

# 14th EuCheMS International Conference on Chemistry and the Environment



**ICCE 2013, Barcelona, June 25 - 28, 2013**

**Book of abstracts**

(updated August 9<sup>th</sup>)



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<b>PL3</b> - Urs Baltensperger – <i>Sources, processes and impact of atmospheric aerosols</i>	
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<b>KN1/ Green and sustainable industrial chemistry</b> – Roger Sheldon - <i>Green &amp; sustainable chemistry: Methods &amp; metrics</i>	
<b>KN2/ Atmospheric chemistry and aerosols</b> – Roy Harrison - <i>Characterisation and behaviour of nanoparticles from road traffic exhaust</i>	
<b>KN3/ Water pollution and treatment</b> - Ivana Ivancev-Tumbas - <i>Universe of organics in drinking water treatment processes</i>	
<b>KN4/ Soil and sediment pollution, wastes</b> – Greame Paton - <i>Quantification of bioavailable fractions of elements and organic pollutants and sustainable steps to remediate these at the field scale.</i>	
<b>KN5/ Emerging pollutants</b> – Klaus Kuemmerer - <i>Emerging pollutants: Of old compounds and new ones, of micrograms and tonnes, from the past to the future.</i>	
<b>KN6/ Water pollution and treatment</b> – Susan Richardson - <i>The next generation of drinking water disinfection by-products: Occurrence, formation, toxicity, and new links with human epidemiology</i>	
<b>KN7/ Soil and sediment pollution, wastes</b> – Emmanuel Naffrechoux - <i>Fate of PCB in aquatic ecosystems : cold case or hot topic ?</i>	
<b>KN8/ Atmospheric chemistry and aerosols</b> – Andrés Alastuey - <i>Geochemistry of atmospheric particulate matter: from remote to urban environments</i>	

**KN9/ (Eco-)Toxicology: pollutants exposure and effects on biota and ecosystems –**  
Kevin Thomas - *Effect-directed analytical approaches for the identification of  
contaminants of emerging concern*

**KN10/ Green and sustainable industrial chemistry –** Joel Barrault - *Sustainable  
Chemistry: from renewable resources to chemicals via catalysis*

**KN11/ Modelling, management and risk assessment –** Andrea Rizzoli - *Advances in  
software system for supporting environmental decision making*

**KN12/ Transformation and fate of pollutants –** Sixto Malato - *Removal of Pollutants  
in Water and Wastewater by Solar Advanced Oxidation Processes*

**KN13/ Transformation and fate of pollutants -** Dionysios Dionysiou - *Oxidative  
transformation of Cyanotoxins and other Contaminants of Emerging Concern in Water  
using advanced oxidation processes*

**KN14/ Emerging pollutantats –** Maite Galceran - *Novel strategies for the analysis of  
fullerenes in environmental samples*

**KN15/ (Eco-)Toxicology: pollutants exposure and effects on biota and ecosystems -**  
Cinta Porte - *Development of in-vitro bioassays for the assessment of reprotoxicity in  
fish*

**KN16/ Modelling, management and risk assessment –** Manuel Poch - *Decisions in  
wastewater systems: different tools for different decisions' levels*

**KN17/ Water pollution and treatment –** Josep Bayona - *Atmospheric plasma. A new  
technology to remove recalcitrant organic microcontaminants from water*

## **ATMOSPHERIC CHEMISTRY AND AEROSOLS**

**Oral presentations** ..... 55

**OA1 -** Maxence Mendez - *Modelling the chemically speciated PM2.5 over the French  
Northern region using the WRF-Chem system coupled to EMEP and regional emission  
inventories*

**OA2 -** Nuno Ratola - *POPs and PAHs in Norway and the UK – levels and distribution  
in pine needles, litter, soils and air*

**OA3 -** Marie Danielle Mulder - *Gas-particle partitioning and air-sea exchange of  
polycyclic aromatic hydrocarbons in the central and eastern Mediterranean*

**OA4** - Barend L. Van Drooge - *Seasonal and spatial variation of PM1 organic tracers in densely populated and highly insolated urban areas of humid and dry atmospheres*

**OA5** - Elisa Venturini - *PM2.5 source apportionment by directional sampling and Positive Matrix Factorization (PMF)*

**OA6** - Marta Fort - *Association between metal body burden in pregnant women and atmospheric traffic pollution*

**OA7** - Davide Vione - *Photochemical formation of humic-like substances: Phenol di/oligomerisation sensitised by the triplet state of 1-nitronaphthalene*

**OA8** - Staci Massey Simonich - *Prediction, Identification, and Mutagenicity of Novel Nitro-PAHs Formed via Atmospheric Heterogeneous Reactions*

**OA9** - Jordi Diaz-Ferrero - *Dioxins, furans and dioxin-like PCBs in ambient air from Catalonia (Spain)*

**OA10** - Akos Redey - *Monitoring nitrogen-dioxide and benzene in air in the Central Transdanub Region, in the City of Veszprém*

**OA11** - H.J. Grimm - *New real time portable atmospheric aerosol sizer and counter*

**Poster presentations** ..... 65

**PA1** - Mireia Aragón - *Determination of N-nitrosamines and nicotine in particulate matter from air samples by pressurised liquid extraction and gas chromatography-ion trap tandem mass spectrometry*

**PA2** - Marta Alier - *Comparison of water-soluble organic tracer compounds in fine aerosols in two cities: Los Angeles and Barcelona*

**PA3** - Maria Chropenova - *The using of pine needles for long-term monitoring of air pollution*

**PA4** - Slawomira M. Dumala - *The survey for tin in dust samples from apartments in Lublin area, Poland*

**PA5** - Marzenna R. Dudzinska - *Heavy metals in settled dust from educational institutions, Poland*

**PA6** - Vicente Esteve-Cano - *Trends of heavy metals levels in PM10 and PM2.5 in an industrialized area*

**PA7** - Hermann Fromme - *Organophosphate flame retardants in air and dust of German daycare centers and metabolite levels in urine (LUPE 3)*

**PA8** - Mariana Godinho - *Reduction, Evaluation and Monitoring of Chemical Waste in Power Transformers Insulation Systems by Multivariate Image Analysis and Chemometrics*

**PA9** - Tomasz Jankowski - *Investigation of contaminants filtration in metal fluid environments - laboratory evaluations*

**PA10** - Cancelled

**PA11** - Marie D. Mulder - *Legacy POPs and polybrominated diphenylethers in the central and eastern Mediterranean – levels in ambient air and gas-particle partitioning*

**PA12** - Luciano Morselli - *Cor-Ten exposed to a urban-coastal environment: preliminary study on metal release*

**PA13** - Nuno Ratola - *Comprehensive evaluation of the patterns of air pollution by PAHs over Europe by combining modelling and observational data under a climatic perspective*

**PA14** - WG Sayre - *The Atmospheric Chemistry of Three Common Gases*

**PA15** - Cancelled

**PA16** - Dragana Dordevic - *The sea salts contribution on inorganic ions in wet deposition of the central Balkans*

**PA17** - Clara Coscolla - *Size distribution of particle-bound Currently Used Pesticides in the ambient air of a rural station in Centre Region (France)*

**PA18** - Cancelled

**PA19** - Cancelled

**PA20** - Maxence Mendez - *Reactivity of chlorine radical on palmitic acid particles: kinetic measurements and products identification*

**PA21** - Cristina M. Oliveira - *Comparison of two atmospheric aerosol samplers*

**PA22** - Cancelled

**PA23** - Monika Paládi - *Determination of CO<sub>2</sub>-emission in the case of country houses heated by firewood*

**PA24** - Maria Grazia Perrone - *Investigating the chemical components of aerosol from an urban, a rural and a remote site (North Italy) and their relation with the observed biological responses.*

