumthiosalicylate (TOMATS)

has proven its efficiency in terms of Hg extraction [4], thus it has been chosen to act as a carrier.

The aim of this work is to study the possibility of using a system based on a PIM with made of 50%CTA+30%TOMATS+20%NPOE.

Several experiments have been performed to evaluate this new device using 5L of natural water spiked with $10\mu\text{g L}^{-1}$ Hg in constant agitation and PIM-devices with 5 mL of 10^{-3} M cysteine as receiving phase. The effect of flow pattern was investigated, and Hg transport was not affected by water agitation. This is of paramount importance since flow pattern cannot be controlled in natural environments.

Moreover, results were compared with DGT devices. It was found that both showed a linear tendency on the uptake kinetics. However, the slope of the corresponding calibration curve for PIM was higher than the one obtained for DGT. It is important to take into account that it is possible to correlate Hg adsorbed in DGT with the original metal present in the source solution but, in the case of PIM-device, it is necessary to perform a modelling study to obtain this relationship. A good option can be to perform external calibration curve, since it has been proved that there is no water matrix effect.

The exposed surfaces of passive samplers in natural water can be colonized by microorganisms in biofilms. We have also studied this effect on PIMs for the first time.

Acknowledgements

The financial support of the research project CTM2016-78798-C2-2-P (AEI/FEDER/UE) and the scholarship IFUdG2016-2018 from University of Girona are acknowledged.

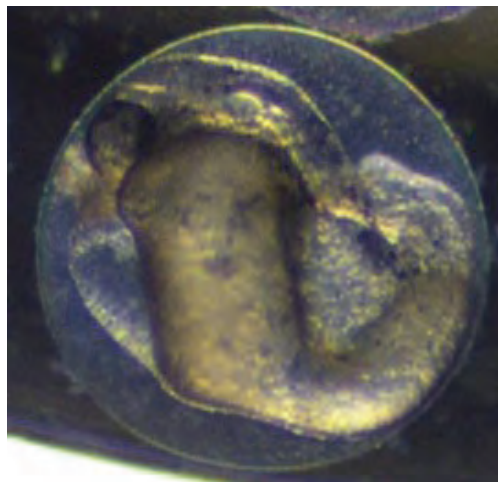
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Zebrafish Embryo Bioassays For Evaluating The Toxicity Of Diclofenac Effluents From Microalgae Treatment

PP Env Monit #15

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In the recent years, the use of microalgae in the removal of both organic and inorganic pollutants has gained attention [1-2]. However, little is still known about microalgae ability to remove emerging contaminants (ECs), such as pharmaceuticals, from contaminated waters.

The generation of toxic products during biodegradation of ECs is an important field of research [3]. In this context, zebrafish (*Danio rerio*) is one of the most popular model organisms in (eco) toxicology [4]. Currently, it has been proved the capability of microalgae, namely *C. sorokiniana*, *C. vulgaris* and *S. obliquus*, as bioremediation systems to remove diclofenac from water [5].

The present work aimed at giving a step forward to further evaluate the efficiency of these systems on the basis of toxicological data from zebrafish embryo toxicity tests. To the best of our knowledge, this is the first time that such a study is carried out, thus fostering a new approach to the assessment of microalgae-based treatments of pharmaceuticals contaminated waters.

The obtained results evidenced that bioremediation by microalgae reduced the negative effects caused by diclofenac on the embryonic development of

zebrafish, namely on mortality and morphological abnormalities. The observed effects were equal to those associated to the remaining concentration of diclofenac after microalgae bioremediation. Therefore, the metabolic removal of this compound by the strains here studied did not mean an input of toxic biotransformation products into the water, at least to this experimental animal model.

S. obliquus was the strain that obtained the best results, eliminating the mortality and reducing the abnormalities up to 30% at 144 hours post-fertilization. Indeed, these abnormalities only affected the larvae mobility.

Results achieved by microalgae bioremediation of diclofenac contaminated water highlight that the considered strains not only reduced the diclofenac concentration, but also the toxicity effects on zebrafish embryo.

Acknowledgements

Authors would like to acknowledge University of León (Spain) for funding given to the project MICROTRAT (UXXI2016/00128). Carla Escapa acknowledges the Spanish Ministry of Educations, Culture and Sports for her PhD fellowship (FPU12/03073). Teresa Neuparth thanks the Portuguese Science and Technology Foundation (FCT) for her Postdoctoral fellowship (SFRH/BPD/77912/2011).

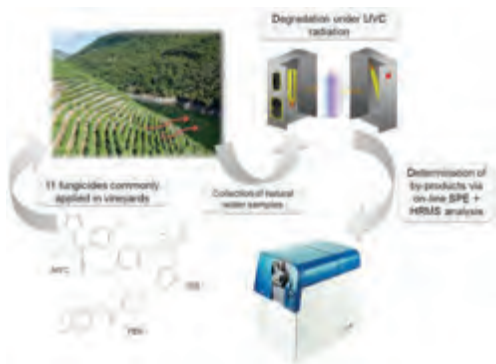
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Photodegradation Rate of Fungicides in Natural Environmental Waters and Identification of By-Products by On-Line SPE – High Resolution Mass Spectrometry (SWATH Mode)

PP Env Monit #16

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Fungicides are a pesticide class of widespread used in agriculture to avoid fungi infection. Even though most pesticides are applied once per season, fungicides require a more frequent application during the whole year and this continuous appliance induces a persistent entrance of fungicide residues into the different environmental compartments, and specially into the aquatic environment, since the final fungicide fate are usually ground- and superficial waters through the lixiviation of the agricultural soils.

Prior to the analysis of these contaminants in water, a pre-concentration step is often required to achieve low limits of detection. On-line SPE is an automated procedure used for this purpose, which, apart from offering a simultaneous clean-up step, requires a low amount of sample and minimizes the handling of organic solvents.

In an attempt to both evaluate the degradation rates of the target fungicides and to identify the formed photodegradation by-products under UVC radiation, Liquid Chromatography High Resolution Mass Spectrometry (LC-HRMS) was employed. A SCIEX TripleTOF® 5600+ equipped with a DuoSpray™ ion source and an Electrospray Ionization (ESI) probe was used. A HPLC system consisting of a low pressure pump and two high pressure pumps (Shimadzu Nexera X2 HPLC with two LC-30AD pumps) was used, equipped with a Phenomenex Kinetex EVO C18 (100x2.1mm, 2.6 µm) column at 50°C. A gradient of water (A)

and methanol (B) buffered with 3 mM ammonium formate, was applied. A Strata-X (25 µm, 20 x 2 mm) and a Strata-C8 (20 µm, 20 x 2 mm) cartridges were tested for on-line SPE in conjunction with the above described HPLC system. 50 µl of water sample were injected into the SPE cartridge.

A workflow performing data-independent fragmentation of all precursor ions entering the mass spectrometer in 20-30 m/z isolation windows (Sequential Windowed Acquisition of All Theoretical Fragment Ion Mass Spectra, (SWATH) was implemented. Here, this SWATH was divided in 30 windows ranging from 80 to 1000 Da, enabling the quantification of the parent fungicide residues and the identification of their photodegradation products with a high level of confidence, especially in terms of mass accuracy and isotope score, after importing a list of 40 suspected by-products and metabolites. High resolution MS/MS spectra of the degradation products could be acquired, as well.

The fungicide degradation in different types of real water samples has been evaluated through direct photolysis under UVC radiation, showing removal efficiency of about 60% after 30 minutes of irradiation for most compounds. Seven photodegradation by-products were tentatively identified by HRMS after UVC photolysis. The three main by-products of the fenhexamide were identified (FEN-1, FEN-2, FEN-3) after 30 minutes under UVC photolysis. They are arising from dechlorination reactions. In all cases, the relative abundance of the formed by-products in comparison with fenhexamide was lower than 10%. Two acidic compounds derived from benalaxyl (benalaxyl acid, BEN-1) and from metalaxyl (N-2,6-dimethylphenyl)-N-(methoxyacetyl), MET-1) were also identified as by-products. Further studies will be conducted soon, especially aiming at improving the acquisition workflow and the identification criteria for the suspected by-products.

Acknowledgements

R.F. would like to acknowledge the Spanish Ministry of Economy and Competitiveness for her contract. M.C. would like to acknowledge CRETUS for her postdoc contract.

NUNATAK: Natural Laboratory on Glacier Contamination and Climate Change

PP Env Monit #17

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Climate change is one of the most important environmental problems of the 21st century and is currently the subject of countless studies and discussions [1,2]. Many of these studies indicate that human influence has caused changes in climate to exceed known thresholds in natural variability [3]. Environmental pollution, especially gases and particulates, contribute and exacerbate the effects of climate change. Particularly, particulate matter can be transported from a city like Santiago de Chile, to Los Andes glaciers and to be deposited on the snow and the ice. These mainly carbonaceous particles absorb solar radiation and heat up, increasing the speed of melting snow, accelerating the loss of mass of the glacier, modifying the albedo and finally impacting on the phenomenon of global climate change. This problem is relevant in Chile, for having one of the largest glacier cover areas in the world, with more than 3,000 glaciers in its territory and a total area estimated at 25,500 Km², representing 90% of the surface area of glaciers of South America.

With the objective of conducting research to try to establish the relationship between anthropogenic pollution and its effects on the glaciers, the first portable environmental research scientific shelter “NUNATAK” was created. This laboratory shelter facility is designed to conduct long term environmental monitoring, and specific monitoring campaigns in extreme zones like Andes glaciers giving habitability, safety and thermal comfort conditions for up to three researchers.

Laboratory-shelter NUNATAK consists in a panelized metal container, made especially for extreme sites, built with materials resistant to the inclemency of the mountain weather as it has thermal insulation and thermocouple windows, which ensure the well-being and comfort of its occupants. The shelter laboratory is fully equipped with drawers and work tables, 3 different types of plugs, a rectifier and voltage stabilizer, as well as a UPS to allow more autonomy and allow the operation and safety of the monitoring equipment during the time in that are operating under field conditions. The shelter laboratory also has an infrastructure for the habitability of 3 people, with bunk beds for sleeping, kitchen and bathroom.

Laboratory-shelter NUNATAK is energetically autonomous, as it has a modern photovoltaic power system capable of generating enough energy to power the monitoring equipment and life support systems inside.

Actually, Laboratory-shelter NUNATAK is equipped for long term monitoring of concentration and size distribution of particulate matter using an aerosol laser spectrometer (EDM 107, Grimm, Germany), Black Carbon concentration using an multi angle absorption photometer (MAAP 5012, Thermo, USA), net solar radiation using an net radiometer (CNR4, Kipp & Zonen, Netherlands), and meteorological parameters using a portable weather station (HOBO, Onset, USA).

Acknowledgements

Authors acknowledge the financial support of Project NAC-I048-2014 from FPA, Environmental Ministry, Chilean Government and Chilean Army and CRESCO Renewal Energies for their logistical support.

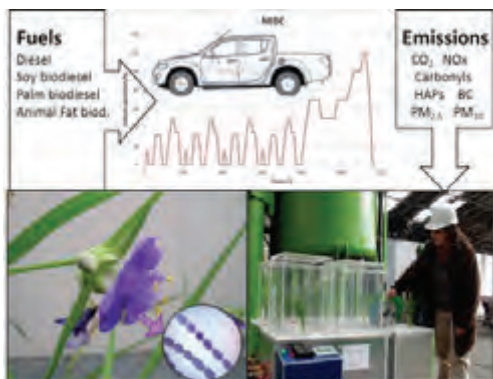
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Genotoxicity Evaluation of Vehicular Emissions from Diesel and Biodiesel of Different Feedstock's Using *Tradescantia* as Biomonitor

PP Env Monit #18

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The incorporation of liquid biofuels into the energy matrix introduces new questions about its possible effect on environment and population health. Vehicle emissions consist in a heterogeneous mixture of gases, volatile and semi-volatile organic compounds which can be found freely in the gaseous phase or adsorbed on the particulate matter. Some of them of mutagenic nature [1].

The genus *Tradescantia*, from the family Commelinaceae, is a multicellular and eukaryotic upper plant with more than 500 species. The *Tradescantia* stamens bioassay (Trad-SH) is reported to be highly sensitive to environmental pollutants and is therefore used to detect toxic effects in urban and industrial studies, including in situ exposure. This test uses the inflorescences of *Tradescantia* clon KU-20 for the evaluation of the mutation frequency induced by chemical compounds, through changes in the colour of the stamen hair cells, from blue to pink, due to the expression of a recessive gene [2,3].

The aim of this study was to evaluate the genotoxicity of vehicular emissions of diesel (B0) and commercial biodiesel (B80) from three different feedstocks (soybean oil, animal fat and palm oil), based on the use of Trad-SH bioassay under controlled conditions. The plant biomonitor was exposed to exhaust emissions of a Mitsubishi Katana L200 (without DPF) driven on a chassis dynamometer following the New European Driving Cycle (NEDC). *Tradescantia* exposure was made in a special chamber named BioToxMonitor, designed and built by CETAM, where diluted emission gases and particles were also analysed to

know the biomonitor exposure levels to CO₂, NO_x, BC, Carbonyls, HAPs, PM_{2.5} and PM₁₀. However, in the present abstract we focus on carbonyl emissions and their relationship with *Tradescantia* mutations. Emission samples were pumped from a dilution tunnel into the Biotoxmonitor. Cartridges of 2,4-dinitrophenylhydrazine (DNPH) were used and eluted with acetonitrile for carbonyl determination in HPLC-UV.

The results show significant differences between mutation frequencies (Mf) of the negative control (deionized water) and the positive controls (sodium azide 40 mg L⁻¹ and formaldehyde 4.35 mg L⁻¹), diesel (B0), animal fat (AF-B80) and soy biodiesel (S-B80). Only palm biodiesel (P-B80) had no significant differences to negative control. The Mf for S-B80 and AF-B80 were 3 and 2.4 times higher than P-B80. These results correlate positively with formaldehyde concentrations found inside the BiotoxMonitor.

Most of literature relates carbonyl emissions with incomplete combustion and oxygen content in the biodiesel blend. However, given that this study compared the emissions of three different B80 biodiesel, the increase in carbonyl concentration seems to be related more likely to the biodiesel ester composition and to some quality fuel parameter, like viscosity and cetane number [4, 5], but not to oxygen content in the biodiesel.

Acknowledgements

Authors thanks the founding of FONDEF D09-I-1070 project, Becas de Doctorado Nacional CONICYT 2014 and the Programa Incentivo Iniciación Científica (PIIC) of the UTFSM for the financial support.

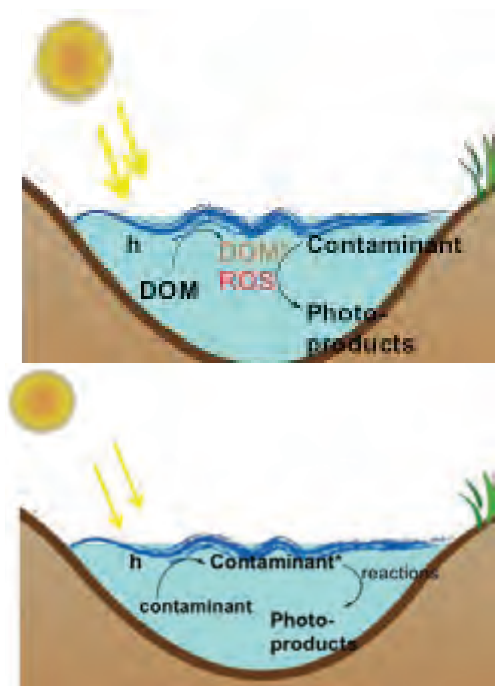
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Environmental Fate of Contaminants in Natural Waters: Effect of Sunlight

PP Env Monit #19

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The environmental impact of contaminants has raised a growing concern over the years, mainly due to their world wide application. Information about possible degradation pathways of contaminants in the environment is important in order to understand their transport and fate in surface and ground waters and to identify the degradation products to which they can give rise.

Photodegradation is one of the factors that can affect the environmental behaviour and persistence of organic contaminants mainly in surface waters exposed to sunlight [1]. Many studies are reported in literature about the role of the sunlight in the degradation of organic contaminants.

In this work three organic contaminants were studied: thiram (THI), a dithiocarbamate pesticide; metoprolol (MET) a pharmaceutical from the b-blockers' group and 4-MBC, an UV filter used in sunscreen. Several studies were performed in solutions with and without natural organic matter and natural waters, in order to evaluate the direct and indirect photodegradation of the different target compounds.

The results obtained showed that THI and 4-MBC suffer direct photodegradation in aqueous solution whereas MET did not photodegrade. In fact, we observed that the photodegradation of MET only occurs in the presence of natural organic matter.

Acknowledgements

Thanks are due to FCT/MEC (POPH/FSE) for the financial support to CERNAS (UID/AMB/00681/2013) and CESAM (UID/AMB/50017/2013) through national funds and, where applicable, co-financed by FEDER, within the PT2020 Partnership Agreement.

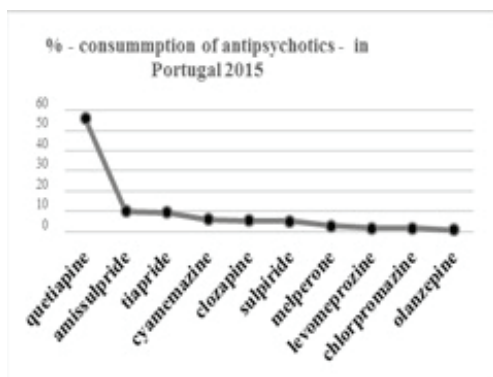
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Improving the Prioritization of Antipsychotic Medicine to Implement Monitoring Programs

PP Env Monit #20

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The patterns of antipsychotic are the treatment of psychosis-mania-aggression. Nevertheless, they are currently used to relieve behavioural and psychological symptoms of dementia among older people [1]. In Portugal during the 2000-2012, the antipsychotic group showed a strong increase of 171%. (DDD by 1000 inhabitants) [2]. Therefore, potential risk of these substances in environment is nowadays one of the major concerns.

Main objective: to develop a prioritisation approach in order to select the antipsychotic substances to survey in the monitoring programs.

Prioritization strategy: 1) simple equation to calculate the PEC (predicted exposure data) [3], involving 3 main parameters: a) crude amount of each antipsychotic drug - primary health care sector - consumed in 2015 (Kg) b) the excretion of active substance (100%); and c) the number of inhabitants in Portugal in 2015. 2) Only antipsychotic substances, with a crude PEC-value greater than the trigger value of 0.01 µg/L, were picked 3) the selected substances were correlated with: a) its excretion fraction as well as its active / conjugates metabolites b) chemical properties c) occurrence, based on literature studies.

Results: During 2015, around 7.4 tonnes of antipsychotic drugs were used. Half of these substances authorised on the market (20

substances) presented an environmental exposure greater than 0.01 µg/L. The representative active substances in descending order of use were quetiapine, amisulpride, tiapride, cyamemazine, clozapine, sulpiride, melperone, levomepromazine, chlorpromazine and olanzapine. The most consumed antipsychotic was quetiapine (4.0 tonnes). Except for levomepromazine and melperone, which are excreted in small proportion of parent compound and active / conjugated metabolites, the remaining substances have excretion percentages over 70%. All the substances are ionisable, demonstrating that the majority of them have a possible lipophilicity profile (log Kow ≥3). The occurrence studies in environment are scarce. In Portugal, olanzapine has been found in WWTP influents [4]. However, it seems that quetiapine showed the most frequent environmental detection in the other countries. Amisulpride was found in groundwater in Germany [5].

Conclusion:

The ecotoxicological/occurrence studies are scarce for the antipsychotic medicines, which makes the environmental risk evaluation a difficult task. Hence, it is important to establish a list of priority for these medicines, prior to implement a comprehensive survey in environmental compartments.

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Quality Assurance and Identification of Sources in PM_{2.5} Lisbon Sub-Urban Aerosol

PP Env Monit #21

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Sub-urban areas contain a large concentration of people and anthropogenic industrial and traffic activities. Hence, they exhibit both the highest levels of pollution and the largest targets of impact. Several studies shown significant correlations between particulate matter (PM) levels and amplified respiratory and cardiovascular diseases, and mortality [1, 2]. Although understanding and monitoring air pollution in these areas is important, it is difficult, mostly for particulate pollutants that have a mixture of primary and secondary sources. The main objective of this study is to identify sources and processes that affect air particulate matter concentrations, at a sub-urban area located in the north outskirts of Lisbon. Particles with an aerodynamic diameter $<2.5 \mu\text{m}$ (PM_{2.5}) were collected with a medium volume Leckel sampler, during 24h twice a week for one year. Elemental concentrations were assessed by inductively coupled plasma mass spectrometry (ICP-MS) for the determination of ^{26}Mg , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{111}Cd , ^{121}Sb , ^{208}Pb . Prior to ICP-MS analysis, samples were digested in a microwave system with a mixture of nitric and hydrofluoric (1:4) acid, and evaporated until near to dryness. Quality control of elemental determination was assured by analyses of the Certificated Reference Material No.28 Urban Aerosols from

National Institute for Environmental Studies.

Firstly, the optimization of the procedure of analysis of aerosol samples by ICP-MS analysis was accomplished, using PTFE, quartz and polycarbonate filters. Quality assurance of PM_{2.5} sampling and analysis based on a precision study, involving sampling and analysis of APM, using 3 samplers operating side by side showed good reproducibility.

Positive Matrix Factorization analysis was used to identify possible emission sources and determine their contribution for the total mass concentration of PM_{2.5}. Hysplit Model was used to identify the air mass trajectories influencing each one of the sampling days.

Due to the geographical position, the Atlantic Ocean serves as an important source of particles and plays an important role in many atmospheric processes. Besides sea, this area also presents other characteristic sources: soil, secondary aerosols, road traffic, fuel-oil combustion and coal combustion. Maritime transport scenarios are frequent and promote the decrease of anthropogenic and mineral aerosol concentrations. South Continental episodes are common and are characterized by high mineral aerosol contents, due to the transport of dust from the interior of Iberian Peninsula and the Sahara desert.

Acknowledgements

This work was funded by the International Atomic Energy Agency under the Technical Project RER/1/015 and by the Portuguese Foundation for the Science and the Technology (Fundação para a Ciência e a Tecnologia, FCT; Portugal) project UID/Multi/04349/2013 to C2TN/IST.

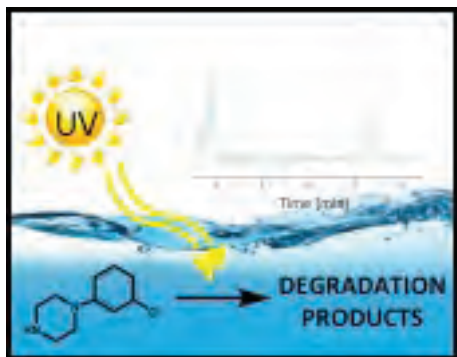
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Environmental Degradation of the Psychoactive Phenylpiperazine Derivative mCPP

PP Env Monit #22

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Illicit drugs (ID) are a classe of new so-called ‘emerging’ contaminants that have raised great concern in the last years. Due to their continuous input into the aquatic media through wastewater as a main point-source, IDs are considered to be ‘pseudo-persistent’ contaminants.

Several studies have reported that illicit drugs are detectable in wastewater from municipal sewage treatment plants (STPs) and surface waters [1,2]. These substances are excreted in urine and faeces unchanged or as active metabolites in high percentages after consumption and continuously discharged into domestic wastewaters. Residues of illicit drugs can therefore reach STPs in substantial amounts, escaping degradation, and are then released into surface waters.

Current research efforts are focused on the monitoring of parent compounds, while transformation products are usually not included. However, transformation products can be relevant for environmental and health risk assessment. After consumption IDs can be transformed within the consumer (i.e. human metabolism), undergo various chemical and biological processes during wastewater treatment (e.g. hydrolysis, oxidation, de-conjugation, photodegradation) and/or they can be transformed in the environment by similar processes as those that may occur in the wastewater treatment plant.

The so-called designer drugs are a heterogeneous group of psychoactive substances obtained through the modification of chemical structure of some natural products or drugs [3]. The most common designer drugs are derived from phenylethylamine, as 3,4-methylenedioxymethamphetamine (MDMA). As these drugs become forbidden, new derivatives appear in the market to evade the law as was the case of piperazine derived drugs.

The new ecstasy-like substance 1-(3-chlorophenyl)piperazine (mCPP) has been found in 26 member states of European Union (EU) and in Norway. Chemically, the piperazinic compounds are derived from piperazine, a cyclic molecule containing two nitrogens in opposite positions and four carbons distributed between the two nitrogen atoms.

In this study, we investigated the photolysis mechanisms of mCPP in water under the irradiation of a simulated sunlight source. The main purpose of this study was to understand the photochemical degradation of mCPP and to characterize its intermediates and photoproducts and propose the possible photodegradation pathways. The results obtained will be presented in this communication.

Acknowledgements

This project was supported by Foundation for Science and Technology (FCT) and FEDER/COMPETE (Grants UID/QUI/00081/2013 POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028).

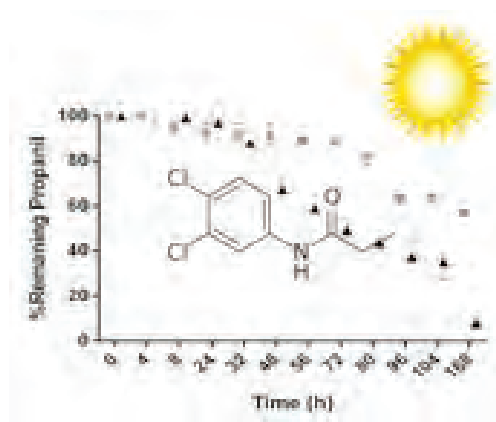
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The Role of Chemical and Photochemical Degradation in The Environmental Fate of Herbicide Propanil

PP Env Monit #23

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The use of pesticides in modern agriculture has considerably improved productivity, but it has also significantly increased the concentration of these compounds in food and in our environment, with associated negative effects on human health. As a result of their ubiquitous application, pesticides are commonly found in surface and groundwaters worldwide [1]. In addition, contamination of aquatic systems by pesticide residues around the world repeatedly compromised also aquatic food resources, fisheries, and aquaculture. Once in the environment, most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions.

Propanil (*N*-(3,4-dichlorophenyl) propanamide) is a synthetic anilide herbicide used to control grasses and broad-leaf weeds primarily during the production of rice. It is a short duration postemergent herbicide of selective action, used in the inhibition of photosynthetic electron transport in wide leaf herbs. Propanil is hydrolysed in acidic and alkaline media to 3,4-dichloroaniline (3,4-DCA) and propionic acid. In water, propanil and 3,4-DCA are rapidly degraded by sunlight

to phenolic compounds, which then polymerize [2]. The molecule 3,4-DCA is highly toxic and is classified as a secondary poisonous substance.

Photolysis is one of the major transformation processes affecting the fate of pesticides in the aquatic environment. Sunlight photoalteration processes are known to play an important role in the degradation of pesticides and other contaminants in water by generation of highly reactive intermediates, mainly hydroxyl radical ($\bullet\text{OH}$), a powerful non-specific oxidant. As photochemical degradation contributes to the environmental fate of many pesticides in surface waters, a better understanding of the role of direct and indirect photochemical degradation of pesticides is necessary in order to predict their environmental fate and persistence.

Thus, in this work, we have studied the influence of key chemical properties and the environmental conditions that can have an impact on the degradation of herbicide propanil. Chemical and photochemical studies conducted under environmentally relevant conditions (i.e., aqueous solutions with irradiation wavelengths >290 nm) were performed. Comparisons were made between the observed degradation rates in sterile water, pure water and a river water containing dissolved organic matter to assess the extent of pesticide fate. The results obtained will be presented in this communication.

Acknowledgements

This project was supported by Foundation for Science and Technology (FCT) and FEDER/COMPETE (Grants UID/QUI/00081/2013 POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028).

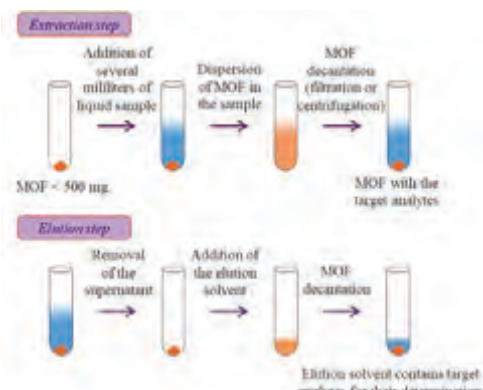
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Monitoring Personal Care Products in Water Samples using Metal-organic Framework in Miniaturized Dispersive Solid-phase Extraction

PP Env Monit #24

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Personal care products (PCPs) refer to a wide group of compounds of diverse chemical nature utilized in dairy products such as gels, lotions, or cosmetics [1]. They can be classified in six groups: UV filters, preservatives, disinfectants, musk, insect repellents, and siloxanes. Its use has increased in recent years, which has caused their excessive accumulation in the environment. Furthermore, PCPs have been categorized as emerging contaminants, due to their toxicity and their probable endocrine disrupting activity. Clearly, humans are exposed to high amounts of PCPs directly or indirectly.

PCPs are present in environmental samples at low concentration levels. Thus, despite modern analytical determination techniques, an adequate extraction and/or preconcentration strategy is normally required as a previous step of the chromatographic method.

Trends in analytical chemistry are focused in the development of green extraction methods, in terms of minimization (and even elimination) of the organic solvent consumption in the sample preparation step, minimization of time and wastes, while maintaining adequate analytical performance in terms of accuracy, sensitivity, and reproducibility. Among green techniques for sample preparation, the miniaturized version of the solid-phase extraction

method (μ SPE), requiring amounts of sorbent <500 mg, has become one of the most frequently used techniques in environmental analysis. μ SPE is characterized by as high preconcentration factors, rapid phase separation when performed in its dispersive version (D- μ SPE), low organic solvent consumption compared with SPE, and simplicity [2].

Recent studies focus on the research of novels materials as sorbents in D- μ SPE, such as molecularly imprinted polymers (MIPs), nanomaterials (NMs), and also metal-organic framework (MOFs) [3].

MOFs are hybrid microporous crystalline materials with three-dimensional structures highly ordered. MOFs are formed by coordination bonds of metal ions (clusters) with organic ligands (linkers). They exhibit the highest surface area known, high mechanical resistance and thermal stability, uniform structured cavities, and high adsorption affinity [2]. Furthermore, MOFs present tailorable polarity and pore size, which permits to be a priori designed with certain affinity for the target analytes.

In the present study, a D- μ SPE method using novel MOFs followed by ultra-high performance liquid chromatography and ultraviolet detection (UHPLC-UV) has been developed to monitor PCPs in waters.

Acknowledgements

P.G.-H. thanks the Fundación Caixa-ULL for her FPI PhD fellowship. V.P. acknowledges funding from the Spanish Ministry of Economy (MINECO) project ref. MAT2014-57465-R.

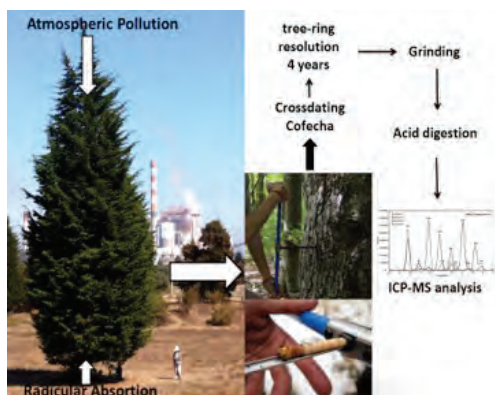
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Evaluation of Tree-rings of *Cupressus macrocarpa* as Environmental Multi Decadal Biomonitoring

PP Env Monit #25

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Anthropogenic contamination by trace elements and heavy metals degrades water, soil and air, affecting the ecology of diverse populations, both natural and human. In central Chile (V Region) is located the Puchuncaví Valley. In this area there is an important industrial complex with diverse industries, which were installed since 1964. The main activities are copper smelting and coal-fired power plants (thermoelectric), but also include liquefied petroleum gas (LPG) terminal, chemical industries and cement companies, among others. Due to the type of activity developed in the area, it is strongly affected by the anthropogenic pollution, such as discharged of atmospheric deposition, gaseous pollutants and deposition of metal-rich particles [1, 2].

In the tree, intake of elements is through the leaves and roots. However, the main pathway uptake of elements to tree-rings is via roots. The roots are influenced for several factors such as the sapwood-heartwood concentration equilibrium, the quantity of macronutrients versus metals, ion solubility, type and pH of soil [3, 4]. Likewise, within the exogenous factors that affect soil pH is found the environmental pollution. The soil pH is influenced directly for environmental pollution through the acid rain that play an important role in soil acidification, affecting the bioavailability of some elements [4].

The goal of this study was to evaluate the *Cupressus macrocarpa* (Cm) tree-rings as environmental multi

decadal biomonitor of trace elements in Puchuncaví Valley. Core samples were drilled from 25 Cm trees of Costa Quilén (4,2 Km N from the industrial complex) were used to crossdating, with Cofecha program. Five trees were selected to trace element analysis. The samples selected was crossdating between 1960 and 2011. For the trace element analysis, tree-rings portions with a resolution of 4 years were milled, acid digested and subsequently analysed by ICP-MS for As, Pb, Mo, Cu, Fe, Al, Cr, Zn, Mn, Ba, Co, Ni, Cd, V and Sb.

The mainly source of pollution in the area is a copper smelting. Based on copper production, 3 periods (1960-1975, 1976-1995 and 1996-2011) were selected to evaluate the trace elements in tree-rings. Significant differences (confidence level 90%) between three periods in Al, As, Zn, Cu, Cr, Fe, Mo, Pb, Mn, Co, Ni, Cd, Ag and V was observed. In all cases, the third period (1995-2011) was presented a higher concentration of the element evaluated, according to copper production. For all elements evaluated, the increase in concentration in the third period (1996-2011) was 88-345% respect to first period (1960-1975), except for Cd which presented a decrease of 1,7%. The tree-rings of Cm are a good multi decadal bioindicator of environmental pollution.

Acknowledgements

CONICYT+PAI/ Concurso Nacional Inserción en el Sector Productivo, Convocatoria 2014 + Folio (781301007) and AES-GENER, Chile.

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Sulfonamides in Wastewaters: Method Development, Occurrence, Mass Loading, Removal Efficiencies and Environmental Risk Assessment

PP Env Monit #26

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Antibiotics, which are an important group of pharmaceuticals in today's medicine, have been used not only to prevent and treat diseases in human and animals but as growth promoters, as well. They are one of the most important xenobiotic contaminants due to their potential development of antimicrobial resistance [1]. As their consumption has been increased, they are being detected in all sectors of the environment and have attracted much public attention in the last decade. Sulfonamides (SAs) are the most highly consumed antibiotics, after tetracyclines, in the European Union (EU). They are commonly used to treat diseases as urinary tract infections, ear infections, bronchitis, bacterial meningitis, certain eye infections, *Pneumocystis carinii* pneumonia, traveler's diarrhea, and a number of the other kinds of infection [2]. Furthermore, they are used in aquaculture and intensive livestock farming.

The presence of SAs residues is of great public concern because some of them might be carcinogenic, promote occurrence of antibiotic resistant bacteria, and cause allergic reactions in humans. Therefore, in the European Union (EU),

the total level of SA residue should not exceed 100 μkg^{-1} [3].

The present work describes the development and application of a method for the determination of nine sulfonamides (sulfacetamide, sulfapyridine, sulfadiazine, sulfamethoxazole, sulfathiazole, sulfamethizole, sulfamethazine, sulfamethoxypyridazine, sulfaquinoxaline) in wastewaters in Greece. A pre-concentration step, based on solid phase extraction (SPE) using different types of sorbent cartridges and followed by LC-ESI-MS system, was used.

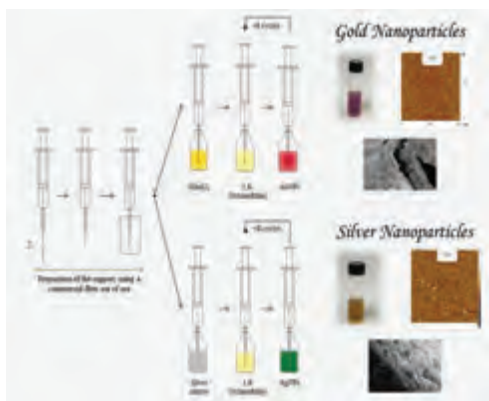
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Comparison of Au and Ag Nanoparticles as Novel Coatings in Solid-Phase Microextraction Fibers for Environmental Analysis

PP Env Monit #27

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Solid-phase microextraction (SPME) has become an extended technique employed for traces analysis in complex samples such as environmental samples since Arthur and Pawliszyn developed it in 1990. This is due to the high simplicity of the technique, the reduction of steps at the sample preparation (performing the extraction and pre-concentration in one single step), and its environmental friendly nature owing to the reduction of organic solvents and sample volumes requirements. SPME is even solvent-free when combined with gas chromatography.

Current trends of the SPME technique focus on the development of more selective and robust coatings, employing novel materials such as ionic-liquids (ILs), polymeric ionic-liquids (PILs), metal-organic frameworks (MOFs), molecularly imprinted polymers (MIPs), carbon nanomaterials and metallic nanomaterials [1]. Among them, metallic nanoparticles (NPs) have been thoroughly used [2]. This is related to their advantages:

robustness, stability, high surface area, feasible functionality, and interesting optical properties. Among metallic NPs, gold (AuNPs) and silver (AgNPs) nanoparticles have been the most studied so far, and at this point higher control over their synthesis can be achieved. Furthermore, both types of NPs merit citation as novel SPME coatings [3].

In this study, a comparison between the use of silver nanoparticles and gold nanoparticles as novel coatings for SPME is accomplished. Particular attention is paid to all the aspects related with the synthesis procedure of the nanoparticles and the preparation of the SPME coatings, their morphological characteristics, and their applicability to the environmental analysis, also comparing their analytical performance for contaminants of different nature.

Acknowledgements

V.P. thanks the Spanish Ministry of Economy and Competitiveness (MINECO) for the Project Ref. MAT2014-57465-R. A.G.-S. thanks his research contract associated to the Project Ref. MAT2014-57465-R. P.G.-H. thanks the Fundación Caixa-ULL for her FPI PhD fellowship.

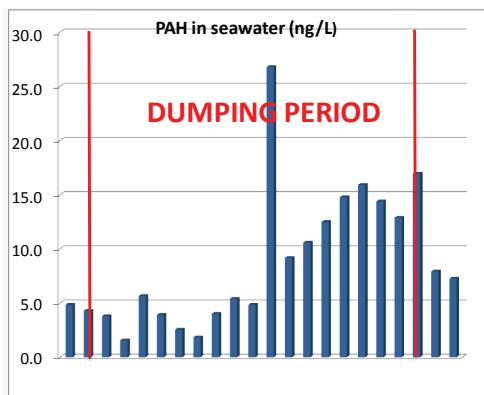
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Pollution Caused by the Dumping of Hydrocarbon Polluted Dredged Sediments in a Coastal Area in Greece

PP Env Monit #28

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The pollution from hydrocarbons and the geochemistry of hydrocarbons were studied in the water column and surface sediments of a coastal area in Saronikos gulf, Greece, where the dredged urban river (Kifissos river) sediments were dumped for a period of 20 months (May 2010 - December 2011). Kifissosriver is the metropolitan river of Athens, the capital of Greece, and is contaminated by hydrocarbons, mainly of petroleum origin, as a result of intense anthropogenic activities in the area. Surface sediment and seawater samples were collected from 5 stations during April 2010 - July 2012. Aliphatic and polycyclic aromatic hydrocarbons (PAH) were determined in both seawater and sediment samples by gas chromatography - mass spectrometry applying the appropriate procedures [1].

In the surface sediments, total aliphatic hydrocarbon concentrations were increased from 98 $\mu\text{g/g}$ to 1800 $\mu\text{g/g}$ during dumping and remained high (1003 $\mu\text{g/g}$) four months after dumping. The examination of various ratios and indices (CPI, U/R ratio, composition of hopanes) showed significant quantities of petroleum residues during and after dumping. Total PAH were also increased insurface sediments from 450 ng/g to 6200 ng/g during dumping and decreased to 3300 ng/g after dumping. Before dumping, the composition of PAH mixtures and the examination of specific isomeric PAH ratios revealed a clear predominance of pyrolytic compounds. During dumping, high abundances of 2-3 aromatic ring compounds were recorded, whereas the methylated PAH were predominant, suggesting petrogenic origin, similar to the contaminated dumped material. After dumping, a part of methylated derivatives were lost, resulting inequal amounts of pyrolytic and petrogenic PAH. In seawater, a 5-fold increase of PAH concentrations was observed 9 months after the beginning of the dumping, while six months after theend of the dumping PAH values in the whole water column were still higher than those prior to dumping. PAH with 2-3 aromatic rings, along with the methyl substitutedoneswere dominant in all cases, before, during and after the dumping.

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Outdoor Spatial Distribution and Indoor Levels of NO₂ and SO₂ in a High Environmental Risk Site of the South Italy

PP Env Monit #29

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In the frame of the project EDOC@WORK3.0, Education and Work on Cloud (2013-2015) founded by MIUR (Italian Ministry for University and Research), a monitoring plan has been carried out in Taranto (one of the most polluted sites of Italy) [1], by using passive sampling devices (Radiello sampling system) [2], in order to investigate contemporary indoor and outdoor concentrations of NO₂ and SO₂.

In Taranto (South Italy), close to the urban centre, an industrial complex, that includes one of the greatest steel manufacturing plants in Europe, an oil refinery, shipbuilding activities, a navy arsenal and a cement plant and two thermoelectric power plants has host [1]. These industrial activities represent important environmental stressors for the area.

Simultaneously indoor and outdoor samplings of NO₂ and SO₂ were performed from 2nd November 2015 to 5th December 2015 in nine sites scattered in the area: three sites were located in the downtown, two sites in the district Tamburi (very close to the industrial area), one site closeness to the high

traffic street, two in the district 'Paolo VI' and one in Statte (a municipality very close to the industrial complex). In the figure, green drops represent the sites monitored during our campaign, while red drops represent the stations of the regional air quality monitoring network managed by Apulian Environmental Protection Agency (ARPA Puglia). Indoor sites were selected among private homes, vicarage, a research institute, the Engineering department and an educational center.

Each indoor and outdoor sampler was exposed for a period of time ranging from three to four days.

NO₂ and SO₂ concentration levels obtained during our campaign were compared with values obtained from ARPA monitoring stations for the same sampling period. Moreover, NO₂ and SO₂ total column maps were obtained for the sampling time period from satellite images (<http://giovanni.gsfc.nasa.gov/giovanni/>), in order to have information on all area of South Italy.

Generally, NO₂ and SO₂ values have shown variability among sites and their respective locations.

In particular, outdoor SO₂ mean values were more homogeneous among sites suggesting a common origin of this pollutant, while outdoor NO₂ mean values among sites were more variable, suggesting the contribution of local sources.

Indoor NO₂ and SO₂ mean values generally indicated kitchen as relevant source.

Acknowledgements

This work was founded by PON Ricerca e Competitività 2007-2013' MIUR program.

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Combined Effect of Copper and Chromium on *Ceratophyllum Demersum* Absorption

PP Env Monit #30

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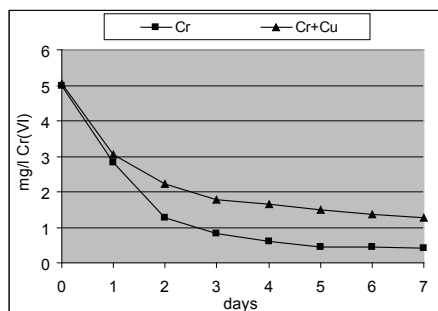


Figure 1. Change of concentration Cr when alone and in the presence of Cu

Heavy metals are very persistent natural or anthropogenic pollutants, especially in the aquatic environment. The biological effects of individual metals are more or less known, but even though combinations of heavy metals are common in nature their combined effects are still to be thoroughly investigated. Metals in mixtures may act independently or interact to produce additive, synergistic, or antagonistic effects, which depends on their concentrations and factors such as temperature, pH, and light [1]. So far, only a few studies have investigated combined effects of metals on plant species.

The aim of our study was to investigate remove from water copper (in the concentrations of 5 mg/l) and chromium (5 mg/l) using aquatic plant *Ceratophyllum demersum* L by exposing it to either metal or to their combinations for seven days.

Copper is an important essential microelement for plants, but it can be toxic at higher concentrations. Copper contributes to several physiological processes in plants [2]. Cr is not essential for plants and it is toxic even at low concentrations [3].

Ceratophyllum demersum is a perennial submerged, free-floating aquatic rootless plant, which grows in

stagnant or slow-moving waters. The buds grow in the winter at the bottom of lake water and form a new plant in the spring. *C. demersum* can be used as a measure of the lake pollution, as its tissue may contain toxic metals, such as Cd and Pb. It could also be used to remove low concentrations of heavy metals from aquatic ecosystems [4]. For our experiments plant was taken from Lake Skadar, Montenegro.

Water samples for analyzed were filtered through a 0.45 μm Millipore filter and stored in plastic 1L bottles to which 2 mL of 70 % super pure nitric acid was added. Water samples were prepared in triplicate and their average value was assessed. Blank solutions were added to the series of samples and measured after every tenth sample determination. The set of standards applied for preparation of calibration curve for metal concentration determination was obtained from Merck (Darmstadt, Germany). The concentrations of Cu and Cr were determined by the ICP-OES technique using a Spectro Arcos instrument.

C. demersum removed from water 78.5% of the copper, and 91.6% of the chromium when metal given alone. No effect was noted on the removal Cu in the presence of Cr. However, the removal of Cr from water is reduced in the presence of Cu. In the presence of Cu, *C. demersum* removed 73.8% of Cr from the solution for seven days.

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Organic-geochemical Characteristics of the Mud from the Techirghiol Lake, Romania

PP Env Monit #31

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Figure 1. Location of samples in the Lake Techirghiol (Romania).

The lake Techirghiol is located on the east of Romania, separated from Black Sea by a sand-belt, 100 m wide and 3 km long. It is the largest salt lake in Romania, with an area of 10.68 km² and a maximum depth of the 9 m. [1, 2]. Techirghiol Lake is supplied with groundwater and surface water from Movilita, Biruinta and Techirghiol rivers. Also, Techirghiol lake was declared protected area in 2000 [1].

As a result of low annual precipitation and high evaporation the lake water has become hypersaline. During the last few years the salinity of the water varies between 55 g/l and 66 g/l [1]. In this hypersaline environment, a unique ecosystem in Europe has developed with the specific capacity of producing mud from organic matter (saprogenic sludge) which is used for therapeutic purposes.

The aim of this paper is to investigate origin and maturation level of organic substances of Techirghiol Lake mud. This type of research has not been conducted so far. Five mud samples were collected at distinct locations (Figure 1).

After bitumen extraction from the samples and isolation of saturated, aromatic and NSO fraction, saturated and aromatic hydrocarbons were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The saturated hydrocarbon fraction was subsequently analysed for *n*-alkanes, and polycyclic alkanes of the sterane and terpane types.

The chain length distributions of the *n*-alkanes of all samples are bimodal with predominance of odd-over-even chain lengths in most of samples. Relatively high abundance of high-chain *n*-alkane homologues with *n*-alkane maximum at C₂₉, followed by presence of homologue series of *n*-alkenes in that range implies the recent organic substances.

On the other hand, distribution of hopanes and steranes indicates presence of matured organic substances.

The predominant hopane in all samples is C₃₀17 α (H)21 β (H)-hopane and it is followed by C₃₀17 α (H)21 β (H)-hopane, C₃₁-C₃₅17 α (H)21 β (H) 22S and 22R-hopanes, C₂₉Ts, C₂₉-moretane, C₃₀-moretanes, gammacerane, oleanane, as well as C₂₇, C₃₀ and C₃₁ hopens. Tricyclic and tetracyclic hopanes are also present.

In sterane fractions, besides the biolipid isomers C₂₇-C₂₉ 14 α (H)17 α (H) (20R), geolipid isomers were also found, like diasteranes, as well as C₂₇-C₂₉ 14 β (H) 17 β (H) (20S) steranes.

Abundance and distributions of *n*-alkanes, *n*-alkenes and steranes indices suggests that investigated muds contain mixture of recent and matured organic substances.

Considering the unexpected presence of the mature organic substance in analyzed mud samples from the Techirghiol Lake, further analyses are necessary to determine its origin.

Acknowledgements

This work was supported in part by the Ministry of Science and Environmental Protection of the Republic Serbia (Project No.176006).

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Capsule Phase Microextraction: A Field Deployable Sample Preparation Technique for Rapid Environmental Pollution Monitoring

PP Env Monit #32

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Recent decades have witnessed a massive surge in environmental pollution across the world. As such, the importance of a robust pollution monitoring plan can not be overemphasized. Current analytical work-flow dedicated to environmental pollution monitoring regimen consists of a number of steps including collection of representative samples from the field in prescribed containers, adding preservative to cease microbial activity, transport to the laboratory, storing at controlled temperature, thawing to ambient temperature, filtration, extraction of the target analytes using any or a group of sample preparation techniques, elution of the analytes in organic solvent, solvent evaporation, sample reconstitution in a small volume of organic solvent and finally injecting an aliquot into the chromatographic system. This long list of sequential steps involved in sample pretreatment, sample preparation, and sample post-treatment often incur substantial loss of the target analyte(s), and consequently, result in under reporting of the analyte concentration in the environmental water. One possible solution to minimize the long list of steps involve in sample preparation is to develop a field deployable sample preparation device that would allow the entire sample preparation directly in the field.

Although the new generation sample preparation techniques represent improvements in sample preparation technologies, most of these techniques cannot directly handle real-life environmental samples which often contain high volume of particulates, debris, biomasses and other matrix interferents and do inevitably require a series of sample pretreatment steps such as filtration,

centrifugation etc.

Capsule phase microextraction (CPME) has been developed to culminate majority of the shortcomings still haven't been adequately addressed by other sample preparation techniques. CPME completely eliminates sample pretreatment/clean-up step from the sample preparation work-flow. CPME utilizes a porous tubular polypropylene membrane capsule with 0.2 μm pore size and 1.8 mm internal diameter to encapsulate sol-gel hybrid organic-inorganic sorbent in the form of monolithic bed or spherical particles. The porous membrane capsule allows easy permeation of aqueous sample containing the target analyte(s) while protecting the sorbent from being contaminated by matrix interferents. A magnetic metal rod is embedded into the microextraction capsule that allows spinning the device when placed on a magnetic stirrer and diffuses the sample matrix for fast analyte-sorbent interaction and rapid extraction equilibrium. High loading of sol-gel sorbent providing excessive sample capacity for target analyte(s), fast extraction kinetic due to sponge-like porous architecture of the sol-gel sorbent, protection of the sorbent from contamination *via* encapsulation into a porous tubular membrane capsule have made capsule phase microextraction (CPME) an impressive and robust sample preparation technique. After the extraction, a small volume of organic solvent can be used to desorb the accumulated analyte(s). Due to high preconcentration factor achieved in CPME, no solvent evaporation and sample reconstitution is required. The prepared sample can be analyzed in gas chromatograph, liquid chromatograph or capillary electro chromatograph to obtain complimentary information if a mutual solvent equally compatible with these chromatographic techniques is chosen.

Analytical data obtained from a number of real-life applications of CPME including EPA priority pollutants, endocrine disrupting chemicals (EDCs), pharmaceutical and personal care products (PPCPs) from environmental water will be presented showcasing CPME's advantages, extraction characteristics, performance superiority, and analytical figures of merit.

Analysis of Three- and Tetracyclic Aromatic Hydrocarbons in the Air of Belgrade (Serbia) Using *Cedrus atlantica* (Atlas cedar) Needles as Passive Samplers

PP Env Monit #33

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Cedrus atlantica (Atlas cedar) is an evergreen conifer decorative tree which is very widespread in green areas in Belgrade, the capital of Serbia. In our previous study we demonstrated that *Cedrus atlantica* pine needles are capable of accumulating three- and tetracyclic aromatic hydrocarbons from the air [1].

The aim of our present research was the analysis of three- and tetracyclic aromatic hydrocarbons in the air of Belgrade using *Cedrus atlantica* needles as passive samplers.

The *Cedrus atlantica* sprouts and one year old needles were collected in spring 2017 at several different locations in the central area of Belgrade, Serbia. The selected polycyclic aromatic hydrocarbons were isolated according to an analytical method by Kelly et al [2]. The obtained extracts were analyzed by gas chromatography – mass spectrometry in the Single Ion Monitoring mode. The ions monitored were: $m/z = 178$ (phenanthrene and anthracene), $m/z = 202$ (fluoranthene and pyrene) and $m/z = 228$ (benzo[a]anthracene and chrysene).

The analyzed three- and tetracyclic aromatic hydrocarbons were quantified against their surrogate standards, phenanthrene- d_{10} and chrysene- d_{12} , according to the previously validated method.

The results indicated that three- and tetracyclic aromatic hydrocarbons in the air of Belgrade at the investigated locations were mainly sourced from traffic. These results were in agreement with the results of earlier analyses of polycyclic aromatic hydrocarbons in the air of Belgrade [3].

The concentration of the investigated analytes in the sprouts was lower than the one in one year old needles. These results are in agreement with the current knowledge on accumulation of polycyclic aromatic hydrocarbons in pine needles and indicate that *Cedrus atlantica* needles different in age can be used for differentiation of temporal trends in concentration of polycyclic aromatic hydrocarbons in the air.

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 176006) for supporting this research.

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Validation of a Gas Chromatographic – Mass Spectrometric Method for Analysis of Three and Tetracyclic Aromatic Hydrocarbons in *Cedrus atlantica* (Atlas Cedar) Needles

PP Env Monit #34

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Pine needles are well known for their ability to accumulate, in their cuticular wax layers, atmospheric polycyclic aromatic hydrocarbons (PAHs). Many different analytical methods are reported useful for their analysis.