**PA25** - Grazia Rovelli - *Experimental measurements of particulate matter DRH and CRH for the prevention of corrosion in Data Centers*

**PA26** - Vania Martins - *Contribution of Barcelona metro train brake pads to atmospheric PMx levels in platforms*

**PA27** - Cancelled

**PA28** - Barend L. Van Drooge - *Environmental Tobacco Smoke (ETS) in the outdoor urban area of Barcelona*

**PA29** - Esther Borrás - *Chemical composition of organic atmospheric particulate matter in the Mediterranean Area*

**PA30** - Cancelled

**PA31** - Gianluigi de Gennaro - *Time-resolved measurements of Particulate Matter ionic fraction: comparison between South and North Italy*

**PA32** - Young-lan Kim - *A study of the dioxin emission from energy facilities used liquid fuel in Korea*

**PA33** - Vania Martins - *Passenger exposure to PM while commuting in the Barcelona metro*

**PA34** - Andrés Alastuey - *Indoor and outdoor levels and composition of air pollutants in primary schools in Barcelona*

**PA35** - Maria Tutino - *Monitoring of nitro-PAHs in Taranto (southern Italy)*

**PA36** - Raffaele Cucciniello - *NOx uptake on Ca-based absorbents*

**PA37** - Arianna Tolloi - *Aerosol studies in the Karst of Trieste (Italy)*

**PA38** - Maria Chropenova - *MONAIRNET - Monitoring network for persistent organic pollutants in ambient air of Czech Republic - Austria region*

**PA39** - Dimitra Voutsas - *Study of aldehydes in rainwater of the urban atmosphere.*

## **SOIL AND SEDIMENT POLLUTION, WASTES**

**Oral presentations** ..... 98

**OS1** - Marc Crampon - *Analytical strategies to evaluate polycyclic aromatic hydrocarbons (PAHs) bioavailability in soils; correlation with their biodegradability*

**OS2** - Martina Furdek - *Persistence of butyltin (BuT) compounds in the contaminated sediments from the Croatian Adriatic coast*

**OS3** - Cancelled

**OS4** - Susan C. Wilson - *Food Crop Accumulation and Bioavailability Assessment for Antimony (Sb) compared with Arsenic (As) in contaminated soils*

**OS5** - Barbara Beckingham - *Sediment PAHs in the Rivers of Ammer (Germany) and Liangtan (China): Differences between Early- and Newly-Industrialized Countries*

**OS6** - Martin Seidl - *Micropollutants as tracers of urbanization history of the Mingoa river watershed (Yaoundé, Cameroon)*

**OS7** - Mi-jeong Jeong - *Comparison of Triglycerides and Fatty acids patterns in burial leachate and raw oils (animal fats, fish oils, cooking oils)*

**OS8** - Peter Grathwohl - *Integrated monitoring of particle associated transport of PAHs in contrasting catchments*

**OS9** - Rahul Kumar - *Geochemical speciation and potential toxicity of trace elements in river sediments*

**OS10** - Perihan Binnur Kurt-Karakus - *Estimation of Health Risk from Indoor dust as a source of Exposure to Heavy Metals in Istanbul*

**Poster presentations** ..... 107

**PS1** - Michel Chalot - *The use of dendrochemistry to reveal pollution history*

**PS2** - Cancelled

**PS3** - Marta Eliane Doumer - *Waste biomass to biochar and bio-oil: conversion of various biomass materials by slow pyrolysis*

**PS4** - Joaquín Guadaño - *Environmental remedial activities in the Sardas landfill, Sabiñánigo, Huesca (Spain). The problem of HCH*

**PS5** - Thilo Hofmann - *Evaluating in situ thermal remediation of a chlorinated solvent source zone*

**PS6** - Cancelled

**PS7** - Cancelled

**PS8** - Maris Klavins - *Analysis of human impact intensity changes during last 300 years using sedimentary records*

**PS9** - Yulia Katzman - *Reduction of 4-nitrophenol to 4-aminophenol over Ag<sub>0</sub> and Au<sub>0</sub> nanoparticles immobilized in SiO<sub>2</sub> matrices prepared via the sol-gel synthesis*

**PS10** - Mario Llusar - *Use of exhausted Y-Faujasite from FCC wastes for the removal of heavy metals*



- PS11** - Erika Levei - *Assessment of water and sediment contamination by mining activities in the Aries river, Romania*
- PS12** - Mireia Lao - *Determination of free Zn<sup>2+</sup> concentration in root extracts of *Hordeum vulgare**
- PS13** - Jelena Milinovic - *Sorption behavior of perfluorinated compounds in sewage sludges and soils*
- PS14** - Guillermo Monrós - *Dynamics of fluoride and borate in soils exposed to the emission of the ceramic industry of tiles and glazes*
- PS15** - Esmeralda Morillo - *Diuron mineralisation in soil affected by the use of hydroxypropyl- $\beta$ -cyclodextrin and different amendments.*
- PS16** - Esmeralda Morillo - *Cyclodextrin enhanced extraction of PAHs from spiked and aged soils. Effect of co-contaminants*
- PS17** - Stephen M. Mudge - *Identifying the sources of chemical contamination after the fact*
- PS18** - Ewa Olkowska - *Comparison of isolation techniques for analysis of cationic surfactants from solid samples*
- PS19** - Diego Martiñá Prieto - *Biofilm systems for the prevention of As (V) problematic concentrations in river environments*
- PS20** - Witold Reczynski - *<sup>137</sup>Cs and <sup>40</sup>K radionuclides activity and heavy metals concentrations in soil samples from East part of the Flysh Carpathian Mountains in Poland*
- PS21** - Witold Reczynski - *General aspects of environmental analysis: choice of methods, methods compatibility, data processing*
- PS22** - Raquel Sousa - *Analysis of trace pesticide contaminants in deposits from water networks*
- PS23** - Angelina Sarapulova - *Dynamics of lead, zincum, copper mobile form and their biological accessibility in tailings dams after processing molybdenite and sulfide-hubnerite ores*
- PS24** - Hugo F. Silva - *Monitoring lead in soils in Lisbon during the last decade*
- PS25** - Dragana D. Tomasevic - *As and Pb immobilisation in contaminated sediment using bentonite and kaolinite supported nano zero valent iron*
- PS26** - Nikoletta Docs - *Heavy metals in the floodplain: a case study of the River Tisza, NE Hungary*
- PS27** - Mari Dahl - *Field scale remediation experiment for oil-contaminated soil*

- PS28** - Mi-jeong Jeong - *Residue patterns of Antibiotics in leachate from carcasses*
- PS29** - Cancelled
- PS30** - Vladimir Nikiforov - *Bacterial degradation and bioremediation of polycyclic aromatic hydrocarbons in the industrially polluted soil*
- PS31** - Yana Russkikh - *Pentabromodiphenyl ether in water and sediment samples from saint-petersburg area*
- PS32** - Kristin Schaefer - *Changes of the soil pollution in the vicinity of a metallurgical plant*
- PS33** - Beata Smolinska - *Leaching of mercury during phytoextraction assisted by compost*
- PS34** - Beata Smolinska - *What do spice plants synthesize in answer to heavy metal stress conditions?*
- PS35** - Barend L. Van Drooge - *Temporal trends of POPs in sediments from a high mountain lake in the Tyrolean Alps*
- PS36** - Tae Wan Jeon - *Results of Monitoring and Strategies for the Reduction of Household Food Waste in Korea*
- PS37** - Tae Wan Jeon - *A Study on Analysis Methods of Heavy Metals and Concentration of Portland Cement in Korea*
- PS38** - Tatiana Yuzhakova - *Study on the possible utilization of the red mud as catalyst*
- PS39** - Dimitry Bolshakov - *Determination of pesticides in soil and waters by dlme/mekc, quechers/mekc*
- PS40** - Chrystelle Bancon-Montigny - *Organotin compounds in lagooning treatment plant: occurrence and behaviour*
- PS41** - Rahul Kumar - *Geochemical Speciation and Potential Toxicity of Trace Elements in River Sediments*
- PS42** - Isabella Lancellotti - *Comparison of phosphonate and carboxylate chelating agents in the Pb extraction from WEEE glass*
- PS43** - Isabella Lancellotti - *Inertization of chromium liquid waste in inorganic polymers by alkali activation of metakaolin*
- PS44** - Gerard Bondoux - *Advances in Atmospheric Pressure Gas Chromatography (APGC) for the analysis of persistent organic pollutants (POPs); background and applications.*

**PS45** - Helena MVM Soares - *Selective leaching of Mo and Ni from spent Ni-Mo catalysts using a two-stage microwave-assisted method*

**PS46** - Ákos Rédey - *A sustainable method of waste cathode ray tubes recycling*

**PS47** - Patricia E. Freitas - *Energy from waste: Using red mud and residual glycerol from biodiesel to produce syngas*

**PS48** - Francois Lestremau - *Application of QuEChERS based methodology for the analysis of pesticides in sediments*

**PS49** - Roland Weber - *Securing HCH deposits of a former Lindane production in Aragone (Spain)*

**PS50** - Ruben Reif - *Pesticides distribution in dust with different particle size collected from urban environments*

**PS51** - Cancelled

## **WATER POLLUTION AND TREATMENT**

**Oral presentations** ..... 154

**OW1** - Jonas Margot - *Laccases: Potential treatment for removal of micropollutants in municipal wastewater?*

**OW2** - Pedro N. Carvalho - *Pharmaceuticals removal from wastewaters in constructed wetlands*

**OW3** - Aida Garcia-Rodriguez - *Biologically-based water reclamation systems: a sustainable alternative for removing pharmaceuticals and endocrine disrupting chemicals from wastewater*

**OW4** - Gianluca Li Puma - *Solar Water Detoxification Processes for the Removal of Estrogens, Antibiotics and other Contaminants of Emerging Concern*

**OW5** - Lucía Prieto-Rodríguez - *Removal of organic micro-contaminants from municipal waste water by an IBR system coupled to a solar photo-Fenton process as tertiary treatment*

**OW6** - Boguslaw Buszewski - *Utilization of diatomite modified by ionic liquids for uranium ions adsorption from aqueous solutions*

**OW7** - Thorsten Reemtsma - *Transformation of Organic Contaminants in Plants*

**OW8** - Ana Assunção - *Palladium biorecovery using anaerobic bacterial communities*

**OW9** - Johannes Kuipers - *Intensified photocatalytic slurry reactor with a multitude of low intensity UV-LEDs for removal of micropollutants*

**OW10** - Jelena Radjenovic - *Application of electrochemical processes for water and wastewater treatment*

**OW11** - Adama M. Sesay - *Rapid and Cost-Effective methods for Detection of Environmentally Harmful Compounds from Waste Waters (RACE)*

**OW12** - Zsofia Kovacs - *Application of early-warning system to identify surface water pollution*

**OW13** - Robert Loos - *EU-wide monitoring survey on wastewater treatment plant effluents*

**OW14** - Grace Lewis - *Boron-Doped Diamond - Boron-Doped Diamond Electroanalytical Detectors for Environmental Monitoring of Pharmacologically Active Compounds and Other Emerging Contaminants*

**OW15** - Gerald Thouand - *Detection of heavy metals, organotins and their toxicity with bioluminescent bacteria*

**OW16** - Claudia Fontas - *Screening of arsenic in groundwater: a novel and green detection method*

**OW17** - Pavlina Pavlova - *Ice cores for the reconstruction of historical input and migration behavior of POPs in Alpine glaciers*

**OW18** - Sebastien Abramson - *Towards Highly Efficient Heterogeneous Magnetic Fenton Catalysts for the Degradation and Mineralization of Aqueous Organic Pollutants*

**OW19** - Jean-marie Fontmorin - *Modification of graphite electrodes for the degradation of halogenated organic compounds: coupling of an electrochemical process with a biological treatment*

**OW20** - Peter A. Behnisch - *Effect-based screening assays for water pollutions with endocrine disrupters, POPs, obesity and other toxicants*

**Poster presentations** ..... 174

**PW1** - Awad Al-rashdi - *A doubly functionalised mesoporous silica nanoscavenger for the analytical extraction of tributyltin from water*

**PW2** - Cancelled

**PW3** - Eliska Cechova - *Determination of estrogens in different types of wastewaters and technologies for their removal*

**PW4** - Molly Costanza-Robinson - *Influence of Surfactant Loading and Interlayer Arrangement on Contaminant Uptake by HDTMA-Modified Montmorillonite*

**PW5** - Jin Wook Chae - *Adsorption of Cr(VI) Using Magnetite Nanoparticles*

**PW6** - Lurdes Ciríaco - *Anodic oxidation of sanitary landfill leachates at a Ti/Pt/PbO<sub>2</sub> electrode*

**PW7** - Cancelled

**PW8** - Cancelled

**PW9** - Estefanía De Torres Socías - *Cork boiling wastewater treatment at pilot plant scale: comparison of solar photo-Fenton and ozone (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> at different initial pH values). Toxicity and biodegradability assessment*

**PW10** - Carlos Escudero - *Divalent heavy metal removal using a natural lignocellulosic based ion exchanger in a continuous bed up-flow process: sorption behaviour and modelling in single and multimetal mixtures*

**PW11** - Annabel Fernandes - *Chemical precipitation and anodic oxidation integrated process to treat sanitary landfill leachates*

**PW12** - Claudia Fontas - *Point-of-use treatment for Arsenic removal based on Adsorbia<sup>TM</sup> As600 resin*

**PW13** - Josep Galceran - *On site determination of free Zn<sup>2+</sup> concentration in river water*

**PW14** - Cancelled

**PW15** - Alba Grau-Martínez - *Induced nitrate attenuation in an artificial recharge pilot pond in Sant Vicenç dels Horts, Catalonia*

**PW16** - Cancelled

**PW17** - Marjan Heidarkhan Tehrani - *Cloud point extraction of Zinc in biological samples and determination by UV-visible spectrophotometry*

**PW18** - Marjan Heidarkhan Tehrani - *Separation and Preconcentration of Trace Aluminum in Biological and Water Samples using Cloud Point Extraction*

**PW19** - Xuexiang He - *Removal of Cyanobacterial Toxin Cylindrospermopsin by UV-mediated Advanced Oxidation Processes*

**PW20** - Meltem Isleyen - *The Elimination of Hazardous Compound for Environmental Protection: Photocatalytic Treatment of 4-Chlorophenol*

**PW21** - Katarzyna Jaworek - *Application of spme/gc/ms method for determination of organoarsenic compounds and their degradation products*

**PW22** - Cancelled

**PW23** - Gianluca Li Puma - *Photodegradation of estrogens in aqueous TiO<sub>2</sub> suspensions with UVA and UVC radiation*