In our previous research we demonstrated that the needles of *Cedrus atlantica* (Atlas cedar) can be considered as passive samplers of three- and tetracyclic aromatic hydrocarbons in the air [1]. The aim of our present research was validation of a gas chromatographic – mass spectrometric (GC-MS) method for quantitative analysis of these PAHs in needles of this coniferous tree.

For the method validation study we used a sample preparation and extraction method by Kelly et al [2]. In order to mimic the analytical method in the best possible way, a matrix spike procedure was used.

The *Cedrus atlantica* needles different in age were collected in spring 2017 in a city park in the central area of Belgrade, Serbia. The needles were homogenized and divided in number of identical subsamples.

Each subsample was spiked with the mixture of three- and tetracyclic aromatic hydrocarbons

of known concentration. The compounds used were: phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene. The concentration range was chosen to be the same as the concentration range of these compounds reported for different pine needles in the scientific literature.

For the quantification purpose, surrogate standards: phenanthrene-d10 and chrysene-d12 were added to each subsample as well.

All subsamples were passed through the same analytical procedure. All analyses were conducted in five replicates. The extracts obtained were analyzed by GC-MS in a Single Ion Monitoring mode.

The validation parameters investigated in this research were: linearity, precision, limit of detection, limit of quantification and recovery.

The results showed that this method can be successfully used for quantitative analysis of three- and tetracyclic aromatic hydrocarbons in the needles of *Cedrus atlantica* in the concentration range of these compounds reported for different pine needles in the literature.

Acknowledgements

We thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 176006) for supporting this research.

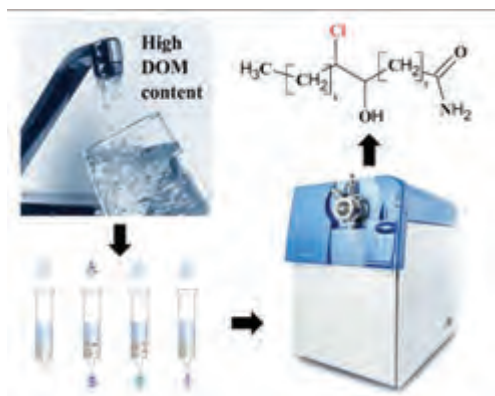
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Non-targeted Screening of Halogen-containing Disinfection by-Products in Tap Water Rich with Organic Matter

PP Env Monit #35

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The quality of drinking water is of great concern, especially in the regions with natural reservoirs enriched with dissolved organic matter (DOM). The application of chlorine-based disinfectants, such as molecular chlorine, hypochlorites, chloramines and others [1] leads to formation of disinfection byproducts (DBPs), which may have a negative impact on human health. Even after flocculation several hundred halogen-containing compounds are detected by HR-MS method [2].

The problem is particularly acute for the European North of Russia, where lakes and rivers are fed with water of peat bogs.

As an object of the present study we chose the tap water of the City of Arkhangelsk collected during spring break and abundant snowmelt. This period is characterized by a sharp increase in the amount of DOM and hypochlorite disinfectant consumption during water treatment.

The fresh samples of tap water (2 L) were acidified and immediately concentrated using solid-phase extraction on polymer sorption cartridges Bond Elute PPL (Agilent, USA) [3]. After desorption of analytes with methanol the obtained extracts were evaporated in nitrogen stream to the final volume of 200 μ L.

Ultra-pure Milli-Q water after the polishing with C18 LC-Pak cartridge (Merk, France) was treated in the same manner and used as a blank sample.

The extracts were analyzed by the high performance liquid chromatography – high resolution time-of-flight mass spectrometry (HPLC-QqTOF) in positive and negative mode of electrospray ionization (ESI). All experiments were carried out using TripleTOF 5600+ instrument (AB Sciex, Canada) coupled to LC-30 Nexera HPLC system (Shimadzu, Japan). Chromatographic separation was performed on a reversed C18 stationary phase in a gradient mode. Mass spectrometry detection was carried out in the information-dependent acquisition mode in the mass range 100–1000 Da (MS), and 20–1000 Da (MS/MS) with resolving power 40 000 FWHM. The collision energy used was 30 eV with a spread of 20 eV.

Chloro- and bromophenols dominated (10 compounds) among the halogenated species in the extracts analyzed. Of particular interest are the data obtained in the positive ionization mode. More than forty compounds of CHNOCl and CHNOBr groups were detected. In accordance with the gross formulae obtained, as well as MS/MS spectra, it can be assumed that the majority of these components are hydroxy halogenated derivatives of fatty amides (picture). These products were not mentioned earlier in literature as disinfection byproducts. They can be formed as a result of HOCl and HOBr addition to double carbon-carbon bonds of unsaturated amides. The latter precursors (eg. oleamide) are widespread in natural water and also can be released during DOM degradation processes.

The results obtained are important for understanding the consequences of using halogen-containing reagents for disinfection of organic rich tap water.

Acknowledgements

The research was performed under financial support of Russian Scientific Foundation (project No. 17-13-01112).

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Biomonitoring of Stockholm Convention POPs in Gull Eggs from National and Natural Parks of the Iberian Peninsula

PP Env Monit #36

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The objective of this study is to investigate the presence and distribution of Persistent Organic Pollutants (POPs) in populations of Yellow-legged Gulls (*Larus michahellis*) and Audouin gulls (*Larus audouinii*) in 9 areas of great ecological interest spread in the Iberian Peninsula. Because of their feeding habits, the great industrial development and the global anthropogenic pressure [1, 2], these colonies are exposed to various pollutants, ranging from POPs historically used in agriculture and industry to compounds recently used such as flame retardants or fluorinated compounds in consumer's goods. POPs are substances that are toxic and bioaccumulable, that can be transported over large distances and are widely distributed in aquatic and terrestrial ecosystems and can cause impairment in marine birds [3, 4, 5]. This study attempts to study all POPs that are comprised under the Stockholm Convention (meeting of 11th September 2016 in Rome). These include legacy compounds such as polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCs) and the more recently included compounds such as polibromodiphenyl ethers (PBDEs), perfluorinated substances (PFASs), short-chain chlorinated paraffins, and other OC pesticides such as endosulfan, lindane, pentachlorobenzene and hexabromobiphenyl. Gull eggs were biomonitoring using optimised and validated analytical techniques based in ultrasonic extraction and gas chromatography coupled to tandem mass spectrometry. POPs were detected in all colonies, with higher levels in the Mediterranean areas compared to Atlantic colonies. The concentration of individual target compounds ranged between 10 and 150 ng/g wet weight and Σ POPs were at the μ g/g

wet weight level. PCBs were the most ubiquitous compounds, followed by OC pesticides, PFAS, PBDEs and other compounds were detected at trace levels. A different POP profile was observed in each colony which reflects a specific contamination pattern according to the activities carried out in each area. Whereas in Medes the pattern was enriched with PFAS, Ebros, Columbretes, Murcia and Chafarinas had high concentrations of PCBs and OC pesticides and the Atlantic colonies had high levels of PBDEs. Surprisingly, the levels of POPs in *L. audouinii*, feeding exclusively on fish, were higher than those of *L. michahellis* which is an opportunistic species.

The proposed monitoring scheme permits to determine possible sources and assess the effects and impacts of POPs with the objective of providing control measures to minimize chemical pollution. Also, the results obtained will contribute to ratify the Stockholm Convention for which data on the levels of POPs in birds should be provided as contamination biomarker to maintain bird population and preserve the biodiversity of protected areas.

Acknowledgements

This study has been financed by the Ministry of the Environment in Spain projects [038/2009] and 2012/768. Dr. R. Chaler and D. Fanjul are thanked for MS assistance and G. Martrat for assisting in the freeze-drying. Parques Nacionales from the Ministry of Environment, the Generalitat de Catalunya, Generalitat Valenciana and personnel of Natural and National Parks (Atlantic Islands, Chafarinas, Columbretes and Medes) are kindly acknowledged for permission for sampling.

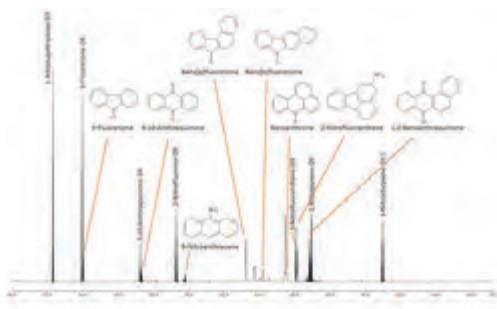
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Nitrated and Oxygenated Mono- and Polyaromatic Hydrocarbons in Polluted Air in Central Europe and Aerosol Toxicities

PP Env Monit #37

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Nitroaromatic compounds in air are more carcinogenic than the parent polycyclic aromatic hydrocarbons (PAHs) [1-2], and quinones, a prominent class of oxy-PAHs (OPAHs), contribute to reactive oxygen species generation upon particle deposition in the lung [3]. Nitro-PAHs (NPAHs) and OPAHs are probably the most potent toxic compounds in ambient air and the most hazardous environmental chemicals for public health in central Europe, but their levels, fate in the environment and toxic potencies are largely unknown [4-5].

Gas and particulate phase concentrations of NPAHs, OPAHs and nitromonoaromatic hydrocarbons (NMAHs i.e., nitrosalicylic acid, -phenols and -catechols) in air and precipitation were determined in urban and rural environments in the Czech Republic (city of Ostrava, a hot spot of air pollution [6], and Pustá Polom and Košetice, respectively), in winters and summer 2016/17. In winter time, concentration levels are higher by 1 (NPAHs, NMAHs) or 2 (OPAHs) orders of magnitude than in summer. At the urban site, nitrocatechols dominated NMAHs and benz(a)anthracene-7,12-dione OPAHs. OPAHs are found to be distributed evenly among gas and particulate phases in both winter and summer, while NPAHs are found to shift

from particulate in the winter-time to gas-phase in the summer-time. NMAHs are found to be washed out effectively by precipitation, unlike OPAHs, NPAHs and the parent PAHs.

The mass size distribution of the targeted substance classes as well as of toxicities (dioxin-like, estrogenicity, androgenicity) peaked in submicrometer size fractions ($PM_{1.0}$). A large part of toxicities is found to be associated with polar fractions of particulate organic matter, in particular in $PM_{1.0}$.

Acknowledgements

We thank M. Váňa, L. Černíkovský, B. Krejci and P. Smolík (Czech Hydrometeorological Institute) for logistical help and provision of meteorological and trace gas data. This research was supported by the Granting Agency of the Czech Republic (#503 16/11537S), the Max Planck Society and the Czech Ministry of Education, Youth and Sports (#LO1214, LM2015037 and LM2015051).

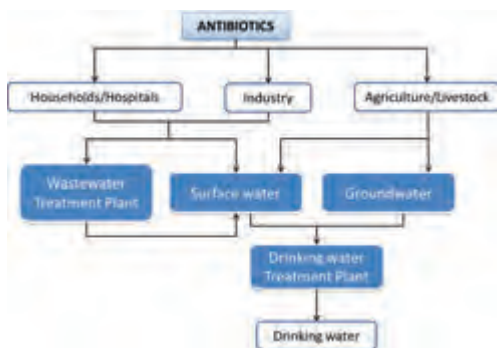
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Multiresidue Determination of Antibiotics in Wastewater Effluents using Liquid Chromatography-Triple Quadrupole Mass Spectrometry

PP Env Monit #38

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It is well known that wastewater treatment plants (WWTPs) release antibiotics into surface waters, which is an important concern to global health, as they lead to the generation of antibiotic resistant bacteria and thus, endangering the effectiveness of antibiotics [1,2]. As such, there is a growing interest in developing analytical methods to monitor the persistence of antibiotics in environmental commodities [3,4].

To this end, a multiresidue analytical method for the determination and quantification of 28 antibiotics in urban wastewater influent and effluent samples from two WWTPs in Almería (Southeastern Spain) was developed in this work. The method involves concentration of the samples using off-line solid phase extraction (SPE), followed by analysis using ultra-high-performance liquid chromatography coupled to hybrid triple quadrupole-linear ion trap mass spectrometry (UHPLC-QqLIT-MS/MS). The performance of several SPE sorbents was studied and also three chromatographic columns were tested in order to optimise the chromatographic parameters. Two selected reaction

monitoring (SRM) transitions were optimised, the most sensitive one for quantification and the other one for confirmation.

Quantification of the antibiotics was carried out by matrix matched calibration and recoveries obtained ranged between 50 and 99% in almost all compounds analysed at three spiked concentration levels. Method detection limits varied from 1 to 392 ng/L, showing satisfactory performance. The analytical method developed was successfully applied to identifying and quantifying antibiotics in wastewater influent and effluent samples with a total analysis run time of 32 minutes. Several antibiotics were found in the samples, Azithromycin, Erythromycin, Ofloxacin, Sulfamethoxazole and Trimethoprim, among others, at levels of ng/L to µg/L in wastewater effluents, demonstrating that both municipal WWTPs monitored are not able to efficiently remove antibiotics.

Acknowledgements

The authors gratefully acknowledge the financial support by the Ministry of Economy, Industry and Competitiveness of Spain (Ref. CTQ2016-78255-R) and the European Regional Development Fund (ERDF).

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Comparison of Semi-volatile Organic Compounds (SVOCs) Levels in Pine Needles Towards a Uniform Assessment Using Different Species

PP Env Monit #39

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Biomonitoring using vegetation is nowadays a common practice in environmental science, but depends a lot on the availability of the species able to be used in the target sampling points. Pine needles are one of the most used matrices in these types of studies, due to their ubiquitous nature associated with relatively long and stable life cycles, able to convey not only spatial but also temporal trends of contamination [1].

However, different species used are prone to show different uptakes of semi-volatile organic compounds (SVOCs) [2]. This makes the direct comparison of databases a very difficult, if not impossible task. The goal of this study is to raise awareness and be a starting point to deal with this important gap.

To achieve these purposes, samples of pine needles from several species (*Pinus* (*P.*) *pinea*, *P. pinaster*, *P. halepensis*, *P. radiata*, *P. sylvestris*, *P. nigra*, *P. canariensis* and *P. strobus*) were collected in 12 sites from different countries (Portugal, Spain, UK and Romania), where at least two species were planted under a similar environmental exposure (next to each other).

A multi-residue analytical protocol previously validated by our group [3] was employed to extract and quantify 4 classes of semi-volatile organic contaminants (SVOCs) - polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs)

and organochlorine pesticides (OCPs) – in order to establish initially the differences between the levels of the target chemicals between them, and then try to produce statistically significant relationships between pine species for as many compounds as possible.

These were found ($p > 0.05$) for the sum of concentrations of the different classes of SVOCs and for some of the individual compounds, especially for the most volatile ones and between *P. pinaster* and *P. pinea* species. These uptake correlations seem to be transversal to the land uses (urban, rural, remote). They were also collected in different times of the year, although always with exposures between 1 and 2 years. For some species analysed, the number of samples was insufficient to draw correlations. But the general results point towards the following uptake trends: *P. pinaster* > *P. sylvestris* > *P. pinea* > *P. radiata* > *P. halepensis* > *P. strobus* > *P. canariensis*.

Acknowledgements

This work was the result of the project: (i) POCI-01-0145-FEDER-006939 (LEPABE – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (ii) NORTE-01-0145-FEDER-000005-LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the ERDF; (iii) Investigador FCT contract IF/01101/2014 (Nuno Ratola).

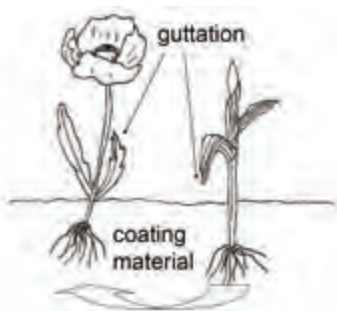
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Appearance of Neonicotinoids in Guttation Liquid of Weeds from Coated Maize Seeds

PP Env Monit #40

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Neonicotinoid residues in wildflowers [1] as well as in guttation liquids [2] were assumed as potential routes of chronic exposure for pollinators. Neonicotinoid uptake by maize plants emerged from coated seeds and cross-contamination via soil readily occurs from neighbouring plants that emerged from coated seeds [3]. Insecticide concentrations in the guttation drops depend on several factors (physicochemical characteristics of the active ingredient, relative humidity, age of the plants) including soil characteristics that play an important role in spreading of insecticides [4].

Two common weeds, grown in close proximity to maize plants that emerged from seeds coated with neonicotinoids, were studied: a well-known, aggressive perennial maize weed, the creeping thistle (*Cirsium arvense*) and a common annual weed, red poppy or Flanders poppy (*Papaver rhoeas*) as model species for laboratory and field studies. Uptake of thiamethoxam (TMX) and clothianidin (CLO) by the plants was characterised via guttation liquid measurements using HPLC-UV measurements. The results confirmed that cross-contamination may occur by uptake through soil from neighbouring maize plants that emerged from coated seeds. TMX and CLO residues were detectable in the guttation liquid of the weeds for up to 20 to 35 days after planting of maize seeds, although levels were substantially lower than those in maize emerged from coated seeds. Peak concentrations of TMX and CLO in the guttation liquid of maize were 160 and 70 µg/mL, while both appeared in creeping thistle and red poppy at 21 and 0.7 µg/mL, respectively. The significantly lower levels detected in red poppy are explained by

its higher guttation intensity. The average mass of guttation liquids collected were 0.0057 and 0.097 g/day for creeping thistle and red poppy, respectively, although with a high day-to-day variation during the sampling period. Guttation liquids of plants derived from TMX coated seeds generally contained both ingredients, as CLO is a metabolite of TMX. In these cases, the ratio of CLO to TMX increased to approximately 40% in 2 weeks, and then remained constant. The levels of the active ingredient applied showed a steep increase in a few days upon emergence and a gradual decrease later with fluctuations in the field experiments due to weather conditions influencing the evaporation of the droplets. Vertical and in depth diffusion of the ingredients in soil, and their leaching upon irrigation were also monitored, and results were similar to our previous findings [5].

Due to their wide scale use, neonicotinoids became ubiquitous contaminants. Pollution of soil by systemic ingredients results in translocation of these compounds to weeds growing in arable field margins that play an important role in maintenance of ecosystem services. In addition to the exposure to neonicotinoids via pollen and nectar, exposure via guttation liquid also occurs, and is not restricted to the blooming period of flowering crops, and as our results indicate, untreated weeds and wildflowers may also have to be considered among the possible routes of exposure.

Acknowledgements

This work was supported by project K112978 (Hungarian Scientific Research Fund, OTKA).

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Assessment of Exposure to Polycyclic Aromatic Hydrocarbons by Biomonitoring

PP Env Monit #41

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Polycyclic aromatic hydrocarbons (PAHs) are a large group of ubiquitous and persistent organic compounds that are formed during pyrolysis and incomplete combustion of organic matter. Many PAHs present cytotoxic and mutagenic properties being some of them considered carcinogenic or probable/possible carcinogenic to humans [1-2]. However, PAHs monitoring is complicated by their partitioning between vapour and particulate phases and by the absorption of these chemicals from inhalation, food ingestion, and dermal contact, which make biomonitoring the most appropriated way to assess total exposure to PAHs. Thus urinary metabolites of PAHs, monohydroxyl-PAHs (OH-PAHs), constitute an accurate tool to determine the total internal dose of PAHs. Still, the obtained OH-PAHs data should be combined with information reached by environmental monitoring to attain a comprehensive characterization of exposure.

Children are a sensitive group because their respiratory, immune, reproductive, central nervous, and digestive systems are not fully developed [3-4]. Firefighters are an occupational group that are regularly exposed to a countless number of pollutants released during fires [5]. Thus children and firefighters are at high risk to suffer potential harmful effects due to their exposure to health-relevant pollutants, including PAHs. The present work aimed to assess the total exposure to PAHs by both environmental monitoring and biomonitoring in schoolchildren (3-5 years old) and firefighters involved in firefighting activities.

Airborne PAHs with 2-3 rings were the most abundant compounds, being followed by 4-6 ring PAHs. A similar distribution profile was observed between airborne PAHs and urinary OH-PAHs, with 1-hydroxynaphthalene and 1-hydroxyacenaphthene being the compounds that contributed the most for total OH-PAHs, followed by 2-hydroxyfluorene, 1-hydroxypyrene, and 1-hydroxyphenanthrene. Levels of 1-hydroxypyrene were lower than the benchmark level (0.5 $\mu\text{mol/mol}$ creatinine) proposed by the American Conference of Governmental Industrial Hygienists and urinary 3-hydroxybenzo[a]pyrene, the PAH biomarker of carcinogenicity, was not detected. Regardless the group considered, strong to moderate Spearman correlations were observed between the levels of total PAHs, and total OH-PAHs, suggesting air pollution as the one of the major exposure source of PAHs.

Acknowledgements

This work received financial support from European (FEDER funds through COMPETE) and National (Fundação para a Ciência e Tecnologia project UID/QUI/50006/2013) funds and in the scope of the P2020 Partnership Agreement Project POCI-01-0145-FEDER-006939 (LEPABE) funded by FEDER funds through COMPETE2020. K. Slezakova is also grateful for their fellowship (SFRH/BPD/105100/2014).

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Platinum Group Elements Geochemistry in the Urban Road Environments

PP Env Monit #42

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Platinum-Group Elements (PGEs), in particular platinum (Pt), palladium (Pd), and rhodium (Rh), are rare metals which are used in automotive catalytic converters to catalyse the harmful emissions from exhaust fumes such as polycyclic aromatic oxides, hydrocarbons, carbon monoxide and nitrogen oxides into carbon dioxide, nitrogen and water [1].

Three converters were studied together with the distribution of these elements in road dust and in storm water detention and infiltration pond sediments, in Nantes area, France. The objective of this research is to study the behaviour of PGEs in environmental systems to provide more important information about the alteration and transportation of PGEs in nature to make a realistic assessment of the risk for man and environment. For all samples, Pt, Pd and Rh were determined by ICP-MS after an aqua regia digestion. The accuracy of data was assessed by means of the certified values of PGEs for BCR-723 (road dust). Batch experiments were carried out on catalytic converters with runoff

water. The mobility and speciation of PGEs were investigated in road dust and in sediments by means of the sequential extraction scheme using the BCR protocol [2,3]. Moreover, microscopic observations were carried out on the different samples.

Results show variable content for PGEs for the three converters (in the ranges of 6-511, 0.5-2507 and 0.1-312 mg.kg⁻¹ for respectively Pt, Pd and Rh) which could release up to 47%, 62% and 43% of Rh, Pd and Pt, respectively in runoff water. Elevated concentrations of PGEs have been found in samples of road dust and pond sediments (which ranges for Pt, Pd, and Rh respectively between 57-148, 107-5882, and 20-589 µg.kg⁻¹ in the road dust, and between 51-170, 108-1203, and 19-127 µg.kg⁻¹ in the sediments). Besides, the sequential extractions indicate that Pt is bound to organic matter and oxides (37-51% of Pt was bound to organic matter and 14-19% to iron/manganese oxides in sediments and road dust respectively). Microscopic observations (SEM/EDX) of catalyst surfaces show the dispersion of individual EGPs nanoparticles. The PGEs observed on road dust and pond sediments suggest that these elements can be associated with clay minerals or organic matter.

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Is the Groundwater in Cemetery Areas Contaminated by Pharmaceuticals? A Case Study

PP Env Monit #43

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Studies in the cemeteries areas are normally for historical and architectural research and questions of the potential risk for the adverse impact of cemeteries in environment have never received enough attention [1]. Cemeteries are placed in areas that are vulnerable to contamination and may have serious environmental consequences, particularly on the quality of adjacent groundwater. This is because the infiltration and percolation of rainwater through the soil graves allows migration of a number of organic and inorganic chemicals which can pollute aquifers. If the cemeteries is on vulnerable soil or if the soil reaches its depurative limit, the pollution may reach the groundwater [2]. Only a few studies embracing the subject's "cemetery" and "groundwater" are found and most of these works cover the studies of the presence of metals or bacteria and viruses [1].

It was observed that in some cemeteries, a warning message "Do not drink, Non-potable water" or "Unfit for consumption" are on the taps. Information's of the water sample source was obtained near to the responsible entities and groundwater was confirmed in these cemeteries. Thus, the analysis of 33 pharmaceuticals covering various therapeutic groups (nonsteroidal anti-inflammatory drugs (NSAIDs)/ analgesics, antibiotics and psychiatric drugs), and some of their main metabolites were

analysed in the groundwater collected in the taps inside of five cemeteries areas.

A Shimadzu Nexera UHPLC–MS/MS system triple-quadrupole mass spectrometer (LCMS-8030, Shimadzu Corporation, Kyoto, Japan) with an electrospray ionization source (ESI) was used. The LCMS-8030 is equipped with a LC-30 CE pump (two solvent delivery modules), a CTO-20 AC column oven, a DGU-30A3 degasser, a SIL-30 AC auto injector, and a CBM-20A system controller. LabSolutions software was used for control and data processing. Electrospray ionization (ESI) mode was used. Solid phase extraction (SPE) was performed using Strata-X cartridges (200 mg, 3 mL) from Phenomenex (USA). Sample preparation using SPE extraction, chromatographic separation and MS conditions were based on the author's previous work [3].

Acetaminophen, salicylic acid, ibuprofen, ketoprofen, and nimesulide were the NSAIDs/ analgesics and carbamazepine, fluoxetine, and sertraline were the psychiatric drugs detected. 100% of detection frequency was observed for salicylic acid, ibuprofen, ketoprofen, and carbamazepine. The highest concentration was obtained for carbamazepine and salicylic acid with concentrations in range of 20.0 to 22.3 ng/L and 33.7 to 71.0 ng/L, respectively.

The present work can be a basis for future studies and others therapeutic classes could be analysed and attention must be redoubled because groundwater is an important source of water for streams, rivers, lakes, wetlands, and bays and consequently is important to monitor all water cycles.

Acknowledgements

This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e Tecnologia) through project UID/QUI/50006/2013. To all financing sources the authors are greatly indebted.

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Caffeine Contribution to Portuguese Atlantic Coastal Waters in Bathing Season

PP Env Monit #44

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Sewage effluent from wastewater treatment plants (WWTPs) is recognized as a major source of human pollution and is discharged into marine environments through coastal areas and through rivers receiving WWTP effluents [1]. Due to their location, coastal areas represent a major advantage as many economic activities may take place, including tourism, commercial ports, and harbours, thus making them more vulnerable to higher levels of pollution than other seawater samples [2]. Bathing water quality standards are based on international standards and legislations. However, in Europe, only the microbiological parameters are to be accomplished. Recent research has focused on chemical indicators that can determine human fecal contaminants in water [3]. Suitable markers are therefore necessary to detect and locate the sources of water pollution [4]. From all the markers investigated the one that received the most attention in recent times is caffeine [5].

Caffeine naturally occurs in plants (e.g., coffee beans, tea leaves) and the consumption of caffeine is mainly from beverages (e.g., coffee, tea), foods (e.g., chocolate), and as stimulant in certain medications (e.g., analgesics).

Caffeine is a very good tracer because its detection in the aquatic system indicates human waste source [6].

The suitability of caffeine as a chemical marker for seawater pollution in the North Portuguese coastal area in the Atlantic Ocean was assessed. Five cities were monitored, and 101 samples were collected in fourteen beaches during the seasonal period.

Beaches classified as having sufficient, good, and excellent water quality were monitoring.

Multiple SPE cartridges were processed simultaneously with a 12-position SPE vacuum manifold. Caffeine was extracted using Strata-X cartridges (200 mg, 3 mL) from Phenomenex (USA) and analysed by liquid chromatography coupled to tandem mass spectrometry (LCMS-8030, Shimadzu Corporation, Kyoto C, Japan)) with an electrospray ionization source (ESI).

Caffeine was detected in all seawater samples and concentrations obtained were in the range of 18 to 525 ng/L. The highest level of caffeine and the highest average of caffeine were found in samples collected in July, in beaches classified with a yellow flag and located in cities with high density population and with high tourist affluence. The highest and the lowest level of caffeine reported in the study not pose toxic effect either on fish or on daphnia but can have a possible toxic effect on algae.

Acknowledgements

This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e Tecnologia) through projects UID/QUI/50006/2013. The authors are greatly indebted to all financing sources.

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Methodologies for the Identification of Polycyclic Aromatic Hydrocarbons Sources

PP Env Monit #45

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	PC1	PC2	PC3	PC4
Variance (%)	50.8	17.4	12.5	5.6
Source	Biogenic (biomass) and Biogenic	Pyrogenic (crude) #	Pyrogenic (crude) #	Petrogenic
N		0.93		
F			0.73	
Phe			0.94	
A			0.87	
Fluo	0.52		0.58	
P	0.53		0.57	
BaA	0.66		0.47	
Chr	0.62			
B(b+k)F	0.95			
BaP	0.89			
Ind	0.95			
DBA	0.89			
BghiP	0.95			
BeP	0.97			
Per	-0.79			
C1-N		-0.66		0.58
C2-N				0.77
C3-N				0.66
C1-Phe				0.81
C2-Phe				0.81

Table 1 – Source profile obtained from PCA.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that tend to rapidly adsorb to particulate organic matter in sediments and tissues due to their hydrophobic characteristics, inducing toxic effects, carcinogens and mutagens to many living organisms. According to their origin or temperature of formation PAHs are classified into three classes: pyrogenic, petrogenic and biogenic/natural. The monitoring and identification of the sources is relevant especially in sediments because they are the main reservoir and secondary source of contamination of aquatic systems. To identify the sources there are different methods for data treatment that complement each other: pattern recognition, spatio-temporal analysis, source-specific diagnostic ratios of PAHs and principal component analysis (PCA) [1-4]. To demonstrate the applicability of these different methods were used the concentrations of PAHs from sediments of four Portuguese estuarine systems: Ria de Aveiro, Tagus River, Sado River and Ria Formosa, in order to identify the sources.

For example the PCA was used for 27 samples with 20 variables, and four components were extracted, which account for 86.3% of the total variance. The components loading matrix is shown in Table 1. The first component (PC1) is responsible for 50.8%

of the total variance and is related with combustion processes (positive weights) and biogenic sources (negative weights).

The second component (PC2) representing 17.4% of the variance is loaded on C1-C2-N PAHs and related with degradation since these PAHs are more soluble in water.

The third component (PC3) accounts for 12.5% of the total variance and is related with pyrogenic sources. The average weights for Fluo and P (the most abundant emitted by combustion processes) [5] are similar to those found in PC1. In addition, this component don't have the alkylated PAHs that are common in fuel oil. As such, this component can be related with combustion of fossil fuels. The negative relative weight for Per also assigned this component to the biogenic source. Finally the fourth component representing 5.6% of the total variance with positive loadings for alkylated homologue series is related with petrogenic sources.

In this study the obtained results demonstrate that for the different stations of the four Portuguese estuaries, the main source is the pyrogenic (burning of biomass and fossil fuels, on a smaller scale). In some stations near ports/docks denote a slight petrogenic signature.

According to the PCA this results are confirmed.

Thus, it is concluded that this type of approach to data, provides distinct information beneficial in identifying the source of PAHs.

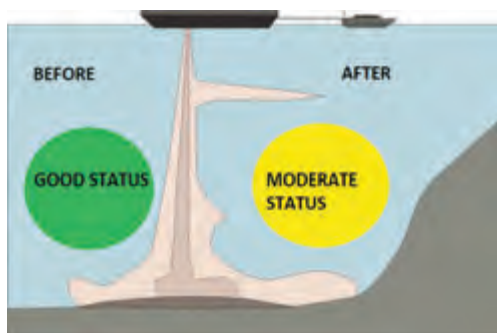
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Nutrient Dynamics in a Coastal Area Affected by Dredged Sediments from a Polluted Estuary: Saronikos Gulf, East Mediterranean Sea

PP Env Monit #46

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Dredging activities could locally release pollutants (organic compounds and nutrients) to the overlying water, and affect the water quality of a coastal area. Dredged sediments derived by the low course and estuary of the metropolitan river of Athens, Greece (Kifissos river), were dumped every day for 21 months at a coastal site in the Saronikos Gulf in east Mediterranean. Fine-grained sediments (muddy sand, sandy mud and mud) dominated in the area around the river mouth. From May 2010 to January 2012, the dredging of Kifissos estuary resulted to the production of significant amounts of sediments, which were licensed to be dumped further seawards in a designated coastal sea area of surface 1 nmi². For 21 months, a total of ~700.000 m³ of dredged-material were dumped, with a mean monthly discharge of 33.333 m³ [1]. The coastal area of the licensed dumping site was monitored, prior during and post to dumping for 24 months. Sampling stations in a distance from the dumping site were also monitored for 24 months.

The dredged sediments contained 2-3 times more organic C and P than the dumping area in Saronikos gulf. The dissolved oxygen concentrations in the

near bottom layer were relatively high during the period of dumping (~4.0 mL/L). Increase in phosphates and ammonium concentrations was observed during and after the dumping, which was not statistically significant. In the near bottom layer, increase of nutrients (phosphate, silicate, ammonium, nitrite and nitrate) was observed during and after the dumping. Dredged sediments may release ammonium through remineralization process of the organic nutrients released from the sediment plume and the recycling of nitrogen and phosphorus compounds. In the presence of oxygen, the released ammonium could be further oxidized to nitrites and nitrates through the biological process of nitrification. The nitrogen to phosphorus ratio decreased during and after the dumping indicating N-limitation in the study area.

Five months after the beginning of the dredging activities in the area, the trophic status of the area receiving the dredged sediments downgraded from good trophic status into moderate and in some cases into poor status. Not only the two sampling stations located into the licensed dumping area, but also other sampling stations near the dumping site seemed to be affected. Hydrology and the prevailing water mass circulation during the samplings play an important role on nutrient dynamics in the area. On the other hand, biological processes determined the nutrient dynamics in the water column. According to this, it seems that the dredged sediments affect the inorganic nutrient distribution of the coastal area where they were dumped, but not significantly.

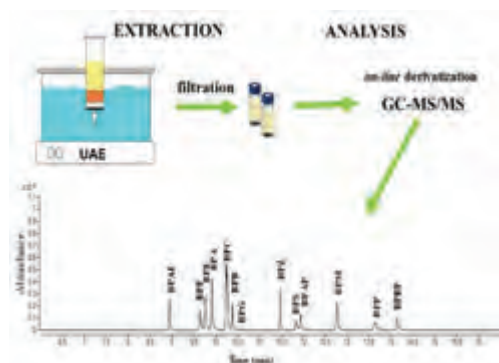
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Simultaneous Determination of Thirteen Bisphenols in Soil Samples

PP Env Monit #47

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Bisphenol A (BPA) is one of the most widely used chemicals because it has many industrial and commercial applications. The concern over widespread human exposure to BPA and its potential health effects has led to regulations on the production and usage of BPA in the European Union. For this reason, the development and production of alternative substances to replace BPA has been encouraged and compounds, structurally similar to BPA, are being used in the manufacture of polycarbonate plastics and epoxy resins.

The main objective of this study was to develop a quick, selective, sensitive and efficient analytical method for quantitative simultaneous determination of thirteen bisphenols in soil samples by GC-MS/MS with on-line derivatization in the GC system. The extraction method developed was based on ultrasound assisted extraction (UAE) in small columns, due to its main advantages as miniaturization of the extraction procedure, short processing time and use of conventional laboratory equipment. For this study, soil samples were collected from several agricultural fields and industrial soils from Spain.

Derivatization efficiency mainly depends on the reagent amount and the reaction time. Thus, the optimization of these parameters was firstly evaluated to obtain the best chromatographic response of the bisphenol analogues. Then, manual and on-line derivatizations were compared and results showed that significant higher chromatographic responses were achieved with on-line derivatization. The quantification was done by matrix-matched calibration, using fortified blank

extracts as standards instead of standard solutions in solvent, in order to overcome matrix effects and to achieve a better analysis of the bisphenol analogues.

The effect of different parameters in the analysis of the compounds was assayed. Taking into account that the extraction solvent and the extraction time are the two main factors that affect UAE methods, a statistical analysis was done to improve the efficiency of the procedure and simultaneously estimate the influence of the extraction time and different EtAc:MeOH ratios using a multilevel experimental factorial design. In general, MeOH percentage significantly affected the extraction efficiency for nine of the thirteen bisphenols, whereas the extraction time did not show significant differences, except for BPG and BPF. Then, an extraction time of 15 min was selected, as a compromise for all bisphenols evaluated.

After optimization, the method was evaluated in terms of linearity, precision, accuracy and detection limits. A good linearity was obtained, with correlation coefficients equal or higher than 0.996 for all the compounds studied. The detection limits for all target bisphenols ranged from 0.04 to 0.27 ng g⁻¹, for BPC and BPA respectively. Analysis of spiked soil samples gave satisfactory recovery results, from 70 to 111 %, for all the compounds.

In order to assess the suitability for the analysis of real samples, the developed method was applied to analyze agricultural and industrial soils collected in different areas of Spain. Three of the thirteen target bisphenols were detected in the soil samples analysed.

These results demonstrate that different bisphenols are found in soil samples; although, only the presence of BPA has been previously reported and methods for the determination of bisphenol analogues in environmental samples are scarce and focused in a few bisphenol compounds.

The use of reclaimed waters for irrigation of agricultural fields was related with the presence of bisphenol analogues in soil.

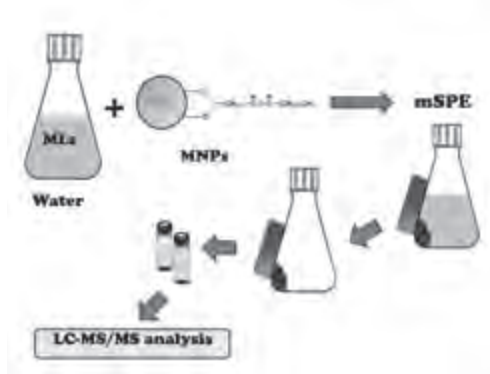
Acknowledgements

Authors wish to thank the Spanish Ministry of Economy, Industry and Competitiveness for financial support, project (RTA2014-00012C03), and for the contract of M. Ferriz.

Application of Magnetic Nanoparticles for the Determination of Macrolides in Water by Liquid Chromatography–tandem Mass Spectrometry

PP Env Monit #48

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Pharmaceuticals cover a large group of substances that belong to different chemical families which are introduced into the environment as a result of medical and veterinary use. They are emerging contaminants because they are not commonly monitored due to the lack of regulation, and they are continuously introduced into the environment at rates that exceed their degradation rate. Among pharmaceuticals, antibiotics have received particular attention due to the development and rapid expansion of antibiotic resistance that threatens the effectiveness of the treatment of infectious diseases in humans and animals. Macrolides (MLs) are synthetic broad-spectrum antibiotics commonly used in human and poultry treatment. They belong to one of the most commonly used families of antibiotics, although occurrence of MLs in aquatic environment at high concentrations is not expectable, due to their relatively low water solubility. Nevertheless, they have been often found in different aqueous matrices as a result of their significant and continuous consumption in both human and veterinary medicine.

Magnetic solid-phase extraction (mSPE) methods using MNPs of magnetite (Fe_3O_4) have been described as an interesting technique for the analysis of pollutants in liquid samples [1,2].

The main objective of this study was to develop a quick, cheap and efficient method for the analysis of MLs in water samples. In this work, the application of oleate-coated Fe_3O_4 MNPs was evaluated for the extraction of three MLs (erythromycin, tylosin

and tilmicosin) and one metabolite (erythromycin- H_2O) from water by mSPE, followed by LC-MS/MS analysis. Various experimental parameters affecting the extraction efficiency were optimized and the selected method was applied to monitor these contaminants in water samples from different sources.

The MNPs were firstly characterised. The effect of several parameters (extraction solvent, pH, extraction solvent volumes, amount of MNPs and extraction time) on the extraction efficiency of MLs from water using oleate-coated MNPs was evaluated.

The matrix effect, the recovery of target analytes spiked at two concentration levels (0.75 and 0.25 ng mL^{-1}), the repeatability intra- and inter-day, and the limits of detection (LODs) and quantification LOQs) were evaluated for method validation. The recovery results obtained were satisfactory (>84%) for most of the compounds, and the LODs and LOQs ranged from 11.5 to 26 ng L^{-1} and from 34 to 77 ng L^{-1} , respectively.

In order to assess the suitability of the developed mSPE method for the analysis of real samples, different water samples (a well water and six surface water from different Spanish regions). The analyses confirmed the presence ERY and ERY- H_2O in river water which shows that both compounds must be simultaneously detected in order to not underestimate the presence of this macrolide in water samples. The present work demonstrates the applicability of the developed method for the determination of these MLs in water.

Acknowledgements

Authors wish to thank the Spanish Ministry of Economy, Industry and Competitiveness for financial support, project (RTA2014-00012C03), and for the contract of M. Ferriz.

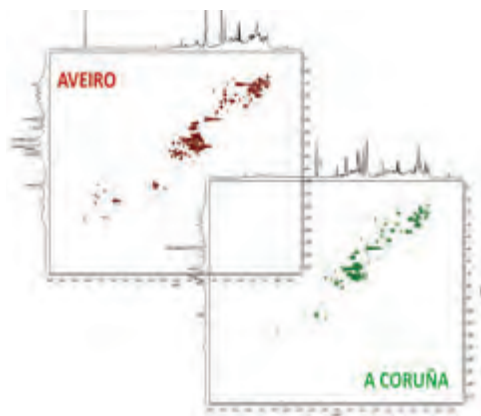
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Comparative Study of Atmospheric Organic Aerosols Composition in Contrasting Suburban Environments in the Iberian Peninsula Coast

PP Env Monit #49

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The atmosphere at the Western European Coast is likely influenced by a variety of emission sources, including both primary (sea salt, mineral dust, fossil fuel, wood burning) and secondary (e.g., atmospheric aging and photooxidation) sources [1,2]. However, important questions still remain: (i) how the levels of atmospheric organic aerosols (OA), in particular of the water-soluble organic fraction, distribute along this region, and (ii) how they compare in terms of their chemical and structural composition.

This study aims at addressing these two questions, using a multidimensional non-targeted analytical strategy [3,4], based on excitation-emission matrix (EEM) fluorescence and 1D and 2D nuclear magnetic resonance (NMR) spectroscopies, to investigate the structural composition of the water-soluble organic carbon (WSOC) fraction from PM_{2.5} samples collected, simultaneously, during summer and winter, in two different suburban sites at the Iberian Peninsula Coast: Aveiro (Portugal) and A Coruña (Spain). Stable isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of the bulk PM_{2.5} samples were also assessed to better understand the contribution of various sources to OA at the studied locations.

The atmospheric levels of PM_{2.5}, total carbon (TC), and WSOC were consistently higher in Aveiro than in A Coruña. At both sites, the highest levels of PM_{2.5}, TC and WSOC were found during winter. During this colder period, the PM_{2.5} samples from

Aveiro and A Coruña are very similar in terms of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ composition. However, during summer, PM_{2.5} samples from A Coruña are somewhat more oxidized and less enriched in ^{15}N than those from Aveiro. Although the EEM fluorescence profiles seemed to be very similar for all WSOC samples, the ^1H NMR source attribution confirmed differences in aging processes or local sources between the two sites. All WSOC samples exhibit the same major ^1H types; however, they differ in terms of their relative distribution. In summer, WSOC from Aveiro are less aliphatic and oxidized, and more aromatic than those collected in A Coruña. In winter, WSOC from Aveiro are clearly impacted by biomass burning for house heating, whereas those collected in A Coruña could have some contribution from this primary source; nevertheless, the later samples seem to be more oxidized and aliphatic than those from Aveiro. The structural features of the WSOC samples were further explored by ^1H - ^{13}C HSQC and HMBC, and ^1H - ^1H COSY NMR, revealing different molecular signatures of meaningful OA source markers in both sites.

Acknowledgements

Centre for Environmental and Marine Studies (UID/AMB/50017/2013); Organic Chemistry Research Unit (QOPNA, UID/QUI/00062/2013); FEDER under the PT2020 Partnership Agreement; and, Portuguese Science and Technology Foundation (FCT), through the European Social Fund (ESF), Portuguese NMR network, “Programa Operacional Potencial Humano - POPH”, and an Investigator FCT Contract (IF/00798/2015). This work was also supported by Xunta de Galicia (GRC2013-047). P. Esperón is greatly acknowledged for her collaboration.

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Microplastics in Aquatic Environments: From Micro Particles to A Macro Problem

PP Env Monit #50

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The ubiquity of plastics in our Oceans is a corollary of their exponential increase in production and subsequent disposal since the 1950's. In the environment, these debris fragment, often originating particles smaller than 5mm in size, known as microplastics. These, nonetheless, can also be directly released into the environment, as they are also key components of products such as face creams and toothpaste [1].

Microplastics have been found to be consumed by over 220 different species, across multiple trophic levels, including zooplankton, protists, echinoderms, annelids, cnidaria, amphipods, decapods, cephalopods, isopods, bivalves, barnacles, fish, birds, turtles and cetaceans [2].

These can then undergo trophic transfers, through indirect ingestion by predators and detritivores. All these hazards are exacerbated by the presence of chemicals in these otherwise relatively inert materials. Such chemicals can either be intentionally added, as sub-micron additives, used, for example, in thermoplastic applications, or adsorbed by the plastic particles from the surrounding environment, as already observed for persistent organic chemicals (POPs) [3]. When ingested, these materials can then leach into organisms, leading to bioaccumulation and bioamplification phenomena.

Furthermore, floating plastic debris can act as vehicles for invasive species, with severe environmental consequences [4].

It is therefore of paramount importance to have a deep understanding and knowledge of the prevalence of these materials in the environment, in order to adequately ascertain their potential

effects, especially when considering that the currently available literature focus on the use of microplastics at concentrations that far exceed those in the environment [5]. These studies also report on findings that deal with largely homogeneous particles, in terms of their physical and chemical characteristics – such as size, colour and composition, among others – that do not mimic real world conditions [1].

A detailed and comprehensive analysis on the presently available sampling methodologies and identification techniques, as well as on the development of appropriate strategies for the determination of the effects of microplastics, including at the ecotoxicological level, is not only recommended, but necessary.

Herein, we describe the most relevant sources of microplastics, their fate, and the most prominent effects of these small particulates, while identifying the key challenges scientists currently face in the research of microplastics in the environment.

Acknowledgements

This work was supported by national funds through FCT/MEC (PIDDAC) under project IF/00407/2013/CP1162/CT0023. Thanks are also due, for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the cofunding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. This work was also funded by Portuguese Science Foundation (FCT) through the scholarship SFRH/BPD/122538/2016, under POCH funds, cofinanced by the European Social Fund and Portuguese National Funds from MEC.

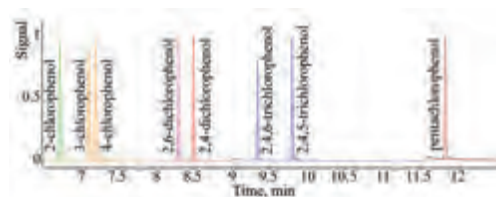
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GC-MS/MS Determination of Chlorinated Phenols in Sea Water and Sediments of Western Russian Arctic

PP Env Monit #51

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The increasing human activity in the Arctic and sub Arctic territories leads to the higher contamination of the Northern rivers and sea water of the Arctic ocean. Chlorinated phenols penetrate Arctic environment with the wastes of industrial and agricultural enterprises, pulp and paper mills. These compounds are highly toxic and are easily accumulated in the lipid tissues and liver of aquatic animals. To monitor chlorophenols' levels in the marine environment one should deal with water as well as sediments. Since highly sensitive and selective methods are required for the qualitative analysis of chlorophenols in complex matrix we used gas chromatography – tandem mass spectrometry (GC-MS/MS) in electron ionization mode. Anyway mass spectrometry is the best analytical tool to deal with complex mixtures of organic compounds [1]. Sample preparation involved concentration on the sorption cartridges followed by acetylation. 2-, 3-, 4-Chloro-, 2,4-, 2,6-dichloro-, 2,4,5-

, 2,4,6-trichloro, and pentachlorophenols were selected for the analysis of the environmental Arctic samples, while 2-chlorophenol-d4 was used as an internal standard. All GC and MS parameters were optimized for the better detection and quantification of the corresponding compounds. Cartridges Strata C-18 were used for water analysis while sediments samples were subjected to the extraction with water at pH 11. To analyze environmental situation water and sediment samples were collected in the vicinity of the Bolshaya Zemlya peninsula (Barentz sea). The detection limits of the sea water samples were 0.2-0.9 ng/l, of the sediment samples - 0.1-μg/kg. Arctic water samples contained up to 15 ng/l of 2,4-dichlorophenol and up to 7 ng/l 2,6-dichlorophenol. Other chlorophenols were measured at the levels 1-4 ng/l or lower. Sediments samples contained 2,4,6-trichlorophenols at the level 0.3-0.8 μg/kg, while concentration of other chlorophenols were lower than 0.3 μg/kg.

The obtained results allowed estimating the human influence on the Arctic environment and proposing efficient measures to decrease this influence.

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A New Approach to Extract Synthetic Musks and UV-Filters From Sludge Using a QuEChERS/GC-MS/MS Methodology

PP Env Monit #52

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The presence of Personal Care Products (PCPs), namely the classes of Synthetic Musk Compounds (SMCs) and UV-Filters (UVFs) in sewage sludge is unquestionable. So far, several studies have shown their presence in this matrix in high amounts, ranging the $\mu\text{g/g-dw}$ [1-2]. However, the methodologies developed for the extraction of these compounds are often expensive and time consuming, like pressurised liquid extraction (PLE) or solid-phase extraction (SPE).

A new approach is being developed in order to extract SMCs (6 polycyclic, 2 macrocyclic and 5 nitro musks) and UVFs (6 compounds) from sludge, using the QuEChERS methodology followed from GC-MS/MS analysis. This methodology does not require any specific equipment and relies in small amounts of sample, extraction solvent and clean-up sorbents.

So far, it has been tested several types of organic solvents like acetonitrile, ethyl acetate, acetone and dichloromethane/hexane (1:1), according to the literature. Different kind of sorbents have also been tested like Florisil, Alumina, C18 and PSA. To develop this new methodology, a Design of Experiments (DoE) approach was used to optimize the experiments, understanding the best operation conditions. Because several parameters may affect the extraction procedure, the DoE was divided in two steps. First, a screening design (SD), which consisted in a fraction factorial design, where performed, studying the type and amount of solvent and sorbents, time of ultrasound

extraction and mixing. The % of recovery of the selected compounds was chosen as response and the main effects were determined by the statistic tool F-distribution applied to each factor. Then, a central composite design (CCD) was applied to the selected factors to optimize the procedure. Using the surface response, mathematical relationships between the dependent and independent variables were established. The variables and interactions were identified by the t-Student test and the 3-D surface responses were obtained, using the JMP 13© software and the best conditions to extract the 19 compounds simultaneously were defined.

The method was then validated, evaluating the linearity ranges, coefficients of determination, limits of detection (LODs) and quantification (LOQs), accuracy and precision (intra and inter-day).

Therefore, the main goal of this work was to develop a reliable, fast and cheap method to analyse several SMCs and UVFs classes.

Acknowledgements

This work was the result of the project: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (ii) NORTE - 01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); (iii) Post-doctoral Grant SFRH/BPD/76974/2011 - Vera Homem; (iv) Doctoral Grant SFRH/BD/110831/2015 – Sara Ramos.

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Multi-Matrix Assessment of Airborne SVOCs in a Norway-UK Transect

PP Env Monit #53

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Semi-volatile organic contaminants (SVOCs) have been cause for concern among the scientific community and stakeholders due to their numerous emission sources, ubiquitous environmental distribution and potential damage to wildlife and humans [1]. Their presence in sediments, air and water are often reported, but soils and particularly vegetation, an excellent matrix to assess airborne SVOCs like persistent organic pollutants (POPs) or polycyclic aromatic hydrocarbons (PAHs) still fall behind in terms of monitoring efforts.

Data obtained from multi-matrix studies conveys the possibility of a comprehensive understanding and reduction of the gaps still remaining regarding the trends and behaviour of these chemicals [2], combined with trans-national efforts that help to enhance the maps of spatial distribution. In this work, the concentrations of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and PAH in pine needles and litter were determined and combined with the levels available in air and soil in previous studies in the same sampling area (a transect covering over 30 sites in Norway and the UK).

Previously validated extraction and clean-up protocols involving Soxhlet, solid-phase extraction

(SPE) columns and gel-permeation chromatography (GPC) were employed in the analysis of the samples, before GC/MS for identification and quantification of a total of 13 OCPs, 40 PCBs, 21 PBDEs and 16 PAHs.

In terms of results, total PCBs and OCPs predominate in litter and pine needle samples comparing to PBDEs, reaching levels up to 5000 pg/g each. Total PAH concentrations are about 10 times higher than the sum of all POPs. Limited significant correlations with latitude were found, but in litter samples, some correlations can be perceived between total PCB and total OCPs with total PAHs and between total PCBs and total OCPs. Source apportionment suggests long-range atmospheric transport (LRAT) for some POPs to the higher latitudes and mixed sources for PAHs, with stronger influence of nearby sources. Combining all matrices, different PCB patterns emerged for pine needles, litter, soils and air.

Acknowledgements

This work was the result of the project: (i) POCI-01-0145-FEDER-006939 (LEPABE – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT – Fundação para a Ciência e a Tecnologia; (ii) NORTE-01-0145-FEDER-000005-LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the ERDF; (iii) Investigador FCT contract IF/01101/2014 (Nuno Ratola). The UK Department of Environment, Food and Rural Affairs (DEFRA) is also acknowledged for financial support.

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Selected Methods for Determination of Surfactants

PP Env Monit #54

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Surfactants (surface-active agents) are compounds that decrease the surface or interfacial tension. Their molecules usually consist of non-polar (hydrophobic) and polar (hydrophilic) group. It is possible to classify surfactants with respect to the nature of their hydrophilic part as anionic, cationic, amphoteric and non-ionic. Surfactants are the main component of commonly used detergents, wetting agents, emulsifiers, foaming agents and dispersants.