**PW24** - Silvia Claudia Mosneag - *Comparative study regarding the treatment of contaminated groundwater from Căpuș area, Cluj region, Romania, by processes of adsorption on granular activated carbon and natural zeolite from Mirșid*

**PW25** - Cancelled

**PW26** - Moussa Mahdi Ahmed - *Enhanced photo-Fenton oxidation of carbamazepine for water decontamination by using persulfate as an oxidant*

**PW27** - Cancelled

**PW28** - Betty Niazov - *Bioethanol production using water hyacinth grown in wastewater*

**PW29** - Ewa Niewiara - *Application of inorganic sorbents for removal of humic acids and heavy metals from water solutions*

**PW30** - Ewa Niewiara - *Determination of organo-tin compounds with the renewable film mercury sensor*

**PW31** - Mohammed Omer Khatab - *Characterizing Water Quality for Photosynthesis Zone of Mosul Dam Lake, Northern Iraq by Means of Field Parameters*

**PW32** - Ewa Olkowska - *Occurrence of ionic and non-ionic surface active agents in liquid samples collected in regions of varying intensity of anthropopression*

**PW33** - Alexandro Papageorgiou - *Occurrence and fate of ozonation by-products in Drinking Water Treatment Plant of Thessaloniki, Greece*

**PW34** - Valery S. Petrosyan - *Monitoring of Water Quality Using the Optical Cardiography of Shellfish*

**PW35** - Adi Radian - *Pollutant Uptake from Water by Polycation-Clay Composites: an Experimental and Quantative Structural Activity Relationships (QSAR) Approach*

**PW36** - Maria J. Pacheco - *COD and heavy metal content variation during a combined electrocoagulation-electrooxidation treatment of a landfill leachate*

**PW37** - Noemí Santiago Sánchez - *New device for continuous measurement of trihalomethanes (TRIADEC)*

**PW38** - Eda Sinirtas - *Advances in the Environmental Applications: The Photocatalytic Removal of Organic Contaminant from Wastewater*

- PW39** - Alaa Salma - *Effect of pH on the photolysis and photocatalytic degradation of ciprofloxacin (kinetic and mechanism)*
- PW40** - Susanna Sonny - *Electrochemical biosensor development for detection of ecotoxicological compounds in wastewater*
- PW41** - Maciej Tankiewicz - *Fast and 'green' multi-residue methods for the determination of emerging pesticides from various chemical groups in water samples by gas chromatography*
- PW42** - Tomas Undabeytia - *Removal of priority pollutants from water by clay-vesicle complexes*
- PW43** - Anton Valkov - *Photodynamic Disinfection of Wastewater Using Photosensitizers Immobilized in Polymers*
- PW44** - Ulrika Winnberg - *Synthesis of a novel octabrominated dimethoxydiphenyl ether (diMeO-octaBDE) and identification of its phenolic analogue in blue mussels from the Swedish west coast*
- PW45** - Sebastian Zabczynski - *Physicochemical degradation of iodipamide – quantum yield calculation*
- PW46** - Sebastian Zabczynski - *The influence of sludge retention time on the efficiency of the iodinated X – ray contrast media removal in aerobic and anaerobic membrane bioreactors*
- PW47** - Cancelled
- PW48** - Cancelled
- PW49** - Aisha N. Bismillah - *Water Purification by Photo-catalytic Destruction of Pollutants*
- PW50** - Alessandra Bianco Prevot - *Use of soluble bio-based substances isolated from urban biowastes as organic photocatalysts for the degradation of 4-chlorophenol.*
- PW51** - Cancelled
- PW52** - Cancelled
- PW53** - Ekaterina Chernova - *Organotin compounds in marine environment of the Eastern Part of the Gulf of Finland*
- PW54** - Leonardo Cerasino - *Cyanotoxins in the Italian Deep Subalpine Lakes (DSL): distribution and controlling factors*
- PW55** - Maria Clara Costa - *Liquid-liquid extraction studies for platinum recovery from chloride media using N,N'-dimethyl-N,N'-diphenyl succinamide*

- PW56** - Christophoros Christophoridis - *Education in Environmental Analysis – Leonardo da Vinci CHEMLAB II project*
- PW57** - Cancelled
- PW58** - Cancelled
- PW59** - Cancelled
- PW60** - Frimmer Fritz - *Toxic effects of nano particles on aquatic microorganisms*
- PW61** - Noor Gulamussen - *Evaluation of the effect of sorbent morphology for SPE application*
- PW62** - Cristian Gómez-Canela - *Development of a novel Liquid Chromatography - tandem Mass Spectrometry method for the determination of rodenticides in wastewater*
- PW63** - Cancelled
- PW64** - Cancelled
- PW65** - Ana Lopes - *Treatment of cork processing wastewaters by anodic oxidation*
- PW66** - Carolina Martínez de Peón - *Simultaneous determination of disinfection by products in water samples by headspace solid phase microextraction and gas chromatography-mass spectrometry*
- PW67** - Cancelled
- PW68** - Jan Sebastian Manz - *Impact of a tar contaminated site on an adjacent river – NSO-Heterocycles, PAHs, PAH-Derivatives and Phenols*
- PW69** - Semanur Saribuga - *The analytical examination of the magnetic nanoparticles*
- PW70** - Shailesh S. Sable - *Clofibric acid degradation by heterogeneous Fenton-like process using Fe-zirconia catalysts*
- PW71** - Cancelled
- PW72** - Jana Uhlig - *Removal of pharmaceutical residues from wastewater by polymer-based spherical activated carbon (PBSAC)*
- PW73** - Roberto Lava - *Biota monitoring of hexachlorobenzene and hexachlorobutadiene in *Silurus glanis* from a heavily polluted aquatic environment*
- PW74** - Costas Michael - *UV light-activated persulfate for the removal of erythromycin and antibiotic resistance from secondary wastewater*



**PW75** - Costas Michael - *The effectiveness of sulfate radicals on the abatement of ethyl-paraben in aqueous media*

**PW76** - Jennifer Bowen - *Effects of ionic strength, oxygen level and humic acid concentration on photochemical degradation of fluoranthene in aqueous solution*

**PW77** - Samane Mehrandoost - *Determination of inorganic and organic species of selenium in Iranian walnut by spectrophotometry after cloud point extraction*

**PW78** - Gilles Varrault - *Effect of dissolved organic matter on micropollutants sorption by clays and oxides in aquatic system under strong urban pressure*

**PW79** - Attila Sarkady - *Alternative possibilities of the bio fraction handling of municipal solid waste*

**PW80** - Cancelled

**PW81** - Mohammad Algamdi - *Degradation of phenolic compounds in industrial effluents by ionizing radiation*

**PW82** - Vigilija Cidzikiene - *Assessment of tritium activity in groundwater at Visaginas Nuclear Power Plant site, Lithuania*

**PW83** - Marcelo G.Rosmaninho - *Water Purifying Using Waste of Electrical and Electronic Equipment (WEEE) as Fenton and Photo-Fenton Catalyst*

**PW84** - Juliana C. Tristao - *Use of Highly Oxygenated Biochar as Catalyst for Sulfide Oxidation*

**PW85** - Khalid Alhooshani - *Efficient photocatalytic degradation of Methyl Tertiary Butyl Ether (MTBE) in aqueous suspension of Pt/WO<sub>3</sub> nanocomposite under sunlight-type excitation*

**PW86** - Cancelled

**PW87** - Antonia Garrido Frenich - *Highly sensitive determination of polybrominated diphenyl ethers in surface water by gas chromatography coupled to high resolution mass spectrometry according to Directive 2008/105/EC*