Determination of surfactants in water can be carried out in various ways, according to the specific requirements for the resulting information.

Because of the diversity of the surfactants, specific procedures for group determination have been developed. The titration methods, colorimetry, polarography or spectrophotometry can be used for particular purposes. The results of group determination refer to the selected standard.

The concentrations of anionic surfactants in water are routinely determined using the spectrophotometric method, according to ISO 7875-1 [1]. This method is based on the association of anionic surfactants with a cationic dye - methylene blue. The resulting ionic associate is extracted into chloroform and the intensity of the blue complex measured at $\lambda = 650$ nm is proportional to the amount of surfactant.

Chromatographic methods can be used to determine individual surfactants. These methods belong to the most used because of their separation efficiency and sensitivity. Liquid chromatography (LC) is among the commonly used methods due to the low volatility of surfactants [2]. Capillary electrophoresis (CE) can also be used in order to separate and determine specific surfactants [3]. This paper presents the results of application of

the above mentioned methods for determination of various surfactants with focus on the following:

- a) Effect of possible interferences of Ajatin, Diclofenac, Humic Acids, Nitrate and Phenol was studied in spectrophotometric determination of anionic surfactants. Only effect of Ajatin was confirmed after two-steps chloroform extraction.
- b) The HPLC method with UV detection was optimized and used for the determination of three cationic surfactants (benzyltrialkylammonium halogenides) and Triton X-100 as a non-ionic surfactant. Limits of detection for studied analytes were about one tenth mg.L^{-1} and for Triton X-100 0,2 mg.L^{-1} .
- c) Anionic surfactants with non-aromatic structure (alkyl sulfates) were determined by an optimized LC / MS method. Their concentrations in output of WWTP were in order of tenths mg.L^{-1} .
- d) CE was used to determine selected anionic surfactants. The total of the content of these three analytes was determined in „environmental friendly“ and „common“ household cleaner.

Acknowledgements

This work was supported by Project No. **FCH-S-17-4766** of the Ministry of Education of the Czech Republic.

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Assessment Of Trace Metal Contamination of Water, Sediments and Flora From Douro River Estuary, Portugal

PP Env Monit #55

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Human activities are major sources of pollutants released into the aquatic environment. Most of these pollutants are considerably toxic and have the potential of accumulation in organisms [1]. Among them are trace metals due to their high persistence and low degradability in the environment [2]. The aim of this study regards the presence, distribution, sources and biotic accumulation of trace metals in water, sediments and local flora from Douro River estuary. The Douro River is one of the largest of the Iberian Peninsula, with a watershed shared between Spain and Portugal. The estuary is located between two densely populated cities and is highly impacted by anthropogenic activities, such as industry and agriculture. For this purpose, estuarine water samples and sediments were collected at five sampling points along the estuary at low tide to evaluate spatial distribution, possible sources and accumulation of trace elements into the estuary. Algae and plants were collected on the riverside at the same sampling points. Water, sediments and flora tissues were digested by a microwave-assisted digestion procedure and analysed by ICP-MS for their trace elements concentration (Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb and U). Physicochemical parameters, such as pH, conductivity, dissolved oxygen, nitrates, nitrites, ammonium, orthophosphates were also determined in waters and sediments for evaluation of anthropogenic impact and influence on metals availability. Results showed high levels of nitrates and ammonium, above the limits set in the Portuguese legislation (Decreto-Lei n° 236/98, up to 50 mg L⁻¹ and 0.5 mg L⁻¹, respectively). All

selected trace elements were detected in water and sediments. Water levels for most trace elements were lower than the limits established by the EU for drinking water quality [3]. Nevertheless, Al and Pb (up to 924.7 and 55.5 µg L⁻¹, respectively) were above the maximum permissible values of 200 µg L⁻¹ for Al and 10 µg L⁻¹ for Pb [3]. This is of high concern since surface water of Douro River is used for irrigation of local rural activities and for the production of drinking water. Highest metals levels were found at the mouth and at sampling stations located near discharges of wastewater treatment plants. Aluminum was one of the most abundant elements in water and sediments. Mean values for Al were up to 924.7 µg L⁻¹ in water and 12,400 µg Kg⁻¹ in sediments. Considering local flora, all trace metals were also found, showing uptake and accumulation of these trace elements in plants and algae. Highest values were found in roots and leaves tissues. Similarly to water and sediments, Al was the most abundant element found in plants and algae. Al concentration was higher in roots and leaves of various species compared with surrounding sediments and water demonstrating a possible bioaccumulation of these element in local flora. Data shows the occurrence of trace metal in estuarine water from Douro river estuary and their accumulation in sediments and biota.

Acknowledgements

This work was supported by FCT, Ministério da Ciência, Tecnologia e Ensino Superior (MCTES), under Project PTDC/SAU-ESA/108871/2008, and CESPU, through Projects MYCO-CESPU-2016 and ChiralDrugs-CESPU-2017.

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Differentiation of Crude Oils Using Indices Between Adamantanes

PP Env Monit #56

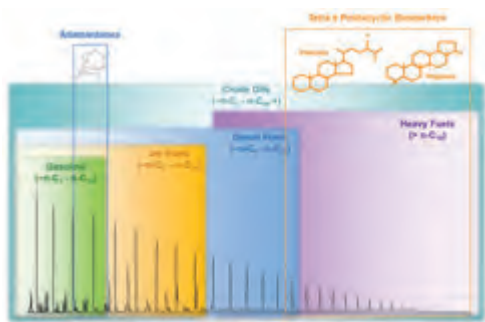
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Figure 1 – Total ion chromatogram of a crude oil organic extract.

The Gas Chromatography-Mass Spectrometry (GC-MSD) have been applied to forensic analysis of spilled petroleum products (Figure 1). These analysis are carried out by correlation between molecular indices determined for spill sample, collected in the contaminated area, and for source samples, collected in the suspected sources of the incident. The indices are calculated based on chromatographic signals of biomarkers, especially tetra and pentacyclic terpanes. However, during petroleum refining process these components are removed from the composition of light and medium oil products due to its high boiling point and molecular weight. The source identification of the spillages for this kind of products could be compromise if the tetra and pentacyclic biomarkers are absent which cause decrease in the corroboration level due to the fact that the number of indices determined are less. The adamantanes (ADs) proved to be an alternative to tetra and pentacyclic biomarker because they are present in the composition of light and medium oil products. However, to apply ratios between them it is necessary that certain criteria are met: resistance to degradation of ADs and analytical precision, independence and discriminatory character of the indices [1-3].

This study aims to get a larger group of indices that will improve the corroboration level of the method used for the resolution of pollution illicit processes by oil spills. For this purpose, 20 different crude oils were analysed and the ratios between ADs were evaluated in terms of independence and discriminatory power, as well as, the resolution and abundance of the chromatographic peaks of these components [4].

It was obtained a larger number of adamantanes ratios than typically observed in literature. Other indices observed in literature were excluded in this study for not having discriminatory power or for showing dependencies with other indices that exhibited better differentiating character.

Selected ratios already allow discrimination between some crude oils and refining products which may be complementary in forensic analysis of the spilled oils, especially in cases where tetra and pentacyclic biomarkers are absent.

The weathering impact on indices was not addressed in this study but this topic will be assessed further. However, it was taken into account some studies already made in this area [5, 6].

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Validation and Field Test of an Atmospheric Elemental Fractionation Sampler for Pollution Monitoring around Industrial Areas

PP Env Monit #57

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Elemental composition of atmospheric aerosol and precipitation is crucial for estimating risks for humans and natural ecosystems derived from pollution, and also for pollution sources assignment and apportionment. In consequence, analytical methodologies for measuring the presence and concentration of trace element of environmental concern are highly demanded within the frame of air quality monitoring networks and campaigns.

Whereas most of the studies dealing with determination of trace metals in atmospheric deposition are focused on the determination of total metal concentration, the speciation or at least fractionation of the analytes is very relevant for risk assessment of metal toxicity, since elemental solubility provides useful information about the biological and environmental availability of specific elements contained in environmental samples [1]. As a result, growing research interest is focused on novel, optimized procedures for extracting airborne elements, and for acquiring and interpreting data on their solubility.

In the present study, we propose the new concept of “in situ” fractionation of elements in atmospheric deposition by a passive atmospheric total deposition collector modified with a quartz fiber filter. This concept, designed as filtrating-bulk sampler, has been explored by some researchers for pH and major ions monitoring in the frame of acid rain investigations [2-4] but no reference has been

found about its use for elemental fractionation. So we propose this system and a simple and convenient analytical tool to obtain this relevant analytical information with significant cost savings in atmospheric monitoring activities.

The proposed methodology is based on the modification of a standard total deposition passive sampler by integrating a quartz fiber filter that retains the insoluble material, allowing the soluble fraction to pass through and flow to a receiving bottle. After operation for an extended period of time (typically one week), the quartz filter containing the insoluble fraction and the filtered solution containing the soluble fraction are separated and separately assayed by standardized ICP-MS protocols.

The atmospheric elemental fractionation sampler (AEFS) was validated by analyzing a NIST Coal Fly Ash 1633c certified reference material with good results, and then tested for field fractionation of a set of environmentally relevant trace elements. The samplers were installed at air quality monitoring units placed around the industrial area of Puchuncavi-Ventanas, Chile. The proposed AEFS was applicable for pollution assessment and also for identifying variability of the soluble and insoluble fractions of the selected elements within the study area (derived from different degrees of exposure to the industrial sources), allowing to improve the analytical information given by standard passive samplers for total deposition, avoiding the need of operating sophisticated equipment like wet-only / dry only collectors.

Acknowledgements

We acknowledge MEyC, Spain (project CTQ2014-52309-P) Junta de Extremadura, Spain (projects PRI IB16114, GR15087 and REPICA network), all partially financed by European Union Funds for Regional Development (FEDER).

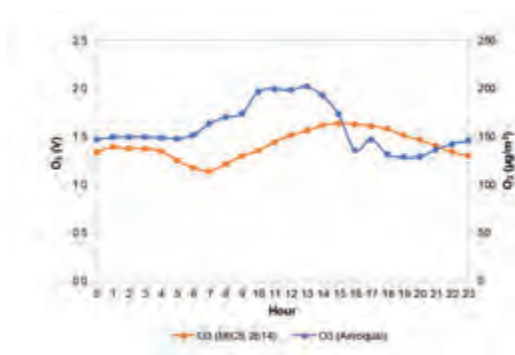
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Air Quality Monitoring Using Low-cost Sensors Based on URBANSENSE Platform

PP Env Monit #58

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Urban air quality poses a global concern to human health [1]. Air pollution is increasingly recognized as a contributing factor to the burden of diseases (e.g. lung cancer and cardiovascular problems) and it is also responsible for premature deaths in Europe [2]. In this sense, citizens in urban areas are continuously exposed to critical levels of air pollution in their daily lives, such as ozone (O_3). Therefore, control and monitoring air pollution are a pressing need. Traditionally, air pollution is monitored by measuring air pollutants concentrations at fixed sites by using accurate and expensive instrumentation [1]. Nevertheless, recent studies suggest low-cost sensors as a potentially more attractive alternative to conventional monitoring instruments [1]. Moreover, using a network of low-cost sensors (like the URBANSENSE platform) for the urban-scale air quality monitoring has been gaining more and more interest [1]. Thus, this study aims to evaluate O_3 data from low-cost sensor located at Fernão Magalhães avenue (near Dr. Francisco Sá Carneiro square) in Porto city (Portugal).

UrbanSense is a platform for pervasive environmental monitoring. It is composed by 23 monitoring units called Data Collection Units (DCUs), containing different sensors, that were deployed at relevant sites in Porto city [3]. For the purpose of this study, one of the 23 locations (Fernão Magalhães avenue) was selected to evaluate the O_3 daily mean profile. The air quality monitoring with O_3 low-cost sensor (MICS 2614) was performed between 11 May and 12 July 2016. During this period, the Aeroqual S500 was used as reference sensor enabling accurate real-time surveying, aiming the calibration of the O_3 low-cost

sensor. The O_3 daily mean profiles for the reference and low-cost sensors are showed in the figure. It is possible to observe a typical O_3 profile of urban environment for the reference sensor, characterized by an increase of concentrations at 7h and a decrease at 17h., with a maximum value of $202 \mu\text{g}/\text{m}^3$. However, the O_3 mean daily profile given by the low-cost sensor was different, presenting a slightly delay in O_3 concentrations. Linear regression (LR) and multiple linear regression (MLR) were applied to calibrate the O_3 low-cost sensor data. MLR model considered temperature and relative humidity as explanatory variables. The correlation coefficients (r) achieved were, respectively, 0.46 and 0.48 for LR and MLR. Both models presented a similar profile and were not able to fully describe O_3 variations, maintaining an almost constant concentration along the day. Thus, simple linear responses might not be the best models to describe O_3 variations.

Accordingly, in the future, more in-depth studies with more sophisticated calibration models, as artificial neural networks, should be developed and applied.

Acknowledgements

Authors are grateful to the municipality of Porto for all the support in deploying, operating and maintaining the DCUs and to Ana Aguiar and her team at Instituto de Telecomunicações for the management of the data platform. This work was financially supported by: Project POCI-01-0145-FEDER-006939 (LEPABE funded by FEDER funds through COMPETE2020 - POCI - and by national funds through FCT), European Project Future Cities FP7-REGPOT-2012-2013-1, and grant SFRD/BPD/91918/2012 for SIV Sousa, funded by FCT, POPH/QREN and ESF.

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Plastic Organic Additives in Surface Seawater and Zooplankton from the Gulf of Lion (NW Mediterranean Sea)

PP Env Monit #59

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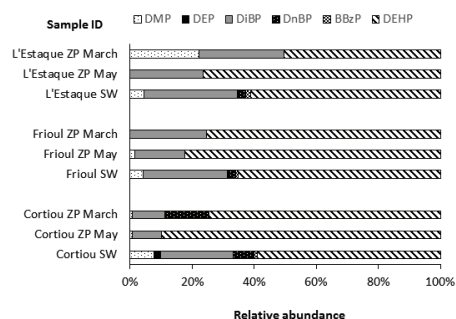


Figure 1. Relative abundance of PAEs in zooplankton (ZP) and seawater (SW) samples in 3 sites (Estaque, Frioul and Cortiou) from the Gulf of Lion (NW MED)

The Mediterranean Sea has been reported to be one of the most polluted seas of the world by plastics. [1] Small plastic fragments, the so-called microlastics (MP) (fragments in the range of 0.1 μm and 5mm) can enter the marine environment via rivers and runoffs, wastewater treatment plant (WWTP) effluents, air-borne transportation and direct inputs [2]. Marine organisms can be impacted by both the physical damage and the chemical pollution resulting from MP ingestion. MP may sorb, transport and release a variety of toxic chemicals, like persistent organic pollutants (POPs) and organic additives. Still little is known about their real impact in the environment. Representing a pivotal component of the marine food web, zooplankton (ZP) plays a vital role in the ecosystem functioning, yet the actual occurrence and impacts of MP (and associated organic additives) on these organisms have been poorly studied. Phthalic acid esters (PAEs) and organophosphate ester (OPE) flame retardants and plasticizers are among the most important plastic additives. Previous reports proved their overall occurrence in the aquatic environments [3-5]. However, there is still very little information on their concentrations in seawater and at the first levels of marine trophic webs. Here, we report the first existing data on the PAE and OPE occurrence in seawater and ZP from the NW Mediterranean Sea. Samples were collected in March and May 2017 at three different locations in the Bay of

Marseille (France): in the proximity of a harbour (L'Estaque), at the outflow area of Marseilles WWTP (Cortiou), and near a sparsely inhabited island (Frioul). ZP was sampled using a 150 μm mesh-sized neuston net and water was gathered in using an inox collector and then transfer into pre-combusted 1 L glass bottles. ZP samples were accelerated solvent extracted (ASE), while solid phase extraction (SPE) was used for processing water samples. Instrumental analysis was performed by GC/MS. Good method recoveries were obtained PAEs in ZP (80 to 131 %) and water (82 to 97 %) samples. OPE recoveries in water were also good (66 to 107 %). No blank problems were observed. Higher water concentrations of $\Sigma_9\text{OPEs}$ and $\Sigma_6\text{PAEs}$ (~ 700 and 180 ngL^{-1} , respectively) were measured in Cortiou, at the outlet of the WWTP, and lower levels were observed in the other sites ($50\text{--}75 \text{ ngL}^{-1}$ ($\Sigma_9\text{OPEs}$) and $100\text{--}135 \text{ ngL}^{-1}$ ($\Sigma_6\text{PAEs}$). TCPPOP dominated in all sites, while DEHP was the most abundant PAE, also in the ZP samples (Figure 1), which reflected the highest PAE levels at Cortiou site too.

Acknowledgements

This work was funded by the French Agence de l'Eau (Blue-POLUT project) and the Labex OT-Med (no. ANR-11-LABX-0061) – MEDPOP, funded by the French Government “Investissements d'Avenir” (ANR) through the A*MIDEX project (no ANR-11-IDEX-0001-02) and takes place

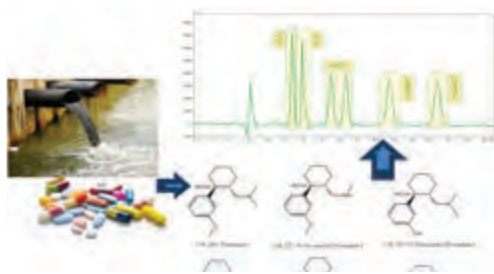
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Enantiomeric Separation of Tramadol and Its Metabolites: Method Development, Validation and Application to Environmental Samples

PP Env Monit #60

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Pharmaceutical compounds are an important group of emergent environmental pollutants due to their high consumption and continuous discharge [1, 2]. Besides, many pharmaceuticals are chiral and are found in environmental matrices as single enantiomers or as enantiomeric mixtures [3]. Each enantiomer can have distinct biological and chemical behaviors triggering different concerns. Thus, the accurate assessment of chiral pharmaceuticals requires enantioselective analytical methods [3]. This study presents the development and validation of an enantioselective liquid chromatography with a fluorescence detection method for the concomitant quantification of the enantiomers of tramadol and their metabolites, *N*-desmethyltramadol and *O*-desmethyltramadol, in wastewater samples. Sample preparation was carried out by solid phase extraction using 150 mg Oasis[®] mixed-mode cation exchange (MCX) cartridges. Optimized chromatographic conditions were achieved using a Lux Cellulose-4 column (150 × 4.6 mm, 3 μm; Phenomenex) in isocratic mode, with 0.1% diethylamine in hexane and ethanol (96:4, v/v) at a flow rate of 0.7 mL min⁻¹ and excitation and emission wavelengths set at 275 and 300 nm,

respectively. The validated method demonstrated to be selective, accurate, and linear ($r^2 > 0.99$) over the range of 56 ng L⁻¹ to 392 ng L⁻¹. The detection and the quantification limits of each enantiomer were 8 ng L⁻¹ and 28 ng L⁻¹ for tramadol and *N*-desmethyltramadol, and 20 ng L⁻¹ and 56 ng L⁻¹ for *O*-desmethyltramadol. The feasibility of the method was demonstrated in a screening study in influent and effluent samples from a wastewater treatment plant. The results demonstrated the occurrence of tramadol enantiomers up to 325.1 ng L⁻¹ and 357.9 ng L⁻¹, in the effluent and influent samples, respectively. Both metabolites were detected in influents and effluents.

Acknowledgements

The author acknowledges the financial support from PHARMADRUUGS-CESPU-2014 and ChiralDrugs CESPU_2017. The authors wish to thank Grünenthal, GmbH for their kind donation of tramadol and *O*-DT enantiomers. This research was partially supported through national funds provided by FCT/MCTES and Higher Education (PIDDAC) and European Regional Development Fund (ERDF) through the COMPETE: Programa Operacional Factores de Competitividade (POFC), under the Strategic Funding UID/Multi/04423/2013, in the framework of the programme PT2020.

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Assessment of Toxicity Potential of Raw Olive Mill Wastewater and Polar Subfraction using Set of Bioassays

PP Env Monit #61

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Olive processing is one of the fastest growing agro-food sectors in EU with more than 4% of annual growth rate [1]. Although very important for the economy of the Mediterranean region, olive processing has been recognized as one of the most problematic in terms of environmental pollution, which is evident from the fact that next to the olive oil (only 20 % of the input volume), two waste matrices known as pomace (30 %) and wastewater (50 %) are also produced. Released into environment they can within a short period cause irrecoverable impact to the environment and environmental organisms. Although olive processing lasts only three months, 10-30 m³ of olive mill wastewater (OMW) is produced annually, which is equal with pollution of municipal wastewater that is produced by 20-22 million people [2]. Though there is an unquestionable need for monitoring, there are still no data concerning the level of OMW in the receiving water, and there are no established protocols in order to accurately assess the toxic potential of OMW. Previous studies already reported negative impact of raw OMW on microorganism, marine and freshwater organisms and plants [2, 3], but all those results are difficult to compare due to the different exposure times, concentrations and selected endpoints, and also does not tell much about toxic potential of polyphenols contained in those OMW samples.

For this reason, within our research solid phase, extraction was preformed and concentration of polyphenols were determined using HPLC-UV. Four toxicity tests which covered different modes of action were conducted for the evaluation of the environmental impact of unfractionated OMW sample, and also polar subfraction: i) algal growth inhibition test using *Chlorella vulgaris* [4]; ii) germination seed test with two plants – *Trifolium repens* and *Hordeum vulgare*; iii) *Daphnia* sp. acute immobilization test [5]; iv) zebrafish embryotoxicity test [6]. All experiments were performed on undiluted (100 %) and diluted raw OMW/polar subfraction samples (1, 5, 10, 25, 50 and 75 %).

Obtained results showed a clear correlation between polyphenols concentration and observed toxicity. Those findings may contribute to the understanding of OMW induced toxic effects on primary producers, plants, invertebrates and vertebrates.

Acknowledgements

»The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. J2-8162«.

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Nutrient Concentration Signature and Trophic State of the Shallow Poti-y Sub-Reservoir From The Large Subtropical Reservoir of Yacyreta

PP Env Monit #62

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In South America large artificial reservoirs have been built mainly for energy generation, irrigation of agriculture lands and flood control [1]. Yacyreta dam was built during the 1980s and 90s, but in 2008 was flooded to the designed level, forming several sub-reservoirs. Its Trophic Status Index (TSI) [2, 3], water chemistry, and nutrient inputs are still not characterized. Poti-y is a shallow sub-reservoir and its watershed has a mixed use: agriculture, pasture lands and urban area over 30Km². We aimed to determine the nutrients signature and trophic state and its evolution during from 2008. Under this study samples were collected monthly in six monitoring points. In order to look for spacial trends and correlation with trophic state evolution, we examined physico-chemical parameters, total phosphorus (TP) and nitrogen, chlorophyll α (Chl) concentrations, phytoplankton density and climatologic parameters [4]. Principal component analysis/ factor analysis [5], was used to analyze the seasonal, and spatial variations of water quality from May 2016 to April 2017 in controlling points of the Poti-y sub reservoir. The results indicated that the water quality and structure of the subreservoir were mainly affected by external inputs of nutrients from urban and agriculture activities as well as from internal forces as rain and fetch. Pearson test shows a strong correlation between Total Solids and Total Suspended Solids with a trend to

increase this correlation in spring and summer and decrease in autumn. The limiting factor for nutrients is phosphorus and no correlations were found between chlorophyll α and TP over the 12-month timeframe. TP presented a mean of 0,045 mg.L⁻¹, with a range between 0,018 mg.L⁻¹ and 0,11 mg.L⁻¹, while chlorophyll α presented a mean of 2,35 $\mu\text{g.L}^{-1}$ with a range between 0,13 $\mu\text{g.L}^{-1}$ and 7,25 $\mu\text{g.L}^{-1}$. Results of TSI for P and Chl suggest an mezotrophic state with some periods of eutrophic state. The relatively small nutrient concentrations in the riverine zone were probably related to the effect of the cascade reservoirs upstream of Itaipu and led to relatively low removal fractions. Our study suggested that water quality problems may be more pronounced immediately after the filling phase of the artificial reservoir, associated with the initial decomposition of drowned vegetation at the very beginning of reservoir operation.

Acknowledgements

The authors acknowledge the Entidad Binacional Yacyreta Margen Derecha, for facilitating the means for monitoring and water quality analysis.

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Different Approaches for the Analysis of UV Filters in Beach Sand

PP Env Monit #63

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UV filters are substances added to cosmetics such as sunscreen products, and also to lipsticks, and skin care and make up products, with the aim of protecting the skin against solar radiation. They are also added to other products like plastics, adhesives, paints and rubber to protect them from UV degradation. UV filters enter the environment mainly due to discharges into sewage treatment plants or directly into the aquatic environment, for example, through the bathing of cosmetics users. In the case of the matrix object of study in this work, beach sand, UV filters can be easily deposited in it, either applying the sunscreen in the beach or by direct contact of the person impregnated with the sunscreen with the sand or indirect through the bathing water. There are evidences of that these compounds are toxic and present adverse effects like estrogenic activity on biota and human beings. For these reasons, they are considered emerging pollutants.

Five methods based on ultrasounds, vortex, on-column lixiviation and two different alternatives of SPME extractions followed by gas chromatography–tandem mass spectrometry (GC-MS/MS) were developed for the simultaneous analysis of eleven UV filters (2-ethylhexyl methoxycinnamate, 4-methylbenzylidene camphor, benzophenone-3, benzyl salicylate, 2-ethylhexyl 4-dimethylaminobenzoate, ethyl hexyl salicylate, octocrylene, homosalate, isomyl-

methoxycinnamate, menthyl anthranilate and octocrylene) in sand samples. Only 1 g of sand was employed with any of the techniques. For US and vortex extractions, and lixiviation, 1 mL of ethyl acetate was used and then the extract was filtered before analysis. Regarding SPME, two options were tried: the SPME of an US extract diluted 1:10 with water and the direct SPME of the sand with 1 mL of water. One of the advantages of using SPME is that, for the major part of the compounds, a much higher response is obtained using SPME against the other techniques. However, as a consequence of high procedural blanks for some of them, LODs were not as lower as expected according the signal/noise ratio. Even so, LODs were in the low ng g⁻¹ level in all cases, being an order of magnitude inferior for some compounds using SPME. Other benefits are the possibility of automate the process and that it is not necessary the use of organic solvents. Nevertheless, US and vortex assisted extractions constitute a fast and economic approach for extracting UV filters from sand samples. Lixiviation provided the worst results, with recoveries lower than 75% for most compounds, while with the rest of techniques recoveries were acceptable. Therefore, all methods excluding lixiviation, were suitable for the analysis of these compounds in real beach sand samples. Finally, some beach sand samples from the northern coast of the Iberian Peninsula were analysed, showing the presence of eight out eleven studied compounds.

Acknowledgements

This research was supported by European Regional Development Fund 2007-2013 (ERDF), UNST10-1E-491 (Infrastructure Program, Ministry of Science and Innovation) and projects CTQ2013-46545-P (Ministry of Economy and Competitiveness, Spain) and GPC2014/035 (Consolidated Research Groups Program, Xunta de Galicia). M.V. would like to acknowledge Ministry of Education, Culture and Sport for a FPU grant and Red REGATA for a doctoral stay abroad grant. Some of the authors belong to the CRETUS Strategic Partnership (AGRUP2015/02).

V. Homem acknowledges her Post-doctoral Grant SFRH/BPD/76974/2011.

Analysis of Preservatives, Allergenic Fragrances, Musks, Plasticizers and UV Filters in Environmental Water by SPME-GC-MS/MS

PP Env Monit #64

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Preservatives, allergenic fragrances, musks, plasticizers and UV filters are compounds added in the majority of the cosmetics and personal care products. The fate of these ingredients is the rivers, lakes, seawater, sand, etc. since they enter the environment through domestic discharges or aquatic activities of the consumers of cosmetics. In addition, some of them are suspected to be harmful to health. For these reasons, they are considered emerging pollutants, and are starting to be included in environmental monitoring programs. One UV filter, 2-ethylhexyl methoxycinnamate, was recently incorporated in the watch list of substances for Union-wide monitoring in the field of water policy. The lack of suitable analytical methodologies makes necessary to develop multiresidue methods that include a high number of target compounds of different families in one analysis.

A method based on solid-phase microextraction-gas chromatography tandem mass spectrometry (SPME-GC-MS/MS) is proposed to determine almost 50 compounds including preservatives, allergenic fragrances, musks, plasticizers and UV filters in water samples. SPME is a good and environmentally friendly technique since it does not involve the use of organic solvents. In addition,

it can be easily automated, and it employs few mL of sample (10 mL of water in this work). Another advantage is that SPME offers a high concentration factor, very necessary in this kind of matrices, where the compounds should be monitored at very low levels. The method was optimized, and a multifactorial ANOVA was carried out. The selected conditions comprise the head-space extraction mode, with the polyacrylate fibre at 100 °C and the addition of 20% (w/v) of sodium chloride. This method was validated and applied to the analysis of several environmental water samples.

Acknowledgements

This research was supported by European Regional Development Fund 2007-2013 (ERDF), UNST10-1E-491 (Infrastructure Program, Ministry of Science and Innovation) and projects CTQ2013-46545-P (Ministry of Economy and Competitiveness, Spain) and GPC2014/035 (Consolidated Research Groups Program, Xunta de Galicia). M.V. would like to acknowledge Ministry of Education, Culture and Sport for a FPU grant. Some of the authors belong to the CRETUS Strategic Partnership (AGRUP2015/02).

This work was also financially supported by the projects: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE 2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT–Fundação para a Ciência e a Tecnologia. (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF), (iii) Post-doctoral Grant SFRH/BPD/76974/2011-Vera Homem and (iv) IACOBUS Program IV – V. Homem.

Assessment the Level of Self-cleaning of the Soils Around the Former Metallurgical Plant – Kremikovtsi, Bulgaria

PP Env Monit #65

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The aim of our research is to study the natural self-cleaning ability of soils around the metallurgical plant – Kremikovtsi, Bulgaria, closed since 2009. On the basis of results from previous survey, with soil samples collected nearby operating Kremikovtsi plant, we had prepared a new sampling plan including sample points of contaminated soils according to the current Bulgarian soil legislation [1]. The new set of samples was processed and analyzed in accordance with internationally accepted ISO standards for soils [2, 3, 4]. Appropriate analytical techniques (flame atomic absorption spectrometry and electrothermal atomic absorption spectrometry) were used for quantification of both pseudo-total concentrations (aqua regia

extraction) and concentrations of selected toxic elements in soil extracts obtained according to the classical BCR extraction procedure. The content of polycyclic aromatic hydrocarbons (PAHs) in soil samples was determined by gas chromatography after a Soxhlet extraction. Comparing the data from the previous studies and the newly obtained results, self-purification coefficients for the sampling points were calculated with respect to the different analytes (toxic chemical elements and PAHs).

Acknowledgements

Authors are grateful for the financial support from the Sofia University Science Fund – Grant № 8010-40/2017. One of the authors (Ts. V.) is grateful to Operational programme “Science and Education for Smart Growth”, project BG05M2OP001-2.009-0028.

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The Analysis of Environmental Samples Using High Resolution Mass Spectrometry to Identify Novel PFAS Compounds

PP Env Monit #66

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Introduction

There are a very wide number of PFAS compounds that are actually present in environmental samples that are not part of the current EPA methods for PFAS analysis. The goal of this work was to use a QTOF mass spectrometer with Non Target Screening workflow to locate and identify unique PFAS compounds that were not known to be in the sample.

Methods

Water samples were analyzed using a Sciex X500R QTOF system set up to acquire data in a Non Target Screening workflow. The instrument first performed

a TOF scan from 100-1500. This scan was followed by a data dependent scan where ions above a set threshold were selected for fragmentation and acquisition of a full scan MS/MS spectrum. The resulting MS/MS spectra were searched against a high resolution library to identify potential PFAS of compounds seen present in the samples.

Preliminary Data

Perfluoroalkyl substances (PFASs) encompass a range of fully fluorinated alkyl compounds and are prevalent in Aqueous Film Fire Foam (AFFF). In addition, PFASs are ubiquitous as they are used in many household goods and have been found in various environmental and biological samples. Here, we demonstrate the use of QTOF technology to exploit the power of high resolution mass spectrometry and the use of product ion spectra to identify novel compounds in AFFF contaminated samples. The use of library searching to identify unique and unexpected compounds in these samples will be presented.

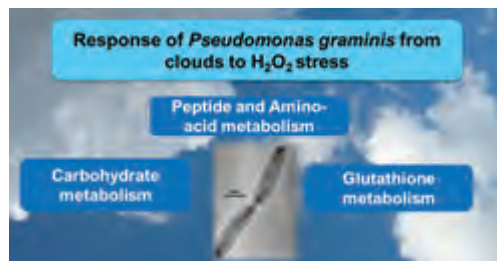
Novel Aspect

Novel PFAS compounds are identified using high resolution mass spectrometry

Modulation and Resilience of the Metabolome of *Pseudomonas Graminis*, a Cloud Bacterium, Facing H₂O₂ Atmospheric Stress

PP Env Monit #67

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In cloud waters microorganisms are metabolically active although they are exposed to very strong stresses, especially due to the presence of reactive oxygenated species, including H₂O₂ and radicals. In order to understand how microorganisms can modulate their metabolism facing H₂O₂ stress, we have investigated by a metabolomics approach the response of a *Pseudomonas graminis* strain, isolated from cloud waters, to hydrogen peroxide exposure. For this purpose *P. graminis* cells were incubated in microcosms containing artificial cloud waters in the presence or absence of H₂O₂. Metabolites were extracted at two time points (50 min and 24 h) that were important regarding the evolution of ATP cellular content and H₂O₂ degradation over time. These bacterial extracts were analyzed by LC-MS and ¹H-NMR using the Metabolic Profiler[®] facility (Bruker). Metabolic profiles were converted into matrices and statistical analyses (PCA, PLS-DA) were performed; key markers of this oxidative stress were identified by 2D NMR and LC-MS-Orbitrap.

At time 50 min, when H₂O₂ was still present in the incubations, the bacteria adapted and modulated their metabolome facing this stress.

The major metabolic pathways of *Pseudomonas graminis* (13b-3) impacted by the presence of hydrogen peroxide were the carbohydrate pathway, glutathione, energy, lipid and amino-acid metabolisms. Unexpectedly, the concentration of a few dipeptides containing mainly Ala, Val, Leu (Ile) was also highly modified in the presence of H₂O₂. These dipeptides are reported here for the first time as biomarkers of oxidative stress. Interestingly, at time 24 h, when H₂O₂ has been completely biodegraded by the cells, no more significant difference was observed between the metabolites of exposed and non-exposed cells to H₂O₂. This shows the resilience of this bacterium metabolome after H₂O₂ stress exposure. These results are discussed in terms of impacts on cloud chemistry.

Acknowledgements

Financial support from the TGIR-RMN-THC Fr3050 CNRS for conducting the research is gratefully acknowledged. N. Wirgot thanks the French Ministry of Research for her PhD scholarship. Part of the work was funded in the frame of the ANR BIOCAP French program. Developers of the web-based platform Galaxy are acknowledged. We used this platform for LC-MS data treatment and also for the statistical analyses.

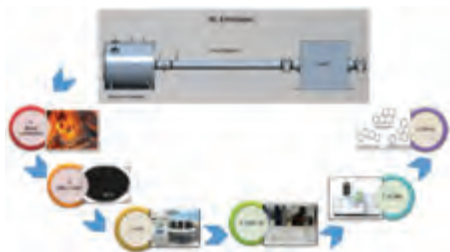
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Emission Factor and Toxic Concentration Equivalent of PAHs Generated by Combustion of *Pinus Radiate*, *Eucalyptus globulus* and *Nothofagusobliqua* at Two Different Wood Humidity

PP Env Monit #68

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In Chile there is a large consumption of firewood as a primary energy source, being the second most important source of energy after petroleum, where 59% of the firewood consumption is for domestic heating (chimneys and fireplaces), stoves and cookers. Wood burning generates lot of air pollutants which are mainly affecting the cities of central-south Chile) [1], especially Temuco city. In general, the investigations associated to wood burning have being focused on particulate matter less than 2.5 and 10 μm ($\text{PM}_{2.5}$ and PM_{10}), where highlights have reported a strong relationship between daily mortality cases among PM_{10} and subjects aged 65 years old with a greater Relative Risk (RR) for Temuco city (RR 1.1-1.2) respect to Santiago city (RR 1.0) [2]. It is well known that $\text{PM}_{2.5}$ can be deposited on the respiratory tract increasing their health effects [3] and it has been reported that between a 70 and 90% of the total PAHs from wood combustion is adsorbed on $\text{PM}_{2.5}$ surface (inhalable particles) [4]. Unfortunately, in our country there are not studies about the chemical composition of $\text{PM}_{2.5}$, more specifically Polycyclic Aromatic Hydrocarbons (PAHs) concentration from wood combustion, compounds widely known by their carcinogenic and mutagenic effects [4]. Although there is a large amount PAHs, the US-EPA has defined 16 compounds as priority, named 16 EPA-PAHs, of which, according to European Committee for Standardization, benzo(a) pyrene (BAP) compound is proposed as a marker for cancer risk on ambient air [5]. In this research, an analytical methodology was optimized using Accelerated Solvent Extraction (ASE) and GC-MS for determination of Emission Factor (EFs) of priority 16 EPA-PAHs adsorbed

in $\text{PM}_{2.5}$ generated by the combustion of the most common woods used in the south central zone of Chile: *Eucalyptus globulus* (EG), *Nothofagusobliqua* (NO) and *Pinus radiata* (PR) using the Controlled Combustion Chamber for Emissions (3CE, CETAM patent application No. 843-2008, 2010 in Chile and International Patent Application No. PCT / CL 00058, 2010, pending) [6].

The objective of the present work is to evaluate the variation of EF and Toxic Concentration Equivalent (TCE) for combustion of EG, NO and PR at 0% and 25% humidity (H) using the 11 Equivalent Toxicity Factor (ETF) of the authors Larsen and Larsen (1998). In this study the species that generated the greater Total TCE at 0% H was PR followed by NO and EG. While at 25% H, in decreasing order was EG, NO and PR. In all of species to both humidities, benzo(a)pyrene represents between 66 and 77% to the Total TCE. Additionally, if all parameters are compared for the same wood specie at 0% H (PR) the EF of $\text{PM}_{2.5}$ was the lowest and EF of Total PAHs and Total TCE was the highest.

Finally, we conclude that it is not enough to know EF of $\text{PM}_{2.5}$ in order to evaluate the population health risk, it is also necessary to know the PM toxicity by analyzing the HAPs concentration and their TCE.

Acknowledgements

CONICYT-PAI/Concurso nacional tesis de doctorado en la empresa 2014-78141103; FONDEF IDEA en 2 Etapas N° ID15I10580, Proyecto CONICYT-FONDECYT/postdoctorado 3150685, FONDECYT 1161793 and 1131028. DGIP-UTFSM-PICC- 2015.

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Geochemical Properties of the Sediments of the Great War Island, Belgrade (Serbia)

PP Env Monit #69

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Fig 1. Great War Island, Belgrade.

Rivers, which approximately deliver 20 billion metric tons of transported sediment to oceans every year, play a key role in Earth surface processes. Determining the content of potentially harmful heavy metals in rivers sediments is essential for estimating the environmental risk. The main sources of heavy metals in drainage basins are weathering of rocks and anthropogenic activities.

The aim of this study is to determine the geochemical properties in river sediments in order to assess the intensity of possible anthropogenic influence. Sediments were collected from the Great War Island in Belgrade, located at the confluence of Sava and Danube River (Fig. 1).

Number of authors analyzed Danube and Sava sediments [e.g. 1, 2], but so far no studies have been conducted on the confluence of these two rivers. Contents of Cr and Ni are of particularly interest since high concentrations of these two elements were reported in previous studies, but their origin is still not completely understood.

For the purpose of this study sediment samples were collected on five locations: 3 locations along the shore of the island (Kalemegdan, Lido and Small port) and 2 inland locations (at the Big and Small Galijas channels) (Fig. 1).

Mineralogical and geochemical properties were determined on 27 samples. Grain size composition

was determined using the Laser Microsizer 2000, contents of major and minor elements using X-ray fluorescence diffraction (XRF). Content of organic carbon (Corg) was determined with CHNOS Elemental analyzer.

Grain size analysis shows that analyzed sediments form four groups: sands, silty sands, sandy silts and clayey silts. Sediments from the shores show very high variation in dominant grain size, while sediments from the inner part of the island are clayey silts. This is in accordance with hydrological conditions since Island shores and the Big Galijas are under constant sediment input, although very low energy flows occur in the channel. Sediment deposition in the Small Galijas occurs only during extreme floods and consequently fine grain sediments are deposited.

Clay content and Corg content have positive correlation. Sediments from the Small Galijas have highest Corg (~5%) and lowest carbonate content indicating calm reduce deposition environment. Future organic geochemical analyses will give important insight into distribution of organic compound at the molecular level.

Contents of Cr and Ni in all samples have a positive correlation indicating the same geogenic origin. Content of Cr is grain size controlled in sediments that are under constant water flux, meaning higher Cr concentration in coarser sediments. Sediments in the Small Galijas do not obey this rule due to its specific depositional environment.

Acknowledgement

The study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 176006).

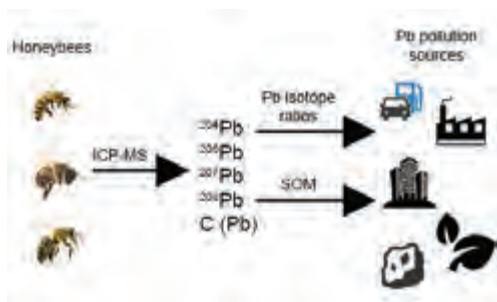
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Honeybees as Sentinels of Lead Pollution: Source Identification Using Stable Isotopes and the Kohonen Self-organizing Maps

PP Env Monit #70

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Honeybees have proven to be good bioindicators of metal pollution [1,2]. They reflect pollution that is present in all aspects of the environment: air by particulate matter (PM) deposition directly on the hairy bodies of the bee, water through drinking and soil either by the uptake by plants and transfer through its organs to flowers (pollen and nectar) consumed by bees, or by resuspension of soil into the air and consequently its deposition directly on bees and on plant organs they visit [3].

Stable lead (Pb) isotopes have earlier been used to determine sources of lead pollution in the environment [4]. Pb sources can be determined based on measured isotopic ratios considering that Pb isotopic composition does not change during different environmental or anthropogenic processes and that it varies only with geological sources of Pb [5]. Pb isotopic ratios cannot always give precise sources of Pb pollution, because some sources of Pb have similar isotopic compositions that are determined by geochemical composition of Pb in parental rock.

The Kohonen self-organizing map (SOM) is an unsupervised method for multidimensional data reduction and display [6]. SOM has been used for different environmental studies, including some biomonitoring studies [7].

The aim of this study was to assess origin of Pb pollution found in adult honeybees collected at apiaries with different environmental impact using

Pb isotope ratios and Kohonen self-organizing map. According to our knowledge this is the first time that Pb isotopes were determined in honeybee samples. Also, this is the first time that SOM is used to interpret data obtained on environmental contaminants using honeybees as bioindicators.

Pb isotope ratios obtained helped us differentiate different sources of Pb according to the environmental conditions around the apiaries where the samples were collected. Considering that there were samples that had similar Pb isotope ratios SOM that uses both Pb isotopes and concentration data as inputs was used to further discriminate these samples.

Acknowledgements

This paper was realized as part of project Nos OI 176006 and OI 172007, which are financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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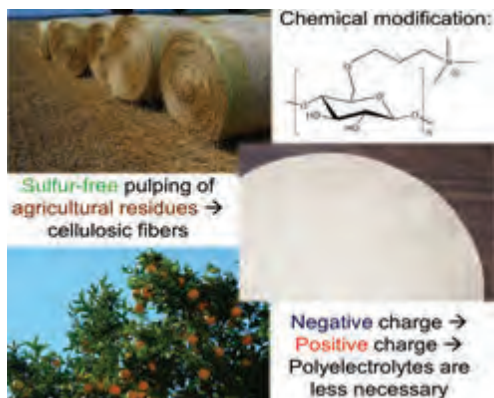
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Environmental Technologies

Can We Persuade Papermakers to Use More Lignocellulosic Residues and Less Cationic Polyelectrolytes?

PP Env Tech #1

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In the 1990s, nearly all predictions agreed on what would happen with the pulp and paper industries of developed countries: non-wood fibers would become increasingly used by manufacturers. The European production of pulp from alternative materials in the present decade could be up to 5 million tonnes per year, ten times that of 1993 [1]. Actually, current production of paper from non-wood sources in Europe is lower than that of 1993. Papermakers were held back by issues related to silica, fines and sheet formation [2].

At the same time, the paper industry is the largest consumer of cationic polyacrylamides. These polyelectrolytes are highly toxic to fish, given the negative charge which their gills bear, so the polymer chains hinder oxygen transfer [3]. It can be alleged that they are discharged in residual amounts, but cationic polyacrylamides are very poorly biodegradable [4]. To make things worse, measuring their concentration in the environment is a very complicated task.

We have the twofold aim of reusing waste from agriculture and making cationic polyelectrolytes less necessary. Considering this, we pulped various lignocellulosic residues by soda-anthraquinone processes, avoiding the use of sulfur compounds, and functionalized the pulps.

The functionalization was carried out with (3-chloro-2-hydroxypropyl) trimethylammonium

chloride (CHPTAC). Quaternary ammonium ethers of cellulose are formed. With degrees of substitution comprised between 0.1 and 0.2, the positive charge is low enough for fibers to remain insoluble [4], so they do not pass through the wire during sheet formation. Nonetheless, it is high enough to neutralize the negative charge of commercial pulps (around 0.02 meq/g) by adding approximately 5% of cationic fibers.

Results indicated that cationic fibers from agricultural waste improved the retention of fines, even with better performance than a conventional polyacrylamide. The retention of negatively-charged fillers was also enhanced. This would mean replacing a poorly biodegradable polyelectrolyte with a product that is not even discharged.

Acknowledgements

We want to thank the Ministry of Science and Innovation of Spain for the financial support (project *FIBRALT*); the auxiliary research centers at the Complutense University of Madrid, for the elemental analysis, and the research group LEPAMAP (University of Girona), for providing pulps.

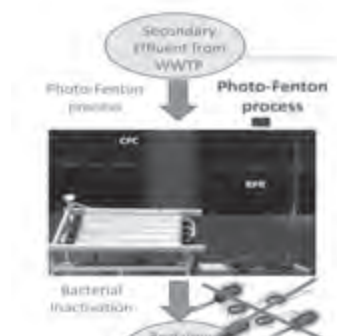
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Disinfection of Secondary Effluent from WWTP by Solar Photo-Fenton Process at Neutral pH in Raceway

PP Env Tech #2

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Since water is a limited resource, it is necessary to develop technologies for wastewater regeneration. These treatments are needed to improve water quality so that the limits imposed by legislation (RD 1620/2007) are achieved. *Enterococcus* and *Escherichia coli* (*E. coli*) are common indicator microorganisms of faecal contamination in water. Chlorination and ozonisation are common methods used to inactivate pathogenic microorganisms in wastewater, however its use increases the toxicity of treated effluents due to the generation of toxic products [1]. Advanced oxidation processes (AOPs) are a reliable alternative to traditional treatments. These processes are mainly characterized by the generation of hydroxyl radicals (non-selective), which are highly oxidizing. Among them, solar photo-Fenton process was studied in CPC for wastewater disinfection obtaining bacteria inactivation times around 60 min in compound parabolic collectors (CPC) [2]. A new option is proposed in this study using raceway pond reactors (RPRs) based on its high efficiency to eliminate micropollutants in discontinuous mode [3]. Consequently, the purpose of this research was

to analyse the bacteria inactivation of a secondary effluent from urban WWTP by solar photo-Fenton at neutral pH in RPR of 5 cm of liquid depth. These set experimental were carried out in CPC simultaneously for comparison the efficiency of process. To perform these experiments were used 50 mg $\text{H}_2\text{O}_2/\text{L}$ and 20 mg Fe/L , concentration values based on previous studies [2]. Therefore, assay of chronic and acute toxicity were carried out after and before treatment in both reactors obtaining non-significant changes in treated effluents. The total inactivation of three bacteria selected (total coliforms, *E. coli* and *Enterococcus*) was similar in both reactors reaching inactivation times of 80 min in both reactors. Additionally, an economic assessment of the treatment in the RPR was carried out. Estimated costs for a 400 m^3/d scale solar photo-Fenton plant for disinfection were 0.15 €/m³. This value is the range of reclaimed water rates.

Acknowledgements

This research was supported by the Ministry of Economy and Competitiveness (Government of Spain) and the European Regional Development Fund (ERDF), project CTQ2016-78255-R. G. Rivas and B. Esteban would like to acknowledge the Andalusian Regional Government for their PhD fellowships.

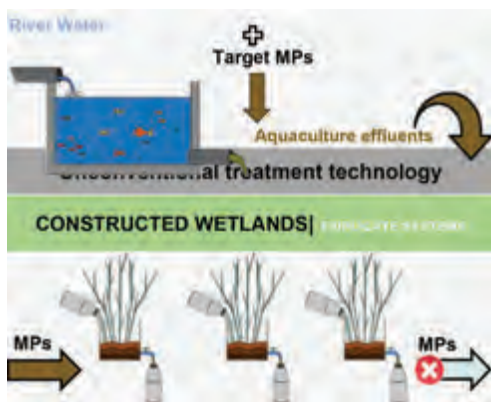
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Removal of Organic Micropollutants from a Freshwater Aquaculture Effluent Using Constructed Wetlands

PP Env Tech #3

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Fresh water is one of the most important resources on Earth and for this reason its contamination represents a serious worldwide issue of increasing environmental concern. Until very recently the attention in terms of water pollution has been focused on a specific group of pollutants (e.g. metals and persistent pollutants); however, in the last two decades, organic micropollutants (MPs) have been targeted as a growing challenge in the context of protection of aquatic systems [1, 2]. In fact, MPs may cause adverse effects in wildlife and human health, as bacterial and/or genes resistance and endocrine disruption. Typically present in the water at trace concentrations (between ng L^{-1} and $\mu\text{g L}^{-1}$), MPs encompass different classes of compounds, in general very difficult to eliminate by conventional water/wastewater treatment processes. Although there is no regulation for MPs legal discharge, Directive 2013/39/EU and Decision 2015/495/EU indicates, respectively, 41 organic priority organic substances (PSs) and 17 contaminants of emerging concern (CECs) for monitoring in surface waters within the EU [1, 3]. Despite general recognition of this problematic, alternative technologies to eliminate organic MPs from water/wastewater have been still poorly investigated, even more for aquaculture effluents [2, 3]. Constructed wetlands (CWs) are complex systems including water, a substrate, native microorganisms and usually plants, where the interaction among these components and the contaminants (dependent upon

several biotic and abiotic factors), promotes the elimination of several pollutants, including MPs. CWs have exceptional advantages as low-cost, simple operation/maintenance and eco-friendly. Nonetheless, their application has been essentially studied for the removal of conventional pollutants (e.g. organic matter, nutrients and metals), existing a huge investigation interest in the context of MPs elimination [2].

In this study, bench-scale experiments were performed using planted vertical subsurface flow CWs microcosms (VSSF-CWs), assembled for evaluating their capacity to eliminate a set of 36 organic MPs from aquaculture effluents. CWs microcosms (in triplicate) were supplemented with 2 L of aquaculture effluents spiked with 100 ng L^{-1} of each selected MP. The CW microcosms were operated in one-week cycle during four weeks, in order to assess the performance of the CWs systems along time. Removal efficiencies of CWs were weekly estimated by the difference of MPs concentrations at CWs inlet and outlet, determined by LC-MS/MS. The obtained results revealed excellent removal rates (varying between 85 and 100%) of the target MPs by CWs, emphasizing the potential of this unconventional technology still under-exploited.

Acknowledgements

Project POCI-01-0145-FEDER-006984 - Associate Laboratory LSRE-LCM, ERDF COMPETE2020 - POCI, AIPProcMat@N2020, FCT -SFRH/BD/133117/2017, SFRH/BPD/101703/2014 and IF/01501/2013, R&D&I INNOVMAR NORTE01-0145-FEDER-000035 and NORTE-01-0145-FEDER-000006, NORTE2020 - ERDF.

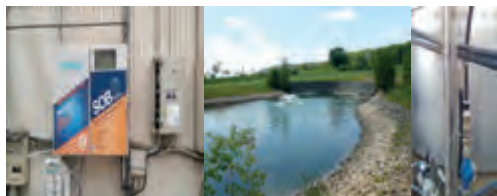
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Removal of Diclofenac in Wastewaters Using Different Advanced Oxidation Techniques (AOPs).

PP Env Tech #4

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Biodiozon and UV radiation equipment

The aqueous effluents that come to the sewage treatment plants of used urban waters show a complex composition associated to the current human and industrial development. So, the presence of certain pollutants, in many cases, may interfere the proper operation of the biological wastewater treatment systems. Between these pollutants, emerging contaminants are considered [1].

Emerging contaminant is considered any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/ health effects. It is important to know its incidence in the environment to be included in future legal regulations. So, several advanced oxidation treatments are proposed combined with photooxidation processes to get a fully satisfactory outcome as regards their degradation [2,3].

Emerging contaminants present high rates of transformation/removal, which may compensate their continual introduction in the environment. For this reason, it is necessary to raise awareness about their origin, transformation and the effects that can have this new generation pollutants to propose modifications or improvements in the mechanisms of water treatment, in order to ensure good quality and without detrimental effects on human health.