**PW88** - Antonia Garrido Frenich - *Occurrence of organic contaminants in wastewater treatment plant effluents from the Mediterranean and Atlantic basins of Andalusia (Spain)*

## **(ECO-)TOXICOLOGY: POLLUTANTS EXPOSURE AND EFFECTS ON BIOTA AND ECOSYSTEMS**

**Oral presentation** ..... 242

**OT1** - Tvrtko Smital - *Prioritisation of organic contaminants in the Sava River basin using chemical analyses and bioassays*

**OT2** - Sofia Raquel Mesquita - *Toxic assessment of particle-bound PAHs: a novel environmental perspective.*

**OT3** - Maria Tarapoulouzi - *Ecotoxic and mutagenic effects of photolytic transformation products of pharmaceuticals: an experimental design for the investigation of mixtures*

**OT4** - Ivana Mihajlovic - *Exposure of breastfed newborn to DDT and metabolites from 1982 to 2009 in the Province of Vojvodina, Serbia*

**OT5** - Eva Gorrochategui - *Perfluorinated compounds: a cause for lipogenic disorder in JEG-3 cells?*

**OT6** - G. Buttiglieri - *Influence of sulfamethoxazole on activated sludge bacterial community and removal efficiencies*

**OT7** - Melissa Faria - *Development of oxidative stress biomarkers in developing zebra fish *Danio rerio* embryos.*

**OT8** - Claudia Rivetti - *The use of gene, biochemical and individual markers in transplanted *Daphnia magna* to characterize impacts in the field*

**OT9** - Monika Mortimer - *Uptake and clearance of non-toxic CdSe/ZnS quantum dots by the ciliated protozoa *Tetrahymena thermophila**

**OT10** - Evy Van Ael - *The influence of bioaccumulated POP and metal contamination on ecological water quality and fish communities*

**Poster presentation** ..... 252

**PT1** - Riikka Airaksinen - *Time trends of PCDD/Fs, PCBs, and PBDEs in Baltic herring in the Finnish coast of the Baltic Sea during 1978–2009*

**PT2** - Cancelled

**PT3** - Magdalena Boshoff - *Transfer and accumulation of Cd, Cu, Ni, Pb and Zn in a soil – plant – snail food web and the effect of metal pollution on physiological and morphological biomarkers in *Cepaea nemoralis* (Gastropoda: Pulmonata).*

**PT4** - Cancelled

**PT5** - Zaneta Barganska - *Levels of selected pesticides in honey samples from Pomerania, Poland*

**PT6** - Zaneta Barganska - *Determination of pesticide residues in honeybee samples with LC-MS/MS and GC-MS/MS*

- PT7** - Paola Avetta - *Evaluation of environmental impact of silica-based nanoparticles*
- PT8** - Joyce Cristale - *Priority and emerging brominated flame retardants in gull eggs (*Larus michahellis*) from Atlantic and Mediterranean colonies: trends and impact*
- PT9** - Maciej Durkalec - *The concentration of toxic metals in wild boars (*Sus scrofa ferus*) from industrial area in Poland*
- PT10** - Mehmet Emin Diken - *Inhibition effect of some pesticides on glutathion reductase and glutathion peroxidase*
- PT11** - Doga Erturk - *On the acute toxicity of polyphenols to freshwater alga *Chlorella vulgaris**
- PT12** - Jean Froment - *Identification of neurotoxic compounds in produced water discharges from offshore oil production platforms by high-throughput effect-directed analysis*
- PT13** - Leandro Figueiredo - *Human exposure to melamine from milk and related products – new molecularly imprinted polymer for melamine analysis*
- PT14** - Cancelled
- PT15** - Filipa Gomes - *Polycyclic aromatic hydrocarbon levels in octopuses from different geographical origins: inter- and intra-specific variability*
- PT16** - Angelika Hofer - *Monitoring the air quality in Venice-Mestre with *Tillandsia aernanthes**
- PT17** - Vera Homem - *Human Exposure Assessment to Musks in the Metropolitan Area of Porto (Portugal)*
- PT18** - Sergio Jarque - *Recombinant yeast bioassay and strategies towards a ready-to-use alternative for detection of endocrine disruptive compounds*
- PT19** - Rita Jordao - *Development of an obesogenic test in *Daphnia magna**
- PT20** - Laura Klavina - *Pollution stress biomarkers in bryophytes and their composition*
- PT21** - Berker Kocaturk - *Effect of some pesticides on antioxidant enzymes obtained from *cyprinus carpio carpio**
- PT22** - Szczepan Mikolajczyk - *Persistent Organic Pollutants (PCDD/Fs, DI-PCBs) in Wild Fish from Two Polish Main Rivers*
- PT23** - Alicja Niewiadowska - *Occurrence and levels of organochlorine pesticides and polychlorinated biphenyls in freshwater fish species from Poland*
- PT24** - Alicja Niewiadowska - *Environmental contamination of game animals by chlorinated hydrocarbons*

**PT25** - Felix Stibany - *Poorly Soluble Compounds in Cosmetics – an approach for a reliable environmental risk assessment (the ECOSM project)*

**PT26** - Josef Szkoda - *Toxic elements in free-living freshwater fish in Poland*

**PT27** - José Avelino Silva - *Comparison of different methods to quantify POPs and emergent pollutants using pine needles*

**PT28** - Melek Saçan - *Comparative performance of descriptors in a Multiple Linear and Kriging Models: A case study on the acute toxicity of organic chemicals to algae*

**PT29** - Agata Smalec - *Honey significance as bio-monitor for the environment*

**PT30** - Agata Smalec - *Toxic metals and trace elements in soil and fruiting bodies of selected mushroom species*

**PT31** - Jon Sanz-Landaluze - *Alternative bioaccumulation test using zebrafish (*Danio rerio*) eleutheroembryos*

**PT32** - Montserrat Tobajas - *Evaluation of toxicity and biodegradability of priority chlorinated compounds*

**PT33** - Malgorzata Warenik-Bany - *Bioaccumulation of PCDD/Fs and DL-PCBs in Wild Boars Tissue From Industrial and Agricultural Region of Poland*

**PT34** - Angela Dago - *Evaluation of the mercury stress produced in plants by the analysis of phytochelatin and its Hg complexes induced in *Asparagus acutifolius* and *Retama sphaerocarpa* from the Almadén mining district*

**PT35** - Cancelled

**PT36** - Cancelled

**PT37** - Tugba Yildiz - *Determination of tetracycline and  $\beta$ -lactam residues in chicken meat by hplc method*

**PT38** - Marta Wasielewska - *Malodorous monocarboxylic acids in the neighbourhood of animal farms. Determination in the air and wastewater*

**PT39** - Giulio Pojana - *Harmful algae in the Venice Lagoon and in the Po River Delta (northern Adriatic Sea, Italy)*

## **MODELLING, MANAGEMENT AND RISK ASSESSMENT**

**Oral presentation** ..... 287

**OM1** - Amrita Malik Baliyan - *Resolution of Environmental Pollution Profiles in Polluted River Waters by Chemometric methods*

**OM2** - Sven Kralisch - *Integrated Environmental Modelling with JAMS*

**OM3** - Montse Dalmau - *Membrane bioreactor modelling: deterministic vs data driven models*

**OM4** - Henry Wohrnschimmel - *Modeling the Environmental legacy of technical HCH usage and Lindane production*

**OM5** - Enrico Turrini - *Integrated assessment modelling to plan local optimal air quality policies harmonized with national and European actions*

**OM6** - Andreas M. Buser - *Physicochemical properties of dimethylsiloxanes and their impact on the environmental fate*

**OM7** - Xianming Zhang - *Integrating Near-field and Far-field Environmental Fate and Exposure Models for Screening-Level Exposure and Risk Assessment*

**OM8** - Sebastien Schenker - *Will Persistent Organic Pollutants reach a global equilibrium distribution?*

**OM9** - Mathieu Cladiere - *Assessing the impact of global change on micropollutants in aquatic ecosystems: Modelling the fate of nonylphenolic compounds in the Seine River*

**Poster presentation** ..... 296

**PM1** - Isabel M.H.R. Antunes - *Spatial vulnerability assessment and stochastic modelling of groundwater contamination in a transboundary watershed*

**PM2** - Florence Bonvin - *Micropollutant dynamics in Vidy Bay- a coupled photolysis-hydrodynamic model to assess the spatial extent of ecotoxicological risk*

**PM3** - Andreas Buser - *Emissions of cyclic volatile methylsiloxanes and polychlorinated biphenyls from Zurich, Switzerland*

**PM4** - Neus Collado - *Evaluating partial nitrification capability to degrade Sulfamethoxazole and their greenhouse gases emissions*

**PM5** - Mathieu Cladiere - *Determination of in-situ biodegradation rate constants of nonylphenolic compounds in the Seine River*

**PM6** - Jillian L. Goldfarb - *Assessing Vapor Pressure Models of PAC Mixtures*

**PM7** - Gerhard Lammel - *Evidence of the return of past organic pollution in the ocean – a model study*

**PM8** - Ramon López-Roldán - *Prediction of water sources contribution in Barcelona supply system by real time UV-Vis spectrophotometry*

**PM9** - Fabrizio Passarini - *The anthropogenic aluminium cycle through integration of MFA and LCA*

**PM10** - Christoph Schulte - *Poly- and perfluorinated compounds – global risks need global management*

**PM11** - Arngrimur Thorlacius - *Source-tracking of airborne dust by PLS modelling of spectrometric data*

**PM12** - Anett Utasi - *Advanced quantitative environmental impact assessment for red mud disposal facility*

**PM13** - Vuokko Malk - *Risk assessment of chemical accidents: Application of a screening model and a scoring method to a real accident case*

**PM14** - Antonio Marcomini - *Persistent Organic Pollutants' data in European Alps: A decade of multi-compartment monitoring*

**PM15** - Cancelled

**PM16** - Racha El-Osmani - *Monthly variation of geochemical parameters in the North Sea. From experimental to modelling*

**PM17** - Marta Roca - *Children exposure to pesticides in Valencia Region (Spain)*

## **TRANSFORMATION AND FATE OF POLLUTANTS**

**Oral presentation** ..... 313

**OTF1** - Florence Bonvin - *Direct photolysis of human metabolites of antibiotic sulfamethoxazole: Evidence for abiotic back-transformation*

**OTF2** - Elisa De Laurentiis - *A model approach to link indirect photochemistry in surface waters with climate change and human impact: the case of polymictic Lake Peipsi (Estonia/Russia) over the last three decades*

**OTF3** - Jagos Radovic - *Assessment of photochemical processes in marine oil spill fingerprinting*

**OTF4** - Tina Kosjek - *Fluorouracil in the environment: analysis, occurrence and transformation*

**OTF5** - Vladimir Nikiforov - *DFT study on hydrolysis of polyhalogenated pollutants for estimation of environmental degradation rates*

**OTF6** - Bozo Zonja - *Formation of phototransformation products of iodinated contrast media; natural attenuation or disinfection process?*

**OTF7** - Veronica French - *Evidence for Exposure to Chemical Contaminants in the Tropical Marine Snail Telescopium telescopium (Gastropoda:Potamididae)*

**OTF8** - Meritxell Gros - *Biodegradation of pharmaceuticals by the white rot fungus Trametes versicolor in hospital wastewaters; study of iopromide and ofloxacin as model compounds*

**OTF9** - Andreas Schaffer - *Biotransformation products of ibuprofen in soil - a new view on the relevance of non-extractable residues*

**OTF10** - Roland Kallenborn - *Enantiomer distribution of chiral pesticides in traditional food from Arctic Greenland. Elucidation of selected up-take and distribution processes*

**Poster presentation** ..... 323

**PTF1** - Jaume Aceña - *Fate and behaviour of erectile dysfunction drugs in wastewater treatment plants and receiving waters*

**PTF2** - Despina Athanasiadou - *Bio-Transformation Products of pharmaceuticals after biological wastewater treatment. A potential risk for the aquatic environment?*

**PTF3** - Maria Estrella Baez - *Sorption-desorption Behavior of Pesticides and their Degradation Products in Chilean Volcanic and Non-volcanic Ash-derived Soils*

**PTF4** - Monica Brienza - *Evolution of toxicity in an effluent containing hormone, Estradiol, during mineralization processes by heterogeneous photocatalysis and photo-Fenton*

**PTF5** - Michel Chalot - *The fate of trace elements during the combustion of phytoremediation wood*

**PTF6** - Jakub Cedrowski - *Antiradical activity of sulforaphane, a phytochemical considered as a protector against ultraviolet radiation.*

**PTF7** - Christophoros Christophoridis - *Simulation of the redox metabolism of antidepressant active compounds (emerging pollutants) by electrochemistry/mass spectrometry.*

**PTF8** - Elisa De Laurentiis - *Assessment of the photoreactivity of surface freshwater in extreme ecosystems: lakes in Terra Nova Bay, Antarctica, as a case study.*

**PTF9** - Antonella De Luca - *Atrazine removal in municipal secondary effluents by Fenton and Photo-Fenton treatments*

**PTF10** - Anko Fischer - *Assessing sources and sinks of hexachlorocyclohexane (HCH) isomers at contaminated field sites using stable carbon isotope analysis*

**PTF11** - Carlos Hurtado - *Fate of waterborne organic microcontaminants in the soil-plant system: Effect of biochar and nanoparticles*

**PTF12** - Xuexiang He - *Thermal and Transition Metal Activation of Peroxides for the Destruction of Emerging Cyanobacterial Toxin Cylindrospermopsin in Water Environment*

**PTF13** - Sebastian Huntscha - *Biotransformation of benzotriazoles: Insights from transformation product identification and compound-specific isotope analysis*

**PTF14** - Cancelled

**PTF15** - Axel Meierjohann - *Phototransformation of acidic pharmaceuticals in riverwater*

**PTF16** - Kaoruko Mizukawa - *Debromination of Polybrominated Diphenyl Ethers (PBDEs) by hepatic microsome of marine and freshwater fishes.*

**PTF17** - Monika Moeder - *In-vitro hydrolysis of asymmetric phthalates*

**PTF18** - Monika Moeder - *Efficient biodegradation of flumequine using ligninolytic fungi*

**PTF19** - Reinhard Oertel - *Determination of clindamycin and its metabolite clindamycin sulfoxide in diverse sewage samples*

**PTF20** - Julien Omlin - *Investigating the presence of phototransformation products of pharmaceuticals and their human metabolites in Lake Geneva*

**PTF21** - Christian Piechotta - *Identification and Characterization of New Disinfection By-products of Polycyclic Musks (AHTN and HHCB) in Swimming pool water*

**PTF22** - Sandra Perez - *Occurrence, fate, and transformation of the antiepileptic Lamotrigine*

**PTF23** - José Benito Quintana - *Oxidation of several pharmaceuticals with aqueous permanganate: reactivity, kinetics and transformation products.*