Within emerging contaminants occupy an important place pharmaceutical compounds and

more specifically the diclofenac. In this study, different combinations of advanced oxidation treatments have been studied to remove diclofenac in urban wastewater. In all cases, the analytical determination of diclofenac, was done by high-performance liquid chromatography (HPLC).

The output produced on site electrolysis of sodium chloride (Biodiozon) in situ at different concentrations was used in treatments, different doses of ultraviolet radiation (using a low-pressure UVC lamp of 8 Watts), various concentrations of hydrogen peroxide, and various combinations of the above technologies.

Initially, a synthetic wastewater was prepared with an initial concentration of diclofenac of 38 mg/L. With a dose of Biodiozon of 2 ppm of free chlorine and 72 hours of contact, all diclofenac was removed. With used doses of ultraviolet radiation was achieved to remove 88.5 % of initial diclofenac. The combination of UV radiation and Biodiozon, as well as combining ultraviolet radiation and hydrogen peroxide, allowed to eliminate 100% of initial diclofenac.

Acknowledgements

The authors are grateful to the personal of the company “S.O.B. Distribuidores” to provide Biodiozon generating equipment and its economic contribution for the present study.

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Nanomagnetism in the Environment

PP Env Tech #5

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Nanomagnetism was once seen as a utopia, and although its potential use was foreseen, there was no real observed development for a long time. All this changed, since the development of magnetic carriers and tagging technologies, as these techniques enable to manipulate the surface of the nanomagnetic particles, making possible to attach them to virtually any given substance, and therefore create agglomerates that we then may manipulate magnetically. Therefore, a huge effort has been put, in the last decade, to optimize the size and shape of these nanomagnetic particles, and many methods have been proposed and successfully implemented, among which we may stand out co-precipitation, hydrothermal, micro-emulsion, decomposition and pyrolysis. The applications are many and in the environmental area these nanomagnetic particles have been used effectively for water and waste water treatment, namely by effectively removing heavy metals and other important contaminants, for soil and underground water treatment, by the use of zero valent iron, in environmental catalytical degradation of contaminants, in environmental analytical chemistry, in greener alternative routes, etc.

In this work we will review the current status of the nanomagnetic particle applications in the environment, including regeneration of the particles and the final destination of the spent solutions.

Acknowledgements

This work was supported by the projects:

(i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development

Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia. (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). (iii) Project MINECO-17-MAT2016-76824-C3-2-R (MINECO, Spain)

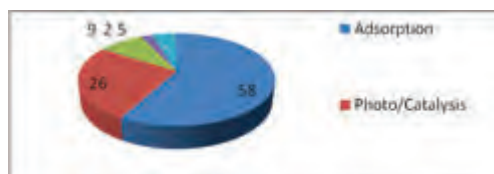


Figure 1 – Spectrum of environmental application areas of magnetic particles

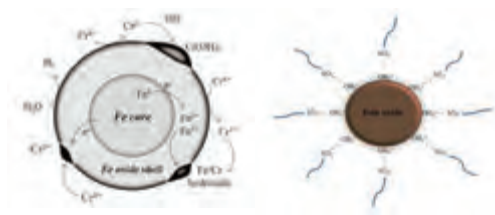
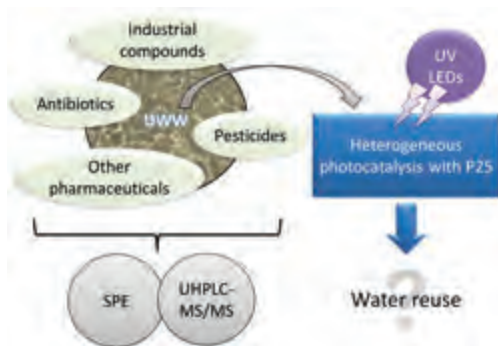


Figure 2 - Examples of particles used in the adsorption of environmental contaminants

Removal of Organic Micropollutants in Urban Wastewater by using UV-LEDs – Heterogeneous Photocatalysis

PP Env Tech #6

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Despite the positive contribution of urban wastewater (UWW) reuse practices for a sustainable water management, crop irrigation with treated UWW is an environmental and health concern within the European Union. Uptake of contaminants by plants and crops has a negative effect on the food chain and increases the risk of antibiotic resistance spread, which is presently considered serious concern to the public health [1]. The most recent European Decision 2015/495/EU identified a set of substances (including antibiotics) to be included in a watch list of environmental concern, including macrolide antibiotics [2]. Current tertiary treatment technologies are not able to mineralize many contaminants of emerging concern (CECs) occurring in UWW [3].

The present study focuses on the application of light-emitting diodes (LEDs) in a particular advanced oxidation process (heterogeneous photocatalysis) for the treatment of organic micropollutants. Lab-scale experiments were carried out in a slurry batch reactor (150 mL) using UV-LEDs and a commercially available TiO_2 photocatalyst (P25 from Degussa, Evonik). In order to optimize the reaction, the antibiotics azithromycin, trimethoprim, ofloxacin and sulfamethoxazole were used as model compounds, and were spiked in secondary UWW effluent at an initial concentration of ca. $100 \mu\text{g L}^{-1}$ each. Several light configurations were tested using TiO_2 photocatalyst at different

loadings. The removal of the CECs was monitored by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). The most efficient catalyst load and light configuration (in spiked UWW) were used for the treatment of non-spiked samples, to study the removal of a wide range of CECs in realistic concentrations (ng L^{-1} range). The samples were analysed by UHPLC-MS/MS, after solid phase extraction (SPE). In general, the concentration of all detected CECs decreased significantly after 10 min of photocatalytic treatment, which is not due to physical removal since no significant adsorption of the CECs over TiO_2 could be found within 30 min of contact. The biodegradability of the treated UWW is the next issue to be addressed.

Acknowledgements

This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. Part of the work presented in this paper is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675530. ARR, NFFM and AMTS acknowledge FCT (SFRH/BPD/101703/2014, PD/BD/114318/2016 and IF/01501/2013, respectively).

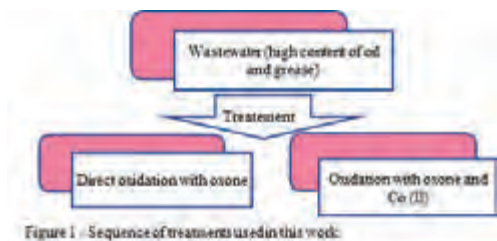
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Chemical Treatment of Biodiesel Production Wastewater with Monoperoxysulfate; Preliminary Studies.

PP Env Tech #7

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Biodiesel has become very attractive as a biofuel due to its environmental benefits [1-3] and it has been mainly produced from edible vegetable oils all over the world, which are easily available [4].

The untreated biodiesel contains several impurities, which will impact on the performance and durability of the diesel engine. Therefore, the purification stage is essential. The more traditional purification method is wet washing. However, the inclusion of additional water into the process offers many disadvantages, including the generation of a highly polluting wastewater that needs to be treated prior to environmental discharge and the significant loss of biodiesel into the wastewater phase [5]. This type of effluent presents high values of chemical oxygen demand (COD), oils and fats, among other contaminants.

The use of monoperoxysulfate (HSO_5^-) is an emerging technology in situ of chemical oxidation of organic compounds [5].

The monoperoxysulfate can directly react with organic molecules, because its redox potential is comparable to hydrogen peroxide and also can be decomposed into radicals by means of transition metals such as Co(II) , Ru(II) and Mn(II) [6,7].

The aim of this work was the study of the effect of the potassium monopersulfate compound ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), marketed under the name of Oxone, in the removal of COD in residual water from the biodiesel purification stage.

Two types of tests were performed (figure 1): Direct oxidation and oxidation using the metal catalyst Co(II) .

The results showed that the direct oxidation tests for the potassium monopersulfate concentrations of

$1.0 \times 10^{-2} \text{ M}$ and $4.0 \times 10^{-3} \text{ M}$ were not effective because there was no significant decomposition of the same over more than three hours.

The removal of COD was almost non-existent.

In the catalytic tests the combinations tested were:

- i) $[\text{Co}^{2+}] = 1.0 \times 10^{-7} \text{ M}$; $[\text{oxone}] = 1.0 \times 10^{-2} \text{ M}$,
- ii) $[\text{Co}^{2+}] = 1.0 \times 10^{-7} \text{ M}$; $[\text{oxone}] = 5.0 \times 10^{-3} \text{ M}$,
- iii) $[\text{Co}^{2+}] = 1.0 \times 10^{-6} \text{ M}$; $[\text{oxone}] = 1.0 \times 10^{-2} \text{ M}$,
- iv) $[\text{Co}^{2+}] = 1.0 \times 10^{-6} \text{ M}$; $[\text{oxone}] = 3.0 \times 10^{-2} \text{ M}$,
- v) $[\text{Co}^{2+}] = 1.0 \times 10^{-6} \text{ M}$; $[\text{oxone}] = 5.0 \times 10^{-2} \text{ M}$,
- vi) $[\text{Co}^{2+}] = 1.0 \times 10^{-6} \text{ M}$; $[\text{oxone}] = 7.5 \times 10^{-2} \text{ M}$.

In all of these tests the complete decomposition of the oxidant was verified for contact times ranging from 2h to 15min.

The tests with low cobalt concentration showed COD removal rates of 16% and 20%, respectively, and with the highest concentrations of 17%, 21%, 46% and 43%, respectively.

These results showed that assay (v) was the most favorable, although the 150 mgL^{-1} imposed by portuguese legislation for discharges in aquatic means has not yet been achieved.

This type of treatment can be considered as a pretreatment of this type of effluent, after monitoring the content of cobalt and sulphates in the final effluent.

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Detailed Characterization of Pyrolysis Oil by Comprehensive Two-Dimensional Gas Chromatography/Mass Spectrometry

PP Env Tech #8

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The importance and utilization of renewable energy sources during last decades is constantly increasing due to increasing contamination of the environment resulting from energy production by burning of fossil fuels. Therefore, energy from fossil fuels is - where it is possible - partially or fully replaced by energy from renewable sources - wind, water, sun, geothermal, or by energy produced from biomass. The last mentioned source is neutral from the point of view of carbon balance; CO₂ is incorporated from atmosphere to biomass during photosynthesis and it is released back during burning. Energy gained in this process is energy of sun radiation converted to chemical energy during photosynthesis.

The most common way of biomass conversion to energy is burning. This is not very effective because the calorific value of biomass is substantially lower than that of fossil fuels, moreover some kinds of biomass burn hard (e.g. wet wood) or not at all (e.g. manure). Various processes have been applied to overcome these drawbacks. These could be divided into two groups: biochemical and thermochemical. Biochemical processes are based on the activity of microorganism, converting complex biopolymers from biomass to simple compounds, which could be consequently transformed to gaseous fuel (methane), liquid bio-gasoline or bio-diesel, bio-ethanol and other products [1]. In thermochemical processes the chemical bonds in biopolymers are cleaved by heat. The heat could be applied either in the presence of stoichiometric or higher amount of oxygen (oxidative processes - burning) or in the presence of substoichiometric amount of oxygen, eventually without it (reductive processes - pyrolysis producing pyrolysis oil together with gas and solid residue, and gasification producing also gas and solid residue, but more or less without oil) [2].

The aim of this work is detailed characterization of pyrolysis oil from woodchips (4 samples) and sewage sludge from wastewater treatment plant Brno-Modřice (1 sample). Samples of pyrolysis oil were provided by Bionic Laboratories Company. Condensable part of vapours and aerosols formed during pyrolysis results to pyrolysis oil, which was subjected to detailed characteristic using complex chromatographic separation methods with mass spectrometric detection.

In the first step the sample of pyrolysis oil was precipitated in n-pentane. Soluble fraction was subjected to column chromatography on activated silica with stepwise elution (n-pentane; n-pentane/dichloromethane 1:1; dichloromethane, dichloromethane/methanol 1:1). Comprehensive orthogonal two-dimensional gas chromatography with mass spectrometric detection using electron ionization and time of flight analyser was used for detailed characterization of each fraction.

The first fraction typically contained alkanes, alkenes and cycloalkanes. Number of identified compounds was usually almost one thousand. The second fraction was dominated by aromatic and polyaromatic compounds, including heterocycles (mainly containing nitrogen). Number of identified compounds varied from 500 to more than two thousands. In the third fraction mainly oxygen containing compounds were found. Number of identified compounds varied between 40 and 400. Similar compounds were found also in the fourth fraction, where number of identified compounds was from 40 to more than 1200.

The composition of pyrolysis oil obtained from wooden chips under different conditions was quite similar. The pyrolysis oil obtained from sewage sludge was characterized by higher amount of heterocyclic compounds together with nitrogen and sulphur derivatives.

GCxGC-TOF MS was found to be very efficient analytical tool for analysis of such complex mixtures like pyrolysis oil from various kinds of biomass.

Acknowledgements

This study was supported by project No. FCH-S-17-4766 from the Ministry of Education, Youth and Sports of the Czech Republic.

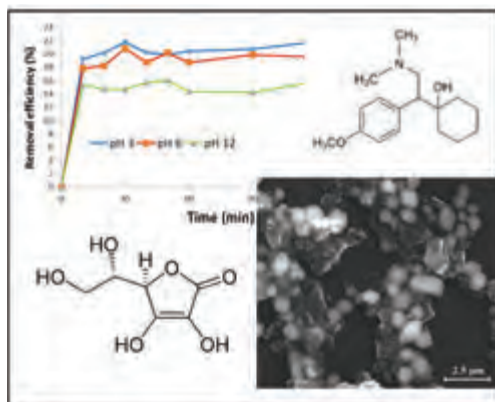
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Polyoxometalate@Graphene Nanocomposites as Photo and Electrocatalysts

PP Env Tech #9

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Pharmaceuticals play an important role in assuring populations' health. However their use is not exempt from negative effects whose importance just more recently has been recognized. Many pharmaceutical compounds are highly persistent in the environment as they are not efficiently removed in wastewater treatment plants [1]. Nanocomposites based on graphene and other species like semiconductor nanoparticles and metal oxides stand out as new advanced photo/ electrocatalytic solutions for efficient and sustainable removal of water pollutants, with a triple role as photo (electro) catalysts, adsorbents and antimicrobial agents. Among the several species that can be immobilised on graphene are the polyoxometalates (POMs) [2]. In this work, tetrabutylammonium salts of phosphomolybdate (PMo_{12}) and vanadium-phosphomolybdates (PMo_{11}V , $\text{PMo}_{10}\text{V}_2$), graphene flakes and POM@GF nanocomposites were used to evaluate the photocatalytic removal efficiency of venlafaxine in aqueous solutions and the electrocatalytic determination of dopamine and ascorbic acid. For photocatalytic studies, the nanomaterials were tested under natural sunlight irradiation during 150 minutes. The nanomaterial masses ranged between 2.6 – 28.81 mg added to 200 mL aqueous solutions of venlafaxine (2 mg/L) and pH values of 3.0 or 6.0. Pharmaceutical removal was monitored by HPLC-FLD.

The POMs tested presented lower removal efficiencies when compared to graphene, which presented a removal efficiency of 68.3% (10.12 mg, pH 6.0). For isolated POMs, the best result

was obtained for PMo_{12} (28 mg, pH 3.0), with 29.3% removal efficiency. $\text{PMo}_{10}\text{V}_2$ (28.0 mg, pH 3.0) removal efficiency was slightly better than the one for PMo_{11}V (20.0 mg, pH 3.0), 11.4% vs. 6.5%, respectively. For the POM@GF , the removal efficiency increased when compared with the values obtained for the isolated materials, probably due to the excellent adsorption properties of graphene, outweighing the POM action in the process. At pH 6.0, removal efficiencies values of 54.5% for $\text{PMo}_{12}\text{@GF}$, 65.0% for $\text{PMo}_{11}\text{V@GF}$, and 61.4% for $\text{PMo}_{10}\text{V}_2$ were attained.

Regarding electrochemical characterization and electrocatalytic properties, the immobilization of POMs onto GF lead to better resolved peaks with much higher peak currents when compared to the free POMs. For $\text{PMo}_{11}\text{V@GF}$ and $\text{PMo}_{10}\text{V}_2\text{@GF}$ the peak at $E_p \approx 0.350$ V increased with increasing ascorbic acid (AA) concentration, whereas the corresponding reduction peak currents decreased, suggesting that the V-centre acts as the active site for AA oxidation. Tests with free V-POMs showed that, although there was an increase in peak currents, this was not clearly attributed to the electrocatalysis of AA by the V-centre in the POMs. For $\text{PMo}_{12}\text{@GF}$ the peak at $E_p \approx 0.200$ V (Mo centre) is the active site for AA oxidation. Electrocatalytic efficiency values of 93.0, 666.3 and 273.7% were obtained for $\text{PMo}_{12}\text{@GF}$, $\text{PMo}_{11}\text{V@GF}$ and $\text{PMo}_{10}\text{V}_2\text{@GF}$, respectively.

$\text{PMo}_{11}\text{V@GF}$ was further used in the dopamine (DA) determination in a solution containing both the DA and AA. A detection limit of $0.88 \mu\text{mol dm}^{-3}$ and a linear range of 2 to $300 \mu\text{mol dm}^{-3}$ were obtained.

Acknowledgements

Fundação para a Ciência e a Tecnologia (FCT), FEDER under Programme PT2020 (Project UID/QUI/50006/2013) and Programme FCT-UT Austin, Emerging Technologies (Project UTAP-ICDT/CTM-NAN/0025/2014) is acknowledged for the financial funding.

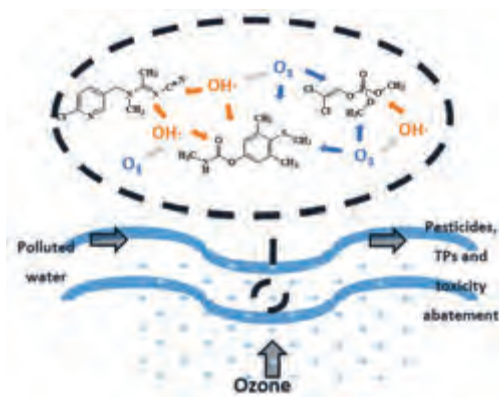
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Elimination of Priority Pesticides During Wastewater Ozonation: Reaction Characterization and Application in Real Matrices

PP Env Tech #10

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Last European laws regarding the monitoring and control of priority substances in the field of water policy include in their lists several pesticides, which represent about a 50% of all the considered compounds [1, 2]. This fact points out the special concern regarding the presence of these hazardous pollutants in water compartments. Increasing attention is now being paid to the development and implementation of innovative remediation technologies aimed to remove these substances from water and wastewater, since a lack of knowledge still exists regarding this issue.

One of the most promising advanced water technologies for micropollutants removal is ozonation. However, in order to elucidate if this treatment can constitute a viable alternative for the elimination of particular priority pesticides from water it is necessary to first characterize the behavior of these chemicals when subjected to ozonation. Reaction kinetics, degradation mechanisms and the residual toxicity associated to the generation of transformation products (TPs) are important aspects that need to be addressed prior to the implementation of this technology. Once this is properly studied, the removal of these chemicals in real waters should be tested in order to elucidate the matrix influence on the process performance and determine the necessary extent of the oxidative treatment in order to achieve the desired depletion level.

In this work, the removal by means of ozonation of three selected priority pesticides (Methiocarb

(MC), Acetamiprid (ACMP) and Dichlorvos (DDVP)) was inspected for the first time. The second-order rate constant of each pesticide with the main oxidants involved in ozonation process (i.e., O_3 and formed $OH\cdot$) were determined by means of competition or pseudo-first order batch kinetic experiments. Rate constants of pesticides with hydroxyl radical were $8.2 \cdot 10^9$, $2.1 \cdot 10^9$ and $2.2 \cdot 10^9$ $M^{-1} s^{-1}$ for MC, ACMP and DDVP, respectively. Rate constants of these substances with molecular ozone presented higher variability: they were determined to be $1.7 \cdot 10^6$ (MC), 0.25 (ACMP) and $590 M^{-1} s^{-1}$ (DDVP). Reaction mechanisms were studied by means of LC-MS analysis, whose results permitted to propose the main degradation pathways followed by these chemicals during ozonation. Microtox® tests revealed that some of these TPs may cause a significant increase in the medium toxicity throughout the process, especially in the case of MC ozonation. This problem is expected to be solved by enhancing the generation of $OH\cdot$ during the process, since this oxidant is able to remove all, parent and formed compounds [3, 4]. Finally, the removal of the three pesticides (spiked at $100 \mu g L^{-1}$) from a conventional wastewater effluent was tested in semi-batch ozonation experiments. Obtained degradation patterns were totally consistent with the rate constants determined for reactions of each compound and molecular ozone.

Acknowledgements

This work was financially supported by the Spanish Ministry of Economy and Competitiveness (project CTQ2014-52607-R and Alberto's Cruz FPI research fellowship BES-2015-074109).

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Preliminary Results of A New LIFE for Mar Piccolo Project

PP Env Tech #11

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The main object of A New LIFE for Mar Piccolo project is the requalification of the Mar Piccolo basin (Ionian Sea, Southern Italy) thought to restore a reasonable portion of the basin (about 3000 square meters) using a purification pilot plant based on membrane microfiltration able to protect the present ecosystem.

This approach will allow us to bring down contamination of PCBs, PAHs and heavy metals that are the principal contaminants present in the sediment [1, 2] and consequently in the water column, reaching concentrations within the limits imposed by existing National and Community legislation.

These pollutants, besides, representing a serious disturbance to the delicate balance of the basin, have also affected mariculture activities, with significant damage to this economic sector of national importance.

To make purification plant eco-friendly, a photovoltaic system able to produce the energy needed to ensure the plant self-sufficiency will be installed.

Moreover the project aims to provide valuable tools for the sustainable management of marine areas to bodies in charge.

For this purpose, an intervention protocol for the environmental recovery of Italian and European coastal marine sites (inland lagoons, port areas, etc..) with similar pollution problems to those of the Mar Piccolo of Taranto will be developed.

The development of this protocol will include the construction of a multi-assay diagnostic kit for assessing the quality of marine waters.

At the end of the project activities, the reclaimed area of 3000 square meters will have its sea bottom free of bioavailable pollutants and it will be again usable.

Therefore, the prototype developed during the project can be re-used, and in case re-modulated, for reclaiming wider areas within Mar Piccolo and in other Italian and European marine and coastal areas.

In this work we show preliminary analysis of the selected site, through a detailed chemical and physico-chemical characterization of water and sediments. Moreover we report first results on resuspension and water diffusion of contaminants through on-site and laboratory experiments with pilot plant.

Acknowledgements

The activities described in this publication were funded by EC LIFE Project (LIFE14 ENV/IT/000461).

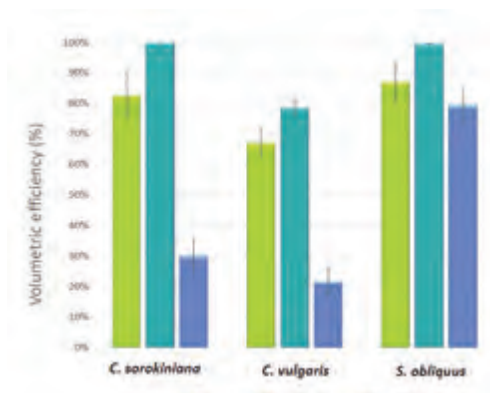
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Microalgae Removal of Nutrients and Diclofenac from Water

PP Env Tech #12

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Emerging contaminants (ECs) are compounds that are not currently covered by existing regulations but are thought to be a threat to environmental ecosystems and human health [1]. Among ECs, pharmaceuticals represent an especially worrying class since they were designed to cause a physiological response and their presence in the environment may affect non-target individuals [3]. This concern has led to the recent inclusion (Decision 2015/495/EU) of seven pharmaceuticals, including diclofenac, in the first watch list of substances to be monitored in all member states to support future reviews of the priority substances list within the Water Framework Directive (2000/60/EC) (WFD). Furthermore, the European Commission (Directive 2013/39/EU) highlighted the compromise of facing water pollution by pharmaceuticals and “propose measures [...] in view to reducing discharges, emissions and losses of such substances into the aquatic environment, taking into account public health needs and the cost-effectiveness”. Mixed microalgal systems have been recently pointed as a sustainable wastewater treatment for the removal of pharmaceuticals from water [3,4]. However, it is also important to study the applicability of different microalgae strains. Therefore, this work aimed at evaluating and comparing the simultaneous removal of nutrients and diclofenac by *Chlorella sorokiniana*, *Chlorella vulgaris* and *Scenedesmus obliquus*.

Microalgae were cultured inside bubbling column

photobioreactors (PBRs) of 250 ml in the Mann and Meyers (nutrients rich) medium, under controlled temperature ($25 \pm 1^\circ\text{C}$), irradiance ($370 \mu\text{E m}^{-2} \text{s}^{-1}$) and photoperiod (12:12). PBRs were operated in batch mode until the end of the exponential growth phase, and then under semicontinuous mode until the growth parameters remained steady. Experiments in the absence and presence of diclofenac ($C_{\text{feed}} = 25 \text{ mg l}^{-1}$) were carried out in parallel with controls containing just diclofenac so to verify its stability. All experiments and controls were run in triplicate and the microalgae growth, nutrients and diclofenac removal were monitored throughout time.

The obtained results showed that, except for *S. obliquus*, growth was favoured under the presence of diclofenac, which suggests that microalgae were mostly able to use this drug as a source of carbon. Among the three strains considered, *C. sorokiniana* showed the largest growth while *S. obliquus* was the most efficient in the removal of nutrients and diclofenac. The obtained results point to the possible application of these microalgae strains in bioremediation systems, not only for removing the excess of nutrients from wastewater, but also for the removal of pharmaceuticals.

Acknowledgements

Authors would like to acknowledge University of León (Spain) for funding given to the project MICROTRAT (UXXI2016/00128). Carla Escapa acknowledges the Spanish Ministry of Educations, Culture and Sports for her PhD fellowship (FPU12/03073).

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Membrane and Resins Technologies to Concentrate Extracts from the Brown Seaweed *Sargassum muticum*

PP Env Tech #13

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Sargassum muticum (Sm) is an invasive brown seaweed on the western coasts, causing a negative impact on ecology, fishing and recreative activities. Marine brown seaweeds contain alginate, laminaran, phlorotannins and fucoidan. On the one hand, sulfated polysaccharides known as fucoidan, are not found in terrestrial plants. Activities such as antioxidant, antiviral, antitumoral, anticoagulant, anti-inflammatory¹ were found for these compounds. However, these biological properties depend on the algal species, harvesting conditions, life cycle and the extraction and purification conditions².

The aim in this study is to compare membrane and resin technologies to obtain extracts rich in oligosaccharides and phenolic compounds of interest.

S. muticum was collected in Mourisca beach (Pontevedra, Spain) in August 2016, washed with water and stored at -18°C until use. Hydrothermal process (autohydrolysis) with compressed hot water in a liquid:solid ratio 30:1 was proposed.

Two temperatures were chosen: 170 °C to attain the maximum in sulfated oligosaccharides³ and 220 °C, to obtain the maximum in phenolic compounds⁴. Liquid and solid phases were separated, and the liquid phase was processed by membranes (100-5 kDa), and by polymeric non ionic commercial resins. Operating in a sequence of membranes, the retentates and permeates fractions were obtained and analysed. On the other hand, the phenolic compounds adsorbed onto resins were eluted with ethanolic solutions and analyzed.

Oligosaccharides were determined by HPLC. Process yield were gravimetrically determined, total phenolics and antioxidant activity were determined by spectrophotometric methods.

Acknowledgements

The authors are grateful to the Ministry of Economy and Competitiveness of Spain for the support of the research project CTM2015-68503-R and Xunta de Galicia for the CINBIO project (2016-2019). Both projects were partially funded by the FEDER Program of the European Union ("Unha maneira de facer Europa"). N.F.F. thanks the Spanish Ministry of Economy and Competitiveness for her FPI grant (BES-2013-064701).

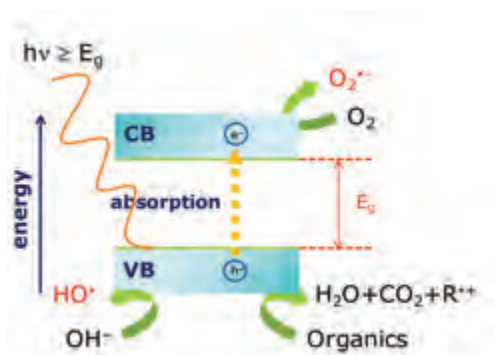
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Photoactive Microfiltration Membranes for Degradation of Organic Micropollutants in Water

PP Env Tech #14

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In recent decades, the usage of pharmaceuticals has increased dramatically originating many contaminant derivatives[1]. Some of those are contaminants of emerging concern and are not completely biodegradable, making them persistent in wastewater although subject to conventional treatments [2]. In order to overcome this limitation, heterogeneous photocatalysis has been paid most attention in many research works. However, most of studies employed suspended particle catalysts (slurries) [3], requiring the separation of the material from the treated water. Aiming to develop novel efficient separation strategies, in the present work, we prepared photocatalytic membranes containing immobilized TiO_2 particles, by a two-step method adapted from elsewhere [4] using commercial polysulfone (PS) and polyvinylidene fluoride (PVDF) microfiltration membranes.

The analysis of both PS and PVDF membranes by scanning electron microscopy (SEM) allowed observing a well-assembled layer of TiO_2 particles on the membrane surface, being the TiO_2 content superior in PS membranes. Higher surface hydrophilicity was obtained for all TiO_2 -immobilized membranes in comparison with neat membranes, *i.e.* without TiO_2 . The X-ray diffraction (XRD) patterns of all TiO_2 -membranes showed a well-crystallized anatase phase with particles around 7-9 nm. Thus, the hydrothermal

treatment of TiO_2 membranes by water vapour was effective to crystallize TiO_2 . Dark adsorption and UV-LED photocatalytic experiments were performed under recirculation mode, in order to study the performances of the developed membranes to degrade the pharmaceuticals tested, diclofenac (DCF) and 17- α -ethinylestradiol (EE2) in water. A high degradation of both contaminants was obtained in the case of TiO_2 -PS membrane.

Acknowledgements

Projects POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT and “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). SK acknowledges to the Erasmus Mundus Euphrates Fellowship. SMT, ARR and AMTS acknowledge the financial support from FCT (IF/00573/2015, SFRH/BPD/101703/2014 and IF/01501/2013, respectively), with financing from the European Social Fund and the Human Potential Operational Programme.

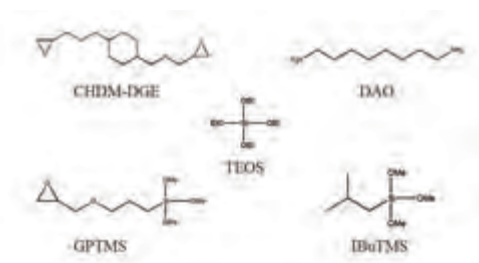
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Development of TiO_2 Nanostructured BPA-free Epoxy-silica Resins as Stone Conservation Hybrid Materials

PP Env Tech #15

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Our built heritage is constantly exposed to irreversible physical, chemical and biological deterioration processes that severely affect the long-term conservation of stone materials [1]. Accordingly, the design of new eco-friendly multifunctional products with consolidating, water repellent and biocidal properties is today industrially required to ensure a proper stone treatment.

Following this goal, the work here addressed is focused on the development of multifunctional epoxy-silica hybrids to obtain the advantages and minimize the drawbacks derived from the individual use of both classes of materials [2-3].

For this purpose, epoxy resins free of bisphenol A, were synthesized from a low molecular weight cycloaliphatic compound, 1,4-cyclohexanedimethanol diglycidylether (CHDM-DGE), by reaction with 1,8-diamineoctane (DAO) in the presence of different siloxane precursors, i.e. glycidoxypromethylmethyldiethoxysilane (GPTMS), tetraethyl orthosilicate (TEOS) and isobutyltrimethoxysilane (iBuTMS).

Besides, TiO_2 nanoparticles, in anatase form, were synthesized and incorporated during the hybrid materials synthesis to gain photocatalytic activity and biocidal properties.

After the selection of the most appropriate synthetic parameters, the cross-linking degree of the organic/inorganic networks obtained were studied by a combination of Raman spectroscopy and SEM-EDS. The thermal stability, dynamic mechanical behaviour and water repellence capability of the most promising samples were investigated by TGA, DSC, DMA and contact angles analysis.

According to the results, the materials obtained evidenced GPTMS as a good siloxane precursor to obtain stable materials against temperature degradation with considerable hydrophobicity to be tested in the field of stone conservation.

Acknowledgements

This work has been financially supported by the Research Groups Program (ref. IT-742-13) of Basque Government (GV/EJ). O. Gómez-Laserna gratefully acknowledges her post-doctoral contract from the University of the Basque Country (UPV-EHU). The authors are grateful to the technical support provided by the Raman-LASPEA laboratory of The Advanced Research Facilities of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF).

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Phosphorus Recovery from Sewage Sludge by Electrokinetic Based Technologies

PP Env Tech #16

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Phosphorus (P) is essential to all life being and a key ingredient in fertilizers to sustain high crop yields. It is an indispensable nutrient for food production and in a world of 9 billion people by 2050, securing sufficient P will be critical for future food security. Phosphorus has no substitute, but can be continually reused, being an example of a critical resource that could be utilized more efficiently in a circular economy to support sustainable growth and decrease pollution sources.

Electrokinetically based technologies can be effective and viable options for P recovery from sewage sludge [1,2]. Simultaneous phosphorus (P) recovery and removal of four emerging organic contaminants (caffeine, bisphenol A, 17 α -ethinylestradiol and oxybenzone) from sewage sludge was assessed using the electrodialytic (ED) process.

The application of a low level direct current improved the degradation of all emerging organic contaminants while allowing P recovery. In this study, a high pH favoured P solubilisation from the sludge. A 2 compartment cell design in which the sludge was placed in the cathode end using an anion exchange membrane, was the best option. This design allowed the migration of P to the anode end.

In total, 78% of P were recovered after 5 days using 50 mA (0.10 mA/cm²) and 70% of P in 3 days using 100 mA (0.21 mA/cm²). Still, the obtained results showed that 55% were recovered in 24 h using 100 mA. This suggests that P recovery, for the studied experimental conditions, can be carried out only for 24 h, decreasing the associated energy costs. The analysis of the microbiological community showed that the conditions within the cell were not appropriated to the protozoa and metazoan communities, as the number of individuals decreased with increasing ED experiments duration. Accounting the best recovery percentage achieved in these studies, 70% in 3 days using 0.21 mA/cm², ED technology has the potential to recover 280 000 tP/y of the total P in the sewage sludge.

Acknowledgements

Authors would like to thank AdP, Dr. Cristina Santos for providing the sewage sludge samples, Eng. Olga Paredes and the Laboratory of Control and Processes for the samples' characterization. Financial support was provided by CENSE-Center for Environmental and Sustainability Research which is financed by national funds from FCT/MEC (UID/AMB/04085/2013) and National Natural Science Foundation of China (21177135). N. Couto acknowledges Fundação para a Ciência e a Tecnologia for her Post-Doc fellowship (SFRH/BPD/81122/2011).

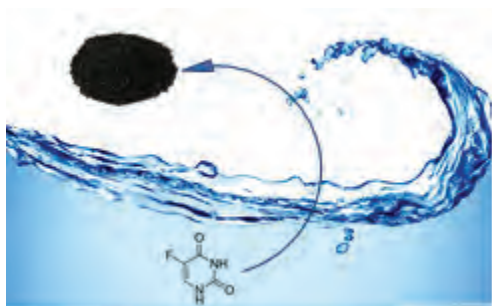
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Removal of the Anticancer Drug 5-Fluorouracil from Water by Adsorption on Carbonaceous Materials

PP Env Tech #17

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Anticancer drugs, widely used in chemotherapy, have emerged as new water contaminants due to their increasing consumption trends and poor elimination efficiency in conventional water treatment processes. As a result, anticancer drugs have been reported in surface and even drinking waters, posing the environment and human health at risk [1-3]. The search for effective treatment solutions are therefore of paramount importance and constitutes the scope of the present study, which is focused on the adsorption of 5-Fluorouracil (5-Fu) on different carbonaceous materials (four activated carbons and two carbon blacks). 5-Fu is one of the most used anticancer drugs in Portugal and in Europe, in combination with its pro-drug (capecitabine) [3, 4].

A comprehensive textural and elemental characterization of the adsorbent materials was performed, based on which their kinetics and equilibrium adsorption performances for 5-Fu uptake were compared. The equilibrium data revealed that the adsorption capacities are generally in line with the surface area of the carbonaceous materials; the carbon blacks, BP2000 and Vulcan (with respective BET surface areas of 1401 and 228 m²/g), exhibit the highest (112 mg/g) and lowest (19 mg/g) adsorption capacities, respectively. The linear driving force model was successfully used to describe the rate of 5-Fu adsorption on

the carbonaceous materials and the effect of some parameters (agitation speed, adsorbent particle size and initial 5-Fu concentration) on the sorption kinetics was evaluated. It was found that the oxygen content and the mesopore volume are the most relevant properties of the adsorbent affecting the kinetics.

Acknowledgements

This work was the result of the project: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Mónica S. F. Santos is grateful to the Portuguese Foundation for Science and Technology (FCT) for her postdoctoral grant (ref. SFRH/BPD/104039/2014).

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Metal Levels in Soil and Plants of Abandoned Gold Mines from Portugal

PP Env Tech #18

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As a consequence of ore exploitation, mining areas often encompass soils that present low cohesion, shortage of nutrients and organic matter, low pH, elevated potential for acid mine drainage generation, and high concentrations of metals [1]. Plants growing on mine sites usually tolerate toxic metal levels through mechanisms that include metal accumulation or exclusion. Hence, these metal-tolerant plants (known as metallophytes) can sometimes be used for biogeochemical prospecting, environmental biomonitoring, and soil reclamation through phytoremediation [2,3]. In this study, nine abandoned gold mines from Portugal were surveyed to determine metal concentrations in their soils and colonizing plants.

Soil and plant samples were collected at the following mines: Grovelas (Ponte da Barca), Marrancos (Vila Verde), Castromil (Paredes), Banjas (Paredes), Santo António (Penedono), Escádia Grande (Góis), Lousal (Grândola), Aljustrel (Aljustrel), and São Domingos (Mértola). Metal contents in soil and plant tissue were assessed by inductively coupled plasma mass spectrometry (ICP-MS).

In soils, the highest concentration ranges (expressed in mg kg⁻¹) for selected metals were found at:

- Aljustrel (6.5<[Ag]<15.62)
- Marrancos (1.16<[Au]<12.75)
- Penedono, (2,725<[As]<10,000)
- Castromil (104.1<[Cr]<157.1)
- Aljustrel (3.03<[Hg]<19.74)
- Aljustrel, (5,463<[Pb]<10,000)

In addition to highlighting the elevated levels of polluting metals, these results may also hint at the possibility of using another plant-based technique known as phytomining [4], to recover valuable metals from these soils (particularly Au).

Among plants, the most noteworthy results were observed on *Polytrichum commune* (common haircap), and two *Agrostis* species, *Agrostis delicatula* and *Agrostis curtisii* (hereinafter referred to as bentgrass plants). Common haircap exhibited shoot Ag concentrations up to 1.15 mg kg⁻¹ at the mine of Castromil, and up to 8.31 mg kg⁻¹ at the mine of Penedono. These findings suggest the aptitude of this species for Ag bioindication given that the concentrations were 1-2 orders of magnitude greater than those measured on every other species from all mines. The bentgrass plants, found solely at the Penedono mine, displayed root and shoot As levels up to 3,129 and 1,227 mg kg⁻¹, respectively. On average, these concentrations were at least 100-fold those registered on the majority of plant species from all mines. Thus, these bentgrass plants constitute promising prospects for biomonitoring soil As, as well as to promote the restoration of As polluted mine lands via phytostabilization.

Additional analysis to the comprehensive array of data obtained in this study (over 40 elements and several physicochemical parameters have been investigated), may provide greater understanding about the selected mines, their environmental risks, future challenges and opportunities.

Acknowledgements

The authors gratefully acknowledge financial support from the ERDF Interreg Sudoe Program (PhytoSUDOE-SOE1/P5/E0189) and the Portuguese Foundation for Science and Technology (FCT) (SFRH/BPD/103476/2014)

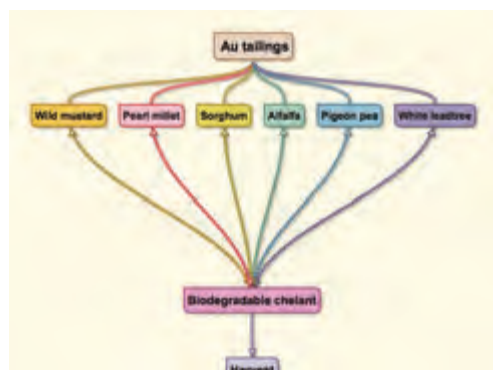
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Assessing the Potential of Six Common Brazilian Crops for Gold Phytoextraction from Mine Tailings

PP Env Tech #19

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In recent years, the ever-growing price of rare and valuable elements, the inability of conventional mining to extract the totality of metals from mineral ores, and the build-up of billions of tons of mine waste worldwide [1], have emphasized the importance of alternative solutions like phytotechnologies. These inexpensive and environment-friendly plant-based techniques have demonstrated their competence to not only mitigate pollution (phytoremediation), but also to recover critical metals (phytomining/agromining) and generate carbon-neutral energy from harvested biomass [2–4]. In this study, six naturalized crops that can be extensively found in Brazil, were assessed for their capacity to uptake Au from the tailings of a gold mine.

Seeds of *Pennisetum glaucum* (pearl millet), *Sorghum bicolor* (sorghum), *Sinapsis arvensis* (wild mustard), *Medicago sativa* (alfalfa), *Cajanus cajan* (pigeon pea), and *Leucaena leucocephala* (white leadtree), were sown on a 2:1 perlite:sand mixture (2:1 v/v), and allowed to germinate and grow till two fully expanded leaves. Seedlings were then transferred to pots at the rate of 1 per pot, following uniform criteria. The pots were filled with equal volume of mine tailings (Mina do Morro, Campo Largo, PR-Brazil), presenting 2.15 mg of Au kg⁻¹. One week before harvesting, the pots were treated with a solution of ammonium thiocyanate (NH₄SCN), at a rate of 1 g kg⁻¹. Plants, 3 replicates per species, were harvested 60 days after sowing.

Plants were divided into root and shoot, and their dry weights were measured. Metal contents in plant tissue and tailings (pseudo-total and bioavailable fractions) were assessed by inductively coupled plasma mass spectrometry (ICP-MS). One-way analysis of variance (ANOVA) was carried out to determine significant differences ($p < 0.05$) between plant species.

The biomass yield and metal levels of the shoots are critical for phytomining because they control the quantity of metal to be harvested from each plant (henceforth referred to as harvestable amount). Thus, although the dry weight of the aboveground parts was significantly lower in alfalfa than in the other species, it presented the highest Au levels (24.08 mg kg⁻¹), followed by wild mustard (7.82 mg kg⁻¹), and white leadtree (1.91 mg kg⁻¹). The remaining crops exhibited shoot Au concentrations below 1 mg kg⁻¹. These results translate into maximum harvestable amounts of 27.32^a, 15.17^b, 2.59^c, 2.34^c, 1.28^c, and 0.34^c µg of Au plant⁻¹ in alfalfa, wild mustard, white leadtree, sorghum, pigeon pea, and pearl millet, respectively (different letters indicate significant differences between crops).

Further analysis to the results obtained in this study include an economic assessment to determine the process profitability.

Acknowledgements

The authors gratefully acknowledge financial support from the Portuguese Foundation for Science and Technology (FCT) under grant no. SFRH/BPD/103476/2014.

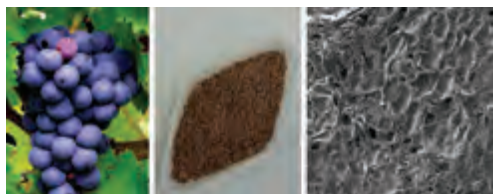
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Food industry By-product for Nitrate Removal

PP Env Tech #20

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Nitrogen compounds discharged in the environment can cause several problems such as eutrophication and deterioration of water sources. Furthermore, nitrates can cause hazards to human health by forming nitrosamines and nitrosamides which are found to be potentially carcinogenic compounds [1].

The food process industry generates a large quantity of by-products, which usually have low or no value and represent a possible environmental pollution. Development of inexpensive and effective water treatment chemicals have been of great interest during the last few years. Therefore, bio-based materials, i.e. by-products could be utilized in the removal of anions from water.

The aim of this work was to remove nitrate from wastewater of the confectionary industry by adsorption/ion exchange process. Chemically modified grape seed anion exchange resin was used in the sorption studies. The modification of grape seeds was carried out using epichlorohydrin, *N,N*-dimethylformamide, ethylenediamine and trimethylamine [2].

The physico-chemical properties of quaternized resin made from grape seeds (MGS) was analysed using techniques like SEM and FTIR. Batch studies were carried out to optimize the conditions for adsorption:

- the concentration range of nitrate was 10 mg/L to 300 mg/L
- the pH was adjusted from 2 to 10 using HCl and NaOH
- the effect of contact time was studied with nitrate solution of 30 mg/L and 0.2 mg MGS for varying periods of time (2 to 1440 minutes)
- the resin dose was varied from 0.05 g to 0.5 g in a 50 mL nitrate solution of 30 mg/L NO_3^- .

The removal efficiency of real wastewater generated from a local confectionary industry containing approximately 30 – 35 mg/L NO_3^- was about 80%. The nitrate removal capacity of resin from real wastewater with 300 mg/L nitrates was 16.21 mg/g. Langmuir, Freundlich and Dubinin-Raduschkevich adsorption isotherms were used to fit the equilibrium data. The Dubinin-Raduschkevich isotherm gave a better fit than Langmuir or Freundlich isotherm. The values of E (free energy) obtained in Dubinin-Raduschkevich model found to be greater than 14 kJ/mol, indicating the adsorption process as chemical ion-exchange process [3].

The adsorption kinetics followed the pseudo-second order kinetic model with higher correlation coefficient ($R^2 > 0.995$) compared to pseudo-first order kinetic model, suggesting that the adsorption limiting step may be chemisorption. In addition, the results indicate that intraparticle diffusion model was not the sole rate controlling step ($C \neq 0$) which indicates that both intraparticle diffusion and boundary diffusion affected the nitrate adsorption on MGS.

Modified grape seed was tested in column as well. The resin could only absorb a certain amount of nitrates and therefore the saturation capacity was very low (1.43 mg/g) after first cycle. Other anions present in wastewater had higher affinity for MGS.

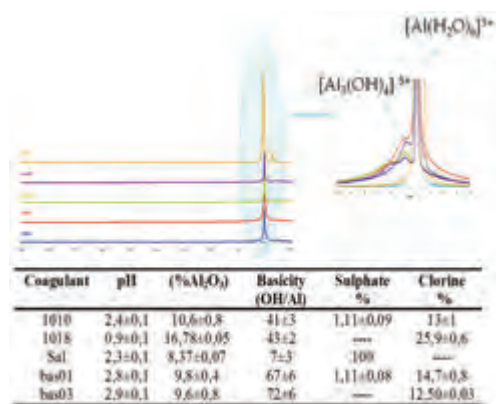
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Spectroscopic Characterization and Effectiveness Study of Aluminium Salt Coagulants in Water Treatment

PP Env Tech #21

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The study addressed is focused on identifying the species responsible of the coagulation process on the water treatment to enhance the design of aluminium salt coagulants. In this way, the effectiveness of the selected coagulants was correlated to their composition as well as the responsible species of the process were estimated.

For that purpose, five coagulants commonly employed in the water treatment (1010, 1018, sal, bas01 and bas03) were studied. Firstly, a spectroscopic characterization, based on RMN and Raman, was carried out to establish the species contained in them (see figure).

Subsequently, Jar-tests [1] were used to compare their effectiveness and select the optimal composition to encourage the formation of the desirable species. Besides, to select the maximum yield, the pH, temperature, and concentration variables and their effect on the residual amount of aluminium, turbidity and organic matter were also studied.

The results of aluminium hydrolysis distribution diagrams showed the greater effectiveness of the coagulant at high basicity conditions and no sulphate content. From the data obtained, it can be concluded that to design more effective coagulants for water treatment high basicity conditions and the biggest percentage of $[Al_3(OH)_4]^{5+}$ polymeric species are required since, it is the precursor of the $[Al_{13}O_4(OH)_{24}]^{7+}$ formation and then, the responsible of the coagulation process.

Acknowledgements

This work has been financially supported by the Research Groups Program (ref. IT-742-13) of Basque Government (GV/EJ). O. Gómez-Laserna gratefully acknowledges her post-doctoral contract from the University of the Basque Country (UPV-EHU).

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Wastewater Management in Shale Gas Industry: Alternatives for Water Reuse and Recycling, Challenges and Perspectives

PP Env Tech #22

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Wastewater management is nowadays one of the major concerns faced by the shale gas industry to improve its cost-effectiveness, while preserving the human health and environment [1]. Horizontal drilling and hydraulic fracturing «fracking» operations—required for the economically viable natural gas production from tight shale rocks—usually demand excessive freshwater consumption and generate large wastewater volumes [2]. Aside from chemical additives present in hydrofracturing fluids, wastewater is also composed by the shale formation constituents, which can include organic matter, naturally occurring radioactive materials (NORM), and high concentrations of salts and scale-forming ions [3]. The highly polluting nature of shale gas wastewater impels the application of energy-intensive pretreatment and desalination, to allow water reuse in hydraulic fracturing processes, water recycling or safe discharge.

Different management alternatives can be used for shale gas wastewater to reduce socioeconomic, public health and environmental risks. Around 95% of the shale gas wastewater totality produced by the U.S., is currently disposed in Class II saline water wells through conventional underground injection [4]. Although deep-well injection still remains as the dominant practice mainly due to economic reasons, factors related to capacity restrictions and potential groundwater and soil contamination and induced seismic activity, have recently arisen as driving forces for the application of advanced managing strategies.

Water reuse for internal shale gas operations is another beneficial alternative to address both the freshwater resources depletion and wastewater

pollution. Yet, direct wastewater reuse is generally inappropriate owing to its elevated contamination, which can hinder the shale well exploration. In this case, onsite pretreatment plants containing primary and secondary treatment technologies for greases, oil, scaling material and total suspended solids (TSS) removal, can be implemented to prevent operating problems. Apart from practical and capacity constraints of onsite treatment units, internal reuse alternative is ultimately dependent on the growth in shale gas production. As the demand for new wells exploitation tends to decrease with the industry maturity, shale gas activity will turn into a wastewater producer. Then, (offsite) desalination units will become inevitable to achieve the high-quality needed for water recycling or release to surface water bodies.

High energy consumption and greenhouse gas emissions, as well as specific operational problems (fouling and scaling) are challenges for the further development of emerging zero-liquid discharge desalination technologies. Firmer environmental regulations on brine discharges and water quality, and regulatory incentives will eventually guide the shale gas industry towards a cleaner future.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No. 640979. The financial support provided by the European Regional Development Fund (FEDER), Regional Operational Program of the Center (CENTRO2020), grant No. CENTRO-01-0145-FEDER-000006, and the Portuguese Foundation for Science and Technology (FCT), grant No. UID/MULTI/00308/2013 are also acknowledged.

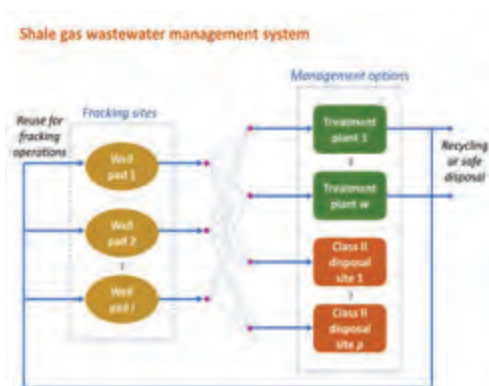
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Robust Stochastic-Fuzzy Modelling Approach for Shale Gas Wastewater Management under Uncertainty

PP Env Tech #23

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Shale gas has attracted growing investments as a new resource to increase primary energy supply, with impact on global energy markets. Over the last decade, advances in horizontal drilling and hydraulic fracturing «fracking» technologies have boosted the natural gas production from tight shale formations. Notwithstanding, shale gas exploration is still a controversial topic since its environmental and social implications are far from being totally elucidated. Concerning wastewater-related impacts alone, shale gas extraction generally produces large volumes of polluting hypersaline wastewater [1]. Hence, wastewater management is especially challenging to enhance overall process efficiency and sustainability in shale gas industry [2].

In this work, a new stochastic-fuzzy-based modelling approach is introduced for the robust optimization of shale gas wastewater management under multiple sources of uncertainty. Different management alternatives are considered to deal with the wastewater produced from fracking sites (well pads), including treatment plants—composed by pre-treatment and zero-liquid discharge (ZLD) desalination units—to allow water recycling or internal reuse in shale gas operations, or final disposal in Class II saline water injection wells (i.e., conventional deep-well injection). Thus, the model is aimed at obtaining an optimal shale gas wastewater network by improving the process cost-effectiveness, while accounting for several planning periods with different wastewater generation scenarios, and uncertain capacities of treatment plants and disposal wells. In this new approach, wastewater flowrate and salinity are

both considered as uncertain correlated parameters described by a set of generation scenarios with a given probability of occurrence. The wastewater generation scenarios are obtained via Monte Carlo sampling technique from a multivariate normal (Gaussian) distribution with symmetric correlation matrix. Uncertain treatment and disposal capacity constraints are mathematically modelled through fuzzy membership functions at different feasibility degrees, and probability functions by stochastic chance-constrained fuzzy programming [3].

The resulting multiscenario stochastic-fuzzy MINLP-based model is implemented in GAMS (version 24.8.5), by minimizing the expected total annualized cost. The objective function accounts for the contributions associated with the capital investment in the expansion of treatment plants (scenario independent decision variable) in the strategic planning periods, and operating expenses (scenario-dependent decision variables) related to transportation, pre-treatment and desalination and disposal in Class II wells, and revenues from water internal reuse in new fracking operations.