**PTF24** - Ana Ruiz - *Natural and reconstituted arkosic sedimentary rocks as landfill barriers for major solutes transport retardation*

**PTF25** - Mark Russell - *Elimination kinetics of perfluorohexanoic acid in humans and comparison with mouse, rat and monkey*

**PTF26** - Mark Russell - *Calculation of elimination half-life with an ongoing source: The example of perfluorooctanoic acid*

**PTF27** - Issac Rodríguez Pereiro - *Kinetics and transformation products of cocaine upon reaction with free chlorine*

**PTF28** - Isaac Rodríguez Pereiro - *Transformation of the fungicides triadimenol and fenhexamid under environmental conditions and UV exposure.*



- PTF29** - Benjamin Ricken - *Ipsso-hydroxylation initiates sulfonamide degradation by *Microbacterium* sp. BR1*
- PTF30** - Liliane Savoye - *Role of forest for atmospheric PAHs input into mid-mountain karst systems*
- PTF31** - Saleh Sulaiman - *Photocatalytic degradation of Spironolactone by using Advanced Process Oxidation (AOP)*
- PTF32** - Saleh Sulaiman - *Photodegradation and photocatalysis of Diazepam in liquid phase*
- PTF33** - Nivis Torres-Fuentes - *Photodegradation of the Mefenamic Acid and Fenofibrate on Soil Surface under Simulated Sunlight*
- PTF34** - Sarka Urcova - *Residues of Extraction and Refining of Crude Oil in Soils and Mobility of Oil Hydrocarbons in Snowpack*
- PTF35** - Konstantin Volchek - *Release of toxic organic compounds from contaminated building materials into air*
- PTF36** - Sian Evans - *Study of Stereoselective Degradation of Pharmaceuticals and Illicit Drugs in Wastewater and Receiving water bodies*
- PTF37** - Cancelled
- PTF38** - Anita Leovac - *Sorption behaviour of trifluralin and alachlor on selected sorbents in aquatic matrices of different origin*
- PTF39** - Mohamad F.Mohd Amin - *Surface to volume ratio effect on atrazine removal by polymer in water: cationic polymer mechanisms*
- PTF40** - Mathilde Monperrus - *The use of isotopic tracers to study the transformation rates, localization and biomolecular binding of Hg species at subcellular level in methylating and non-methylating sulphate-reducing bacteria*
- PTF41** - Gerald Thouand - *ProbaBio (Probability of Biodegradation): a new concept in the evaluation of biodegradation*
- PTF42** - Pascal Wong-Wah-Chung - *Fate of a pharmaceutical compound, pyrimethamine, in water under solar light irradiation*
- PTF43** - Amalia Muñoz - *Atmospheric degradation of pesticides. Studies at EUPHORE Chambers.*
- PTF44** - Amalia Muñoz - *Degradation of ethalfluralin under atmospheric conditions*
- PTF45** - Nareman D.H Khaleel - *Photocatalytic degradation of sulfamethoxypyridazine with TiO<sub>2</sub>, FeCl<sub>3</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub>: Biodegradability, toxicity assessment, and LC-UV-*

*MS/MS identification of the photodegradation products in aqueous and sewage treatment plant effluent*

**PTF46** - Waleed M. Mahmoud Ahmed - *Identification and initial toxicity assessment of Thalidomide and its photo transformation products*

**PTF47** - Pablo Campo - *Biodegradability of Corexit 9500 at 5 °C and 25 °C*

**PTF48** - Sara Rodríguez - *Comparison of Hydrolysis and Oxidation Processes for Degradation of Bisphenol A (BPA) from Wastewater Sludge*

## **GREEN AND SUSTAINABLE INDUSTRIAL CHEMISTRY**

**Oral presentation** ..... 370

**OG1** - Daniele Cespi - *Application of LCA methodology to a chemical process: the production of acrylonitrile by ammoxidation*

**OG2** - Victor Fabregat Tena - *Synthesis of photoactive hydrophilic polymeric materials. Applications in synthetic chemistry and pollutant degradation*

**OG3** - Dana Kralisch - *Chemical engineering of intensified flow-chemistry guided by sustainability issues*

**OG4** - Javier Francisco Da Costa Serra - *Sustainable Production of Hydrogen from Steam Reforming of Bioethanol Using a Recycled Catalytic Material*

**OG5** - Willem De Lange - *Polymers: out of REACH?*

**OG6** - Helena M.V.M Soares - *Pre-treatment of paper pulp in the bleaching process with a biodegradable chelating agent*

**OG7** - C. Estevez - *Transition from hazardous to green solvents: theoretical and practical challenges*

**Poster presentation** ..... 376

**PG1** - Cancelled

**PG2** - Ana Ferreira - *Effect of pickling process in chromium offer for bovine hide tannage*

**PG3** - Paola Galletti - *New solid acid catalysts from waste biomass: synthesis, properties and application to the obtainment of biodiesel from algae and waste oil*

**PG4** - Zeliha Gamze Alp - *Thermal kinetic studies of pva-bentonite nanocomposites*

**PG5** - Cancelled

**PG6** - Silvia Mosca - *Sampling of 5-ethylidene-2-norbornene in industrial flue gas*

**PG7** - Piotr Piotrowski - *Vanillin-derivatized C60 fullerene SAMs on gold electrode surface as example of green engineering*

**PG8** - Jose A.Saltos - *Synthesis, Properties and Performance of Eco-friendly Curcumin-derived Plasticizers for Poly(vinyl chloride)*

**PG9** - Vania F. Silva - *Gelatine recovering from wet-blue shavings*

**PG10** - Begoña Asenjo - *Degradation study based in Ultraviolet light test of EVA encapsulant of photovoltaic modules*

**PG11** - Cancelled

**PG12** - Cancelled

**PG13** - Cancelled

**PG14** - Vicente Martí-Centelles - *Biocompatible Gels from Amino Acids*

**PG15** - Raúl Porcar - *Sustainable Chemical transformations under continuous flow*

**PG16** - Cancelled

**PG17** - Philippe Garrigues - *Porous materials made from a paper mill by-product and the life cycle assessment of their environmental impacts*

**PG18** - Laura González - *Simple Chiral Ionic Liquids (CILs) from amino acids for the development of chiral media*

**PG19** - Yolanda Cesteros - *Calcined hydrocalumites as basic catalysts for the obtention of glycerol carbonate by transesterification of glycerol*

**PG20** - Cancelled

**PG21** - Cancelled

**PG22** - Cancelled

**PG23** - Maria Del C. Cotto-maldonado - *Photocatalytic Hydrogen Production by Water Splitting Using ZnCdFeCuS Nanoparticles Under UV-vis Light Irradiation*

**PG24** - Maria Del C. Cotto-maldonado - *Synthesis, Characterization of Au@TiO<sub>2</sub> Nanowires and their Production of Hydrogen by Water Splitting Under UV-vis Light Irradiation*

## **EMERGING POLLUTANTS**

**Oral presentation** ..... 393

**OE1** - Benny Chefetz - *Contaminants of emerging concern in the agro-environment: Uptake by crops, fate and processes*

**OE2** - Laurine Barritaud - *Occurrence of emerging organic micropollutants in urban wastewaters – Non-targeted analysis using GCxGC TOF MS and LC-HRMS*

**OE3** - Seyed Mohammad Majedi - *Toward a robust method for in situ separation, speciation analysis, and toxicity assessment of nanoparticles in natural water samples: Cloud point extraction of CuO nanoparticles*

**OE4** - Antonio Marcomini - *Agglomeration and sedimentation of Titanium dioxide nanoparticles (n-TiO<sub>2</sub>) in synthetic and real waters*