Results from risk analysis reveals optimal trade-offs between economic performance and system reliability. This methodology is a useful tool to support decision-makers towards the application of more robust and reliable systems for shale gas wastewater management.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No. 640979. The financial support provided by the European Regional Development Fund (FEDER), Regional Operational Program of the Center (CENTRO2020), grant No. CENTRO-01-0145-FEDER-000006, and the Portuguese Foundation for Science and Technology (FCT), grant No. UID/MULTI/00308/2013 are also acknowledged.

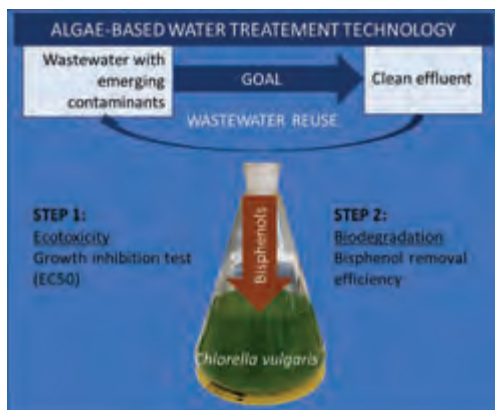
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Algae-based Water Treatment Technology: Ecotoxicity and Biodegradation of Bisphenols by *Chlorella vulgaris*

PP Env Tech #24

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Water shortage and water quality degradation are global concerns and are expected to intensify with increasing water demand mainly due to the rise of the world population and to climate change. Already now, the competition between the different water end-users (e.g. municipality, agriculture, industry) is enhancing, which demonstrates the urgent need to shift to a more sustainable water management. In this context, reuse of wastewater (WW) appears as a key solution to help preserving water resources. Nowadays, reuse of treated WW is generally considered as a reliable alternative water source for irrigation and replenishment among other applications. However, the potential health risks and environmental impacts due to pathogens and micropollutants usually present in WWs should not be overlooked. Thus, it is necessary to develop appropriate WW treatment systems which can deliver treated water adapted to its further utilization.

Emerging microcontaminants that can be present in WW treatment plant outflow constitute a major threat to the environment since their removal by common treatment processes is limited therefore efficient alternatives needs to be developed. Microalgae-based WW treatment technologies (ABT) have received considerable attention in recent years due to the resource recovery of algal biomass (e.g. fertilizers and bioplastics) and high-quality effluent obtained.

The aim of this study is to assess the removal efficiency of selected organic micropollutants by ABT. To this end, bisphenol A and its alternatives (BPs) have been selected as model of emerging industrial chemicals. The studied algal culture consists of a single strain *Chlorella vulgaris*, which exhibits great potential in WW treatment since it has a fast growth rate and a short generation time. The investigation consists of two main steps: i) determination of the acute ecotoxicity (EC50) of selected BP on *C. vulgaris* and, ii) degradation of a mixture of 18 BPs by *C. vulgaris*.

The experimental set-up involves placing the individual BP or mixture of BPs solutions (stock solution of 100 mg L⁻¹) in BBM (Bold's Basal Medium) under fluorescent illumination (4000 lux) at constant shaking. The ecotoxicity test is performed following the standard protocol OECD 201 (2011) with a 72-h exposure time of algae to BPs. The optical density (OD) of algae as well as chlorophyll a (Cha) content are monitored by spectrophotometer. BP concentrations are determined by HPLC-UV. The following parameters are monitored during the 10-days degradation experiments: i) OD and Cha by spectrophotometer, ii) pH, conductivity, redox potential and dissolved oxygen by selective sensors, iii) total nitrogen and phosphorus, phosphate, nitrite, nitrate and ammonium by fast colorimetric tests, and iv) BP residual concentrations by GC-MS. The eventual degradation products will be identified, as well.

The results of this investigation will allow to determine the ability of the microalgae *C. vulgaris* to degrade BPs present in WW and to optimize the basic parameters in order to scale up the experiment at a pilot level. Further steps of this study will include the testing of other emerging contaminants such as neonicotinoid pesticides.

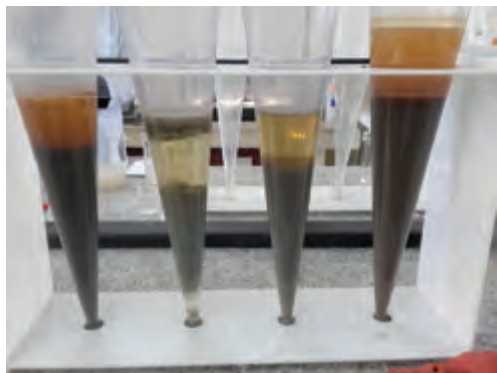
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The authors acknowledge the financial support from the Slovenian Research Agency; research core funding No. P3-0388, the projects Improved treatment and monitoring of Water Framework Directive priority pollutants (ID L1-7544) and Closing material flows by wastewater treatment with green technologies (ID J2-8162).

Wastewater Treatment of Leachates of El Inga Landfill in Quito using Conventional and Natural Coagulants

PP Env Tech #25

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Leachate results from the percolation of wastes found in landfills. One of the biggest problems when not given adequate treatment is filtration and percolation in the soil itself, ending in groundwater, aquifers, lakes, rivers or marshes thus diminishing the utility of this resource. The objective of the present investigation was to create natural coagulants in replacement of commercial and conventional coagulants in order to treat leachate water from the landfill. A simple sampling work was carried out in the “El Inga” sanitary landfill in Quito-Ecuador. A treatment based on the application of different unit operations was carried out; a greater emphasis was placed on the coagulation phase by coagulants of natural origin. Within the treatment phases, a maceration process was used in ethyl alcohol to obtain the coagulants, as well as the principles of electrochemistry to achieve a destabilization of the different contaminants to the treatment. The leachates were investigated in a jar test with three

compounds: PAC, PAC-R and $Al_2(SO_4)_3$, obtaining on this basis the conventional or commercial coagulant of better performance and thus be able to combine proportional in percentages of 25%, 50 %, 75% and 100% with the natural coagulants prepared (EUTANIFLOG and EUCOFLOC names given by the authors) to determine the best efficiency based on the measurement of parameters: turbidity, color, SST, pH and conductivity before and after. The combination of 25% EUTANIFLOG coagulant and 75% aluminum sulphate at a concentration of 30000 ppm with a turbidity of 8.27 NTU reducing turbidity by 99.58%. Dissolved Oxygen 3.5 mg / L suspended solids 26 mg / L color 449 PtCo and pH = 5.67, then passed through a column with zeolite, sand and activated charcoal to remove color, odor and SST.

Acknowledgements

We especially thank the teachers who were behind this investigation as well as the laboratory managers: Alfredo Maldonado, Veronica Rodriguez and Gabriel Cevallos who had the patience to guide us in this investigation. Also to the people of EP-EMGIRS in Quito.

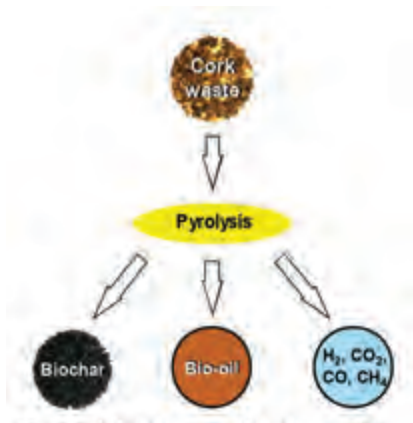
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Valorisation of Cork Wastes via Slow Pyrolysis

PP Env Tech #26

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Portugal holds a worldwide position on cork production, with a cork oak forest area of 7.35×10^9 m², corresponding to 34 % of the world's area and 23 % of its national forest [1]. In 2010, Portugal contributed with 52.5 % of the global production of cork, followed by Spain with 29.5 %. Waste management in the cork industry is crucial to its sustainability. Thermochemical conversion of residues has been an effective alternative in order to valorise these residues [2].

In this study cork waste, specifically high density cork granules obtained from Portugal's cork industry, were characterized and used to evaluate the effect of bed temperature on the yields of pyrolysis products (biochar, bio-oil and gas phase) and on the composition of the producer gas. The process was performed in a refractory steel vertical batch reactor with an internal diameter of 9.7 cm and height of 78 cm, heated by an electrical furnace of 5 kW. Pyrolysis products were analysed and each yield was determined.

Regarding the solid and liquid phases, higher values were obtained at 500 °C, with 33 % and 30 %, respectively. However, as expected the gas phase yield increased with an increase in bed temperature. The best results were obtained at the highest tested temperature, around 715 °C, with 54 % of producer gas. The influence of bed temperature on the average composition of producer gas is shown in figure 1.

The increase in bed temperature raised the mean volumetric composition of H₂ and CO in the producer gas. However, CH₄ composition showed a fairly constant behaviour along the tested temperatures.

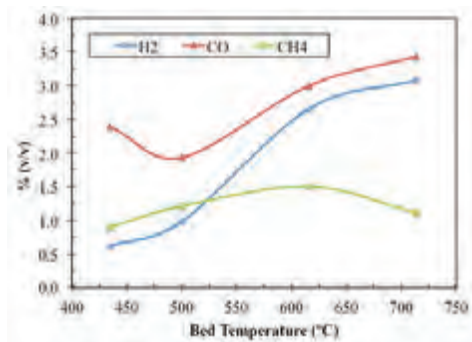


Figure 1 – Influence of bed temperature on producer gas composition.

The higher heating values (HHV) of the producer gas and solid phase were determined, and are shown in Table I.

Table I – Influence of bed temperature on the HHV of cork waste pyrolysis products.

	Bed temperature [°C]			
	453	500	615	715
Solid [kJ/g]	28.0	25.3	27.8	29.7
Gas [kJ/Nm ³]	7.4	8.5	13.2	12.8

Increasing the temperature does not appear to significantly influence the HHV of the solid phase. However, it does cause an increase in H₂ and CO concentrations, with a consequent increase in the HHV of the producer gas. Temperature was shown to play an important role in cork pyrolysis, affecting the three different phases. The choice of a specific bed temperature depends on the final purpose of pyrolysis. Nevertheless, this study shows that cork pyrolysis is a viable alternative to simple waste disposal.

Acknowledgements

Financial support from the FCT, under the Research Project UID/EQU/00305/2013.

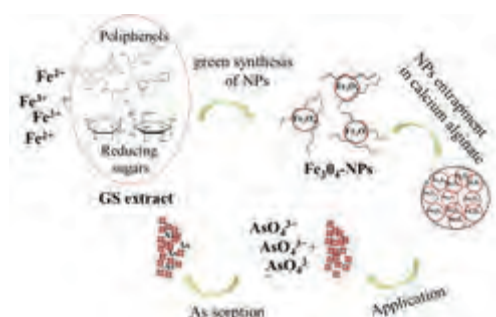
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Green Synthesis of Magnetite (Fe_3O_4) Nanoparticles Using Grape Stalk Waste Extract: Entrapment in Calcium Alginate Beads and Application for Arsenic Biosorption.

PP Env Tech #27

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Nanoscale iron oxide particles represent a new generation of cost-effective sorbent materials for the remediation of some challenging pollutants. Among the various synthesis procedures of the magnetite nanoparticles (Fe_3O_4 -NPs), the selected procedure has been the co-precipitation of Fe^{2+} and Fe^{3+} ions by NaOH in an aqueous solution. The chemical reaction occurring during co-precipitation of magnetite from iron salts mixture by raising the pH can be represented as: $2\text{Fe}^{3+} + \text{Fe}^{2+} + 8\text{OH}^- \rightarrow \text{FeO} \cdot \text{Fe}_2\text{O}_3 + 8\text{H}_2\text{O}$ [1,2].

Biosynthesis of Fe_3O_4 -NPs has been recently recognized to be a simple, environmentally friendly, pollutant-free and low cost approach. When biosynthesis is the selected method to produce Fe_3O_4 -NPs the iron salts mixture is previously contacted with the natural solution and then NaOH is added to raise the pH to get total precipitation of the iron oxide. It has been reported that green synthesis of nanoparticles produces NPs of smaller size with good stability as the bioagent acts as reducing and capping agent. In this work magnetite nanoparticles have been synthesized using the extract of grape stalks waste. A factorial

experimental design [3] was used to investigate the effect of four independent variables on Fe_3O_4 -NPs size: concentration of iron salts mixture, volume of grape stalks extract, time of contact between iron salts and extract and reaction time of the alkaline mixture. The synthesis experiments were conducted randomly at four different levels of independent variables coded as $-\alpha$, -1 , 0 , 1 , $+\alpha$ for high and low values, respectively with eight central points to give a total of 32 synthesis runs.

All possible combinations of these variables were tested, and a matrix was established. The low and high levels of the variables values were selected according to the results obtained in some preliminary experiments. The predicted response was NPs average diameter size that was measured by dynamic light scattering (DLS). The Fe_3O_4 -NPs synthesized at optimal conditions to get the lowest average diameter size were encapsulated in calcium alginate beads and used for arsenic removal.

Acknowledgements

This research was funded by the Spanish Ministry of Science and Innovation as part of the project CTM2015-68859-C2-1-R (MINECO-FEDER). Giusy Maria Rita Rizzo was financially supported by a fellowship from ERASMUS + Traineeship 2016-2017.

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Characterization of Agroforestry Residues: Their Potential in the Biorefinery Context

PP Env Tech #28

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Biorefinery concept is nowadays a very interesting strategy to convert biomass resources into value-added products. This approach has mainly emerged due to the price increase and less abundance of fossil resources. A number of biomass resources has been explored, including wood, grasses, corn, among others. Those substrates can be transformed into chemicals, energy, biofuel, or other marketable products [1, 2]. In this context, it is important to characterize those materials to assess their potential for energy or biochemical products production.

Thus, the aim of this work is to characterize four residues from agro-forestry industry, including pine branches (PB) and stump (PS), tomato (TW) and winery waste (WW) for analysing their potential within the biorefinery context. Young branches were sampled from four *Pine* spp and volatile fraction was analysed by SPME-GC/MS method. For *P. pinaster*, branches were extracted by supercritical CO₂ and antioxidant (DPPH) activity analysed. Stump samples were obtained from *P. pinaster* sp., washed, milled and sieved and analysed following incineration, extraction, and acid hydrolysis to determine ash, extractives, total lignin and carbohydrates. Also, elemental analysis, SPME-GC/MS, antioxidant and flavonoid content analyses were performed as well as solvolysis. WW was obtained from wine distillation and frozen until analysis. TW (*S. lycopersicum*) was purchased on a local store in a semi-rotten state, minced mechanically and frozen. Both WW and TW were characterized regarding to elemental analysis, antioxidant activity, flavonoid content, and biochemical methane potential (BMP).

Results from volatile fraction of PB indicated that the component in the highest percentage for *P. halepensis* was β -myrcene, for which antibacterial and anti-metastatic activity have already been reported [3]. Limonene appears as the main volatile for the remaining species, being a natural repellent for some insects. For volatile extracts, the yield ranged from 0.94 to 3.12 % (d.b.) and the antioxidant activity takes the IC₅₀ value of ~795 μ g/mL. Regarding PS residue, a smaller particle size (0.210 – 0.425 mm) resulted in high ash (~5 %), extractives (~11 %) and lignin content (~30 %) but in low carbohydrate content (~48 %). The elemental analysis revealed ~47% C, ~6% H, ~47% O, 0.3% N and <0.01% S; Solvolysis process of PS was effective in the production of a bio-oil. In addition, the α -pinene was the predominant volatile compound. For this residue, both high antioxidant activity (IC₅₀ = ~6 μ g/mL and IC₅₀ = ~26 μ g/mL, for aqueous and ethanol extract, respectively) and high flavonoid content (~12 % of aqueous extracts and ~4.0 % for both ethanol and acetone extracts) were observed. The BMP of WW and TW substrates was 412 and 425 L CH₄/kg SV, respectively. A low value of flavonoid content (~2 %) and antioxidant activity (IC₅₀ = ~232 μ g/mL) was obtained for WW, and benzenethanol appeared as the main volatile. Overall, the analysed residues are promising for a bio-based economy.

Acknowledgements

This work was financially supported by “Fundação para a Ciência e Tecnologia (FCT, Portugal)” through the project “MultiBiorefinery - Multi-purpose strategies for broadband Agro-forest and fisheries by-products: a step forward for a truly integrated biorefinery - POCI-01-0145-FEDER-016403”.

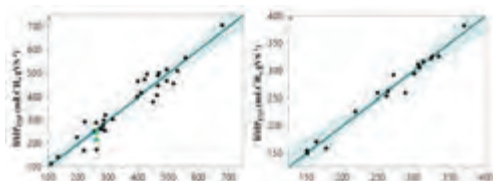
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Development of Models for Biochemical Methane Potential Prediction for Diverse Substrates

PP Env Tech #29

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Biochemical methane potential (BMP) is referred as the ultimate methane yield or the maximum methane production at infinite anaerobic digestion time [1]. This parameter allows to evaluate not only the biodegradability, but also the suitability of a substrate to produce methane. This could be particularly important to determine the optimum ratio between co-substrates if co-digestion is considered [2]. In this study, BMP was determined through experimental and theoretical methods for different substrates with interest for anaerobic digestion (AD) process. Since the experimental procedure is time-consuming, laborious and with low reproducibility, the main objective of this work is to develop predictive models able to estimate BMP based on substrates characteristics commonly indicated in the literature [3]. Thus, about 40 scientific papers were analysed, for collecting data to assess the relationship between BMP (determined experimentally) and chemical properties of substrates. From these papers, it was possible to get BMP values for about 149 different substrates, grouped into 10 categories: beverages, cereals, diet, fruit, manure, plants, sludge, vegetables, municipal wastes and others. In general, these data reveal that based on a specific category it is not possible to predict easily BMP. The parameters often determined simultaneously with BMP in the literature are: volatile solids (VS), lipids (LP), proteins (PT), carbohydrates (CRB), elemental composition (C, N, H, O), lignin (LG), hemicelluloses (HMC), celluloses (CEL), acid detergent fibres (ADF), total chemical oxygen demand (tCOD) and carbon-nitrogen ratio (C/N). As a first screening, the influence of each of these

14 parameters on the BMP value was assessed through simple linear regression analysis. All of these factors are related to the organic part of the substrates.

The results show that none of the single factors is enough to explain the observed BMP, since all coefficient of determination (R^2) are quite low (< 0.40). Therefore, multiple linear regression analysis using JMP® software was carried out involving several parameters. From the analysis of the results, some valuable models were obtained, which were cross-validated. Models based on elemental analysis are able to predict BMP for the substrates in categories like cereals, plants, manure, some fruits and vegetables. Models based on PT, LP, CRB, ADF and LG seems suitable for manures, plants, fruits and vegetables. The models developed appears to have a great potential for a BMP forecast, take into account the elemental composition of the substrate and a combination of lignocellulosic parts and other organic properties of substrates. The application of these models could save time and costs to assess BMP parameter for complex substrates.

Acknowledgements

R.C. Martins acknowledges the financial support under the contract FCT investigator 2014 Program (IF/00215/2014) with financing from the European Social Fund and the Human Potential Operational Program. Authors acknowledge the financial support under the project POCI-01-0145-FEDER-016403 - MultiBiorefinary, with financing from FEEI through COMPETE 2020 and National funds from FCT.

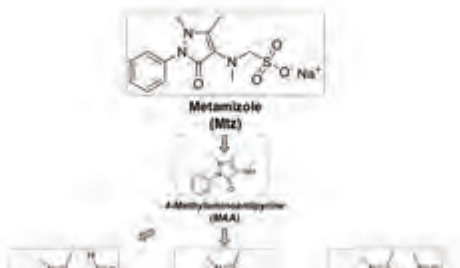
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Chlorination and Chloramination of Metamizole Metabolites

PP Env Tech #30

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Metamizole (Mtz), or dipyrone, is a painkiller, spasm reliever and fever reliever. After oral or intravenous administration, Mtz is metabolized in human body to 4-methylaminoantipyrine (MAA), that in liver is further metabolized to 4-aminoantipyrine (AA), 4-formylaminoantipyrine (FAA) and 4-acetamidoantipyrine (AAA) [1].

The presence of pharmaceuticals and metabolites in environmental water bodies is nowadays widely studied. Several studies reported the presence of these metabolites in environmental water samples, such as wastewater or water sources for drinking water production [1, 2]. Different water treatment techniques are intensively being investigated to limit contamination in the aquatic environment. However, these techniques (especially oxidative treatments) produce transformation products (TPs) that may be equally or even more harmful to aquatic organisms [3].

The aim of this work was to study the transformation of the Mtz metabolites, AA, FAA and AAA, during chlorination and also with monochloramine (NH_2Cl). Half-lives were estimating at different values of pH

(5.7, 7.0 and 8.3) and during chlorination also at different bromide concentrations ($0\text{--}200\text{ ng mL}^{-1}$). Under the evaluated conditions, reaction kinetics with chlorine were faster (half-lives below 30 s at pH 7) than those with chloramine (half-lives above 6 h at pH 7).

The determination of TPs was performed by liquid chromatography (LC) followed by high-resolution mass spectrometry (HRMS) equipped with a quadrupole-time of flight (Q-ToF) mass analyser. Thus, 6 TPs were tentatively identified, showing that, first FAA and AAA are transformed to AA, and then AA reacts further by hydroxylation and opening of the pyrazole ring.

Finally, a preliminary estimation of the toxicity of these TPs by using quantitative structure-activity relationship (QSAR) was performed, indicating that the TPs found are less (eco)toxic than the parent compounds.

Acknowledgements

This work was funded by Xunta de Galicia (EM2014-004, GRC2013-020) and FEDER/ERDF.

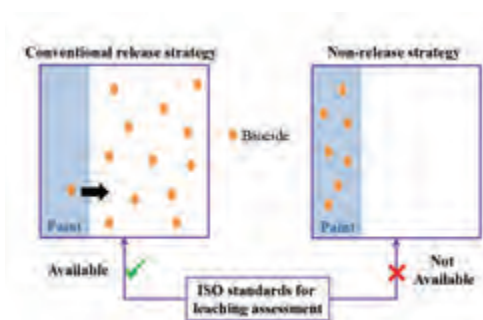
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Non-Toxic Biocidal Coatings: Validation of an Antifouling Non-Release Strategy

PP Env Tech #31

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Marine Biofouling is the unwanted accumulation of a variety of organisms on submerged surfaces, being responsible for adverse ecological and economic effects, particularly in the marine transport industry [1]. Procedures that provide the surface protection against this marine biofouling have been widely pursued. Until now, the most efficient antifouling approaches exploit coatings acting through controllable release of biocides. Nevertheless, the ecotoxicity of the applied biocides has led to harsh regulations for their use, and in the future considerably more restrained guidelines are expected (BPR, EU Regulation n°528/2012). Therefore, a rigid environmental compatibility analysis is crucial for any new developed antifouling systems. Their intrinsic characteristics should envisage a low environmental risk.

In this work, a recent developed non-releasing strategy [1], based on the chemical immobilisation of confirmed biocidal agent(s) (e.g. Ecomea) in marine coatings has been evaluated in terms of environmental compatibility. In particularly leaching experiments of the developed formulations were performed (standard ISO15181) to validate the effective biocide immobilisation in coatings matrix, and the presence and quantity of the biocide

were accurately analysed in the leaching waters (HPLC-DAD, UV-Vis). UV-Vis spectroscopy proved to be a quick qualitative detection method of Ecomea biocide, whereas for its accurate quantification, the HPLC technique is preferred. When Ecomea was incorporated through chemical immobilisation, no detectable Ecomea was found on the leaching waters, suggesting that the chemical immobilisation strategy is effective to provide non-releasing biocide coatings systems.

Furthermore, an ecotoxicity assessment of biocidal coatings following standards included in the EU hazard assessment of substances and European Eco-label was performed [2].

The overall results demonstrate the low ecotoxicity, and the non-releasing ability of the new developed biocidal coatings.

Acknowledgements

Support for this work was provided by FCT through UID/MULTI/00612/2013, PEst-OE/QUI/UI0612/2013, and PTDC/AAG-TEC/0739/2014 and by European Regional Development Fund through the COMPETE (POCI-01-0145-FEDER-016793) and RIDTI (Project 9471). The authors also acknowledge Sara Cravo and Olga Ferreira for technical support. A. E. Ferreira and E. R. Silva also acknowledge FCT for the grant PTDC/AAG-TEC/0739/2014-BI and for the postdoctoral scholarship SFRH/BPD/88135/2012, respectively.

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Biodegradation of Microplastics by Marine Fungi

PP Env Tech #32

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Plastic is one of the biggest pollutant in the oceans, where it can undergo many types of degradation, originating particles of various shapes and sizes. According to the National Oceanic and Atmospheric Administration (NOAA), plastic particles with sizes smaller than 5 mm are classified as microplastics [2-3].

Microplastics are potentially harmful as their small size renders them highly bioavailable for ingestion by a wide variety of marine organisms, leading to accumulation within their gut and possibly in physical harm. Furthermore, these particles can adsorb persistent organic pollutants and heavy metals in greater concentrations than those found in seawater. These substances, along with plastic additives, may be released in organisms, eventually leading to bioaccumulation and bioamplification of these contaminants through the food chain [2-3].

The use of microorganisms for eliminating plastic is a promising approach to mitigate the negative effects of microplastic pollution with low investment, therefore this work underlines the potential of marine fungi *Z. maritimum* and

N. Vibrissa for the biodegradation of polyethylene microplastics, thus corresponding to the need of minimize the presence of these materials in aquatic systems. The marine fungi *Z. maritimum* and *N. Vibrissa* were able to grow in a minimum nutrient supplemented growth medium in the presence of microplastics. Based on FTIR and NMR results it has been observed the use of microplastics by the fungi as substrate. A reduction in lipid and protein content, and an increase in carbohydrate concentration in fungi has been observed with the time of exposure to microplastics.

Acknowledgements

This work was supported by national funds through FCT/MEC (PIDDAC) under project IF/00407/2013/CP1162/CT0023. Thanks, are also due, for the financial support to CESAM (UID/AMB/50017), to FCT/MEC through national funds, and the cofunding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. This work was also funded by Portuguese Science Foundation (FCT) through the scholarship SFRH/BPD/122538/2016, under POCH funds, cofinanced by the European Social Fund and Portuguese National Funds from MEC.

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The Effects of Sub - Inhibitory Concentrations of Fluoroquinolone Antibiotic on Nutrient Removal in Activated Sludge Processes

PP Env Tech #33

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Biological treatment is the most common secondary treatment of wastewater and was designed to purify waters discharged by humans from specific pollutants. Engineers were focused on removal of nutrients, namely: C, N and P compounds. The most commonly used process, allowing removal of those nutrients, is Conventional Activated Sludge process (CAS). Nowadays, ones can observe a raising interest in abundance and the effect of Chemicals of Emerging Concern (CEC) on the environment. It is well known, that many chemical compounds enter Wastewater Treatment Plants (WWTPs) and cannot be effectively treated in CAS. Among those compounds are antibiotics and raw wastewater entering WWTP can contain ppb or ppm concentrations of those CEC [1, 2]. Antibiotics, working as antimicrobial compounds aiming to kill or inhibit bacterial growth, may affect bacterial communities in different ways. It is possible that constant input of antibiotics in sub – inhibitory concentrations leads to changes in the structure of bacterial community [3, 4]. Therefore, changes in communities may give an output in changes in processes carried out by different groups of bacteria. It is not known if input of antibiotics can affect CAS properties, nitrification and denitrification processes.

The main goal of presented study was to investigate the effect of environmentally – relevant concentrations of antibiotic ciprofloxacin on CAS process. Two lab – scale WWTPs working as pre – denitrification CAS systems, fed with synthetic wastewater (according to ISO 11733) were used in this experiment. While maintaining one system as an antibiotic-free control, a second one was spiked with increasing concentrations of ciprofloxacin. Constant input of raising antibiotic concentrations was aimed to induce shifts in bacterial community structure. Nutrients removal processes (nitrification and denitrification) were routinely monitored together with SVI and microscopic observations. By dissecting the CAS processes into a few easy to follow parameters, we provide novel insights into the contribution of sub-inhibitory antibiotic concentrations to the CAS process, and how these can affect the quality of WWTP effluents.

Acknowledgements

The presented work is a part of the ANSWER project receiving funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675530.

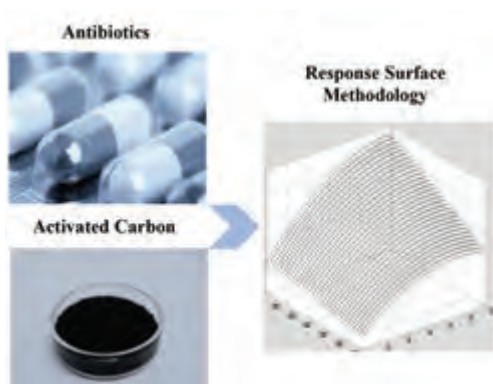
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Application of Experimental Design Methodology to Optimize Antibiotics Removal by Walnut Shell based Activated Carbon

PP Env Tech #34

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The increasing contamination of freshwater systems with thousands of anthropogenic chemical compounds has become a worldwide environmental problem. Several monitoring studies have shown that a diversity of organic pollutants can be found in surface waters, groundwater, effluents, sewage sludge, soils, marine waters and even drinking water [1, 2]. These substances comprise a wide range of industrial and household chemicals, pesticides, pharmaceuticals and personal care products (PPCPs).

Antibiotics are among the most commonly reported PPCPs currently reported to occur in the water cycle (surface water, groundwater, drinking water and wastewaters) as well as in the soil, sewage sludge and sediments [2, 3]. Antibiotics are released to water bodies both directly and indirectly through a range of diffuse and point source pathways, with treatment facilities, primarily wastewater treatment plants (WWTPs) playing a key role in the introduction of these substances into the aquatic environment [2, 3]. Though, the existing treatment technologies produce water that meets current legislation on water-quality standards, it has been demonstrated that the removal of several PPCPs, including antibiotics, is incomplete, with many of these contaminants being detected in treated effluents.

The PPCPs efficiency removal is strongly dependent on the technology implemented in the WWTPs. Advanced treatment technologies of secondary effluents are widely discussed as one

of the most promising options for the mitigation of PPCPs entering the aqueous environment via discharges from WWTPs [3].

Activated carbon (AC) is being increasingly adopted in water treatment to remove pesticides and improve taste and odour. AC has been shown to be able to remove several pharmaceuticals, including antibiotics [3]. However, the availability of adsorption data for antibiotics is still limited. There is a need to study and optimized the removal conditions for a better understanding of the removal mechanism(s) and higher AC performance.

In this study a three-level *Box–Behnken* design was employed with response surface methodology (RSM) to maximize the removal of Metronidazole (MNZ) and Sulfamethoxazole (SMX) antibiotics by a walnut shell based activated carbon. Both antibiotics are widely used in human and veterinary medicine and ineffectively removed by conventional water treatment systems. The discussion will highlight the influence of pH, temperature and antibiotic characteristics on the sorption process.

Acknowledgements

This work was financially supported by the projects: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE 2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT–Fundação para a Ciência e a Tecnologia. (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

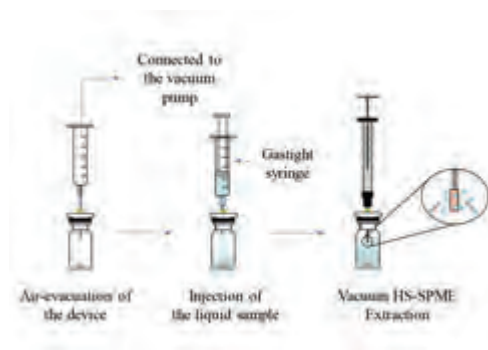
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Vacuum Headspace Solid-phase Microextraction to Monitor Phenols in Wastewaters

PP Env Tech #35

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Vacuum headspace solid-phase microextraction (Vacuum HS-SPME) is a powerful technique for enhancing the HS-SPME extraction kinetics of less volatile compounds [1]. This strategy is based on the use of reduced-pressure conditions during the HS-SPME extraction step. Vacuum HS-SPME is particularly beneficial for the extraction of semi-volatile organic compounds with low Henry's law constants, since mass transfer resistance for these analytes is concentrated in the gas-phase [2]. A group of compounds with these characteristics are phenols, including some chlorophenols, and some alkylphenols such as 3-*t*-butylphenol, 4-octylphenol, 4-cumylphenol and 4-nonylphenol. Furthermore, all these compounds are recognized as endocrine disrupting compounds, causing severe and wide-ranging diseases associated to the endocrine system [3]. Thus, the development of novel, faster and simpler technologies to monitor phenols in the environment has received increasing interest in the last years.

The main aim of this study is the development of a methodology for the monitorization of phenols with recognized endocrine disrupting activity in complex wastewaters. The methodology is based on vacuum HS-SPME coupled with gas chromatography – mass spectrometry. With this purpose, a homemade device has been developed in order to achieve reduced pressure conditions during the extraction. A comparison of the extraction efficiency using this method and HS-SPME at atmospheric pressure was performed, and using different commercial SPME fibers. After demonstrating the superior extraction performance of the vacuum method, it was applied to the analysis of water samples.

Acknowledgements

MJT-R thanks the Agencia Canaria de Investigación, Innovación y Sociedad de la Información (ACIISI), co-funded by the European Social Fund, for her FPI PhD fellowship. PR-B thanks the Spanish Ministry of Economy (MINECO) for her FPI PhD research contract associated to the Project Ref. MAT2014-57465-R. IP-F acknowledge her PhD research contract from ULL-La Caixa fellowship. VP acknowledges funding from the MINECO project ref. MAT2014-57465-R.

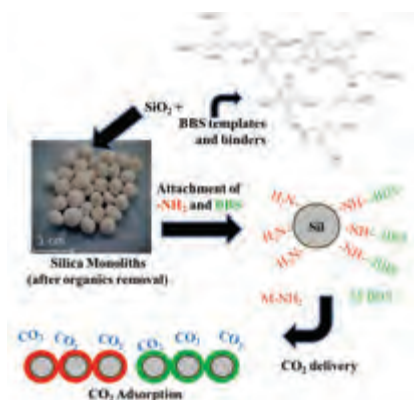
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Surface-modified Siliceous Monoliths for CO₂ Capture Produced from Low Cost and Green Bio-based Substances as Multifunctional Additive

PP Env Tech #36

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Industrialization and accelerated population growth have been creating tremendous air pollution. Carbon dioxide (CO₂) from fossil fuels combustion is a concerning waste gas, responsible of greenhouse effect: it increases atmospheric temperature contributing to more than 60% of global warming. Hence, reduction of CO₂ emissions is one of the biggest challenges for environmental safety, but in the meantime CO₂ levels need to be decreased. Several approaches should be adopted for this purpose, for instance physical absorption using solvents, membrane separation or capture by materials with adsorptive properties (*i.e.* zeolites and activated carbons). [1]

In this work, some low cost silica-based materials were prepared as CO₂ adsorbents. Silica monoliths were synthesized according to a reported procedure [2], from a concentrated dispersion of a commercial silica powder in a solution of bio-based substances (BBS) isolated from composted urban green wastes, which act as templates and binders. After the formation of a wet and workable paste, pellets were yielded in the desired shape (spheres of about 0.5 cm diameter) and calcined in order to remove all organics. The obtained siliceous monoliths were maintained as prepared (M-sil) or further modified by a covalent functionalization of the surface with (3-Aminopropyl) triethoxysilane (M-NH₂) and BBS (M-BBS), in order to improve the adsorption features thanks to the introduction of CO₂-philic

functional groups.

Moreover, a sample of SBA-BBS was produced immobilizing BBS on powdery mesoporous SBA silica to check the influence of an ordered porous structure on CO₂ capture [3].

All the samples were characterized by N₂ adsorption at 77K (for specific surface area and porosity determination) and thermogravimetric analysis (for evaluating the functionalization extent on silica surface and the thermal stability of the functionalized materials). CO₂ uptake and the related molar heats of adsorption were measured at 30°C by an adsorption microcalorimeter Tian-Calvet type equipped with a lab-made gas-volumetric apparatus.

The use of BBS as multifunctional additive was successful: on one hand, they resulted convenient and eco-friendly reaction intermediate; on the other hand they represented an active phase towards CO₂ uptake. In general, the functionalized siliceous monoliths showed good performances in CO₂ adsorption in terms of uptake and low interaction energy, suggesting an easy regeneration of the adsorbing material after a simple outgassing *in vacuo* at 30°C. Finally, the shape of the monoliths can be advantageous for a possible scale-up of the process.

Acknowledgements

This work was realized with the financial support of European Commission (Mat4TreaT project, H2020-MSCA-RISE-2014, project number 655541) and Compagnia di San Paolo and University of Torino (Microbuster project, Torino_call2014_L2_126).

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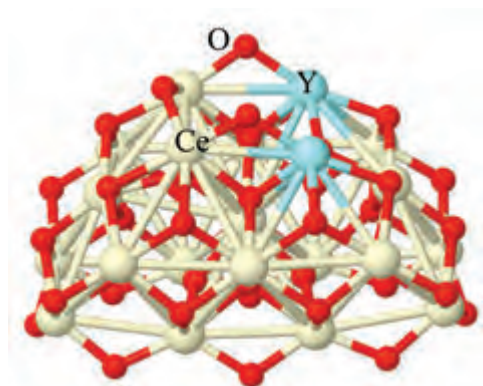
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Environmental Modelling

Modelling of Ceria Surface and Nanoparticle Models Doped by Y^{3+} Cations Relevant for Environmental Applications

PP Env Model #1

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Ceria-based systems are materials with various applications in energy technologies and environmental chemistry. They are used as catalysts for various important processes. For instance, they convert harmful automotive exhaust gases into non-toxic ones, catalyze processes of water gas shift reaction, preferential CO oxidation, reforming of alcohols, conversions in fuel cell catalysts [1,2], etc. Ceria is a reducible oxide, where O vacancies can be created at elevated temperatures. This is accompanied by reduction of two Ce^{4+} to Ce^{3+} cations per each O vacancy and the process is reversible depending on the conditions.

When CeO_2 is doped by a trivalent metal cation, such as Y^{3+} , initial structure contains O vacancies for compensation of the effective negative charge induced by the substitution of Ce^{4+} with Y^{3+} . In this way distortion is induced in the lattice of the resulting $\text{Y}_2\text{O}_3\text{-CeO}_2$ mixed oxide leading to changes in the catalytic behaviour of the obtained system.

We performed periodic density functional calculations to provide information about the distribution of Y^{3+} cations in the $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ systems and how the presence of these cations affects the reducibility of ceria. To achieve our goals we modeled various structures where Y^{3+} replace Ce^{4+} cations on/in periodic slab and nanoparticle models at several Y:Ce ratios.

We found that on pristine $\text{CeO}_2(111)$ surface creation of O vacancy is most favorable in the first subsurface layer. When two of the Ce^{4+} cations are replaced by Y^{3+} cations the most favorable is the structure with an O vacancy located again in the first subsurface layer and Y^{3+} cations are located on neighboring sites close to the vacancy.

Our calculations showed that the presence of Y^{3+} does not change the reducibility of ceria slab model for the most stable structure, where first vacancy is created in the first subsurface layer. Alternatively, in the other two cases where O vacancy is created on the surface or in the second subsurface layer, the energies for O vacancy formation slightly decreases by $\sim 0.2\text{-}0.3$ eV in the presence of Y^{3+} cations compared to the corresponding values calculated for the pristine ceria system. This result is important from a practical point of view since yttrium increases the mobility of the surface oxygen and in this way facilitates oxidation of the adsorbates with participation of those species.

Our $\text{CeO}_2(111)$ slab models containing four Y^{3+} cations in the $3' \times 6$ surface unit cell showed that in the most stable structures both Y^{3+} couples prefer to stay isolated.

Acknowledgements

The authors acknowledge financial support by the Horizon 2020 program of the European Commission (project Materials Networking - grant agreement 692146) and the Bulgarian Science Fund (project DN09/5). Authors are also grateful to Operational programme "Science and Education for Smart Growth", project BG05M2OP001-2.009-0028

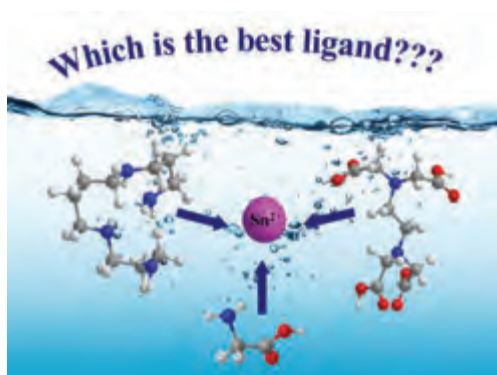
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Exploring Various Ligand Classes For The Efficient Sequestration Of Stannous Cations In The Environment

PP Env Model #2

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The metal pollution has become one of the most serious environmental problems. The presence of heavy metals is due to both natural and anthropogenic sources. Tin is not generally considered to be among the most important “pollutants”, although some compounds are of great importance from an environmental point of view. Beside the reputation of organotin (IV) compounds, inorganic tin species are important from a geochemical and hydrological perspective. In fact, tin is the 24th most abundant element in the Earth’s crust and has ten isotopes, the largest number in the periodic table. Among them, ¹²⁶Sn is a radionuclide produced by nuclear fission, and it is often present in radioactive wastes, with a half-life of 10⁵ years [1]. In this contribution, the sequestering ability of several ligands will be evaluated towards the Sn²⁺ cation in the conditions of several natural fluids, for example sea water ($I = 0.72 \text{ mol kg}^{-1}$, pH = 8.0), fresh water ($I = 0.0034 \text{ mol kg}^{-1}$, pH = 7.0), and an acidic waste water (e.g., $I = 0.05 \text{ mol kg}^{-1}$, pH = 4.0). Several organic and inorganic ligands will be explored, on the basis of the functional group(s) in the molecule (carboxylic acids, amines, amino acids, phosphonates etc...), molecular weight (low and high), number of sites available for binding (monodentate, polydentate, chelants), environmental persistence (biodegradable or not). According to this classification, some ligands such as carbonate, mellitic acid, glycine, EDTA, polyacrylates, spermine, thiomalic acid will be tested. The assessment of the sequestering ability of the ligands is done in terms of evaluation of different parameters, such as the pM (residual concentration of free metal cation), and the $pL_{0.5}$

(concentration of ligand necessary to bind the 50% of metal in solution). It is fundamental to mention the difference between pM and $pL_{0.5}$; in fact, while in the computing of pM, the contribution of all the species that may form complexes with M^{n+} is considered (e.g., OH⁻, other ligands), this is not in the evaluation of $pL_{0.5}$, which on the contrary takes into account only the contribution of the M^{n+}/L species, free from other side reactions, and from our point of view it is more objective than pM.

This research group has introduced a new empirical parameter, called $pL_{0.5}$, for the evaluation of the sequestering ability of a ligand towards a metal cation. Details about the calculation procedure and the features can be found elsewhere [2]. Briefly, a Boltzmann type equation is built calculating the molar fraction of the metal cation, present in trace concentration, complexed to the ligand vs. the ligand concentration (expressed as $-\log c_L$).

$$x = \frac{1}{1 + 10^{(pL - pL_{0.5})}}$$

The value of the pL when 0.5 molar fraction is complexed to the ligand is called $pL_{0.5}$. This simple parameter is useful for the comparison of the sequestering ability of different ligands towards the same cation and vice versa, because it takes into account all the side reactions (ligand protonation, metal cation hydrolysis, presence of a second ligand) and does not depend on the speciation scheme, but only on the experimental conditions (pH, ionic strength and temperature) in which it is determined.

Acknowledgements

We thank MIUR (Ministero dell’Istruzione, dell’Università e della Ricerca) for partial financial support (co-funded PRIN project with Prot.2015MP34H3).

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Effects of Acidification on Metal Mobility in Estuarine Sediments

PP Env Model #3

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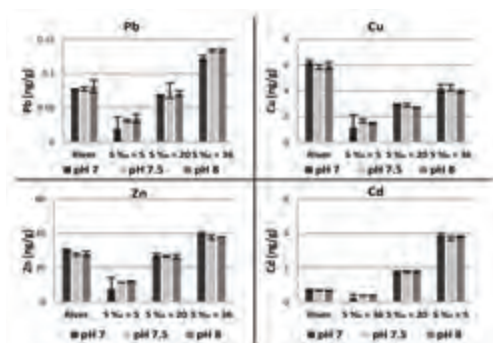


Figure 1: Concentrations of Pb, Cu, Zn and Cd mobilized from sediments to real estuarine water at different pHs and salinities

CO₂ concentration in the atmosphere has increased from its pre-industrial value of 280 ppm to an approximate value of 370 ppm nowadays mainly due to the combustion of fossil fuels, cement production, agriculture and deforestation. Atmospheric CO₂ levels may reach values up to 1000 ppm by the year 2100 [1]. One of its effects is the decrease of pH known as ocean acidification. The pH of the ocean has lowered about 0.1 in 200 years [2], which is about a 30% increase in the concentration of H⁺. The decrease of [OH⁻] and [CO₃²⁻] can affect the solubility, adsorption, toxicity, and rates of redox processes of metals in seawater [3]. Also, the speciation of metal complexes will change and their free concentration increase, which will affect greatly to the marine life. Some trace metals such as Mn, Fe, Co, Ni, Cu, and Zn are essential nutrients [4] but some heavy metals, such as Hg and Pb, are the most common metallic contaminants detected in waters and sediments.

Chemical speciation models have been used to predict changes in the distribution of organic and inorganic forms of trace metals [3], [4]. But the mobility of trace metals due to the acidification has not been investigated empirically. This work aims to study the mobility of some trace metals (Pb, Cu, Cd and Zn) from sediments to the water column

using water taken at the Nerbioi-Ibaizabal estuary (Northern Spain) (REW, Real Estuarine Water) and synthetic seawater (SSW) at different salinities in laboratory experiments.

Results using SSW showed that a bigger metal release was reached at the higher salinities (35 ‰) and at the lowest pH (pH = 7), following the expected trend, except in the case of the extraction with ultrapure water, which showed higher mobilization capacity. The tendency is not clear at mid (20 ‰) and low (5 ‰) salinities. For Zn and Cd at mid salinities the concentrations were found to be higher at the lower pH but in the lowest salinity no big differences were found between pH values. In the case of Cu and Pb the biggest metal release is found at mid pH (pH = 7,5) at 20 ‰ salinities and, again, no big differences were found at low pH.

In the case of REW (see Figure 1) higher metal mobilities were also achieved at higher salinities, except in the case of the river samples where the metal concentration is pretty high in most cases. In general, results showed the expected trend, being the higher concentrations found at the lowest pH in the case of Cu, Cd, Zn. In the case of Pb, the lowest concentrations were found at the lowest pH and no big differences were found between the other two pH values.

Acknowledgements

L. Kortazar would like to acknowledge the Basque Government for her PhD fellowship and O. Gómez is grateful to the University of The Basque Country (UPV/EHU) for her post-doctoral contract.

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The Reconstruction of Paleoclimate Conditions in Neogene Toplica Basin (Serbia)

PP Env Model #4

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The Neogene lacustrine sedimentary basins are the most widespread geological formations in Serbia, containing significant deposits of coal, oil shales, gas and other mineral resources. Therefore they are interesting from the economical and scientific aspect. One of the most difficult tasks in the geochemistry is reconstruct environmental conditions at the time of sedimentary deposition, which specifically applies to paleoclimate conditions.

In nowadays, interdisciplinary approaches i.e. integrate study of organic and inorganic geochemistry with mineralogy, stratigraphy or with the other scientific disciplines allows favourable interpretation and identify the most reliable paleoclimate parameters [1, 2].

Total of 25 samples of sedimentary rocks (Toplica basin, Serbia) from depth of 1000 m were investigated in this study. In order to obtain the concentrations of macro and micro elements, the XRF and ICP analysis of the sediment samples were done respectively. Qualitative composition of the mineral part was determined using X-ray diffractometer. Composition, quantity, type and maturation degree of the organic matter were determined by elemental analysis and Rock-Eval pyrolysis. Bitumen was extracted from sediments using the Soxhlet extraction with an azeotrope mixture of dichloromethan and methanol. Isolation of the saturated and aromatic fraction was done using column chromatography. Organic compound were analyzed by gas chromatography-mass spectrometry (GC-MS) technique in the fractions of saturated and aromatic hydrocarbons.

The most commonly used paleoclimate parameters are Rb/Sr, Sr/Cu, Mg/Ca, Fe/Mn ratios and C-value [3]. Based on values of mentioned parameters it can be assumed that during deposition climate conditions changed from semiarid to humid. Maximum for humid climate was recorded at 708 m and for semiarid climate at 712 and 979 m, and most substantial or most prominent change, from humid to semiarid, took place between 708 and 712 m. The mineral part of sediments deposited under semiarid climate is dominated by dolomite, while analcime is dominated in sediments deposited under humid conditions. Generally, obtained results indicate

that in the higher parts of investigated borehole the climate was more humid, and in the lower parts the climate was predominantly semiarid.

Paleoclimate organic geochemical proxies have been developed mainly for use in marine systems and often they are not applicable for lacustrine settings. Main reason for this is that the complexity of the physical and chemical properties of lakes disables application of some organic geochemical proxies for lacustrine sediments.

Molecular distribution of *n*-alkanes, namely *n*-alkanes chain length index such as average chain length (ACL), $C_{27}-C_{31}$ *n*-alkane ratios (e.g. C_{27}/C_{31} and C_{29}/C_{31}), *n*-alkane $C_{31}/(C_{29}+C_{31})$ ratio, $(C_{17}+C_{21})/(C_{27}+C_{31})$ ratio, P_{aq} index might serve as conventional proxies of paleoclimate and paleoenvironmental reconstruction [4]. In order to evaluate the validity of those proxies in lacustrine deposits they are correlated with applied inorganic geochemical parameters. Ratio C_{29}/C_{31} best correlates with inorganic parameters and it showed the highest sensitivity especially in periods of significantly paleoclimate changes, namely maximums for humid and semiarid climate.

Regarding everything that has been said, this integration study of parameters could provide a more apprehensive insight in paleoclimate reconstruction of lacustrine settings.

Acknowledgement

The study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 176006).

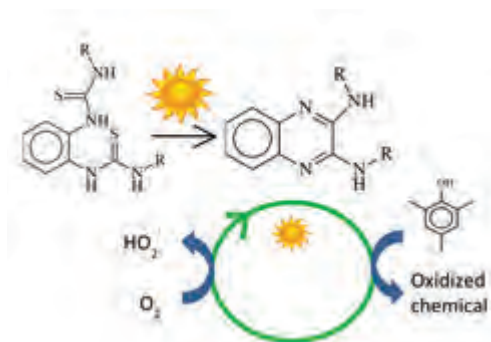
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Thiophanate Methyl: a Case Study Fungicide Capable of Degrading Other Chemicals in the Sun

PP Env Model #5

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The photochemical transformation of chemicals in the environment can result from two different types of reaction: (i) the so-called “direct photolysis” when the chemical absorbs solar light and undergoes phototransformation and (ii) the photoinduced or photosensitized degradation that are mediated by other chemicals present in the neighbourhood of the chemical of interest. A lot of natural and synthetic photoinductors or photosensitizers were described and studied in the literature. We present here an unusual case, that of a fungicide that generates a primary photoproduct showing photosensitizing properties and thus capable of promoting the phototransformation of the fungicide itself and of other chemicals.

Thiophanate-methyl is a benzimidazole fungicide used in Europe, known to undergo photolysis in water and to yield a variety of photoproducts. In this work, we revisited the reaction to understand the mechanism. The degradation profile of aqueous thiophanate-methyl in simulated solar light showed a clear autoaccelerated shape. A possible explanation is the formation of a sensitizing photoproduct able to photodegrade thiophanate-methyl. For this, the following conditions must be fulfilled: the photoproduct must be formed in the early stages of the reaction, the photoproduct must absorb above 290 nm, and it must be photostable

itself. Among the detected photoproducts structure of which was reported in the literature [2], only one was generated in the very beginning of the reaction. This compound, named **I**, that contained a quinoxaline backbone was strongly absorbant above 300 nm ($I_{\text{max}} = 340 \text{ nm}$). Unsubstituted quinoxaline being known sensitizers, **I** appeared as a possible candidate and further experiments were performed to confirm this. The laser flash photolysis ($I_{\text{exc}} = 355 \text{ nm}$) of **I** generated a transient species reminiscent to the triplet excited state of unsubstituted quinoxaline. Both triplets were quenched by the phenolic probe, 2,4,6-trimethylphenol, with $k = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. This probe also readily disappeared when it was irradiated in the presence of thiophanate-methyl and the reaction was auto-accelerated confirming the key role played by the sensitizing photoproduct. We only found that unsubstituted quinoxaline sensitized the degradation of thiophanate-methyl. All these data brought evidence that **I** was the sensitizer responsible for the auto-accelerated phototransformation of thiophanate-methyl. The formation of **I** was explained thanks to quantum calculations.

The capacity of thiophanate-methyl to generate a sensitizing photoproduct may have important consequences in real cases, i.e. on crops in situations where thiophanate methyl is applied in mixture with other pesticides and in surface waters that thiophanate methyl can reach though washing off.

Acknowledgements

S. Hamdache acknowledges the Union of municipalities of Menyeh-north Lebanon LACO, Lebanese University for the PhD grant.

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Application of Central Composite Design for Removal of Cationic and Anionic Dyes by *Thapsia Transtagana* Activated Carbon

PP Env Model #6

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This study investigates the preparation of activated carbons from *Thapsia transtagana* stems using chemical (H_3PO_4) activation and their ability for cationic and anionic dyes removal from aqueous solution. Central composite design (CCD) and response surface methodology (RSM) were used for the optimization of the process. The conditions optimized were impregnation ratio (IR), activation temperature and activation time. Five responses were targeted which are iodine number (IN), methylene blue index (MB index) and removal efficiencies for methyl violet (MV), methyl orange (MO) and indigo carmine (IC). From the experimental results, the maximum iodine number and methylene blue index obtained were 1082.22

mg/g, 397.54 mg/g respectively. The best conditions for the removal of MV were obtained by activated carbon sample activated at 400°C for 145min with an impregnation ratio of 2g/g. For MO, the best condition were activation temperature of 450°C, impregnation ratio of 1.5g/g and activation time of 155min. For IC, activation temperature of 500°C, impregnation ratio of 2g/g and activation time of 145min. Under these conditions, the maximum sorption capacities were 358.67 mg/g for methyl violet, 305.88 mg/g for methyl orange and 196.06 mg/g for indigo carmine. The best activated carbon samples were characterized by FTIR, DRX and SEM-EDX. The functional groups were also determined by Boehm titration. Langmuir isotherm model gave the best description of the adsorption process.

Acknowledgement

The authors would like to thank University Hassan I of Settat for supporting this study.

Temporal Series of Atmospheric Deposition Parameters as Air Quality Assessment Tools in Urban Areas

PP Env Model #7

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Time-series analysis is a very interesting mathematical technique that can be used in the study of temporal evolution of a magnitude when environmental data analysis is required [1]. So, from the analysis of the experimental data, it has been found that there are trend linear and temporal cycles in the value of parameters.

As application a study was made of the temporal evolution of the levels of deposition and pH from the atmosphere of Valparaíso (Chile) during 2000 to 2008.

The sampling and analytical methods are detailed in Arancibia [2].

Firstly, several analytical expressions were used for the temporal trends. So the temporal trend of the time series that best fits the behavior of these data is the linear trend. It is concluded that the deposition values increase with time at a rate of 0.0011 ± 0.0005 ($\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$)/week. The average value was 2.5 ± 1.5 (SD) $\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$. As for pH values also grew at a rate of 0.0012 week^{-1} being 6.4 ± 0.6 (SD) the average value in this period.

Secondly, a study of the time cycles of the data series has been carried out. For that, we analyze the harmonic components of the set of data. So, we obtained the corresponding periodograms based on a Fourier analysis which assumes that each data time series $z(t)$ is formed by the superposition of sinusoidal components of different frequencies. The intensity of the periodogram $I(w)$ is defined as:

$$I(w_i) = \frac{2}{N} \left[\sum_{t=1}^{t=N} z(t) \cos(2\pi w_i t) \right]^2 + \left[\sum_{t=1}^{t=N} z(t) \sin(2\pi w_i t) \right]^2$$

with $i = 1, 2, 3, \dots, q$ where $q = (N-1)/2$ for odd N and $q = N/2$ for even N . The periodogram is then the plot of $I(w_i)$ against w_i where $w_i = i/N$ is the i th harmonic

of the fundamental frequency $1/N$, up to the Nyquist frequency of 0.5 cycles per sampling interval (which corresponds to the smallest identifiable wavelength of two samples). Since $I(w_i)$ is obtained by multiplying $z(t)$ by sine and cosine functions of the harmonic frequency, it will take on relatively large values when this frequency coincides with a periodicity of this frequency occurring in $z(t)$. As a result, the periodogram maps out the spectral content of the series, indicating how its relative power varies over the range of frequencies up to $w_i = 0.5$ [3]. Because the periodograms showed excessive “noise” as a consequence of the abrupt fluctuations of the data, exponential smoothing has become used (see for example, [1]).

From these analyzes it is possible to conclude that all series of data had a cyclic behavior with an annual oscillation period.

Acknowledgements

We acknowledge Junta de Extremadura (PRI IB16114 and GR15087), both partially financed by EU (FEDER).

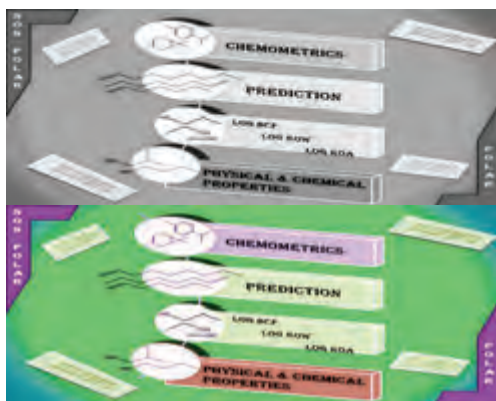
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Computational & Cheminformatics Approach to Characterization of Green Solvents

PP Env Model #8

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The goal of the present communication is to combine chemometric tools with *ab initio* study of 43 nonpolar solvents and 69 polar commonly considered as “green” to estimate the log K_{ow} and log K_{OA}. Each solvent was characterised by 10 parameters, namely melting point, boiling point, density, surface tension, water solubility, vapour pressure and Henry’s law constant and the logarithm of bioconcentration factor (log BCF). This hybrid

approach may serve as a tool for exploring the greenest of the solvents.

As a result, it is expected new specific indicator for the type of polarity in greenest expertise.

The calculations reported in this communications are based on electronic structure calculations performed with the Gaussian 09 software package. The B3LYP functional was applied with the 6-31++G(d,p) basis set. Solvent effects were accounted for by means of SMD method. Calculations were also performed using the M06-2X functional. To ascertain the relationship among the quantum calculations with experimentally available data, the correlation analysis, principal component analysis (PCA), and cluster analysis (CA) were used as classification techniques.

Acknowledgements

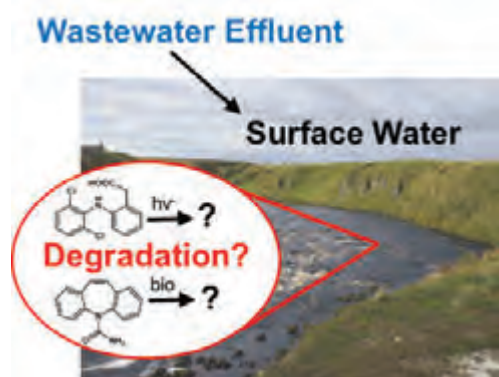
M. Nedyalkova and V. Simeonov are grateful to National Science Fund (NSF), project DCOST 01/6 - 2017.

The support of H2020-TWINN-2015–project „Materials Networking”, Project ID: 692146 is gratefully acknowledged by M. Nedyalkova, V. Simeonov and S. Madurga.

Assessment of the Degradation Behaviour of Diclofenac, Trimethoprim and Carbamazepine Under Controlled Environmental Conditions

PP Env Model #9

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Pharmaceuticals (pharma) are extensively used in contemporary society, and once administered can be introduced into wastewater systems as either the parent drugs or in metabolised form. Inadequate wastewater treatment results in discharge of these biologically active compounds into the aquatic environment via effluent [1, 2]. The effects of wastewater treatment on pharma removal and degradation are not fully understood, and little work has been undertaken to characterise the formation and fate of degradation products in receiving waters [2]. Further research is needed to assess the transformation, persistence and distribution of prioritised pharmaceuticals in order to protect water quality and avoid eco-toxicological impacts in aquatic ecosystems.

The current work identified the degradation behaviour of select pharma in different water matrices under controlled environmental conditions (light exposure, temperature, humidity, oxygenation), with initial transformation product characterisation. Diclofenac (nonsteroidal anti-inflammatory drug), trimethoprim (antibiotic) and carbamazepine (anti-epileptic) were chosen as they are prioritised pharma frequently detected in high concentrations (low to mid microgram per litre range) in final effluent and surface water [1, 2]. Spiked tap water and river water samples were exposed to artificial sunlight and aerobic bacteria in single and mixed process conditions over 10 days. This enabled investigation of photolytic and microbial degradation representative of natural processes in effluent-receiving surface water.

Quantitative analysis was carried out with liquid chromatography tandem mass spectrometry (LC-MS/MS) to determine degradation kinetics, and liquid chromatography time-of-flight mass spectrometry (LC-microTOF) was used for initial product characterisation. All samples were analysed with reference standards and external standard calibration to ensure quality of data. Initial work confirmed the robustness and reliability of the LC-MS/MS technique, with recoveries of $115 \pm 7\%$ and LOQs ranging $0.18 - 0.90 \mu\text{g/L}$ for target compounds. Quantitative results indicated that photolysis was the dominant degradation process for diclofenac in single process samples ($t_{1/2} = 4.7$ h and 91.6 h, photolysis and biodegradation, respectively), and effective diclofenac degradation can be expected under real-water conditions with both light and bacteria exposure ($t_{1/2} = 3.7$ h). Hydroxylated diclofenac was identified as a major diclofenac transformation product, and was observed in select samples after 6 h with varying persistence. Trimethoprim and carbamazepine were recalcitrant to photolytic and biological degradation, with limited removal observed over the 10-day study.

These results suggested that the degradation behaviour varied depending on the process, environmental conditions and pharma. Future work includes investigation of mixed pharma degradation behaviour and confirmation of degradation products with high-resolution mass spectrometry. The outcomes of this research will offer new insight into pharma fate after wastewater treatment and the subsequent effects in receiving waters, with the aim of improving water quality and lessening the environmental risk of these compounds.

Acknowledgements

This research is funded by the Scottish Government Hydro Nation Scholars Programme, with the Centre of Expertise for Waters (CREW).

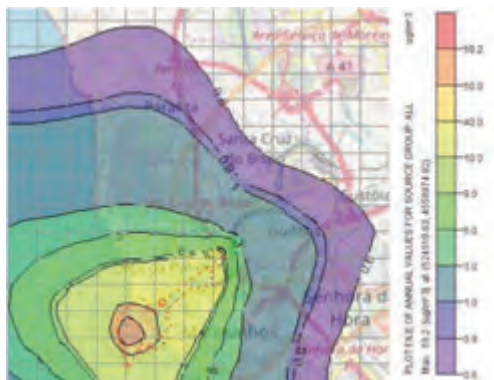
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Dispersion Modelling of NO_x Emissions from Ships Calling Leixões Port

PP Env Model #10

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Introduction

In the last few years concerns regarding the air quality in port cities have attracted growing attention in the scientific community [1]. The main reason is the constant increase of marine emissions over the last twenty years due to the intensification of port traffic (actually maritime transportation is responsible for around 80% of global trade) [2]. Moreover, Nunes et al. (2017), which calculated in-port emissions in four ports of Portugal concluded that if the in-port emissions estimated in these study would have been taken into account to the total national emissions reported by the Portuguese Environment Agency, emissions of NO_x would increase 15% in 2013 [3]. Thus, this study aimed to investigate how the air quality, in terms of NO_x, in the city of Matosinhos is affected by shipping activities at the port of Leixões.

Methods

During 2013, a total of 2564 ships visited the port of Leixões. To determine NO_x concentrations due to shipping activities, in-port emissions (during manoeuvring and hotelling) were obtained from Nunes et al. (2017). For this study AERMOD, an open source Gaussian plume model developed by USEPA, was used to evaluate the dispersion of NO_x emissions. To determine all the necessary input data two stand-alone pre-processor programs, namely AERMET and AERMAP were used. AERMET processes/organizes meteorological data and estimates the necessary boundary layer parameters for dispersion calculations. AERMAP was used to characterize terrain and to generate receptor

grids. Ships activities inside the port (manoeuvring and hotelling) were simulated as an area source and other NO_x emission sources and background pollution were not considered. Using the model, concentrations were calculated at 441 receptors placed in a uniform Cartesian grid.

Results

In general NO_x mean concentrations were low compared to the limit of 40 µg m⁻³ set by the European Union for ambient air pollution. However, for a radius of impact of around 1 km from the point where the maximum concentration was calculated (annual concentration of 59.2 µg m⁻³), concentrations were above of the limit. In this part of the port (southwest) are installed the cruise and oil terminals. It is important to highlight that concentrations are expected to be even higher if other NO_x emission sources and background pollution are considered. Since the highest concentrations of NO_x were estimated near the port, the health of port workers and people living near the port facilities might be at risk.

Acknowledgements

Authors are grateful to APDL for providing data for emissions estimation. Authors are also grateful to Project UID/EQU/00511/2013-LEPABE, funded by FCT/MEC with national funds and when applicable co-funded by FEDER under P2020 Partnership Agreement; Project NORTE-07-0124-FEDER-000025 - RL2_Environment&Health, by FEDER funds through COMPETE, by Programa Operacional do Norte (ON2) and by national funds through Fundação para a Ciência e a Tecnologia (FCT); SIV Sousa is also grateful for grant SFRD/BPD/91918/2012 funded by FCT, POPH/QREN and European Social Fund (ESF).

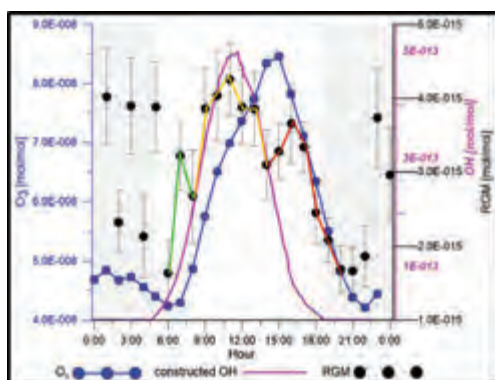
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Measurement-based Modeling of Atmospheric Mercury at a Semiarid Suburban Site

PP Env Model #11

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Over 90% of atmospheric mercury is in the form of gaseous elemental mercury (GEM), with a lifetime of 6 to 24 months. GEM oxidation to Hg^{2+} is associated with the formation of more reactive and soluble species, either in the gaseous phase (reactive gaseous mercury, or RGM) or as particulate matter (fine particulate-bound mercury, or FPM). RGM and FPM are deposited from the atmosphere much more rapidly than GEM, by both dry and wet deposition. Oxidation of GEM is therefore a critical stage in the process of transferring atmospheric mercury to aquatic systems, where it can be further converted into the highly toxic bioaccumulative methyl mercury. Even though many computer-modelling studies in recent years have focused on investigating the oxidation and deposition of GEM, our understanding of the related mechanisms is still far from complete [1]. We used the CAABA/MECCA chemical box model [2] as well as additional kinetics calculations to analyze results from comprehensive field measurements [3] that were recently performed in a semiarid suburban site to investigate night-time and daytime GEM oxidation efficiencies. CAABA/MECCA uses explicit chemical mechanisms of gas- and aqueous-phase reactions, as well as photochemical reactions and heterogeneous reactions for aerosols and clouds. We used O_3 , OH, NO_3 , and H_2O_2 as the only GEM oxidants in the model, and tested the potential contribution of Br to GEM oxidation at the site.

Special attention was given to ensure realistic representation of photochemistry in the model based on in-situ measurements of nitrate radical (NO_3), nitrogen oxides ($\text{NO}_x = [\text{NO}] + [\text{NO}_2]$) and ozone (O_3). Recent studies indicate that in most cases atmospheric oxidation of GEM is multistep, but the chemical mechanisms and associated kinetics is currently not fully resolved. Accordingly, we included three oxidation processes of GEM with O_3 , NO_3 and OH in the model as second-order reactions between GEM and the oxidants. This enabled us to estimate the contribution of each process to observations, by comparing the simulations results with the observations. Our analysis demonstrated efficient night-time and OH-induced GEM oxidation, associated with GEM lifetime of ~15–22 days and ~12–104 days, respectively, depending on the computational method and applied conditions. These findings indicate that under the studied conditions, oxidation involving OH may have a much more important role in GEM oxidation than commonly thought, and that night-time GEM oxidation should be considered in future GEM oxidation studies. This study suggests that GEM oxidation efficiency in the continental boundary layer can be highly sensitive to environmental conditions, calling for improvement in our understanding of the chemical mechanisms of GEM oxidation pathways.

Acknowledgements

E.T. holds the Joseph H. and Belle R. Braun Senior Lectureship in Agriculture.

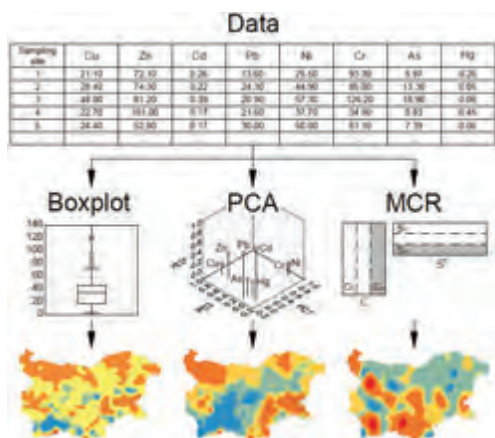
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Geochemical Baseline Determination and Pollution Assessment of Critical Heavy Metals in Bulgarian Monitoring Soil Quality Network

PP Env Model #12

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Defining baseline values of heavy metals in soil is necessary before a soil can be declared to be contaminated. This is of great importance for environmental management and decision makers. The determination of natural background concentration, which is the normal abundance of an element in barren earth material without human influence [1], is almost impossible task because of the long distance transport of pollutants and human activities. Actually baseline values show the expected concentrations for heavy metals specific to one area and time, not influenced by point input due to local human activities but include diffuse or non-point input [2].

The determination of baseline values in networks without geochemical information concerning major element content in soil minerals are often based on statistical approaches. The applied statistical methods can be divided into univariate and multivariate. The univariate methods define baseline values of heavy metals using descriptive statistics, whereas multivariate approaches are geared towards revealing of natural and anthropogenic sources that contribute to heavy metal concentrations in soils. The most used methods from these groups are

boxplot [3,4] and principal component analysis (PCA) [4,5]. Another multivariate approach that can be applied for identifying the contaminated sites is multivariate curve resolution (MCR). In this method, unlike the PCA, the extracted factors are non-orthogonal and non-negativity constraint could be implemented during analysis.

The aim of the study is to use multivariate curve resolution (MCR) for determination of contaminated areas in Bulgarian Monitoring Soil Quality Network and to compare the results with boxplot method and PCA findings. Moreover, the soil clay is included in analysis, as geogenic characteristic for more reliable assessment of "natural" heavy metal content in soils. The spatial distribution of heavy metals or contribution sources is presented by GIS based maps that are a valuable tool for identification and visualization of contaminated regions [5-7].

Acknowledgements

Support from the project No. DFNI E 02/7 12/12/2014 of the National Science Fund of Bulgaria is acknowledged. GY is grateful to Operational programme "Science and Education for Smart Growth", project BG05M2OP001-2.009-0028.

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Sustainable Development

Water-Soluble Organic Matter Present in Inhalable Particles from an Urban Atmosphere Induce a Pro-Inflammatory Profile in Macrophages

PP Sust Devel #1

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Inhalable atmospheric particles (aerodynamic diameter < 2.5 µm) are one of the most serious air pollutants in terms of public health, and most of their effects result from the oxidative stress and inflammatory responses caused by the interaction between the inhalable particles and the epithelial cells and alveolar macrophages. The pro-inflammatory potential of inhaled air particles is generally associated with their chemical constituents (organic and inorganic), particularly the oxidative potential of the water-soluble transition metals present in air particles [1,2]. On the other hand, the pro-inflammatory potential of the water-soluble organic fraction of inhalable particles is still unknown, being therefore a demanding issue to be explored. Within this context, this work aims to characterize the water-soluble organic matter (WSOM) of air particles collected at an urban location, during day- and night-time periods, in autumn and spring seasons, and to evaluate their oxidative and pro-inflammatory potential.

The compositional features of the aerosol WSOM were exploited by 2D nuclear magnetic resonance (NMR), and excitation-emission matrix (EEM) fluorescence spectroscopies. Then, effects of WSOM on nitric oxide production, ROS cellular levels, transcription of the inflammatory genes *IL1B*, *NOS2* and *IL6* as well as activation of associated signalling pathway NF-κB were analysed in Raw264.7 macrophages. Additionally, effects on the transcription levels of genes responding to electrophilic stress (*HMOX*, *NQO1*) were also analysed. It was intended to establish a relationship between the pro-inflammatory

potential of the WSOM from urban air particles and their atmospheric concentrations and structural characteristics.

The results indicate different atmospheric composition and concentration of the aerosol WSOM collected during day- and night-time periods. Our data also indicates that WSOM have dual effects over macrophages depending on the concentration and exposure period. In a model of acute exposure, high concentrations of WSOM induce a moderate pro-inflammatory profile in an oxidative-stress independent manner. Paradoxically, in the same model LPS-induced NO production is significantly impaired by WSOM in a concentration dependent way, indicating the presence of compounds that limit macrophage activation. Finally, in the chronic exposure model, cells treated with physiological concentrations during 21 days also shown a pro-inflammatory status. However, in these cells, LPS exposure results in a synergistic effect, with enhancement of all pro-inflammatory markers tested.

These preliminary data are of utmost importance to advance the current understanding of sources and chemical constituents contributing to aerosol oxidative potential in urban areas.

Acknowledgements

Centre for Environmental and Marine Studies (CESAM, UID/AMB/50017/2013); Organic Chemistry Research Unit (QOPNA, UID/QUI/00062/2013); FEDER under the PT2020 Partnership Agreement; and, Portuguese Science and Technology Foundation (FCT), through the European Social Fund (ESF), Portuguese NMR network, and “Programa Operacional Potencial Humano – POPH”. FCT is also acknowledged for an Investigator FCT Contract (IF/00798/2015).

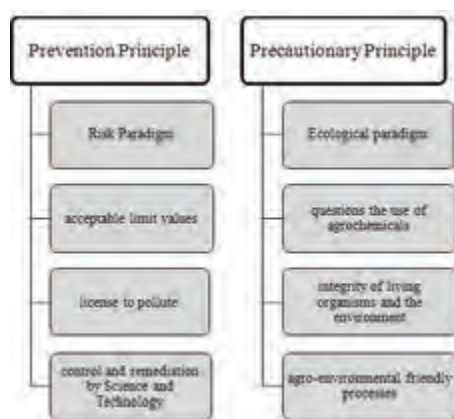
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The High Use of Agrochemicals in Brazilian Agriculture: Analysis by Prevention Principle and Precautionary Principle

PP Sust Devel 82

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The use of agrochemicals in Agriculture

Brazil has a large territorial area used for the production of grains concentrated in plantations and agroindustries, increasing the consumption of agrochemical from 313 thousand tons in 2000 to 823 thousand tons in 2012 [1]. This growth is linked to principles of Risk Management, such as the Prevention Principle and the Precautionary Principle, which may be analyzed underlying Chemistry practices.

The Prevention Principle endorses an action based on the certainty of its known effects. The Risk Paradigm in Chemistry claims for this principle to vouch for the permission of an amount of pollution based on the belief on its ability to account the impacts of and action and to propose technologies to control and remedy them [2,3] – as observed in the No Observed Adverse Effect Level (NOAEL) parameter, for example.

The Precautionary Principle states the need to take precautionary measure when an activity raises threats of harm to human health or the environment, even if some cause and effect relationships are not fully established scientifically [4]. Opposite to the Risk Paradigm, the Ecological Paradigm bases itself on the Precautionary Principle establishing four axes of action. 1) Zero discharge, denying the pollution permission and the exposure limit. 2) Clean production, designing products and processes to abstain the creation of toxic and residual chemicals. 3) Reverse onus, basing the control of substances

on the evidences of safety in its production and use, instead of grounding the decision solely on indications of harmful effects to the environment wrongly assuming the lack of proofs on the noxious impacts as an evidence of security. 4) Chemical classes control, managing entire classes of chemicals, in place of micromanaging individual products [2]. Currently, the Prevention Principle is widely used in regulations on the agrochemicals in Brazil, controlling the exposition of subjects to a maximum amount of permitted pollutants. However, we can achieve the Ecological Paradigm when using the Precautionary Principle to make the following critics during chemists education: inquiring the actual need for such a high use of noxious chemicals; taking into account the integrity of the environment and of its living organisms; searching for less toxic, environmentally friendly processes and products [1]. Green Chemistry and Environmental Chemistry may aid to accomplish these goals, developing biopesticides [5], for example. However, it is necessary to improve the Chemistry education both in chemists training as in compulsory education, embedding them in a culture of environmental sustainability.

Acknowledgements

To the financial support by CAPES to the: a) Research Project “Chemistry Education for Sustainability: relations between classical and emerging postulates of Chemistry”; b) Senior post doctorate of Carlos A. Marques 2017/18 – Portugal.

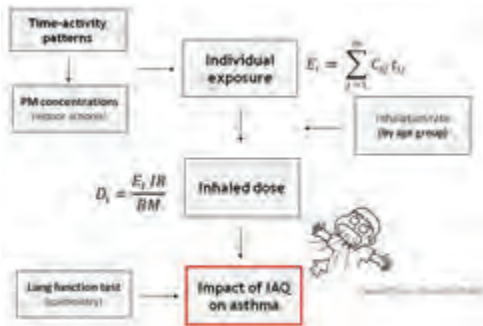
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Children's Inhaled Dose of Indoor PM in Preschools and Primary Schools in Portugal is Associated with Childhood Asthma

PP Sust Devel #3

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Children are more vulnerable to air pollution than adults, being considered a risk group. They spent more than 90% of their time indoors, and 25% of a weekday inside a preschool or a primary school – the first social environments in life – making them relevant on the impact assessment of air pollution on respiratory health. Following INAIRCHILD project [1], this study aimed to assess the association between exposure and inhaled dose to particulate matter (PM) on nursery and primary schools and the development of childhood asthma.

PM_{2.5} and PM₁₀ concentrations were measured in 47 classrooms of 15 nursery and primary school buildings, in rural and urban areas, by using an automatic continuous sampler (TSI DustTrak DRX 8534) for at least 24h. Time-activity-location patterns were also obtained. Lung function indexes (FEV₁, FVC and FEF_{25%-75%}) were obtained by spirometry pre and post bronchodilator administration (200 µg of salbutamol), using Vitalograph ALPHA Track and according to the American Thoracic Society and European Respiratory Society statement [2]. Both preschoolers (130) and primary school children (250) completed spirometry. Children were considered asthmatic when: i) the change in FEV₁ pre and post bronchodilator was equal or higher than 12%; or ii) the change in FEF_{25%-75%} pre and post bronchodilator was equal or higher than 35%. A univariate logistic regression analysis was used to assess the impact of both exposure

and inhaled dose of PM on asthma development, exposure-response and dose-response respectively. PM concentrations were high especially during occupation periods (during exposure), exceeding WHO guideline (84% of times for PM_{2.5}) and Portuguese legislation (54%). Asthma prevalence was 7.5%, higher in primary school children (8.4%) than in pre-schoolers (6.5%). Statistically significant differences were found between asthma prevalence in rural and non-rural children. There were not found statistically significant associations between exposure to indoor PM_{2.5} and PM₁₀ in preschools or primary schools and asthma prevalence (OR~1); however, the association was statistically significant when considering PM_{2.5} (OR = 1.68) and PM₁₀ (OR = 1.49) inhaled doses instead of exposures.

Thus, it is not only the exposure *per se*, but the inhaled dose that may contribute for asthma development on childhood; dose depends not only on concentrations and time of exposure, but also on the type and duration of the activities.

Acknowledgements

The authors are grateful to: i) the children and their parents; ii) the nursery and primary schools' staff involved; iii) the financial support by Project POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia; project PTDC/SAU-SAP/121827/2010 funded by FCT, COMPETE, QREN and EU; grants SFRH/BD/97104/2013 and SFRD/BPD/91918/2012, for PTBS Branco and SIV Sousa, respectively, funded by FCT, POPH/QREN and European Social Fund (ESF).

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Recovery of Rare Earth Elements from Mining, Industrial and Urban Wastes: Economic and Environmental Relevance

PP Sust Devel #4

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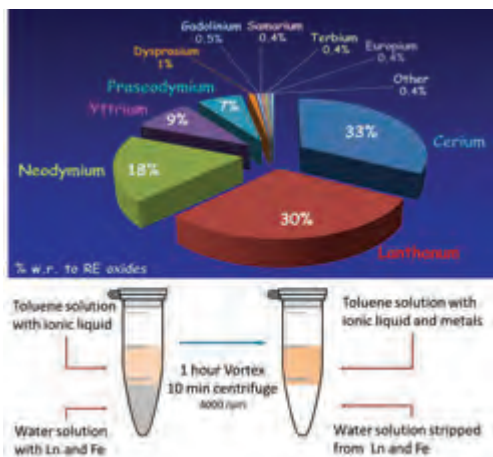


Figure 1 – Top, worldwide end use by element; Bottom, scheme of the extraction process studied.

Rare Earth Elements (REEs; lanthanides, scandium and yttrium) have become a relevant raw material in the industry, playing an essential role in modern electronic technologies, industrial and medical products and innovative environmental technologies (Figure 1, top). REEs are considered as being highly important for societal needs. However, there exists a significant risk of supply for actual demand, namely due to their geographical concentrated sources in only some countries. Therefore, the development of selective, efficient, economical and environmentally friendly separation processes of REEs from different materials is a relevant subject. In this work, ionic liquids (ILs) with only CHON elements in their composition (in order to keep all the process as environmentally appropriate) were used for separation of REEs from other metals, as an alternative to more traditional methods. It is also stressed that advanced mass spectrometry techniques play an important role in this type of studies, as they can provide precise and sensitive elemental analysis via ICP-MS as well as relevant molecular analysis for mechanism elucidation via ESI-MS.

Tetraoctylammonium oleate (IL1) and 1-butyl-3-methylimidazolium - di(2-ethylhexyl) - oxamate (IL2) were the two ILs under investigation. The experiments involved the combination of aqueous solutions of several lanthanides (Ln) and Fe (considered as an archetypal metal to be separated from Ln) in both sulfuric and nitric media, at different pHs, with toluene solutions of IL1 and IL2, in a molar ratio IL:metal 4:1 (Figure 1, down). Metal concentrations in the aqueous phases, before and after extraction, were assessed by ICP-MS in a quadrupole system equipped with a collision/reaction cell. A semi-quantitative analysis of the metals was also performed by ESI-MS in a quadrupole ion trap (QIT), using a method developed by the team. IL2 showed to be a very efficient extractant at moderately acidic pH but not selective for Ln, as Fe was equally extracted; however, at highly acidic pH, Fe was partially extracted while Ln were not. IL1 was clearly less efficient than IL2 but displayed a significant differentiation between Ln. Analyses of the non-aqueous phases were also done by ESI-QIT-MS and indicated that the metal ions were extracted into the organic phase complexed by the IL2 anions, as the detected species corresponded to $M(IL2-anion)_4^-$. Work is in progress with these two ILs and with new ones searching for a selective extraction of REEs in the presence of other metals and an effective separation along the Ln series.

Acknowledgements

We thank the Fundação para a Ciência e a Tecnologia for financial support: projects ENVIREE (ERA-MIN/0002/2014), REEuse (PTDC/QUE-EPR/1249/2014) and UID/Multi/04349/2013, and RNEM – Portuguese Mass Spectrometry Network.

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Biosorption of Pb(II) by *Fucus spiralis* Waste Obtained Through Biorefinery Processing

PP Sust Devel #5

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In the context of developing the circular economy that enables a sustainable use of the available resources and minimum waste generation, marine macroalgae have attracted the attention of researchers and industry due to its many advantages as a renewable bioresource. The current work aims to determine the potential of a macroalgae-derived waste as biosorbent in order to design a complete biorefinery processing of the macroalgae biomass. The macroalgae waste used as biosorbent was obtained after the sequential separation of polyphenols, fucoidan and alginate extracts from *Fucus spiralis* (brown division). In the studies that have been carried out so far, marine macroalgae have demonstrated to be very effective as biosorbents for heavy metals [1], but few endeavours have tested macroalgal waste as biosorbent, and to our knowledge, none have yet analysed the potential of *F. spiralis* waste as biosorbent for Pb(II).

Biosorbent preparation consisted in performing several washings first with HCl 1 mol dm⁻³ and afterwards with distilled water [2], in order to avoid contamination (organic matter leaching) in further biosorption tests. The dried macroalgal residue was then used to evaluate its potential as biosorbent for Pb(II) in aqueous solution. Tests performed with an initial metal concentration of 20 mg dm⁻³ established the best adsorption dosage (0.5 g dm⁻³) and an optimum pH of 4.5. In these conditions, lead was almost completely removed from the aqueous solution.

Adsorption kinetics was studied for initial metal concentrations ranging from 10 to 100 mg dm⁻³.

Kinetic constants, calculated by pseudo-first order fitting, slightly decreased with the initial lead concentration and were in the range 0.02-0.05 min⁻¹. An equilibrium isotherm was also performed with results reasonably described by Langmuir and Freundlich models. Maximum adsorption capacity predicted by Langmuir model was 132±35 mg g⁻¹ (20 °C, pH 4.5).

Desorption studies in batch mode were carried out to identify a suitable reactive for metal recovery. Screening tests were performed with HNO₃ 0.1 mol dm⁻³, NaCl 0.1 mol dm⁻³ and EDTA 0.1 mol dm⁻³ and using a solid:liquid ratio of 2.0 g dm⁻³. The best results were obtained with EDTA 0.1 mol dm⁻³, generating a 95±4% desorption.

The studied macroalgae biomass can therefore be submitted to a complete biorefinery processing and design in the attempt to fulfil the “zero-waste” concept. Further studies should be performed to establish the feasibility and the sustainability of the involved processes.

Acknowledgements

This work is a result of project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C. Filote acknowledges her Erasmus+ scholarship for a traineeship at FEUP (Portugal).

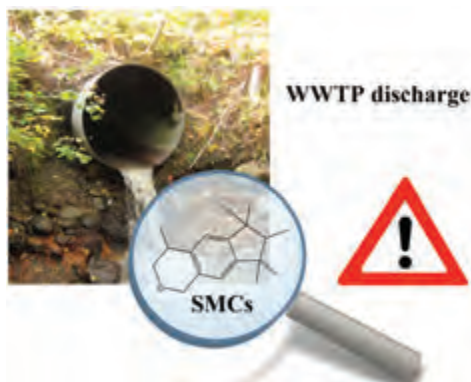
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Back to Nature – A Risk Assessment Case Study of Synthetic Musks in Wastewaters

PP Sust Devel #6

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Synthetic musk compounds (SMCs) are considered fragrance and fixative additives that have been used in several personal care and household products. They are usually classified in four main groups, according to their chemical structure: nitromusks (NMs), polycyclic (PMCs), macrocyclic (MMCs) and alicyclic (AMCs) musks [1].

Being incorporated into products with extremely high frequency of use, SMCs have been widespread and continuously introduced into the environment, mainly through wastewater treatment plants (WWTPs). Due to their (bio)accumulation potential and being only partially biodegradable, SMCs are not completely removed by conventional WWTPs. In fact, SMCs have already been detected in several environmental samples, including river water, seawater, sediments, biota and air [2]. These features make them interesting compounds for further research, especially in the scope of environmental risk assessment.

Therefore, the aim of this study was to evaluate the SMCs concentration profiles at three key points of an urban WWTP, contaminants removal efficiencies from the liquid phase and seasonal variations (Summer/Winter). From the twelve SMCs studied, galaxolide (HHCB), tonalide (AHTN) and

exaltolide (EXA) were the most frequently detected and in higher amounts. Between the raw sewage and final effluent, a decreasing concentration gradient was observed.

Then, based on the WWTP operational parameters and appropriate river conditions, concentrations in the receiving medium were predicted (PEC), following the methodology described in EU Technical Guidance Document [3]. Those values were compared to no-effect concentrations (PNECs determined using previously published toxicological data) and hazard quotients (HQ) were estimated.

Acknowledgements

This work was financially supported by the projects: (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE 2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT–Fundação para a Ciência e a Tecnologia. (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and (iii) Post-doctoral Grant SFRH/BPD/76974/2011-Vera Homem..

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Occurrence of Chemical Contaminants in Peri-urban Agriculture and Assessment of Their Impact on Crops and Human Health.

PP Sust Devel #7

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Peri-urban agriculture performs environmental, social and economic functions and services to the nearby urban areas[1]. Nevertheless, industrialization and water scarcity have led to an increase of the peri-urban agricultural exposure to chemicals. For instance, heavy metal accumulation in soil caused by industrialization, air pollution or the use of reclaimed water with a high content of the so called contaminants of emerging concern (CECs) [2].

Concerns regarding human exposure to CECs and trace elements (TE) have arisen as they have been detected in the edible parts of plants [3], but the risk that accumulated residues may pose to humans via crop consumption is still not well documented. Currently, there are only few field studies done at real scale, none of them in Spain, which demonstrate the uptake of micropollutants in vegetables irrigated with reclaimed water [4].

The aim of this study is to assess the occurrence of chemical pollutants (14 TEs, 34 CECs) in irrigation waters as well as in lettuce crops, their effect in crop composition (i.e., chlorophyll content, nitrates, lipids and carbohydrates) as well as the potential human health risk associated with the consumption of these food crops. This study is carried out in 4 farm plots located in the peri-urban area of Barcelona (NE Spain) and a pristine farm plot far away from the peri-urban area for comparison.

The average concentration levels of TEs and CECs in the irrigation waters impacted by treated

wastewater (TWW) were from 3 ($35 \pm 75 \mu\text{g} \cdot \text{L}^{-1}$) to 13 ($553 \pm 1050 \text{ ng} \cdot \text{L}^{-1}$) times higher than at the pristine site respectively. The most abundant compounds were: B ($>100 \mu\text{g} \cdot \text{L}^{-1}$), 5-methyl-2H-benzotriazole, surfynol 104 and carbamazepine-10,11-epoxide ($>1000 \text{ ng} \cdot \text{L}^{-1}$)[5].

The most abundant pollutants found in lettuce crops were methylparaben, bisphenol F, dimethomorph, Sr, Zn, Mn and B. The results obtained highlight that the occurrence of fungicides by direct application in lettuce crops was higher than the uptake of others CECs ($<10 \text{ ng} \cdot \text{g}^{-1}$) from the irrigation waters (concentration ranged from 0.5 to $22.5 \text{ ng} \cdot \text{g}^{-1}$ for dimethomorph). However, concentrations of pesticides and TEs complied with both Regulation (EC) No 396/2005 and regulation (EC) No 629/2008, for maximum residue levels (MRLs) in foodstuffs.

Furthermore, no significant differences were found in seed phytotoxicity, crop productivity and crop composition.

Human health risk assessment was estimated with the threshold of toxicological concern (TTC) approach using the Toxtree software (Toxtree V2.6.13). Data reveal that the daily consumption of this food crops does not pose a risk.

Acknowledgements

The authors gratefully acknowledge the financial support of the Spanish Ministry of Economy, Industry, and Competitiveness (MEIC) through Project AGL2014-59353-R.

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Influence of Extraction Process on the Luminescent Properties of Carbon Nanomaterials Derived from Olive Mill Wastewaters

PP Sust Devel #8

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In an accompanying communication [1], we have revealed that nanosized carbon materials could be easily obtained from olive mill wastewater (OMWW) using green, sustainable and simple technological processes.

In this contribution we will essentially focus on the study of the impact of the effluent nature on the structural, morphological and luminescent characteristics of synthesized carbon nanodots (CNDs).

CNDs are spherical-shaped nanosized carbogenic particles possessing at its surface acid, alcohol and amine functionalities, which are now intensively used in bioimaging and nanomedicine, photocatalysis, biosensing, and optoelectronics [2], owing to their noteworthy luminescent properties. CNDs may be prepared by a variety of methods (top-down and bottom-up strategies), carbon sources and passivating agents [2].

The OMWW characteristics are dependent on several factors which are intimately linked to the extraction process as well as to external parameters such as the type and stage of maturation of olive fruits, harvesting region and climate conditions. The reported amounts of phenol- and polyphenol-based compounds in OMWW may vary between 1.3-4.0% (dry weight basis) while the total carbohydrates may range from 3.4-33% [3], clearly reflecting the abovementioned dependencies. Particularly, when one considers the classical (batch press) and modern (continuous centrifugation; 3-phase and 2-phase systems) extraction methods, huge differences appear, not only in the concentration of organic matter in the wastewater but also in its composition [4]. Therefore, before any technological process

can be realistically applied to produce carbon nanomaterials from OMWW, one should be aware of their main organic components. Following this line, we have characterized the aqueous effluents of two olive mills, one operating by a batch press (BP) process and the other by a continuous centrifugation 2-phase (2-Ph) system. The results have clearly showed the distinctive nature of the two effluents. Thus, while the amounts of total phenols (8.8-8.9%, expressed in tannic acid) and flavonoids (0.50-0.52%) are similar for both effluents, the tannin content (17.8% and 29.9% for BP and 2-Ph), total sugars (26.5% and 13.8%, respectively) and the lipidic fraction (3.8% and 16.2%, respectively) are quite different. Moreover, the total solids from the two extraction procedures yielded 5.9% (BP) and 0.26% (2-Ph).

The above results deeply contrast with those reported in literature [4], namely for polyphenols, lipids and saccharides, being much higher in current study.

With this information in hand, both effluents were treated by hydrolytic processes, with and without dilution of pristine wastewaters, and in the presence and absence of organic additives. The most important conclusion withdrawn from the study is that whatever the effluent used highly fluorescence CNDs could be obtained, albeit in different efficiencies. Results will be discussed in light of the effluent composition.

Acknowledgements

We thank Instituto Politécnico de Lisboa (Project IPL/2016/NANOLIVE/ISEL) and FCT/MCTES (UID/QUI/00616/2013) for financial support.

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Heavy metals in paints on consumer glassware

PP Sust Devel #9

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Compounds of heavy metals were commonly employed in paints as stabilisers, driers, pigments and biocides. Since the health effects of many metals were realised most metal compounds have been banned or restricted in consumer products, including paints for decorative purposes and that are likely to be contactable by children. One area that has evaded attention in this respect, however, is the use of heavy metals in painted glassware that is available to consumers directly as new products or as re-used, second-hand items. In the present study, painted glassware was purchased from various national chain stores and second-hand stores, including a range of drinking glasses (shot glasses, mugs, children's tumblers, beer glasses, novelty glasses), drinks bottles (water, spirits, beers) and cooking-ware and table-ware (chopping boards, coasters, jugs, measuring beakers). Painted surfaces were measured for 18 elements by portable XRF using a Niton XL3t housed in a test-stand and configured in both a plastics mode and a lead-in-

paint mode. Out of all samples tested ($n = 100$), about 50% contained leaded paint and about 30% contained cadmium-based paints, with other metals-metalloids of toxicological significance detected including chromium, selenium and antimony. In all cases where Pb and Cd were detected, concentrations exceeded allowable limits in paints or consumer products by orders of magnitude, with maximum levels of about 200,000 ppm and 50,000 ppm, respectively. In some cases, painted areas were small and/or centrally located on the glassware, but in many cases, including drinking glasses targeted at children, the painted area extended to within 1 cm of the rim. A standard test of extraction using 4% acetic acid mobilised significant fractions ($> 10\%$) of Pb and Cd from some glassware. The findings suggest that use of Pb and Cd in paint on glassware is an industry-wide practice that may pose health hazards to consumers both directly and through contamination of the waste recycling stream.

Environmental Safety

Useful of New Approaches for Concentration and Separation of Bioactive Analytes in CE in Complex Biological Mixtures

PP Env Safe #1

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Identification and quantification of bioactive substances (such as steroids, catecholamine, polyphenols and proteins) is challenging due to the low levels (ng/ml) in natural matrixes. These require the use of very sensitive and selective analytical methods. Although CE holds great promise as the method of choice for high resolution of biological and environmental samples, it suffers from poor concentration sensitivity, particularly when UV detection is used. *On-line* preconcentration in CE is a very useful way to solve this problem and addition of new materials such as dendrimers and ionic liquids can improve the separation selectivity. We have investigated different techniques of *on-line* concentration (*stacking*, *dynamic pH-junction*, *sweeping*) for ionogenic and neutral analytes (proteins, biogenic amines, neurotransmitter amino acids, steroids) in biological objects by different modes of capillary electrophoresis: zone (CZE) and micellar (micellar electrokinetic chromatography MEKC) modes using modifiers such as cyclodextrin, ionic liquids based on imidazolium and hyperbranched polymers.

It was observed, that dynamic preconcentration techniques (*sweeping* and *stacking*) has provided 20-fold increases in detection sensitivity for steroids by stacking, and for sweeping with the use of β -cyclodextrin in sample matrix – 120-fold.

We investigated the potential of use hyperbranched polymers polyethylenimins, functionalized with maltose (PEI-Mal), with different molecular weights (5 and 25 kDa) and degree of modification with maltose, as a dynamically or covalently bound coating and a pseudostationary phase in capillary electrophoresis for determination bio-active substances. Applying PEI-Mal as a covalent coating for concentrating proteins in the large volume sample stacking (LVSS) combined with the field-enhanced sample injection (FESI),

up to 1320-fold enhancement of sensitivity was achieved. The detection limit of 100 to 500 ng/ml allowed successful analysis of albumin level both in blood and urine samples without additional preconcentration.

Potential possibilities of long chain ionic liquids (ILs) based on imidazole (C_{12} MImCl and C_{16} MImCl) for *on-line* sample concentration techniques (*field amplified sample stacking (FASS)*, *head-column field amplified sample stacking (HC FASS)*, *sweeping*) of ionogenic and neutral analytes (catecholamines and steroid hormones) in different modes of capillary electrophoresis were studied. It was observed a synergistic effect of ILs C_{16} MImCl and sodium dodecyl sulphate on efficiency and separation selectivity of steroid hormones. It was found that using a high conductivity sample matrix in sweeping leads to significant increase of analytes efficiency up to 1×10^6 theoretical plates and reduce the LODs for catecholamines and steroid hormones to 50 ng/mL and 25-100 ng/mL, respectively. This approach is suitable to find out the trace amounts of steroids and catecholamines in natural objects.

All it does method CE comparable on sensitivity with HPLC and exceeds HPLC by efficiency. The received results are claimed in practice of clinical medicine for the determination of catecholamines and steroid hormones in serum and urine at different disease; albumin in urine (~ ng and pg) at microalbuminuria; polyphenols in foodstuff.

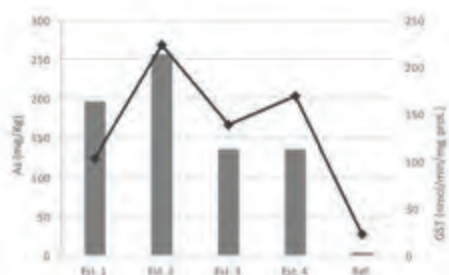
Acknowledgements

This work was supported financially by grant of Russian foundation for basic research no [a_16-03-00791-a](#) and [17-03-012182-a](#). Authors thank Chemistry Educational Centre of Research Park Saint-Petersburg State University for technical support.

Tracking the Distribution and Bioavailability of Contaminants in Ria de Aveiro (Portugal) Using Polychaetes as Bioindicator Species

PP Env Safe #2

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During decades effluents from the Estarreja Chemical Complex were directly discharged in the Ria de Aveiro lagoon through a system of ditches. “Esteiro de Estarreja” was the main channel receiving effluents rich in aromatic based and chlorine compounds and in toxic elements such as As, Hg, Pb and Zn [1]. Consequently, most of the discharged contaminants are settled in this channel, as well as in the inner basin where this channel discharges, the Laranjo Basin [2, 4].

Benthic organisms are in direct and permanent contact with sediments, and despite a decrease in surface sediment contamination, previous studies concluded that biota are still subject to bioaccumulation of contaminants such as PCBs, HCB, Hg, and As [3, 4]. This clearly provides an indication of possible risks for biota, through trophic chains transferences.

Study the potential impact of sediments contamination on the organism’s health is of utmost importance. In this context, molecular biomarkers can provide valuable information about organism’s stress responses that can be translated in effects at higher levels of organization. As a result, the use of biomarkers is becoming increasingly important as early-warning indicators of ecological stress. Thus, this study aims at evaluating the effects of sediment contamination on aquatic invertebrates, by determining some biomarkers, which are sensitive and selective endpoints of exposure and effect.

Four different sites along the “Esteiro de Estarreja” channel, and a reference site (in the Vagueira channel) were selected for sediments and polychaetes (*Hediste diversicolor*) sampling. Organic contaminants (PCBs, HCB) and toxic

elements (including As and Hg) were analysed in sediments. Oxidative stress biomarkers (catalase; glutathione-s-transferase; lipid peroxidation), and biomarkers of neurological activity (acetylcholinesterase activity) were determined.

Very high levels of organic contaminants (both PCBs and HCBs) and toxic elements, such as As and Hg, were found in sediments from the channel, especially when comparing with the reference site. For most contaminants, levels are higher at the beginning of the channel, where the effluents were discharged in the past. Regarding biomarkers, results showed that the contamination levels is affecting the oxidative stress response system as well as the neurological functions of polychaete. Differences between locals were observed, but due to the high levels of contaminants found in all sites and the mixture effect is difficult to conclude which are the ones responsible for the effects observed. Nevertheless, is it possible to conclude that these organisms are good bioindicators of the quality of sediments.

Acknowledgements

This work was supported by: ROHM-CNRS (OHM-Estarreja/2016/Proj.6), and by the Strategic Funding UID/Multi/04423/2013 (CIIMAR) and UID/AMB/50017/2013 (CESAM RU), through national funds provided by FCT (Foundation for Science and Technology) and European Regional Development Fund (ERDF), in the framework of the PT2020 Partnership Agreement. FCT, also supported the work through an individual research grant attributed to A. Cachada (SFRH/BPD/100429/2014).

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Determination of Artificial Sweeteners in Waste Water and Their Potential Impact on the Ecosystem

PP Env Safe #3

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Artificial sweeteners (AS) can be found not only in food, but also in pharmaceuticals and in a range of personal care products. They are also used in animal feed (saccharin). The sweeteners which are authorized in the countries of the European Union are following: acesulfame-K (E950), aspartame (E951), cyclamate and its salts (E952), saccharin (E954), sucralose (E955), thaumatin (E957), neotame (E961) and aspartame-acesulfame sodium salt (E962) [1].

In our work we aimed on the determination of selected AS (saccharin (SAC), cyclamate (CYC), acesulfame-K (ACE) and sucralose (SUC)) in waste water and on their ecotoxicological evaluation. Above mentioned AS were selected because as artificial compounds there are not transformed completely in the human or animal body and enter waste water unchanged; in addition some of them (namely ACE, SUC) are removed to a very limited extent in wastewater treatment plants (WWTPs) and then entered water ecosystem and are detected in surface water. Generally, concentrations of ACE and SUC up to the $\mu\text{g.L}^{-1}$ range can be found in receiving waters, i.e. surface waters, and also in groundwater aquifers and drinking waters. Such concentrations are among the highest known for anthropogenic trace pollutants [2, 3].

The environmental levels of artificial sweeteners depend on the degree of their use in each country and on the type of sweetener. In Europe, the concentration of AS in the inflow of WWTPs is around $100 \mu\text{g.L}^{-1}$, and these concentrations are reduced on effluent. For example, mean sucralose concentrations in the effluent range in $0.71\text{--}11 \mu\text{g.L}^{-1}$ [3, 4].

In our work the 24-hour composite samples (at influent and effluent) were collected at the WWTP Brno-Modřice (capacity 513,000 PE) using an automatic sampler with a sampling interval of 2 hours. Analysis of AS via liquid chromatography with mass spectrometry (Agilent 1100 Series, Agilent Technologies 6320 Series Ion Trap LC/MS), using solid phase extraction (STRATA-X, 200 mg/3 mL, Phenomenex) was carried out.

Ecotoxicity of the sweeteners was evaluated via aquatic organisms, namely the freshwater crustaceans *Thamnocephalus platyurus* and *Daphnia magna* and the water plant *Lemna minor*.

At the inflow of the WWTP, concentration of all monitored sweeteners ranged between 1.40 to $22.67 \mu\text{g.L}^{-1}$. The lowest concentration was found for acesulfame-K (average concentration was $1.67 \mu\text{g.L}^{-1}$), followed by cyclamate ($4.81 \mu\text{g.L}^{-1}$) and saccharin ($17.26 \mu\text{g.L}^{-1}$) and the highest concentration showed sucralose (average level was $18.61 \mu\text{g.L}^{-1}$). At outflow only saccharin at very low concentration (average detected concentration $0.86 \mu\text{g.L}^{-1}$) and sucralose (average detected concentration $14.56 \mu\text{g.L}^{-1}$) were found. Our results correspond with another studies confirming very good degradability of SAC and CYC and limited removal of SUC and ACE [2]. Based on our results we can conclude that only 6% of SUC entered WWTP is removed.

Concerning ecotoxicity evaluation – the most toxic effect exhibits SAC; calculated ecotoxicological values were following: 24hLC50 for *T. platyurus* 115 mg.L^{-1} , 48hEC50 for *D. magna* 131.2 mg.L^{-1} and 168hEC50 for *L. minor* – 27.97 mg.L^{-1} . With respect to this values and to the environmentally relevant concentration of AS we can predict very low acute toxicity of AS, but the question for the future research is chronic toxicity. It is assumed that AS consumption will increase, which will result in increasing penetration of these substances into the environment. Another question is the fate of AS in the environment and their effects in combination with other contaminants.

Acknowledgements

This study was supported by the grant No. FCH-S-17-4766 from the Ministry of Education, Youth and Sports of the Czech Republic.

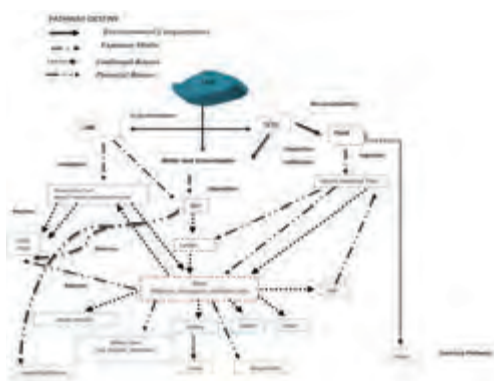
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The Fate of Nanomaterials and Its Consequences

PP Env Safe #4

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Nanoscience is one of the most newsworthy research and development area in modern science and industry. Today's manufacturing and application of nanomaterials in a wide range of areas bring specific issues related to handling of waste containing nanomaterials. The outbreak that has occurred in the proliferation of so many different engineered nanomaterials' (ENM) creates today a big issue to regulators in what concerns hazard identification and environmental/ health legislation [1]. Although the majority of the scientific community is yet unwilling to talk about it, is of the upmost importance to highlight problems related to uncontrolled release of nanoparticles to the environment through waste disposal, and to introduce the topics of nanowaste and toxicology of nanoparticles into the waste management. Some studies associated with usage, precautions, safety and risk perceptions related to ENM were made in some companies [2], and the results suggest that there is insufficient information to establish specific regulations.

In order to evaluate the risks inflicted by the use of nanomaterials in commercial products, and even more important, in environmental applications, is urgent to understand their mobility, bioavailability, and ecotoxicity [3]. The main concern of ENM lies in their toxicology and in the astonishing level of ENM production in the world that leads to an increasing debate on their effects on human occupational settings and on the environment. As a consequence of the increasing production of NMs of all types and the potential for their release in the

environment, their toxicity needs to be addressed. In doing so, it is necessary first to determine the fate and behavior of manufactured NMs in the environment. However, the mechanism of toxicity is still unclear and biocompatibility varies depending on numerous parameters, such as nanoparticle size and shape, surface properties, applied nanoparticle concentration, type of cell and nanomaterial. The toxicity of nanomaterials is often linked to their extremely small size; smaller particles have a greater reactive surface area and are more chemically reactive and produce greater numbers of reactive species, including free radicals [4]. Their high chemical reactivity and their greater capacity to penetrate biological membranes also pose serious new toxicity risks. There are now on the global market over 720 products that contain nanomaterials. Is urgent to wake-up for this new problem, that although with very small visibility (nano size), it will become very quickly a huge problem if we don't take the necessary attention.

The present work is a review of scientific results on the fate and potential negative impact of engineered nanoparticles on the environment.

Acknowledgements

This work was the result of the project:

- (i) POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia.
- (ii) NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

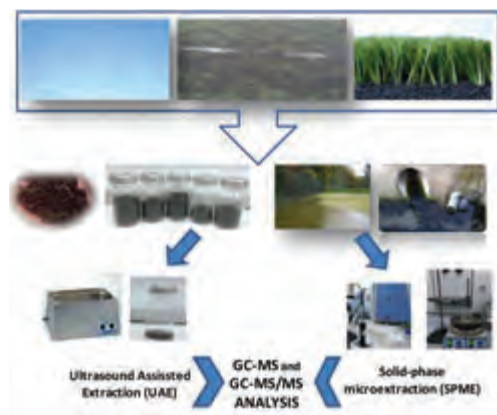
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Monitoring of Hazardous Substances in Rubber Crumb and Leaching Waters from Synthetic Turf Football Fields

PP Env Safe #5

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The recycling of scrap tires through mechanical trituration is a suitable alternative to reuse this material, which is usually employed in all types of indoor (nurseries, gyms) and outdoor (playgrounds, sport fields) surfaces. Nevertheless, in recent years the concern about the safety of these surfaces is increasing. One specific surface consists of football fields of synthetic turf, where the artificial grass is supported by an infill of rubber crumb. The rubber crumb is disintegrated and it easily comes to the surface being more accessible for players. In addition, these outdoor surfaces may reach temperatures higher than 60°C in sunny days, and they are also periodically watered to maintain their physical properties. This practice, together with rainwater, favours the leaching of the hazardous substances present in the rubber crumb, and whose final fate are the aquatic environment.

The presence of priority pollutants such as polycyclic aromatic hydrocarbons (PAHs), and other hazardous chemicals has been demonstrated in recycled rubber tire surfaces such as playgrounds or commercial pavers intended for children playing areas [1].

The objective of this work is the determination of a large number of hazardous organic compounds including PAHs, phthalates, adipates, vulcanisation additives and antioxidants in recycled rubber crumb of synthetic turf football fields from Spain and Portugal.

A comparison between the composition of the commercial rubber crumb material manufactured in both countries was performed. For that purpose, different extraction techniques, Microwave Assisted Extraction (MAE), Pressurized Liquid Extraction (PLE), and Ultrasound Assisted Extraction (UAE), followed by gas chromatography-mass spectrometry (GC-MS) were employed.

More than 40 synthetic turf football fields were extracted and analyzed by solvent extraction followed by GC-MS and GC-MS/MS. Besides, the runoff water of several fields as well as the air in contact with the rubber mulch have been analysed. In this last case, a green non-solvent extraction technique, solid-phase microextraction (SPME), was employed. The high content of toxic chemicals in these materials is clearly shown as well as the likely transfer of the hazardous substances to the related environmental compartments.

Acknowledgements

This research was supported by European Regional Development Fund 2007-2013 (FEDER) and projects GPC2014/035, R2014/013 (Consolidated Research Units Program), CRETUS (AGRUP2015/02) (Xunta de Galicia), and UNST13-IE-2152 and CTQ2013-46545-P (Ministry of Economy and Competitiveness, Spain). M.C. acknowledges CRETUS (Centre for Research in Environmental Technologies) for her contract. This project was partially financially supported by the projects: POCI-01-0145-FEDER-006939 (LEPABE – UID/EQU/00511/2013) funded by the ERDF, COMPETE2020 /POCI and FCT/MCTES/ PIDDAC, NORTE-01-0145-FEDER-000005–LEPABE-2-ECO-INNOVATION funded by the NORTE 2020 programme under the Portugal 2020/ERDF Partnership Agreement and Investigador FCT contract IF/01101/2014 - Nuno Ratola.

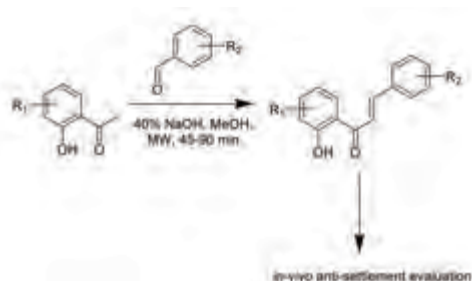
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Synthesis of Chalcone Derivatives and Anti-settlement Activity Against *Mytilus galloprovincialis* Larvae

PP Env Safe #6

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Biofouling is a major concern for maritime industries, increasing the roughness of ship hulls and leading to increase fuel consumption, CO₂ emission and associated costs, as well as safety risks due to material failure resulting from microbiologically induced corrosion [1]. Antifouling paints have been the primary strategy to biofouling control. Nevertheless, because of its toxicity to the marine environment, fisheries and aquaculture, these coatings were banned in several countries since 2008 [1]. Thus, the demand for environmentally benign, nontoxic antifouling agents is urgently required.

Chalcones have been intensively studied for their wide range of biological activities [2,3]. Moreover, these compounds have been used as anticorrosive agents [4], alone and with iodide ions to synergize the activity of the latter in acid-mediated corrosion of steel [5,6].

In this research work, thirteen chalcone derivatives were synthesized by Claisen Schmidt reaction of appropriately substituted acetophenones and benzaldehydes, and their structures were determined through spectroscopic methods, namely nuclear magnetic resonance (¹H and ¹³C NMR, HSQC and HMBC). Additionally, antifouling activity was evaluated using an *in vivo* anti-settlement test with *Mytilus galloprovincialis* plantigrades [7].

Results showed that three chalcone derivatives presented promising activity against the settlement

of plantigrades larvae, with the most potent compound showing an EC₅₀ value of 16.5 μM and low toxicity (LC₅₀ level higher than 200 μM).

Acknowledgements

Support for this work was provided by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT – Foundation for Science and Technology and European Regional Development Fund (ERDF), in the framework of the programme PT2020 and partially supported by Foundation for Science and Technology (FCT) and COMPETE under the projects PTDC/MAR-BIO/4694/2014 - POCI-01-0145-FEDER-016790 - RIDT 3599 and PTDC/AAGTEC /0739/2014 - POCI-01-0145-FEDER-016793 - RIDT 9471. JM and JRA also acknowledge FCT for the grant PTCD/DTP-FTO/1981/2014-BI-2016-054 and postdoctoral scholarship SFRH/BPD/87416/2012, respectively.

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Contribution For The Derivation Of A Soil Screening Level (SSV) For Zinc Using A Portuguese Natural Reference Soil

PP Env Safe #7

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Soil screening values (SSV) often provide the first evaluation of ecological risks of contaminated soils. Several countries across Europe have confirmed the necessity of their derivation, but Portugal still lacks toxicity datasets for this purpose, obtained using Portuguese natural soils. In this context, this work aimed the generation of ecotoxicological data for dominant type of Portuguese soils (PTRS1) [1] and for a preliminary derivation of Zinc SSV, as was already done for uranium, copper and cadmium [2, 3, 4]. A probabilistic method, namely species sensitivity distributions (SSDs), was used to estimate the concentration affecting a given proportion of species (HCp), using effect concentrations (EC) obtained for different species and endpoints. One of these HCp was proposed as a preliminary SSV while more ecotoxicological data is being obtained.

A battery of ecotoxicological tests focusing microbial parameters (arylsulphatase, acid phosphatase, nitrogen mineralization), avoidance of invertebrates

(*Eisenia andrei*), seed germination and plant growth (*Avena sativa*, *Hordeum vulgare*, *Lactuca sativa*, *Lycopersicum esculentum*) were carried out in PTRS1 soil spiked with ZnSO₄.

This metal stimulated the activity of ARS and the NMN at lower concentrations while at higher concentrations caused an inhibition of the same parameters. Seed germination was mainly inhibited for *L. sativa* and *L. esculentum* and the toxic effect on the growth of the different plant species resulted in a range of EC₅₀ between 199.3 and >700 mg Zn kg⁻¹ soil_{dw}. Based on the obtained results, an SSV, EC₁₀-based, of 111.4 mg Zn kg⁻¹ soil_{dw} is proposed.

Acknowledgements

This work was supported by: the Strategic Funding UID/Multi/04423/2013 (CIIMAR) and through national funds provided by FCT (Foundation for Science and Technology) and European Regional Development Fund (ERDF), in the framework of the PT2020 Partnership Agreement.

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Extinguishing Agents and Their Ecotoxicity Assessment

PP Env Safe #8

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Fires could have a negative impact on the environment not only through the production of many toxic products of burning like PAHs, PCDDs, PCDFS, CO etc. but also through application of modern fire extinguishing agents, especially foams based on surfactants. In fact, uncontrolled fires represent significant risk for living organisms, nature ecosystems and also significant threat of material. Due to this fact issue of fire prevention and fire extinguishing has a high priority. In the fight against fires air-mechanical extinguishing foams are often used, which are available in several basic modifications, i.e. protein foam agents, synthetic foam agents and alcohol-resistant foam agents. All these agents help us to inhibit and extinguish spacious fires, but after their application they simultaneously contaminate the environment [1].

Penetration of these substances into the environment causes water and soil contamination and disruption of waste water treatment processes. It results in significant acute toxicity of contaminated matrices and in transfer of pollution to the other environmental compartments. In the soil environment the sorption of various constituents of fire-fighting foams on soil particles can take place and this could lead to the reduction of acute toxicity for aquatic ecosystem, but on the other hand it could increase of acute toxicity for soil organisms [2].

Our work is focused on the evaluation of effects of the most frequently used extinguishing agents on selected aquatic and terrestrial organisms. Extinguishing substances which have been tested were rigid wetting agent TS ECO and TS Turbo and extinguishing powder ABC FAVORIT. Their effects have been tested on aquatic organisms crustacean *Daphnia magna* and algae *Scenedesmus subspicatus* and on terrestrial organisms such as seeds of plant lettuce *Lactuca sativa*, earthworm *Eisenia fetida* and springtail *Folsomia candida*. On the last mentioned organism fire-fighting foam Sthamex F – 15 and Moussol APS F – 15 also have

been tested. Results obtained from tests on aquatic organism *S. subspicatus* predict higher toxicity of rigid wetting agent TS ECO in comparison to the agent from the same group TS Turbo. Value of 72IC50 for above mentioned agent were 0.54 to 3.4 g.L⁻¹. Toxicity of these agents on the other testing organism were comparable ranging in units of grams per liter. Exception was *D. magna*, for which both agents were more toxic. Value of 48EC50 were in the hundredths of grams per liter. All mentioned extinguishing substances were tested on *F. candida*. Toxicities of them were very similar, ranging in units of gram per liter: Sthamex F-15 2.19; Moussol APS E-15 4.47; TS ECO 1.22; TS Turbo 1.10 g.L⁻¹. Exception was ABC FAVORIT fire – extinguishing powder which showed the lowest toxicity to almost all testing organisms (in case *F. candida* its ecotoxicological value of 28dEC50 was 10.17 g.L⁻¹).

Avoidance behaviour and semichronic test on *E. fetida* were for ecotoxicological evaluation of TS ECO, TS Turbo and ABC FAVORIT also used. Both of these tests confirmed low toxicity of ABC FAVORIT fire – extinguishing powder. In case of avoidance behaviour test there were no significant difference from the control group. That means that extinguishing powder exhibited the least negative effect on our testing organisms and therefore could be considered as an environmentally friendly extinguishing agent.

Acknowledgements

This study was supported by the grant No. FCH-S-17-4766 from the Ministry of Education, Youth and Sports of the Czech Republic.

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Cholinesterases as the Biochemical Markers Determined in Terrestrial Gastropods and Earthworms

PP Env Safe #9

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Overuse of chemical fertilizers and pesticides have adverse impact on non-target soil invertebrates such as snails and earthworms [1]. Exposure to these substances affects different levels of biological organization, from molecular to the ecosystem. Biomarkers are used to evaluate the sublethal effect of pesticides in organisms [2].

Cholinesterase is a family of enzymes frequently used as a specific biomarker of exposure to the organophosphate pesticides [3]. These substances disrupt the nervous system due to inhibition of the cholinesterase activity which leads to damage of organism. One of the commonly used organophosphate pesticides in agriculture is chlorpyrifos. It has been shown that chlorpyrifos is harmful to non-target organisms such as soil invertebrates [4].

Therefore, this work is focused on the determination of acetylcholinesterase (AChE), butyrylcholinesterase (BChE) and propionylcholinesterase (PChE) activity in the snail *Helix aspersa* and the earthworm *Eisenia fetida*. The physiological levels and kinetic parameters (Michaelis constant and catalytic efficiency) of cholinesterases were determined in different tissues (head, haemolymph and hepatopancreas in snails; head and body in earthworms). The Ellman method was used for the measurement of enzymatic activity [5]. The difference in sensitivity of tested organisms towards organophosphate pesticides was assessed by *in vitro* exposure to commercially produced pesticide Nurelle D containing chlorpyrifos.

The results indicate a high variability of AChE, BChE and PChE activity between the snail *Helix*

aspersa and the earthworm *Eisenia fetida*. In gastropod, the highest physiological activity was generally measured in their hemolymph, while it was significantly lower in the other tissues. In earthworms, the enzyme activity had very similar values both in the head and the body. The catalytic efficiency was the highest for AChE and the lowest for BChE in both organisms. The presence of organophosphate chlorpyrifos in all samples caused inhibition of cholinesterases in almost all tissues in both organisms. Nevertheless, the most sensitive response was observed in the snails *Helix aspersa*.

Acknowledgements

This work was financially supported by the National Sustainability Programme of the Czech Ministry of Education, Youth and Sports (LO1214) and the RECETOX research infrastructure (LM2015051).

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Investigation of Natural Biodegradation of Contaminated Environmental Samples Near Heating Plant

PP Env Safe #10

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Heating power plant Novi Beograd (Serbia) is the oldest heating plant in Belgrade, with annual consumption of 350 million cubic meters of natural gas. However, beside natural gas, the plant is using app. 45.000 tons of heavy fuel oil app. 3.200 tons of coal [1]. Being located in densely populated areas and near Sava River, heating plant is one of the significant sources of environmental pollution. Presence of different oil pollutants in the sediments and soils of Sava River has already been confirmed [2].

Oil pollutants are complex mixtures of varying composition containing thousands of hydrocarbons each with their own physicochemical properties and degradation kinetics. Biodegradation tests are often performed at high concentrations of individual test substances, whereas environmental biodegradation is taking place at lower concentrations with many chemicals present in a mixture.

In this study we reported natural degradation of oil pollutants in environmental area of heating plant.

O₂ consumption and CO₂ production in period of 68h in soil and water samples from location area of heating plant New Belgrade were measured by using a Columbus Micro-Oxymax respirometer. Total petroleum hydrocarbons was gravimetrically determined before and after respiration experiment. Cells in soil sample consumed 11.52 mL of O₂ within 68 h. By contrast cells in water sample

consumed only 3.61 mL of O₂. The production of CO₂ by soil sample cells was twofold higher than that by water soil cells within 68 h.

Notably, cells in soil sample obtained maximum rate of O₂ consumption after 15 h (4.002 µL/min) while water sample cells obtained maximum rate after 27 h (2.033 µL/min).

Total decrease of TPH at the end of respiration experiment was 87.1 %, and 69.2 % for soil and water sample, respectively.

These results indicate that microbial population in soil is more capable for biodegradation of oil pollutants from this area, and we could suggest that these microorganisms should be used in augmentation approach for bioremediation technology of this contaminated site.

Acknowledgements

This work was supported in part by Ministry of Education, Science and Technological Development of the Republic of Serbia, Project No: III 43004.

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Oil Pollutants in Alluvial Sediments of the Sava River, Serbia

PP Env Safe #11

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In the capital of Serbia, Belgrade, one of the largest heating plants in the Balkan is localized near the Sava River (New Belgrade), and represents a potential source of oil pollution for the alluvial area of the river.

Presence of different oil pollutants in the sediments and soils of Sava River has already been confirmed [1]. The aim of our research was to determine the presence of oil pollutants as well as their vertical migration in the alluvial area of Sava River.

The investigation was started in the summer of 2015. The soil was sampled in 20 different microlocations, at 5 depths (up to depth of 2m). The sampled material was organized in the form of layers, and for each microlocation was made a lithological profile. Most of the samples have had a sandy and clayey structure with low content of organic matter.

Extractions of oil pollutants from soil samples were done using the Soxhlet apparatus with dichloromethane. The extracts were then fractionated by column chromatography into fractions of: saturated hydrocarbons (Fraction I), aromatic hydrocarbons (Fraction II), and polar compounds (alcohols and keto compounds (Fraction III) [2].

In order to monitor changes in the vertical migration of oil pollutants, as well as the relationship of this migration with the soil characteristics, the group composition was determined for each borehole

of all microlocations, taking into account their lithological profiles.

The obtained results showed that in all extracts the most represented were polar compounds (Fraction III), while the saturated hydrocarbon were least represented (Fraction I). This relationship is almost unchanged in samples from different microlocation at different depths.

On the basis of the obtained results, it can be concluded that composition of oil pollutants can be unchanged through the alluvial sediments up to 2m depth. Deeper penetration of these pollutants can be related to the characteristics of the surrounding soil environment.

Acknowledgements

This work was supported in part by Ministry of Education, Science and Technological Development of the Republic of Serbia, Project No: III 43004.

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The Influence of Some Pyrazole Derivatives and Newly Synthetised Cu(II) Complexes to the Inhibition of *Phomopsis Viticola* in Vitro

PP Env Safe #12

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Pyrazole-based compounds and their transition metal complexes have attracted considerable research interest because of their potentially beneficial biological properties. The wide biological activity of this class of compounds (anticancer, antimicrobial, antiviral, anti-inflammatory, antifungal and others) is described in several reviews [1-4]. This results is a part of our continued work with pyrazole based complex [5-6]. In the study inhibitory effects of 4-Nitro-3-pyrazolecarboxylic acid and their copper(II) complex $[\text{Cu}_2(\text{C}_4\text{HN}_3\text{O}_4)_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ were examined to the mycelial growth of *Phomopsis viticola* (pathogenic fungi that causes *Phomopsis* cane and leaf spot disease) in vitro. The compounds were applied in five 5 different concentrations, ranged from 0.12 to 0.0075%. Obtained results

were compared with the commercial fungicide Cabrio Top with active ingredient pyraclostobin that belongs to pyrazole derivates. Both examined compounds expressed weak effect on mycelial growth: only in two initial concentrations of 0.12% and 0.06% the compounds showed a slight inhibition, with a mycelial growth ranged 6.8-7.3 mm (7.5 mm in control).

Acknowledgements

Ž. Jačimović and M. Kosović thank to the Ministry of Science of the Republic of Montenegro for financial support (National project).

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Evaluation development on Monitoring Technique of Soil Toxicity Using Vibration Sensor: Basic Study

PP Env Safe #13

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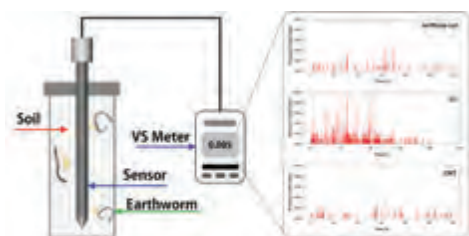


Figure 1. Schematic diagram of experimental equipment (left) and results of signal on movement of earthworms in soil (right).

The guidelines of soil toxicity assessments provided by the OECD or ISO are demanding large amounts of soil and organisms (e.g. earthworms and plants) [1]. Because can only asses the weight and mortality of the organisms after they are long exposed to a contaminated soil (e.g. OECD TG207: 14 days), assessing the probability of death in real time was impossible [2]. Also, the widely accepted guidelines and existing researches are very troublesome when applying to field sites [3]. Hence, to overcome such problem of assessment methods of major organizations, the aim of this study is to introduce a new technology of soil ecotoxicity monitoring. The new monitoring techniques measure the seismometer generated by seismic waves from earthquake, and vibration sensors detect the minute movement of soil particles caused by the earthworm in soil. This study observed the possibility of detecting the movement of earthworms with vibration sensors in both artificial and natural soil. Moreover, it compares the existing results with the results monitored from the movement of earthworm in contaminated soil (Zn and CNT).

The soil used in this experiment had 20 % water content, a volume density of 1.2 g/cm³, and a total of 200g. The total volume of reactor was 116.11 cm³. We exposed five earthworms in each reactor and observed them in periods of five days to 10 days. The concentrations of Zn and CNT was 400 ppm and 500 ppm, and any changes in the weight of earthworm were monitored respectively. The vibration meter used in this experiment was Lutron

BVB- 8207 SDVRs, which is capable of detecting 0.001mm (Fig. 1-left).

The movement of earthworms in both natural and artificial soil was detected using a vibration sensor (Fig. 1-right). The results show that these sensors can detect the movement of earthworms in various soil environments. The earthworms in zinc contaminated soils showed more movements than those of the control soils, which were attributable to the toxic effect of zinc in their skin and digestive system [2]. Moreover, no movement was detected after 200 hours of observation, which indicates that the earthworm died after being long exposed to the contaminated soil. Compared to that of the control soil, the movement of earthworms in CNT contaminated soils observed less activities. The results show that CNT is not toxic to the skin, but it is highly toxic to the digestive system of earthworm [4]. When comparing the weight of exposed earthworm, earthworm of CNT contaminated soil weighed less than the earthworm of control soil. These results will be used as the basic study of soil ecotoxicity monitoring, and need related studies such as the optimization of the equipment, movement patterns of earthworm, toxicity revelation of pollutants (avoidance effect and skin), and bioavailability.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03033490).

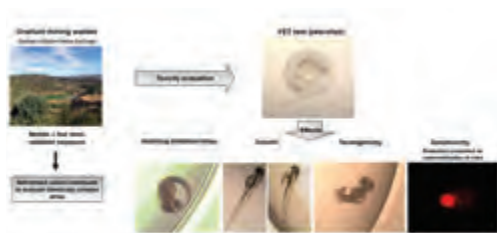
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Uranium Mining Wastes: The Use of the Fish Embryo Acute Toxicity Test (FET) Test to Evaluate Toxicity and Risk of Environmental Discharge

PP Env Safe #14

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Uranium extraction, can represent complex environmental situations, as it causes the surface exposure of geologic material, rich in uranium and its radioactive descendants, as well as other metals and metalloids [1]. Both open pit mine and shaft mines create very large quantities of tailings, which are major sources of the biophysical and biochemical impacts of uranium mining [2–4]. In addition to radionuclides from uranium's decay series, tailings may also contain metals and metalloids (e.g. Ni, Cd, As, Se) and residual chemicals from the milling process [2]. The FET test was employed to evaluate the genotoxic and teratogenic potential of mine liquid effluents and sludge elutriates from a deactivated uranium mine. The aims were: a) to determine the risk of discharge in the environment; b) the effectiveness of the chemical treatment applied to the uranium mine water; c) the suitability of the FET test for uranium mine wastes toxicity evaluation and the added value of including genotoxicity evaluation. The FET test combined with the Comet Assay showed, the genotoxicity of both elutriates and effluents and also the teratogenicity of the mine effluent at low concentrations. Additionally, other parameters were affected namely, growth and hatching. Water

pH alone played an important role in the hatching process. The inclusion of molecular endpoints in the FET test was crucial to prevent the underestimation of the risks posed by such wastes. Care should be taken when using benchmark values calculated for specific stressors to evaluate the risk posed by uranium mining wastes to freshwater ecosystems, due to their chemical complexity.

Acknowledgements

This work was supported by UID/AMB/50017/2013 project, through COMPETE and National Funds awarded by FCT. The Portuguese Foundation for Science and Technology (FCT), through National Funds (Ministry for Science and Education in Portugal), provided financial support to Joana Lourenço and Sérgio Marques by means of a Post- Doc grant (SFRH/BPD/92554/2013 and SFRH/BPD/112803/2015). This research was also partially supported by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT – Foundation for Science and Technology and European Regional Development Fund (ERDF), in the framework of the program PT2020.

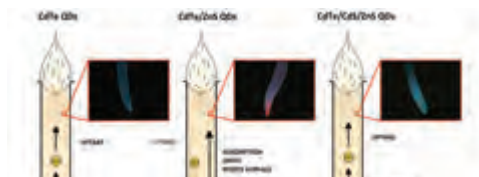
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Toxicity and Uptake of Cadmium from Different Types of Cd-based Quantum Dots in the Model Plant *Allium cepa* L.

PP Env Safe #15

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This study was focus on the determination of toxicity and bioaccumulation of three different types of Cd-based quantum dots (QDs), dispersed in aqueous medium, for a model plant *Allium cepa* L. Core, core/shell, and core/shell/shell QDs (CdTe, CdTe/ZnS, and CdTe/CdS/ZnS QDs capped by 2-mercaptopropionic acid) were tested and CdCl₂ was used as a positive control. After a 24-hour and a 72-hour exposure, total Cd content (M_{Cd}) and bioaccumulation factors (BAFs) were determined in all parts of *A. cepa* plants (roots, bulb, shoot), and the total length of the root system was monitored as a toxicity end-point. Measurements of the total Cd content versus the free Cd²⁺ content (with Differential Pulse Voltammetry, DPV) in exposure media showed differences in chemical stability of the three QD types. Correspondingly, selected QDs showed different toxicity for *A. cepa* and different Cd bioaccumulation patterns.

Similar toxicity of CdTe QDs and CdCl₂ to *A. cepa*, together with high QD core dissolution detected by DPV, points to the conclusion that toxicity of core QDs is predominantly caused by free Cd²⁺ released into aqueous exposure medium, as already suggested by [1].

Plants exposed to CdTe QDs also bioaccumulated the most Cd among all QD exposure groups. CdTe/ZnS QDs showed no toxicity and very low bioaccumulation of Cd in *A. cepa*; the main source of measured Cd in the plants were QDs adsorbed on their roots, which was confirmed by fluorescence microscopy. On the contrary, CdTe/CdS/ZnS QD toxicity and bioaccumulation patterns were similar to those of CdTe QDs and pointed to unstable CdS/ZnS shells.

Acknowledgements

This research has been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020 (LQ1601) and the project FCH-S-17-4766.

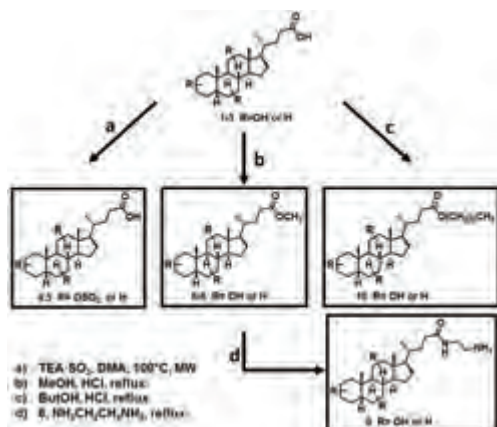
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Synthesis of Steroid Derivatives with Anti-microfouling and Anti-Macrofouling Properties

PP Env Safe #16

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In marine environment is possible to observe species that are always heavily fouled by epibionts, while other species are free of epiphytic growth. Some marine organisms produce biologically active compounds that inhibit the growth of fouling organisms or the settling of their larval forms, namely steroids [1].

The aim of this work was the synthesis of a series of steroid derivatives with different lipophilicities in order to evaluate their antifouling activity (AF) and understand the respective structure-activity relationship.

Seven steroid derivatives were successfully synthesized in moderate to high yields (40-97%): two sulfated derivatives were synthesized using sulfur trioxide complex under microwave irradiation [2]; four ester derivatives were obtained from the steroid with the respective alcohol under reflux [3]; and one amine-amide derivative was obtained by refluxing the methyl ester derivative with the suitable diamine [3]. The structures of the obtained derivatives were confirmed through spectroscopic methods, namely infrared spectroscopy (IR) and nuclear magnetic resonance (¹H and ¹³C NMR, HMBC, and HSQC), as well as high-resolution mass spectrometry (HRMS).

AF activity was tested against macro- and microfouling communities, since an effective AF screening should include the evaluation of the anti-settlement activity against both macro- and microfouling species. Anti-macrofouling activity

was evaluated using an *in vivo* anti-settlement test with *Mytilus galloprovincialis* plantigrades larvae and anti-microfouling activity was evaluated against 5 biofilm-forming marine bacteria, accordingly to previously reported methods [4].

Results showed that five steroid derivatives (compounds 4, 6-8, and 10) presented highly significant differences ($p \leq 0.001$, Dunnet's test) against the settlement of plantigrades larvae, with the most potent compound (compound 8) showing an EC₅₀ value of 3.7 μM, LC₅₀ level higher than 200 μM, and a LC₅₀/EC₅₀ higher than 53.8. Concerning anti-microfouling properties, four synthesized compounds (compounds 6, 7, 9, and 10) showed the ability to inhibit the different species of bacteria biofilm at 12.5 μM (40-80%).

Overall, the ester derivatives were found to be more active than the parent steroids (compounds 1-3).

Acknowledgements

Support for this work was provided by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT – Foundation for Science and Technology and European Regional Development Fund (ERDF), in the framework of the programme PT2020 and partially supported by Structured Program of R&D&I INNOVMAR - Innovation and Sustainability in the Management and Exploitation of Marine Resources, reference NORTE-01-0145-FEDER-000035, Research Line NOVELMAR and the project PTDC/AAG-TEC/0739/2014 - COMPETE (POCI-01-0145-FEDER-016793) - RIDTI (Project 9471). ARN and JRA also acknowledge FCT for the PhD scholarship (SFRH/BD/114856/2016) and postdoctoral scholarship (SFRH/BPD/87416/2012), respectively.

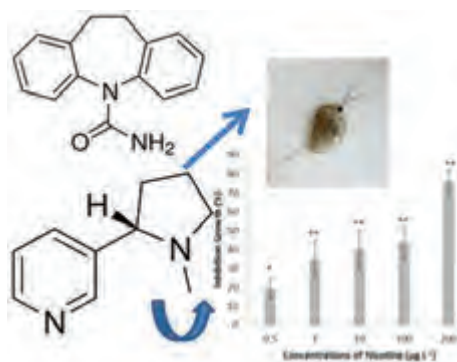
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Comparative Sensitivity of Short-term Bioassays to the Emergent Contaminants Carbamazepine and Nicotine

PP Env Safe #17

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Among the priority substances with biological significance in the aquatic compartment, emergent contaminants (ECs) constitute an environmental relevant group of chemicals, due to their increasing use, environmental persistence, ubiquity and intrinsic biological properties, which can compromise, in a short time, the balance of ecosystems and become a risk to the health of populations. Subsequently, additional data concerning usage, environmental concentrations, fate, absorption rates and toxicity are still needed to develop the accurate risk assessment necessary for the implementation of acceptable management strategies to protect the environmental health. Carbamazepine (CBZ) is one of the most frequently detected antiepileptic drugs in aquatic environments worldwide [1], and it is classified as an IB compound, according to the priority ranking list proposed by Besse and Garric [2], which indicated that this compound is potentially hazardous for the aquatic environment. Nicotine (NIC) is a highly toxic alkaloid found in tobacco and other nightshade plants and classified as “life-style compound” [3]. The principal source of pollution, to the aquatic ecosystem of these ECs, is the domestic wastewater discharges, due to the inefficiency of their degradation at the wastewater treatment plants (WWTP). The aim of the present study was to identify the most sensitive short-term bioassays that can be used in the characterization of ecotoxicological risks of CBZ

and NIC environmental concentrations. The study was performed using species of representative taxa, namely *Vibrio fischeri* (30 min. luminescence inhibition), *Pseudokirchneriella subcapitata* (72h growth inhibition), and *Daphnia magna* (48h mortality/immobility and 24h feeding inhibition), and tested concentrations, ranging from 0.5 to 100 000 $\mu\text{g L}^{-1}$ for CBZ and 0.5 to 1000 $\mu\text{g L}^{-1}$ for NIC. The results highlight that environmental concentrations of CBZ do not induced short-term toxicity at the species used. Contrariwise, short exposures to environmental concentrations of NIC may represent a risk to the aquatic ecosystem. Therefore, among the bioassays used the most sensitive was the *P. subcapitata* inhibition growth with a 72h- IC_{50} (NIC) of 145.14 $\mu\text{g L}^{-1}$ (IC (95% confidence interval): 93.98 – 196.31 $\mu\text{g L}^{-1}$), followed by the feeding bioassay. Hence, results evidence that NIC is a weak feeding inhibitor, inducing a reduction in the *D. magna* feed rate of about 17 and 15 % at the highest concentrations (400 and 600 $\mu\text{g L}^{-1}$), respectively. Further, NIC also induced immobility/ mortality effect to *D. magna* with a 48h- EC_{50} of 790 $\mu\text{g L}^{-1}$ (IC: 702-910 $\mu\text{g L}^{-1}$). As a result, NIC is more toxic in short-term exposition than CBZ. The short-term bioassays with a better response to NIC were 72h growth inhibition of *P. subcapitata* and 24h feed inhibition of *D. magna*.

Acknowledgements

This work was supported by the Portuguese Science Foundation (FCT), through the grant UID/MAR/00350/2013 attributed to CIMA of the University of Algarve and by the Subprograma Estatal de Movilidad (2013-2016)-MEC (Spain) (CAS 15-00049).

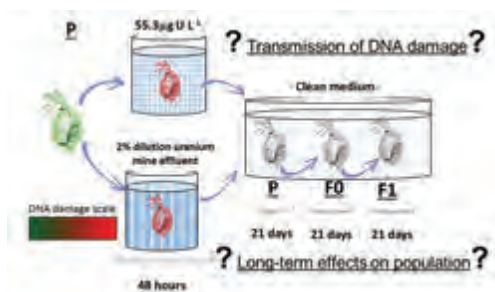
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Long-term Effects on DNA Integrity and Population Parameters of *Daphnia magna* Exposed to Low Doses of a Uranium Mine Effluent and Waterborne Uranium

PP Env Safe #18

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The assessment of the legacy impacts of uranium mine industry in the nearby aquatic ecosystems, with more ecologically relevant endpoints, is vital to secure the long-term health and sustainability of ecosystem services. As so, we designed a transgenerational study on *Daphnia magna* (due to the vital role of cladocerans in freshwater food webs) to perceive if intermittently discharges of uraniferous effluents on water courses may impact daphnids DNA integrity and life history traits, with consequences at the population level in the long-term. Preliminary tests revealed that a 48h exposure of daphnids, to a 2% dilution of a uranium mine effluent (UME) as well as to a matching dose of waterborne uranium (WU) (55.2 mg U L^{-1}) induced significant levels of DNA damage. As so, taking this data into account, daphnids with less than 24h were exposed to both UME and WU, and then passed to a clean medium, where 3 successive generations were monitored for genotoxicity and individual and population effects. Although with some slight variances between WU and UME data, our results reveal that the negative impacts of the short-term exposures gradually fade out in a clean medium. This suggests that under these punctual stressors,

daphnids are able to recover DNA damage, which after a short period (at time of 3rd brood release in the 1st generation) are no longer transmitted to the offspring. As so, DNA damage do not significantly impact its offspring life traits. This lack of long-term impacts contrast with longer and repetitive exposure schemes of exposure to WU and ionizing radiation from other studies [1–3]. Although our results indicate that populations of *D. magna* are not affected by uranium effluents point discharges, this should not be translated as a free-hazardous scenario. Future studies should take into account benthic species, where the exposures are continuous due to the accumulation of these contaminants in the sediments.

Acknowledgements

FCT, through National Funds, provided financial support to Joana Lourenço through Post-Doc grant (SFRH/BPD/92554/2013). This research was also partially supported by the Strategic Funding UID/Multi/04423/2013 and UID/AMB/50017/2013 through COMPETE and national funds provided by FCT and ERDF (PT2020). The authors would like to thanks to EDM for the collaboration given for this work.

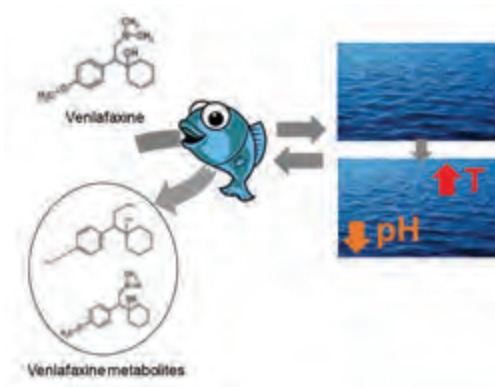
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Influence of Climate Change (sea warming and acidification) on the Metabolization of the Psychiatric Drug Venlafaxine by Meagre

PP Env Safe #19

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Antidepressants are among the most prescribed pharmaceuticals worldwide. Over the last years, venlafaxine, a serotonin-norepinephrine reuptake inhibitor (SNRI) antidepressant, showed to have an improved therapeutic action and, thus its consumption has risen. However, nowadays venlafaxine as well as its main human metabolite, O-desmethylvenlafaxine, have been detected in the aquatic environment [1]. Although there is still a lack of knowledge on the potential toxic effects of venlafaxine for non-target organisms, its potential to bioaccumulate in fish tissues has already been described [2]. Nevertheless, data on the metabolization of venlafaxine by fish, and the presence of their metabolites in the different fish tissues is sparse.

The world is facing global climate changes including warming of the seawater and air, acidification of the oceans, etc. However, little is known about the impact of climate change on uptake, metabolization and depuration of organic contaminants by aquatic organisms.

In this context, this study aimed to evaluate the metabolization of venlafaxine by meagre (*Argyrosomus regius*), as well as the distribution/bioaccumulation of metabolites in different fish tissues, namely brain, liver, muscle and plasma. The influence of environmental factors (e.g. water acidification and increase of water temperature) expected in a climate change scenario, in the metabolization of venlafaxine was also evaluated. Controlled exposure experiments were performed using juvenile meagre *A. regius*. Experiments were

performed in duplicate and 40 fish per tank were exposed to venlafaxine during 28 days under two different exposure routes: via contaminated feed (161 ng/g of venlafaxine) and via water (measured concentration of venlafaxine: c.a. 20 µg/L). The impact of different climate change scenarios (water acidification and/or warming) in the metabolization of venlafaxine was also evaluated. Samples of different fish tissues (brain, liver, muscle and plasma) were collected after 28 and 35 days of exposure. Venlafaxine and 5 known human venlafaxine metabolites were analysed through a novel analytical methodology based on ultrasound assisted extraction of target compounds from these tissues, followed by UHPLC-MS/MS analysis.

Metabolization of venlafaxine was more pronounced when fish was exposed via water than via feed. Two metabolites were detected in almost all fish tissues: N-desmethylvenlafaxine and N,N-didesmethylvenlafaxine, reaching until 8% of venlafaxine levels. The distribution of metabolites was as follow: liver ≈ brain > muscle > plasma. Metabolites were also detected in seawater at 7-23% of the concentration of venlafaxine. Under a climate change scenario a slight decrease in the accumulation of venlafaxine and corresponding metabolites were observed, though only when fish was exposed to the organic contaminant via water.

Acknowledgements

The research leading to these results has received funding from the European Union 7th Framework Programme (2007-2013) under the ECsafeSEAFOOD project (GA n° 311820). A. Marques (IF program) and A.L. Maulvault (SFRH/BD/103569/2014) acknowledge The Portuguese Foundation for Science and Technology. L.H.M.L.M. Santos acknowledges the Juan de la Cierva program (FJCI-2014-22377) and S. Rodriguez-Mozaz acknowledges the Ramon y Cajal program (RYC-2014-16707).

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Assessment of the Application of Encapsulated Glyphosate to Mitigate Environmental and Management Risks

PP Env Safe #20

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Agriculture has coexisted with major paradigms involving food production and the increasing use of crop protection products [1, 2]. How to produce more without harming the environment and without putting at risk the workers of the field and their families? Many studies have been conducted in response to these major challenges [3, 4]. With this purpose, this study evaluated the use of the herbicide **glyphosate** encapsulated in **alginate**: clay **composites** in order to promote an effective action of this pesticide without causing damage to the environment and human health.

Microspheres of average diameter of 3mm were obtained from suspensions of natural clay with granulometry of 100 MESH in aqueous solution

of sodium alginate 2,5% m / v (ratio $m_{\text{clay}} / m_{\text{alginate}} = 1: 2,5$). The experiments were carried out by separating areas of 1x1m² into four parts isolated from each other using an experimental randomized design. In one of the parts was used the conventional application, in the other , the microspheres, a third part without application (as a control) and the last one without removal of the vegetal cover.

It was observed that the efficiency in the action of the encapsulated herbicide was compatible with the conventional application, but using smaller amounts of glyphosate and without the risk of leaching of high amounts of the pesticide.

Acknowledgements

The authors are grateful to CNPq for the financial support.

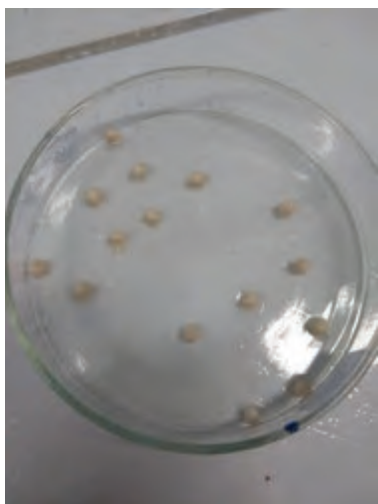
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A Simple System for Controlled Release of Glyphosate and Phosphorous based on Chitosan-clay Composite

PP Env Safe #21

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Controlled released systems on organic and inorganic matrices have been developed over the last years to introduce some pesticides on crop fields at minimal but efficient quantities in order to avoid the environmental and human health effects caused by the use of high amounts of these compounds [1]. Among the various matrices used, chitosan, a natural, low-cost and biodegradable biopolymer have been employed in delivery systems for pesticides and some nutrients [2,3]. Besides, chitosan has antifungal and antibacterial properties being considered too a source of carbon and nitrogen that helping in the mineralization of organic matter and the release of nutrients on soils promoting plants growth [4]. In this study, **glyphosate** one of the most widely used herbicides worldwide was encapsulated in chitosan-clay composite beads.

The natural clay (100 MESH granulometry) and glyphosate were dispersed on chitosan solution 5% (m/v) prepared in acetic acid.

The ratio of clay: chitosan was 1:4 (m/m). After mixing for a period of time the chitosan-clay beads were formed by ionic reticulation after dripping the suspension in sodium tripolyphosphate solution 15 % (m/v). The beads were characterized by elemental analysis (C,H,N), TGA and infrared spectroscopy. Measurements of incorporated phosphorous on beads after reticulation were done using VIS spectrophotometry [5]. The results for P_{total} showed a linear relationship between the mass beads and accumulated phosphorous after reticulation.

The preliminary results obtained in the experiments showed that the developed system may be an efficient way to the slow release of glyphosate herbicide as well as may be a potential source for supply of **phosphorous**, an essential nutrient in the plant metabolism at controlled rates on soils.

Acknowledgements

The authors are grateful to CNPq for the financial support.

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Sublethal Concentrations of Neonicotinoid Insecticides Directly Inhibit the Multixenobiotic Resistance (MXR) Mechanism in the Aquatic Invertebrate Model, *Dreissena* sp.

PP Env Safe #22

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Aquatic animals, both vertebrates and invertebrates are constantly exposed to environmental pollutants, which are easily transported into the body by diffusion through the skin and during respiration or feeding. To prevent the accumulation of harmful xenobiotics, both natural and anthropogenic, a complex cellular mechanism, the multixenobiotic resistance (MXR) provides the efflux mechanism, which removes the toxic xenobiotics from the cells and transports back into the extracellular space. Constant exposure to many toxic pollutants in a longer time enhances the activity of this system, while other chemical act as chemosensitizers, directly inhibiting this defence mechanism.

Mussels are among the most frequently used invertebrate animals in aquatic toxicology as their sessile habitat and filtration activity makes them suitable indicators to detect toxic chemicals in the environment and study the physiological and biochemical alterations evoked by toxic exposure. The presence and activity of the MXR mechanism were also established in these organisms, mediated by specific (Pgp, MRP) transport proteins, members of the membrane bound ATP binding cassette (ABC) protein superfamily.

We tested the isolated gill tissue model of the mussels *Dreissena bugensis* to study the activity of the MXR system in the presence of neonicotinoid insecticides. Adult animals (18-22

mm) were collected locally from Lake Balaton (Hungary). We used the formulated products of neonicotinoids commercially available in Hungary namely imidacloprid (Kohinor, *Makteshim Agan*), acetamiprid (*Mospilan*, Sumi Agro), thiamethoxam (*Actara*, Syngenta), clothianidin (*Apacs*, Arysta Life Science) and thiacloprid (*Calypso*, Bayer). The accurate concentrations of the active ingredients in each neonicotinoid product were confirmed by GC/MS chromatography.

Our results showed that sublethal (50-100 mg/l) concentrations of *Actara*, *Calypso* and *Kohinoor* enhanced the accumulation of (0.5 µM) concentration of rhodamine B (used as model substrate of the MXR) in the gill tissue. These results demonstrated direct inhibitory effects of the MXR system similarly to (20 µM) verapamil used as model inhibitor for reference. Testing *Mospilan*, (containing thiamethoxam) by the same tests, however, did not change significantly the rhodamine B accumulation.

Neonicotinoid type insecticides are generally regarded as selective neurotoxins for insects, inhibiting the nicotinic type acetylcholine receptors (nAChRs) in the central nervous system. Our presented results suggest, however, that neonicotinoid containing insecticides may also act on non-target animals, potentially inhibiting the MXR system as chemosensitizers.

Agro-environmental friendly processes and food chemistry

Bioaccumulation of Persistent and Emergent Pollutants in NW Portuguese Sea Urchins - Is There a Risk for Consumers?

PP AgroFood #1

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The preservation of marine ecosystems and the safety of harvested seafood are currently a global concern. Herein, evaluation of the presence of emerging and persistent contaminants (e.g. butyltins, polycyclic aromatic hydrocarbons, pesticides (including pyrethroids), pharmaceuticals and personal care products (PCPs), and flame retardants) in roe/gonads of sea urchins inhabiting coastal areas was carried out. Sea urchins are a highly prized worldwide delicacy, and the exploitation of this seafood has increased over the last decades, particularly in South West Atlantic coast, where this organism is harvested mainly for exportation. A sampling campaign was performed in three harvesting sites subjected to distinct anthropogenic pressures: Carreço, Praia Norte and Vila Chã, with sea urchins being collected in the north and south areas of each site.

Butyltins, pharmaceuticals and pesticides frequently used in agriculture, as well as several flame retardants and PCPs were not found at measurable levels. But within the large set of contaminants assessed some persistent and emerging contaminants, such as PAHs (e.g. fluorine, phenanthrene, pyrene, benz(a)anthracene and benzo(ghi)perylene), pyrethroids (e.g. transfluthrin, permethrin, cypermethrin and fenvalerate), some PCPs (e.g. galaxolide, tonalide and octocrylene) and some flame retardants (e.g.

some polybrominated diphenyl ethers (PBDEs), some organophosphate flame retardants (OPFRs) and some emerging brominated flame retardants (BFR)), were found at measurable levels in roe/gonads of sea urchins, though in general at low levels. The accumulation of contaminants in sea urchins roe/gonads reflected the anthropogenic pressures in the sampling site. Considering the growing interest in the commercial exploitation of the purple sea urchin *Paracentrotus lividus* in South West Atlantic coast, as a safe and healthy product it is important to monitor harvesting areas and to develop measures to preserve South West Atlantic coastal ecosystems.

Acknowledgements

Work financially supported by the European project 'Real time monitoring of SEA contaminants by an autonomous lab-on-a-chip biosensor (SEA-on-a-CHIP; No. 614168) and the research line INSEAFOD within the Structured Program of R&D&I INNOVMAR – Innovation and Sustainability in the Management and Exploitation of Marine Resources (Reference NORTE-01-145-FEDER-000035) funded by the Northern Regional Operational Programme (NORTE2020) through the European Regional Development Fund (ERDF). A. Marques acknowledges FCT for the IF2014 contract. C. Camacho acknowledges MARINALGAE4aqua Project (ERA-NETCOFASP/004/2015) for the research grant. Part of this work was conducted in the Unit of Environmental, Organic and Biochemical high resolution analysis-Orbitrap-LC-MS analysis of the University of Ioannina, Greece and the authors would like to thank the Unit for providing access to the facilities.

Migration of Bisphenol A (BPA) from Epoxy Can Coating in to Canned Meat Products and Food Simulants

PP AgroFood #2

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Metallic cans are protected against corrosion by the application of inner coatings based on bisphenol A (BPA) epoxy type resins. The synthesis of epoxy resins includes the condensation between BPA and epichlorhydrin to yield linear polymers, which are soluble and fusible. Thermosetting products, used in the internal coating for food and beverage cans, are obtained by curing soluble epoxy polymer with phenolic type reactants (novolacs or resols). Epoxy-phenolics are among the most chemically resistant coatings. Phenolic resins alone give excellent chemical resistance, while crosslinking with epoxy resins improves their adhesion and impact resistance [1]. BPA may remain unreacted when polymerization conditions or the curing process is insufficient. Consumers may be exposed to BPA when the residual monomer migrates from these coatings into foods, especially at elevated temperatures. BPA is among estrogenic xenobiotics that may affect the reproductive system and causes proliferation of breast cancer cells in vitro. Specific migrations limit (SML), which is the amount of the substance that can migrate from the plastic food contact material into the food, based on a specific risk assessment carried out by the European Food Safety Authority (EFSA), is for BPA currently 0.6 mg/kg of food or food simulant. EFSA has lowered the Tolerable Daily Intake (TDI) for BPA from 50 to 4 µg/kg bw/day in January 2015, and is temporary (t-TDI), pending the outcome of further studies [2]. Therefore, a new SML is in turn warranted on the basis of this new t-TDI.

The present study is undertaken to investigate migration of BPA from can coatings into preserved meat products, under different conditions of storage

time period and temperature, and with various degrees of the can damage. The meat products are packaged in cans made of electrolytic tinplate, produced by the special requirements of the Army of the Republic of Serbia, and protected inside with epoxy-phenolic, aluminum-pigmented coating. The structure of the uncured and cured epoxy polymer is examined by NMR and IR spectroscopy. Scanning Electron Microscopy with Energy Dispersive-X-ray Spectrometry (SEM/EDS) was used to identify cracks in the coating during induced mechanical damage. The SEM analysis is used for measuring surface of the induced damages. The concentration of BPA is determined in the meat products stored at room and elevated temperature (20 and 40 °C), within period of several months, in the content of undamaged and damaged cans. After the can is opened, the sample of the meat product was homogenized, extracted with acetonitrile and purified by QuEChERS-based methodology [3]. The concentrations of BPA are determined by LC/MS and compared with the EU maximum permitted levels for the canned food. The specific migration tests of BPA from epoxy coating into different food simulants (3 % acetic acid, 10 % ethanol and 50 % ethanol), were also done. The found level of BPA was in the range of a few tens of ppb.

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172062).

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Tocopherols Profile of Coffee Silverskin (*Coffea canephora*): Influence of Different Geographical Origins

PP AgroFood #3

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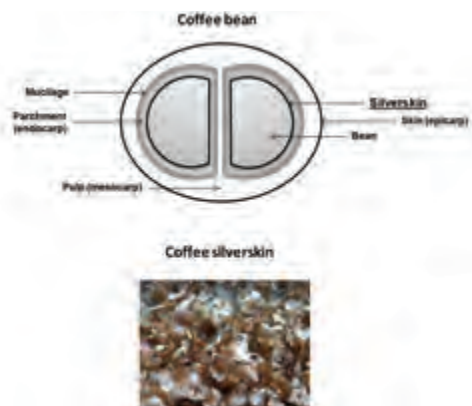


Figure 1. Adapted from [1].

The main coffee production is based on two *Coffea* species - *Coffea arabica* and *Coffea canephora* (arabica and robusta coffee, respectively) - from several coffee-producing countries, mainly localized on the equatorial Latin America, South Asia, India and Africa.

Coffee silverskin is a thin tegument that covers the green coffee beans (outer layer). During coffee roasting, it is discarded leading to a by-product of coffee companies.

The global coffee production in 2016 reached 151 million of 60 kg bags, and an increasing trend of world coffee consumption has been observed in the last years [2]. The industrial coffee production generates around 2 billion tons of waste per year (including coffee silverskin and coffee spent grounds).

Based on recent scientific data, coffee silverskin emerges as an added-value residue. It is a natural source of bioactive compounds that can be used in food, cosmetics or pharmaceutical fields, contributing to a sustainable and economic development of the coffee chain [3].

Vitamin E is known as the most effective natural lipid-soluble antioxidant, protecting cell membranes from peroxyl radicals and mutagenic nitrogen oxide species. Tocopherols (α , β , γ and δ) and the respective tocotrienols (that differ from tocopherols only in the saturation degree of their hydrophobic prenyl side chain) constitute vitamin E. These compounds are exclusively synthesized by photosynthetic organisms, and the vitamers profile varies according

to the species. Tocopherols content can be used in the discrimination of arabica and robusta coffee beans. Specifically, a high β -tocopherol content is usually found in arabica coffees [4].

The aim of this work was to evaluate, for the first time, the influence of six different geographical origins (Brazil, Uganda, Vietnam, Cameroon, Indonesia, and India) on the tocopherols profile of silverskin from *Coffea canephora* beans. Silverskin samples were gently provided by BICAFFÉ, a national coffee roaster.

The samples were extracted according to Alves et al. [3], with minor modifications and analysed by normal-phase HPLC. Three tocopherols (α , β and γ) were found in all silverskin samples, being α -tocopherol the major vitamer found. The Brazilian sample presented a significantly ($p < 0.05$) higher α -tocopherol amount (15.13 mg/100g): approximately 3-4 fold higher values than the remaining samples. Differences were also observed between the β/γ -tocopherol ratio among the different samples, showing that geographical origin can influence the tocopherol profile of coffee silverskin.

Acknowledgements

The authors thank the financial support to the project Operação NORTE-01-0145-FEDER-000011—denominada Qualidade e Segurança Alimentar—uma abordagem (nano)tecnológica. This work was also supported by the project UID/QUI/50006/2013 – POCI/01/0145/FEDER/ 007265 with financial support from FCT/MEC through national funds and co-financed by FEDER. S.M.F. Bessada acknowledges the PhD fellowship (SFRH/BD/122754/2016) funded by FCT.

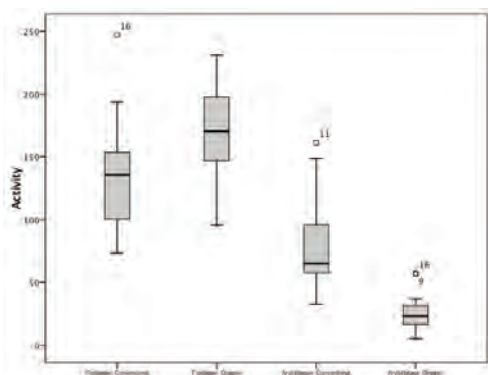
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Organic VS. Conventional Agriculture in the Douro's Vineyards: A Biological Perspective

PP AgroFood #4

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The vineyard landscapes of Douro Demarcated Region represent a strong cultural legacy that must be protected. Thus, it is essential to assure its sustainability in terms of soil functioning, since a decline in soil quality has a marked impact on vine growth, and grape quality. The loss of soil's biodiversity is of special concern since soil biota are involved in several functions and services such as: soil organic matter mineralization processes; soil physical structure maintenance; retention and cycling of nutrients, and various symbiotic relationships with plants [1, 2]. Thus, it is of upmost importance to understand the effects of different agricultural practices on soil's organisms.

Organic farming is seen as a sustainable alternative to conventional farming, mostly due to restrictions on the use of pesticides. In these context, it is expected that organic and integrated management practices have positive impacts on soil quality at long-term. However, this is not yet a clear issue since some studies could not prove that there are benefits of organic farming on global soil quality of vineyards [1]. Thus, with this work it is expected to contribute to understand the benefits of organic farming to soil quality, from a biological perspective.

The objectives of the present study were: a) evaluate the effects of different management practices on the retention functions of soils; b) to notice if there are alterations in the metabolic activity of soils,

mainly in the activity of enzymes of important biogeochemical cycles, in vineyard soils under different production modes.

The study area included two vineyards under conventional mode of production and one under organic mode of production, located in the Douro demarcated region. The main methodologies included the determination of soil physical-chemical parameters (e.g.: pH, organic matter content), tests with aquatic organisms (*V. fischeri*), and the activity of soil enzymes (dehydrogenase, cellulase, and phosphatase) [3]. Preliminary results showed some differences between the two sampling areas (e.g: physical-chemical parameters and enzyme activities). However, based on the results obtained until now, it's not evident which is the more beneficial production mode regarding soil quality. Moreover, in order to better understand the effects of different management practices, more parameters must be included and evaluated in different periods of the year.

Acknowledgements

This work was supported by the structural project INNOVMAR (NORTE-01-0145-FEDER-000035) within the research line (NOVELMAR/INSEAFOD/ECOSERVICES), and by the Strategic Funding UID/Multi/04423/2013 (CIIMAR), UID/GEO/04035/2013 (GEOBIOTEC), and UID/AMB/50017/2013 (CESAM RU), through national funds provided by FCT (Foundation for Science and Technology) and European Regional Development Fund (ERDF), in the framework of the PT2020 Partnership Agreement. FCT, also supported the work through an individual research grant attributed to A. Cachada (SFRH/BPD/100429/2014) and N. Durães (SFRH/BPD/81059/2011).

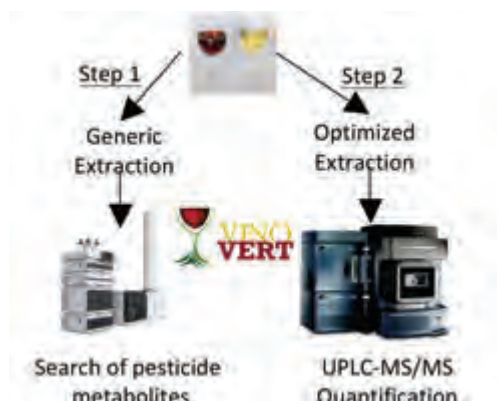
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Determination of Pesticides and Their Metabolites in Wine Using Liquid Chromatography and Mass Spectrometry

PP AgroFood #5

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Fungicides and insecticides are the two main groups of pesticides used in viticulture to prevent and to control diseases caused by fungi, insects and other agents. Their intense application, added to the physico-chemical properties of some systemic compounds, has led to environmental problems (pollution of surface water, persistence in soils,...); moreover, it has turned in the presence of pesticide residues in wines. Although the individual levels of pesticides in this food-stuff are relatively low, wine consumers perceive this contamination as a negative parameter impacting the commercial acceptance of wine. In addition, some scientific studies have highlighted health risk associated to exposure to certain pesticides, such as the neonicotinoid insecticides [1] and certain fungicides [2], which are related to breast cancer development [3]. Thus, European authorities are encouraging wine producers to face the reduction of pesticides uses in viticulture, evaluating the consumer acceptance of wines from vines more resistant to diseases, as well as the economic impact of reducing pesticide applications in the productivity of vineyards. The list of pesticides authorized to be applied in vineyards and their maximum residue levels (MRLs) in vinification grapes (residues in wine are not regulated) vary depending on producing countries [4]; thus, wine exportations can be affected by extremely low levels of residues, permitted in the producer country but not in that of final consumers.

Some recent studies highlight the need to determine not only the residues of pesticides existing in wine, but also to investigate the existence of metabolites and/or transformation products, with unknown toxicities. For example, imidacloprid was detected in white wine at 15 µg/L by Berset et al. [5], while the level of the imidacloprid-olefine metabolite was 331 µg/L in the same sample. Metabolites of other fungicides, often found in wine (e.g. fenhexamide) have also been found in other vegetable origin food-stuffs, although their presence in wine has not been reported.

This presentation shows occurrence frequencies of pesticides in commercial wine samples, from different countries. Moreover, it reports the identification of metabolite residues from their accurate MS and product ion scan spectra, obtained by LC-QTOF-MS, and their further confirmation with authentic standards. Extraction conditions for parent pesticides and identified metabolites are further optimized and their concentrations determine in commercial wines using UPLC-MS/MS. The existence of constant or variable concentration ratios between parent pesticides and metabolites in wine is also evaluated.

Acknowledgements

This study has been financially supported by E.U. FEDER funds through the Interreg Sudoe program (Vinovert project, SOE1/P2/F0246). I.C. acknowledges her postdoctoral grant to Xunta de Galicia.

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Fate and Effects of Uncoated ZnO Nanoparticles on Nine Crops Exposed in Two Agricultural Soils, a Calcareous Soil and an Acidic Soil

PP AgroFood #6

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The nanotechnology has a wide range of applications including those that deliberately release nanoparticles (NPs) into the environment.

The use of nanoformulations containing agrochemicals to soils provides an efficient way to apply pesticides and fertilizers in a controlled mode. The zinc oxide nanoparticles (ZnO NPs) are of particular interest due to their increasing incorporation into agricultural products [1].

Soil components and soil properties affect largely NPs behavior in the soil. Soil pH and organic matter mainly govern Zn chemical speciation, sorption/desorption process and its distribution in the soil [2] and hence, its availability to plants. The increased amount of Zn in the plant tissue displays not only visible toxic impacts but also biochemical ones as the generation of reactive oxygen species (ROS) or enzymatic alterations [3].

This work collects the results of a pot trial conducted to evaluate seed germination, growth and biochemical parameters affectation in nine crops growing in two agricultural soils containing ZnO NPs at soil concentrations of 10, 20, 225, 450 and 900 mg Zn kg⁻¹ (dry weight) (compared to controls non-Zn-treated soils). In addition, the behavior of Zn in these soils was studied by the determination of its potential availability, and by the Zn uptake in roots and later translocation of Zn to the aerial parts of the plants.

Two soils with different physicochemical features were used, a calcareous (pH 8.5) and an acidic soil (pH 5.4). The studied plants were wheat, maize, radish, bean, lettuce, tomato, pea, cucumber and beet. Seeds of the mentioned plants were sown and grown for 45 days under controlled conditions, 16

h light and 20±2 °C. Three replicates of control and treatments were used. After harvest, total and available concentration of Zn ([Zn]) in the soils were analyzed and correlated with [Zn] in plants (both roots and shoots).

As expected, the available [Zn] in the calcareous soil was very low (< 2 mg kg⁻¹) and phytotoxic effects were limited to a slight decrease of biomass of wheat, cucumber and beet at the highest Zn treatment and, an increase of biomass of maize and radish. As a whole, no pattern was found for biomarkers, only ascorbate peroxidase (APX) and catalase (CAT) seemed to decrease in most plant species and [Zn]. By contrast, in the acidic soil, the available [Zn] increased with total [Zn], reaching 35% of initial total Zn at the 450 and 900 mg Zn kg⁻¹ soil treatments. The germination of seeds of bean, tomato, lettuce and beet was reduced and the growth of most of the crops was seriously affected except for maize and pea. The calculated EC₅₀ (growth) values in acidic soil were in a range of 110-520 mg Zn kg⁻¹. The biomarkers as malondialdehyde (MDA) or protein contents increased only in maize. In pea, chlorophyll, MDA and CAT decreased and ROS and APX increased.

The toxic effects on germination and growth correlated better with total [Zn] than with the available [Zn] in both soils. [Zn] in aerial parts of plants showed good correlation with [Zn] in soil (total and bioavailable).

BCFs of most plants grown in the calcareous soil varied in the range 0.5-2 for both shoots and roots. However, under acidic conditions, BCF were in the range 2-6 also for both shoots and roots. Differences in BCF were more due to plant species than to the tested parts of the plants.

Acknowledgements

This work was financed by the Spanish projects RTA2013-00091-C02-01 and 02.

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Soil pH Effects on the Toxicity of Zinc Oxide Nanoparticles to Soil Bacterial Communities

PP AgroFood #7

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The environmental levels of ZnO nanoparticles (nZnO) are increasing continually given the widespread and expanding applications of this material. Soil pH appears to be one of the key factors affecting the behavior and toxicity of metal nanoparticles in soil. Soil microorganisms play a very important function in geologic, hydrologic and ecological cycles, maintaining soil health, ecosystem function and production. Little research has been conducted on the interaction between nZnO and microbial communities in vivo that would mimic the natural environment [1]. In this work, we evaluated the role that soil pH (an acidic soil pH 4.7 and a calcareous soil pH 8.5) plays on the toxicity of nZnO to soil bacterial communities. The soils were spiked with 0 (control), 0.1, 1, 10, 100 and 1000 mg Zn/kg soil as nZnO. Subsamples were taken at 1, 30, 90 and 180 days to analyze available Zn soil concentration and microbial toxicity. The effects studied were the changes on carbon and nitrogen transformation and the alterations on soil microbial metabolisms (dehydrogenase (DH) and acidic (ACP) and alkaline (ALP) phosphatases activities). Moreover, changes in microbial communities were determined by the microbial community-level physiological profiles (CLPP) method.

The available Zn soil concentration was remarkable higher in acidic than in calcareous soil. There were not differences in available Zn soil concentration in the treated soils at low loading rates (<10 and

<100 mg Zn/kg in acidic and calcareous soils, respectively) compared to control soils.

Toxic effects of nZnO in respiration were observed only at the highest concentration and were less than 25% related to control in both soils. nZnO generally did not affect nitrification in both soils. In the calcareous soil, the DH activity increased in the 100 and 1000 mg Zn/kg treatments at 180 days, with percentages between 30-80%. By contrast, it decreased at the highest nZnO dose over the assay (70-87%), in the acidic soil. Dose of 1000 mg Zn/kg inhibited the activity of ACP at 180 days in basic soil and over the assay in acidic soil. The ALP activity showed the maximum differences between both soils, with values very close to the control in calcareous soils and dose-response increases in acidic soil that increased along the time. The higher effects found in acidic soil than in calcareous soil seems related with the highest bioavailability of Zn in the acidic soil. The enzymatic activities did not correlate to microbial biomass (respiration assay). This suggests that the changes in enzymatic activities were not driven by changes in microbial abundance, but in soil microbial populations [2]. The average utilization of the C sources increased in both soils along 30 days. Then, values of average well color development, richness and Shannon-Weaver index were reduced to virtually zero in calcareous soil. In acidic soil, the highest dose produced an elevated increase of bacterial growth without changes in their metabolic profiles over time. Microbial biomass represents the entire spectrum of the catabolic functions of the microbial communities, while CLPP is confined to only a subpopulation of cultivable aerobic microorganisms. This possibly explains the differences between the microbial parameters analysis and microbial physiological profiles results.

Acknowledgements

This work was financed by the Spanish projects RTA2013-00091-C02-01 and RTA2013-00091-C02-02.

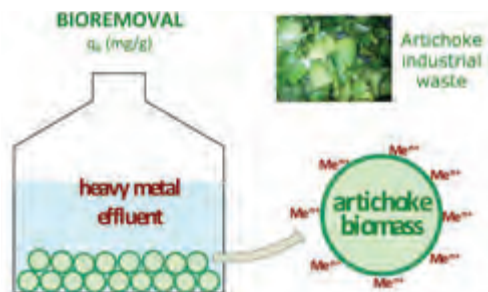
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Taguchi Design-based Enhancement of Heavy Metals Bioremoval by Agroindustrial Waste Biomass from Artichoke.

PP AgroFood #8

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Water pollution by heavy metals is considered a worldwide environmental concern. These pollutants are highly toxic and persistent and therefore tend to bioaccumulate in the food chain, with potential chronic hazards to human beings and adverse impacts to the ecosystem [1].

Recently there has been increased research interest in the application of lignocellulosic agricultural by-products to develop low-cost adsorbents for water detoxification to reduce environmental problems [2]. Food processing activities produce large amounts of waste and by-products. Artichoke is an edible plant native to the Mediterranean region produced abundantly in Spain. The industrial processing of this plant generates a lot of leafy lignocellulosic waste that could be efficiently and sustainably valorized.

Bioremoval with low-cost sorbents is proved to be an excellent alternative technology for the treatment of heavy metal-containing aqueous effluents [3], and agroindustrial waste biomass from artichoke is a promising sorbent that should be investigated. In this work, Taguchi (DOE – Design of Experiment) approach of orthogonal array experimental design was used for multivariate optimization of the bioadsorptive recovery of Cd(II), Pb(II), Cu(II) using agroindustrial waste from artichoke as sorbent.

Agroindustrial waste biomass from artichokes (*Cynarascolymus* L.) grown in the Region of Murcia was used. The starting material, mainly composed of external bracts and stems was dried at 70 °C for 24 hours. The dry material was then milled and passed through a sieve of 18 mesh (1 mm) to obtain the sorbent powder.

Effective factors on adsorption process such as pH, sorbent dosage, initial metal concentration and temperature were considered in each case. So, four factors at three levels each one were investigated according to a $L_9(4^3)$ experimental set for each metal. The levels of each parameter were fixed according to typical values reported in the bibliography [4]. In each run 100 mL of metal solution at different initial concentration, sorbent dosages, temperatures and pH values was shaken at fixed contact time (24 hours). Afterward the supernatant was filtered and collected for analysing metal concentration in an ICP-OES system. The metal uptake capacity (q_e) as, mg of metal bioremoved per gram of sorbent, was then calculated.

The Langmuir, Freundlich and Temkin adsorption isotherm models were applied to the experimental data. To investigate the sorption mechanism the pseudo-first order model, the pseudo-second order model and the intraparticle diffusion model were applied at different experimental conditions.

The results confirm that Taguchi methodology is a suitable tool to determine the operating variables that significantly influence the bioremoval capacity of heavy metals by artichoke biomass.

The artichoke biomass is suited for bioremoving heavy metals from aqueous solution, showing preference for the sequestration of Pb(II), followed of Cd(II) and Cu(II) with q_{max} values of 68,5; 33,3 and 26,3 mg/g respectively.

Acknowledgements

This research is part of the QUIMYTEC R&D group. The excellent technical assistance of M. Vázquez and L.A. Alcolea (SAIT, UPCT) is greatly appreciated.

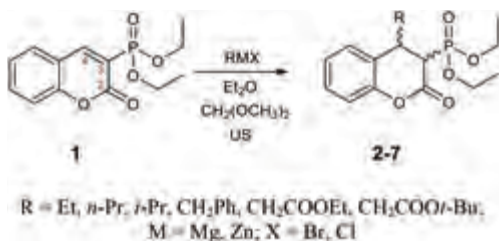
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Efficient Green Method for the Synthesis of 3,4-Disubstituted Coumarin Derivatives

PP AgroFood #9

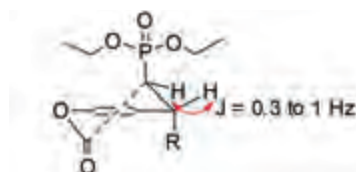
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Coumarins are natural compounds with wide application in the organic synthesis as acceptors in different organic reactions with nucleophilic reagents and dienophiles in Diels-Alder reactions as well in reactions of [2+2] or [2+3] cycloaddition and as intermediates in the synthesis of products of practical interest.

On the other hand, this class of compounds has an important role as antimicrobial, antiviral, anticancer, enzyme inhibition, anti-HIV, and antioxidant agents, they even possess the ability to influence the central nervous system. A third large area of application of the coumarin derivatives is in the modern technologies. They can be applied as excellent luminophores and laser dyes. Coumarin derivatives may be used as ligands for metal complexes and for modification of organic and inorganic supports.

Here in we present our study on the chemical behaviour of 3-ethoxycarbonyl and 3-phosphonocoumarin with series of preformed organomagnesium compounds. Grignard, Reformatsky and Ivanov's reagents were used as nucleophiles too. Our investigations represented them as good acceptor in the 1,4-addition reactions. The group noticed that when ultrasound is used the desired products are isolated with better yields for shorter reaction time and this method has better reproducibility than the typical condition for the Michael reaction. *Syn*-addition to the C3-C4 bond of the 2-oxopyran ring is observed which leads to *anti*-disposal of the incorporated group and the substituent in third position.



Scheme 1. Conformational analysis on the coupling constants of H-3 and H-4.

The compared coupling constants of spin-spin interaction of H3-H4 protons confirmed the formation of the *trans* isomer in all reaction conditions when nucleophilic addition to 3-substituted coumarins took place.

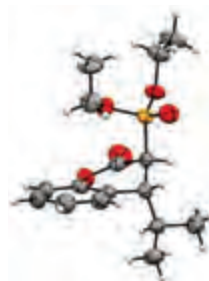


Figure 1. Molecular structures of compound 4 in the crystal. ORTEP representation with thermal ellipsoids.

Importantly, the method is useful for the preparation of 3,4-disubstituted chromanes with an exact configuration of the C3-C4 bond. The stereochemistry of the products 2-7 was determined by NMR spectroscopy and single crystal X-ray spectra of product 4. All products were isolated as *trans* isomers with pseudoaxial antiperiplanar disposition of the substituents at positions 3 and 4.

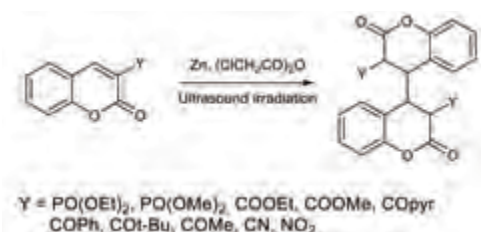
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This work was supported by the H2020 project "Materials Networking".

Eco-friendly Conditions For The Synthesis Of Biscoumarin Derivatives

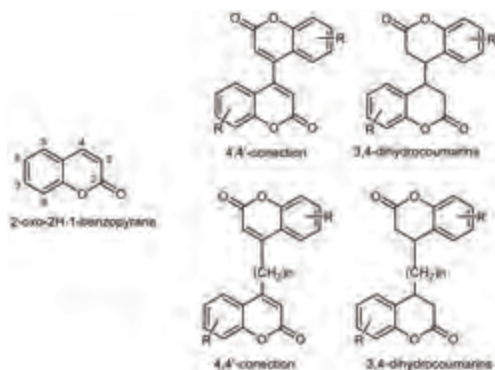
PP AgroFood #10

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Coumarins and their oxo-chroman analogs are a large class of compounds that have attracted the group interest for a long time due to their biological, physical and optical activities as well as for their applications in the agrochemistry. They have shown to be useful as antitumor, anti-HIV agents and as CNS-active compounds. Furthermore, they have been reported to have multiple biological activities – anti-coagulant, anti-inflammatory, anti-microbial, antioxidant as well as good enzyme inhibition properties [1].

During the research of the properties of coumarin compounds and their derivatives, several biscoumarins and their oxo-chroman analogs were isolated from plants and later been synthesized [2]. There are different types of dimerized coumarin systems from which 3,3'-, 4,4'-, 3,8'-, 3,6'-, 8,8'- and 8,6'-biscoumarins are known.



Common features for all these compounds are that they are all isolated from different plants and possess interesting biological activity. The biscoumarins

kotanin and desmethylkotanin, for example, were isolated from *Aspergillus glaucus* that have been found to be mycotoxins. Another examples are toddasiatin (3,3'-linkage), isolated from the root wood of the *T. Asiatica* plant (family Rutaceae), and 4,4'-biisofraxidin (4,4'-linkage), isolated from the root cultures of *Impatiens balsamina* L. and can be used in the case of abscesses, nail ingrowth, and dermatophytosis. We are interested in finding simple procedure for the synthesis of 4,4'-bis-2-oxo-chromans.

For this type of compounds few synthetic procedures were reported in the literature based on the total synthesis of 4,4'-biisofraxidin [3] electroreductive hydrocoupling [4], photoreactions [5] or electrochemical reduction [6]. All of these methods have some disadvantages – long reaction time, unsatisfactory yields or requirement of complex equipment. Therefore the present paper reports the application of ultrasound irradiation in the formation of bis-2-oxo-chromans and their derivatives.

Acknowledgements

Authors are grateful to Operational programme "Science and Education for Smart Growth", project BG05M2OP001-2.009-0028"

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Total and Inorganic Mercury Quantification in Bulgarian Wines

PP AgroFood #11

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Mercury as a priority pollutant with extremely high toxicity is under strict control in all products for human consumption. Wine is a widely consumed alcoholic beverage all over the world. Mercury presence in wines is a result of aerosol particles precipitation on the grape as well as mercury absorption from grape vines from ground waters and soils. Though the mercury content in wines is very low its daily intake could be physiologically significant. Hence, mercury determination in wine is important and requires application of analytical techniques, which ensures quantitative determination with high sensitivity and low detection limits. In the present study 32 samples monovarietal wines with defined geographical and botanical origin from Bulgaria are analyzed in order to determine total and inorganic Hg(II) in them. Analytical methods developed are based on: (i) direct total and Hg(II) measurement in wines by CV-AAS and (ii) total Hg determination after preconcentration using silicagel, modified with L-cysteine, followed by CV-AAS measurement. In the first case optimal conditions for direct Hg(II) determination are defined taking into account matrix interferences from wine components (proteins, polysaccharides, carboxylic acids, complex formation ligands) on the reduction of Hg(II). Various model compounds like cysteine and thiourea (wine proteins), tartaric acid, citric acid and EDTA, ethanol have been used for careful study of the degree of matrix interferences and their elimination by using suitable pH, type and concentration of reducing agent and reduction time. Determination limits of analytical procedure developed is 0.1 µg/L which is much below the

permissible limits of 5 µg/L, according to OIV. More than 30 samples Bulgarian wines with defined botanical and geographical origin have been analyzed. Results obtained showed that for all of them Hg(II) content is below the maximal permissible level, however also below the detection limits of direct CV-AAS determination. In order to define Hg content in Bulgarian wines analytical procedure which includes preliminary Hg enrichment was developed. The procedure is based on solid phase extraction of Hg(II) using L-cysteine modified silica gel followed by CV-AAS measurement [1]. The optimal conditions for preconcentration step are achieved after carefully optimization of amount of sorbent used, pH of wine sample, sample volume, flow rate of sorption and elution stage, type and concentration of eluent. Results obtained show Hg(II) content in Bulgarian wines in the range 0.03 – 0.07 µg/L. The analytical method developed for total Hg determination is validated by parallel analysis of wine samples by ICP-MS after wine digestion.

Acknowledgements

The authors are grateful for financial support of National Bulgarian Science Fund Grant № B02/22. Elisaveta Mladenova is also grateful to Operational programme “Science and Education for Smart Growth”, project BG05M2OP001-2.009-0028.

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Production of Bioethanol from Corncob via Modified Two-Stage Hydrolysis with Different Acids

PP AgroFood #12

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Fermentation Period (h)	Bioethanol Produced (cm ³)/ 50 ml of Sugar Solution		
	HF-P	HF-S	HF-H
12	17	14	13
24	26	19	18
36	34	27	26
44	39	30	28
60	22	23	24

Abstract

Corncob is a biomass waste material generated from maize processing activities with potential for bioethanol production. Therefore, the aim of this work was to study the production of bioethanol from corncob via modified two-stage hydrolysis with different acids. Pretreatment of the corncob was carried out with liquid hot water and then hydrolyzed with three different acids (sulfuric acid, H₂SO₄; phosphoric acid, H₃PO₄; hydrochloric acid, HCl) to obtain Hydrolyzed Filtrate (HF) and Hydrolyzed Residue (HR) samples. This was followed by fermentation of hydrolyzed samples for 72 hours using Baker's yeast and then distillation at 78.5 °C to yield bioethanol. Results

obtained showed that for HF samples, production of bioethanol from corncob using H₃PO₄ gave the highest yield of 151 cm³ and this was followed by 130 cm³ obtained using H₂SO₄, while HCl acid gave the lowest yield of 125 cm³. It was also observed that for HR samples, highest bioethanol yield of 218 cm³ was noted for H₃PO₄, this was followed by 180 cm³ using H₂SO₄, while the lowest yield of 166 cm³ was recorded using HCl. Thus, production of bioethanol from corncob was noted for higher yield using H₃PO₄, this was followed by H₂SO₄, while HCl gave the lowest yield. Furthermore in comparison, production of bioethanol from HR samples was noted for higher yield than production from HF samples.

Acknowledgements

The authors hereby acknowledge the support of Tertiary Education Trust Fund (tETFund) Nigeria for the conference attendance sponsorship.

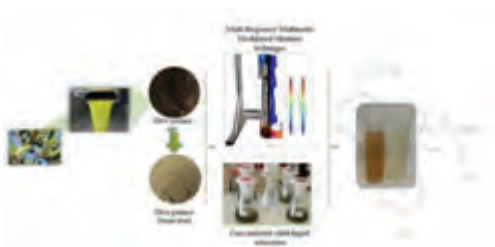
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A New Sustainable Process to Recover Olive Pomace Antioxidants

PP AgroFood #13

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The olive oil industry is becoming one of the larger agro-food business sectors. This industry is related with high amounts of waste production [1]. One of the major outputs is olive pomace (OP). OP characteristics depend of the technique applied for extracting olive oil: two-phase or three-phase processes. In the two-phase process, no water is added and a humid semi-solid pomace is obtained. Despite resulting from an eco-friendly system, this OP has a high water content, which difficult its transport and storage [2]. Moreover, OP is phytotoxic due to its high phenolics content (water-soluble compounds). Although those pomace compounds are a hazard for the environment, they can be recovered for human health/well-being applications [2].

The conversion of OP into added-value products is a great challenge and simultaneously reduces the environmental burden. Green methodologies have been explored to achieve maximum yields of extraction, at low-cost, in a minimum period of time [3].

This work aimed to compare the efficiency of a new sustainable process focused on antioxidants extraction - Multi-frequency Multimode Modulated (MMM) vibration technique - with a conventional solid-liquid extraction (40 °C; 60 min; 600 rpm) using only water as solvent. In the MMM technique, different input electric powers (90 and 160 W) and extraction times (5 and 10 min) were used. OP samples were from an olive oil processing unit in Trás-Os-Montes (Portugal) and freeze-dried before analysis.

The efficacy of extraction was assessed by analysing the total phenolics content (TPC) of

the extracts, as well as their antioxidant activity. This was determined using two complementary methods: DPPH[•] scavenging and FRAP assays.

Compared to the conventional extraction, the acoustic probe allowed a higher recovery of antioxidants. In only 5 min and using an input electric power of 160 W, the sonication probe allowed a significantly higher ($p < 0.05$) yield of extraction (\approx more 60% of total phenolics) when compared to the conventional process (60 min): 402 and 256 μg gallic acid equivalents/mL, respectively. The DPPH[•] scavenging activity and FRAP results were in agreement with TPC. Indeed, significantly high correlations ($r > 0.828$) were obtained between the parameters analyzed, showing that the antioxidant activity is correlated to the phenolic compounds present in the extracts.

MMM vibration process seems to be a very promising sustainable and effective technique to extract antioxidants from OP. Additionally, OP rich extracts can be further valorized and used in food or cosmetic industries.

Acknowledgements

The authors from REQUIMTE/LAQV thank the financial support to the project Operação NORTE-01-0145-FEDER-000011-Qualidade e Segurança Alimentar- uma abordagem (nano) tecnológica. This work was also supported by the project UID/QUI/50006/2013 - POCI/01/0145/FEDER/007265 with financial support from FCT/MEC through national funds and co-financed by FEDER.

M. Antónia Nunes acknowledges the PhD fellowship (SFRH/BD/130131/2017) funded by FCT.

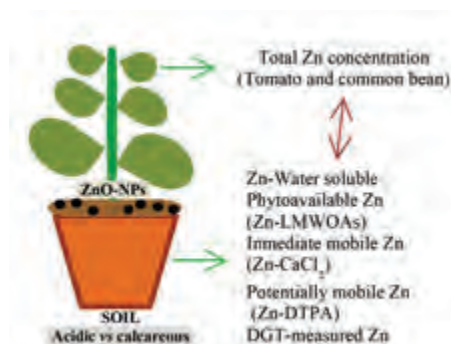
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Soil Chemical Extraction Tests to Estimate Zinc Plant Availability from Engineered ZnO Nanoparticles Applied to Agricultural Soils

PP AgroFood #14

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The Zn oxide nanoparticles (ZnO NPs) have been proposed as a possible Zn fertilizer to alleviate Zn deficiency in soils [1]. The NPs in the soil are subjected to chemical and biological reactions and physical processes, and they can be either retained in the solid matrix or mobilized into pore water, which have a profound impact on their availability. Using the experience gained from studies on chemical availability of trace metals in soils, similar extraction techniques are beginning to be used to assess the availability of metal-based engineered NPs in soils [2]. However, there are still no studies on the selection, comparison and validation of these chemical extraction techniques to estimate in agricultural ecosystems the availability for plant uptake of metals from metal-based NPs in soil. The aim of this investigation was to find effective chemical extraction methods for an effective risk assessment of crop exposure to ZnO NPs in agricultural soils. Chemical measurements in soils could estimate the risk of plant accumulation of Zn if a correlation between the resulting soil chemical values and plant metal amounts can be demonstrated.

A greenhouse pot experiment was performed with two different crops (cherry tomato and common bean), which were grown in two agricultural soils with different pH: an acidic soil (pH 5.4) and a calcareous soil (pH 8.5). The upper layer of the soil in the pots were spiked on average with 3, 20 and 225 mg Zn kg⁻¹ (Zn basis) as dry powder of ZnO NPs (<100 nm, Sigma-Aldrich). The green beans and cherry tomato fruits were recollected gradually. At the end of the experiment the different vegetative parts of plants (root, stem and leaf) were separated

and soil samples were taken from the upper layer of the soil. The total Zn concentrations in soil and plant tissues were determined. The water soluble Zn in soil (Zn-WS) was extracted with double-deionized water. The Zn phytoavailability in soil was assessed by a mixture of LMWOAs (10 mM combined organic acid solution of acetic, lactic, citric, malic and formic acids in a molar ratio of 4:2:1:1:1, respectively) (Zn-LMWOAs). The immediate mobile Zn fraction in the soil was estimated with 0.01 M CaCl₂ (Zn-CaCl₂) and the potentially mobile Zn was predicted with 5 mM DTPA (Zn-DTPA). Additionally, available concentration of Zn in soil was measured using the technique of DGT (diffusive gradients in thin films).

In order to find a valuable extraction method for different crops, the results obtained for common bean and cherry tomato were jointly considered. In acidic soil, Zn bioaccumulation pattern in the different plant tissues (root, stem, leaf or fruit) were successfully simulated by all soil chemical extraction tests used. In contrast, Zn-extractable amounts in calcareous soil were not or poorly correlated with the Zn concentration in plant. The CaCl₂-extractable Zn only weakly correlated with the Zn content in the roots and stems. The Zn amounts in plant fruits exclusively correlated with the LMWOAs-extractable Zn, suggesting that this soil extraction may be a valuable method in order to assess Zn accumulation in edible part of crops of Zn applied to calcareous soils as ZnO NPs. However, the DTPA-extraction method could not predict successfully the Zn accumulation in plant tissues. The results showed that in the high concentration treatments (225 mg kg⁻¹) the amounts of DTPA-extractable Zn were too high in comparison to Zn amounts in plant.

Acknowledgements

This work was financed by the Spanish projects RTA2013-00091-C02-01 and RTA2013-00091-C02-02.

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An Ecofriendly Agar Based Method for Stain Removing from Stone Materials

PP AgroFood #15

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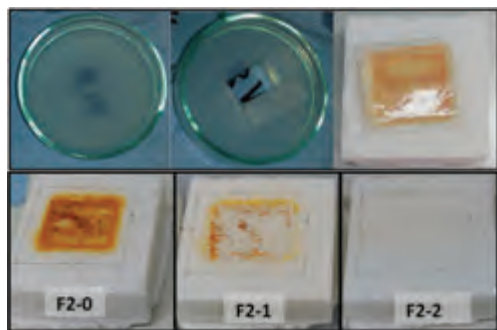


Figure1. Appearance of the pulticesand treated surface at the beginning and after application of 1 and 2 pultices.

Metallic elements composing building facades are often oxidized due to their exposition to the environment. The resulting rusts are the precursor of the unsightly bright colour stains formed on the adjacent stone surfaces due to the continuous leaching of their components. Iron based parts are the most common and thus, iron stains are the most widely studied in order to get effective cleaning methods. The composition of the iron stain depends on the environmental conditions under they form, but it can evolve to other more stable phases. In order to remove the stain formed on the stone materials different kind of strategies can be followed, starting from abrasive methods suchas as sand blasting to more selective stone preservative methods based on liquid formulations. A selective and controled aplication as well as the elimination of cleaner residues (often harmful for the environment and the stone material) is difficult and therefore, they accumulate into the stone. Agel gels have demonstrate to be a suitable ecofriendly alternative cleaning system for other target stains i. e. Black crusts [1]. The aim of this work was to develop a cleaning method based on agar gel pultices to remove iron oxide stains from stones. Agar dissolves in hot water ($T > 85^{\circ}\text{C}$ aproximately) but also other solvents are posible to be used in the preparation of the gel. In this sense, considering that iron oxohydroxides are composing the stains, the cleaning strength of the formula was reinforced taking advantage of the complexant capacity of a ligand. In order to achieve a suitable formulation,

agar and ligand content as well as the pH of the mixture was optimized by means of a Central Composite Design (CCD). Once the reagents were mixed at the required conditions and heated in order to dissolve, each mixture was poured and cooled into a Petri dish to get a 0.5cm thick gel. On the other hand, stone tests (white calcitic marble of $5 \times 5 \times 2$ cm) were prepared by continuously soaking oxidized Corten steel fragments with deionized water till the stain was formed (see F2-0 in Figure 1). The stains were characterized by colorimetry (CIELab2000) and Raman spectroscopy to select the tests the most similar for the assays. Agar gel pultices of the same size were then cut an applied for 24h as shown in Figure 1. The exhaust gel was then dissolved with HNO_3 : HCl (1:3) in order to quantify the extracted total iron by Flame-Atomic Absorption Spectrometry. According to the analyses, the presence of agar does not produce a matrice effect during the measurement and the results of the CCD revealed that %1 agar and %3 ligand at $\text{pH}=7$ were the optimum values in the studied ranges to remove the lepidocrocite composed stain.

Besides, the aplication method was also studied. First aplication times of 4, 8, 16, 24 and 48 hours were studied and 24 was stablished to be the most efficient. Second, 24 hour application replicates were found to be more efficient than a long lasting unique poutlice, which is and advantage because it allows to selectively apply the consecutive gel pultices only in the areas where the stain remains. Finally, the cleaning method was validated at the defined aplication conditions.

Acknowledgements

This work has been supported by the DISILICA-1930 project (ref. BIA2014-59124-P) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

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Proximate, Fatty Acids and Metals in Edible Marine Bivalves: Beneficial and Risk for Consumers Health

PP AgroFood #16

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The dietary habits are among the major concerns of man, since the ingestion, both in amount and quality of the nutrients for good health of the human organism is fundamental. Seafood is a nutrient rich food source and its consumption has been increasing rapidly in view of its nutritional quality. Traditionally bivalves are considered a delicacy in many countries of the world and play an important role in human's diet. [1]

The aim of this study was to determine the proximate, lipid class, fatty acids composition and metals (Hg, Cr, As, Cd, Pb and Ni) content of seven commercially important bivalve species (*Flexopecten glaber*, *Mimachlamys varia*, *Modiolus barbatus*, *Mytilus galloprovincialis*, *Ostrea edulis*, *Ruditapes philippinarum*, *Solen marginatus* and *Venus verrucosa*) from the Ionian Sea (Southern Italy, Mediterranean Sea). In order to investigate public healths associated with consuming seafood from this area the weekly intake of metals in children, adolescents and adults was also estimated. The results showed that all species may be considered as food item with interesting dietetic properties due to their good proteins content that ranged from 10 g/100g in *S. marginatus* to 4.60 g/100g in *R. philippinarum* low lipid (within a range of 1- 3 g/100g for *V. verrucosa* and *M. barbatus*, respectively). Among lipid classes phospholipids are the major group, in all species examined. Cholesterol showed low levels within a range of 3.2-13.7% for *F. glaber* and *V. verrucosa*, respectively. Fatty acid profile, showed significant differences among species ($p < 0.05$).

Both the amount of lipid (rather low) and the proportion of saturated (SAFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids found in these bivalves contribute to a healthful diet. In all species, the relatively high levels of n-3 PUFA and lower amounts of n-6 PUFA provides a high n3/n6 ratio that is favourable for human health. [1]

The n3/n6 and PUFA/SAFA ratios, which are indicators of lipids nutritional quality in food, indicated that the consumption of these species could be beneficial to human health [2,3]. A higher ratio is of great importance in order to diminish coronary heart diseases, plasma lipid levels and cancer risks. The highest ratios of n3/n6 and PUFA/SAFA were obtained from *M. varia* (6.65 and 0.94, respectively) and *M. galloprovincialis* (7.19 and 0.85, respectively). *R. philippinarum* showed the lowest ratios (2.93 and 0.25, respectively).

As regard metals, *M. barbatus* showed the highest values of As (10.5 mg/Kg w.w), Pb (0.7 mg/Kg w.w) and Hg (0.07 mg/Kg w.w). Cd was highest in *F. glaber* (0.95 mg/Kg w.w) while Cr and Ni in *S. marginatus*. In comparison with the permissible limits set by EC Regulation 1881/2006 for Cd (1.0 mg/Kg w.w), Hg (0.5 mg/Kg w.w) and Pb (1.5 mg/Kg w.w), no species showed values above established concentrations.

The estimated intakes of metals through the consumption of these bivalves species not exceed the provisional tolerable weekly intake (PTWI) recommended by the Joint FAO/WHO [4] Expert Committee on Food Additives for all metals except for Cd and As.

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Hydrothermal Extraction of Antioxidants from Paulownia Waste Fractions

PP AgroFood #17

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Paulownia is an arboreal genus in which nine species are considered fast growing [1]. It is native to China although its natural distribution ranges from tropical to temperate-cold climates [2]. Species of this genus have been introduced in different countries such as Japan, the USA and other regions such as Europe. In Spain, species such as *Paulownia elongata* x *fortunei* have been introduced for the production of biomass [3]. This clone differs to others because it corresponds to a natural hybrid that combines in its genotype the characteristics of two species highlighted by rapid growth and good adaptability to climatic conditions of drought and low temperatures [4]. Wood of this specie has been used mainly in the paper and construction industry. In addition, this genus is suitable for recovering abandoned agricultural land or for restoring soils, where special emphasis is placed on the production of biomass [5]. This work aims at selecting the extraction conditions for the utilization of different components present in waste fractions from *Paulownia elongata* x *fortunei* (leaves, petioles and bark) in order to provide a cheap source of bioactives with antioxidant activity, attractive to different industrial applications including wood, food and cosmetics.

The raw material has been provided by Maderas Alvarez Oroza S.L. located in Foz (Lugo), in June 2017. Subsequently, it has been dried at room temperature to a humidity below 10%, in order to facilitating its storage before use. Each of the parts studied (leaves, petioles and bark) have been separated and ground to an optimal particle size for treatment. Firstly, each raw material has

been characterized to know its composition and then a hydrothermal study with pressurized hot water under subcritical conditions (considered an environmental and clean technology) in the range 140-240 °C has been carried out to determine the optimal conditions. Yields were determined gravimetrically, total phenols were determined by the Folin-Ciocalteu method and the ability to scavenge the ABTS radical was expressed as Trolox equivalents.

For leaves, petioles and bark, sugars solubilization ranges were 40-60%, extracts 7-20%, ash 2-10% and the acid insoluble residue was 15-35%. Both the total phenolic content and antioxidant capacity increased with the treatment temperature in the studied range, but maximal yields were attained at 160-180 °C.

Acknowledgements

This work has been funded by the Ministry of Economy and Competitiveness thanks to the project: Multi-stage processes for the integral use of macroalgae and vegetal biomass (CTM2015-68503-R). PRS thanks the Spanish Ministry of Economy and Competitiveness for her FPI grant (BES-2016-076840).

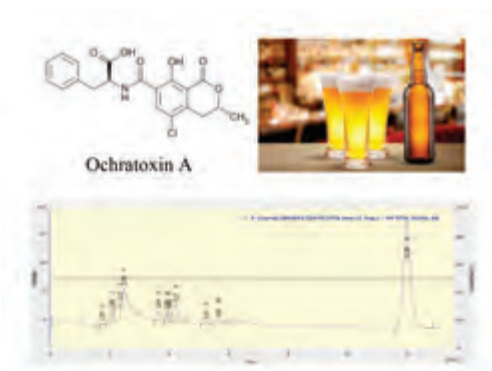
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Ochratoxin A in Different Beers from Portugal: Occurrence and Exposure Evaluation

PP AgroFood #18

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Ochratoxin (OTA) is a mycotoxin produced by some fungi species, namely *Penicillium verrucosum*, *Aspergillus ochraceus* and *Aspergillus niger* [1,2]. Although OTA possesses other toxic properties, it is mainly known for its nephrotoxicity. It is also a cumulative toxic compound due to the fact that it is easily absorbed by the digestive system but slowly excreted through the urinary system. It has been classified by IARC as a possible human carcinogen [1,2].

When compared to other ochratoxins, OTA is considered to be the most toxic, and it is also the most relevant to food safety [1,2]. For this reason, it was deemed essential to determine and quantify the concentration of OTA in the beer [3] consumed in Portugal by liquid chromatography with fluorescence detection (LC-FD).

Ten mL of beer, added of 4% sodium bicarbonate and PBS and centrifuged were loaded into the Ochratoxin IAC columns. After a washing step with Mili-Q water and elution with methanol, the eluate was dried. Twenty μ L were injected using a mobile phase of ACN:H₂O:CH₃COOH (49.5: 49.5: 1). For detection, 333 nm and 460 nm wavelengths were used for excitation and emission, respectively.

The obtained validation results were adequate and both accuracy and precision values met the requirements laid down by EC Directive 401/2006 [4].

The OTA concentration was determined in 33 beer samples, 9 of which (27.27%) were contaminated, with levels ranging between 0.174 and 11.25

μ g/L, and an average level of 3.14 μ g/L. Two of the homemade beer samples exhibit considerable concentrations concentration levels of 9.21 μ g/L and 11.25 μ g/L. The samples of industrial made pale ale presented detection frequencies, and levels lower than those of homemade, self-manufactured and craft production beer.

Three EDI assessments were carried out based on three different scenarios. In the first one the average levels of OTA for the total of the analysed samples were taken into consideration; in the second the average content of OTA in the contaminated samples were considered; and in the third one was based on the worst case scenario. The EDI values obtained were 1.801 ng/kg b.w./day, 6.606 ng/kg p.c./day and 23.67 ng/kg p.c./day, respectively.

For the risk assessment a tolerable weekly intake (TWI) of 120 ng/kg p.c./week, established by EFSA in 2006, was considered [1]. In the first evaluation, the percentage of estimated weekly intake (EWI) versus TWI was 10.5%, in the second, 38.5% and in the third, 138.01%. In the first two situations, the ingestion of OTA through the consumption of beer presents no risk to the respective consumers. Inverse situation was observed for the worst case scenario.

Current legislation does not include limits for the occurrence of OTA in beer, but the identified concentrations, especially of home-made brews, should be considered.

Acknowledgements

The authors are grateful to the POCI/01/0145/FEDER/007265 and to FCT under PT2020 UID/QUI/50006/2013 and the post-PhD fellowship SFRH/BPD/62877/2009.

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Tunisian Olive Oils Geographical Origin Discrimination Using the Potentiometric Fingerprints Recorded by an Electronic Tongue

PP AgroFood #19

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The development of fast and cost-effective analytical techniques for EVOO authentication is a challenging task. Moreover, if a specific meteorological or geographical factor affects different geographical regions similarly, olive oils' geographical discrimination may be a hard task using conventional analytical techniques [1]. E-noses and/or voltammetric E-tongues have already been applied to assess olive oils' geographical origin, mainly to discriminate different countries or quite different regions of the same country [2].

In this work, we used an electronic tongue (E-tongue), with 40 lipid membrane sensors, to extract representative potentiometric fingerprints of Tunisian monovarietal olive oils that, in combination with linear discriminant analysis (LDA), could be used to classify olive oils according to the geographical origin. Aqueous ethanolic (80:20, v/v) extracts of different single-cultivar Tunisian olive oils were electrochemically analysed. According to the literature [3-6], these olive oil extracts are rich in polar compounds that deliver different overall potentiometric responses, which can then be used to evaluate the E-tongue performance for olive oils' geographical origin discrimination. The proposed E-tongue-LDA approach, based on the signal profiles of different sub-sets of sensors (selected with the simulated annealing meta-heuristic

algorithm) allowed the correct geographical origin classification of Tunisian olive oils produced from autochthonous Chemlali or Sahli cultivars (i.e., Kairouan, Sidi Bouzid and Sfax; or, Mahdia, Sousse and Kairouan; respectively). Indeed, predictive correct classifications of 92±7% and 97±8% (for repeated K-fold cross-validation) could be obtained for Chemlali or Sahli olive oils, pointing out the potential use of the E-tongue device for geographical origin identification of olive oils.

Acknowledgements

This work was financially supported by POCI-01-0145-FEDER-006984-Associate Laboratory LSRE-LCM, Project UID/QUI/00616/2013-CQ-VR, Project UID/BIO/04469/2013-CEB and Project UID/AGR/00690/2013-CIMO all funded by FEDER, through COMPETE2020, and by national funds through. Nuno Rodrigues thanks FCT, POPH-QREN and FSE for the Ph.D. Grant (SFRH/BD/104038/2014).

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Electrochemical Taste Sensor for Unmasking Extra-Virgin Olive Oils Adulterated with Rancid or Winey-Vinegary Olive Oils

PP AgroFood #20

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Olive oils may be commercially classified, in a decrease order of quality and economic value, as extra-virgin (EVOO), virgin (VOO) or lampante (LOO) olive oils, being quite prone to frauds. Thus legal protection regulations have been approved by the European Union Commission [1,2], being required the fulfilment of several physicochemical and sensory thresholds [3,4]. Unfortunately, the mixture of expensive olive oils with low quality oils aiming fraudulent economic revenue is still a common practice difficult to detect.

In this work, a potentiometric electronic tongue (E-tongue) was used to detect adulteration of an EVOO with different added levels (2.5%, 5%, 10%, 20% and 40%; v/v) of an LOO with an intense sensory defect (rancid or winey-vinegary). Previously, similar electrochemical devices, also comprising lipid polymeric sensor membranes, showed to be able to give qualitative and/or quantitative responses towards basic taste sensations (acid, bitter, salty, sweet, and umami), positive sensory attributes (bitter, fruity, green and pungency) or defects (e.g., butyric, musty, putrid, winey-vinegary and zapateria) [5-8]. The E-tongue coupled with linear discriminant technique (based on the signal profiles of 19 or 20 E-tongue sensors, chosen using a simulated annealing meta-heuristic variable selection algorithm, for rancid and winey-vinegary adulterations, respectively) allowed to semi-quantitatively distinguish olive oils with

different adulteration levels (repeated K-fold cross-validation predictive correct classifications of $84\pm 10\%$ and $94\pm 8\%$ for rancid and winey-vinegary adulterations, respectively). The preliminary results showed the practical potential of the E-tongue as a taste device for the successful detection of EVOOs adulterated with LOO containing organoleptic defects.

Acknowledgements

This work was financially supported by POCI-01-0145-FEDER-006984–Associate Laboratory LSRE-LCM, Project UID/QUI/00616/2013–CQ-VR, Project UID/BIO/04469/2013–CEB and Project UID/AGR/00690/2013–CIMO all funded by FEDER, through COMPETE2020, and by national funds through Nuno Rodrigues thanks FCT, POPH-QREN and FSE for the Ph.D. Grant (SFRH/BD/104038/2014).

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Porto Map



Venue



Bus Line 502



Metro Lines: A, B, C, E, F



Metro Line D



Porto Wine Cellars and Conference Dinner



1 Quality Inn Portus Cale

2 Bessa Hotel Boavista

3 Hotel Teatro

4 Hotel da Música

5 Hotel Dom Henrique Downtown

6 Hotel Internacional Porto

7 Grande Hotel do Porto

8 Hotel Ibis Porto Centro

9 Moov Hotel Porto Centro

10 In Porto Gallery Guesthouse

11 Porto Lounge Hostel & Guesthouse

12 So Cool Hostel Porto

Social Program

Welcome reception (Porto D'Honra)

Monday, November 27th 18:15-19:30

The Organisation Committee of EMEC18 invites you to a welcome reception at Fundação Dr. António Cupertino de Miranda (the Conference venue). Appetizers will be served, accompanied obviously by Porto Wine and good music.



Visit to Ferreira Porto Wine cellars

Tuesday, November 28th 18:30

EMEC18 offers all participants one exciting tour to the Ferreira Porto Wine cellars. Built by a family of winemakers from the Douro region in 1751, the Ferreira house possessed a rich tradition and a prominent role in the history of Porto Wine. In fact, it is the only major Porto Wine house that has remained in Portuguese hands since its foundation.

Dona Antónia Adelaide Ferreira contributed significantly to the consolidation of the brand. A legendary woman with a unique personality, who became a myth and a symbol of strength, facing the adversities of the nineteenth-century Douro conditions, including the Phylloxera plague. Ferreira cellars invite you to discover a brand over 250 years old, a symbol of the highest quality that encapsulates Portugal's heart and soul.



Conference Dinner at Casa Ferreirinha

Tuesday, November 28th 19:30

Crossing the bridge from Porto, in the city of Vila Nova de Gaia, Casa Ferreirinha is a contemporary venue with a fantastic view to the Douro river, perfectly integrated in the genuine wine cellars of the Ferreira house. The menu will be created by Chef Fernando Santos, who is fluent in different gastronomic concepts and trends, providing a creative fusion cuisine between traditional Portuguese gastronomic delights and modern signature approach. After the dinner, EMEC18 attendees will also have the opportunity to enjoy some national and international music and dance. This will be the perfect time to relax and have fun!!!

CAVES PORTO FERREIRA – Av. Ramos Pinto, 70 – 4400-266 Vila Nova de Gaia – GPS: 41° 8 12,9N/ 8° 37 9,3W



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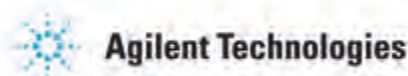


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