**OE5** - Cristina Valhondo - *Enhanced emerging contaminants removal during artificial recharge with a reactive barrier*

**OE6** - Philippe Garrigues - *Chemodiversity of organic xenobiotics in the environment: a naming and scientific nightmare?*

**OE7** - P. Lee Ferguson - *Helping contaminants emerge: The role of high-resolution mass spectrometry in non-targeted analysis of organic micropollutants in aquatic systems*

**OE8** - Leendert Vergeynst - *Development and application of a novel accurate mass based suspect screening methodology for the analysis of pharmaceutical residues in surface water by time-of-flight mass spectrometry*

**OE9** - Melanie Kah - *Environmental fate of nano-pesticides and implications for exposure assessment in the EU*

**OE10** - A. M. Tugulea - *Nano-Silver in drinking water and drinking water sources: stability and influences on disinfection by-products formation*

**OE11** - Daria K. Stepien - *Persistent hydrophilic ethers (1,4-dioxane and glymes) in surface- and groundwaters*

**OE12** - Roland Weber - *The pyridine-analogue of 2,3,7,8-tcdd is formed in the thermal treatment of chlorpyrifos and 3,5,6-trichloro-2-pyridinol*

**OE13** - Wendy D'Hollander - *Characterisation of perfluorooctane sulfonate in a contaminated terrestrial ecosystem in Belgium*

**OE14** - Cancelled

**OE15** - Laura Rohler - *Application of Visual Basic (VB) scripting and comprehensive GC/TOF for the identification of new halogenated contaminants in Norwegian ambient air samples*

**OE16** - Joyce Cristale - *Monitoring of flame-retardants using passive samplers*

**Poster presentation** ..... 408

**PE1** - Carolina Aristizabal-Ciro - *Determination of personal care products and pharmaceuticals in reservoirs water in Colombia by ultra-high performance liquid-chromatography-tandem mass spectrometry*

**PE2** - Alfredo C. Alder - *Occurrence of Perfluoroalkyl Substances in Sewage Sludge and Point Source Characterization*

**PE3** - Alfredo C. Alder - *Screening for Organic Micropollutants in the Prut River Basin at the Romanian-Moldavian border*

**PE4** - M.Rosa Boleda - *Identification of organic compounds migrating from a polymeric material into drinking water*

**PE5** - Esther Borrás - *Particulate matter formation from photochemical degradation of pesticides*

**PE6** - Ekhine Bizkarguenaga - *Determination of musks in vegetables and amended soil samples by stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry*

**PE7** - Ekhine Bizkarguenaga - *Simultaneous extraction of several polar organic pollutants in vegetables and seafood using focused ultrasonic solid-liquid extraction and different clean-up approaches*

**PE8** - Debora Bezerra - *Estrogens in suspended particulate matter: a quick, simple and reliable method*

**PE9** - Enrique Cequier - *Determination of emerging and common flame retardants in norwegian serum samples*

**PE10** - Paola Calza - *Fate of selected emerging contaminants in River waters*

**PE11** - Racha El-Osmani - *Organochlorine pesticides in akkar plain ground waters in north lebanon*

**PE12** - Pilar Fernandez - *Atmospheric deposition of polybrominated diphenyl ethers to remote European regions: geographical trends, congener patterns, and sources.*

- PE13** - Paola Gramatica - *Hazard Assessment of Emerging Pollutants: QSAR/QSPR models developed in the FP7 European Project CADASTER*
- PE14** - Aida Garcia-Rodriguez - *A new membrane-based device for the monitoring of sulfamethoxazole in water samples*
- PE15** - Ester Heath - *Environmental occurrence, fate and transformation of benzodiazepines in water treatment*
- PE16** - Pol Herrero Gil - *Occurrence of benzotriazole, benzothiazole and benzenesulfonamide derivatives in sewage and river water*
- PE17** - Thilo Hofmann - *Analysis of engineered nanoparticles in complex samples: concepts, common pitfalls, and recent solutions*
- PE18** - Melanie Kah - *Sorption behavior of carbon nanotubes: effects of dispersion and surface chemistry*
- PE19** - Pavlina Karaskova - *Perfluorinated Compounds (PFCs) in Modern Textile Materials*
- PE20** - Ivona Krizman - *Occurrence and behaviour of illicit drugs and therapeutic opiates in municipal wastewater treatment*
- PE21** - Sara Losada - *Presence of halogenated flame retardants in marine biota and sediment samples from the UK*
- PE22** - Sara Miralles-Cuevas - *Combined nanofiltration and photo-Fenton for treating water containing pollutants at  $\mu\text{g L}^{-1}$  initial concentration in natural water*
- PE23** - Mary Rosa R. de Marchi - *Multivariate optimization on UV filters extraction from natural water*
- PE24** - Catherine Munsch - *Legacy and emerging brominated flame retardants in shellfish from the French coasts: levels and temporal variations*
- PE25** - Jukka Pellinen - *Screening of emerging environmental contaminants with time-of-flight mass spectrometry*
- PE26** - Noora Perkola - *Occurrence of artificial sweeteners in Finnish rivers and lakes*
- PE27** - Kukka Pakarinen - *Adverse effects of fullerenes (nC60) spiked to sediments on an *Oligochaeta*, *Lumbriculus variegatus**
- PE28** - Fabio Polesel - *Modelling the fate of ciprofloxacin in activated sludge systems – The relevance of the sorption process*
- PE29** - José Benito Quintana - *A novel analytical method for the determination of amphetamines and ecstasy related stimulants from water and urine by solid-phase microextraction combined to gas chromatography-mass spectrometry*

**PE30** - Janine Richter - *Determination of Tributyltin in whole water samples*

**PE31** - Cancelled

**PE32** - Isaac Rodríguez Pereiro - *Matrix solid-phase dispersion followed by gas chromatography quadrupole time-of-flight mass spectrometry (GC-QTOF-MS) for benzotriazole UV absorbers determination in sludge*

**PE33** - Marta Seifertova - *New Method and Procedures of Determination of Alkylphenols in Indoor and Ambient Air*

**PE34** - Amelia Staszowska - *Preliminary assessment of emission of fluorotelomer alcohols from waterproofing impregnation sprays using thermal desorption-gas chromatography-mass spectrometry*

**PE35** - Laura Vallecillos - *On-line coupling of solid-phase extraction to gas chromatography-mass spectrometry to determine musk fragrances in wastewater*

**PE36** - Cancelled

**PE37** - Sebastian Westrup - *Enrichment free LC-HRAM/MS screening method of anthropogenic sewage pollutants in waste water, receiving, ground and drinking water samples*

**PE38** - Alberto Zafra-Gomez - *Removal of quinolone antibiotics from wastewaters by sorption and biological degradation in laboratory-scale membrane bioreactors*

**PE39** - Alberto Zafra-Gomez - *UPLC-MS/MS method for the determination of parabens in compost from sewage sludge. Comparison of the efficiency of two extraction techniques*

**PE40** - Laurine Barritaud - *Biological Tools to Optimize Treatment Technologies to Remove Micropollutants and Endocrine Disrupters (BIOTTOPE).*

**PE41** - Gabino Bolívar-Subirats - *UHPLC-MS/MS for the quantification of plasticizers in water samples and beverages*

**PE42** - Cancelled

**PE43** - Patricia Freixas - *Assessment of pesticide exposure in general population from Catalonia*

**PE44** - Albert Guart - *Migration of plasticizers from Tritan™ and polycarbonate bottles and toxicological evaluation*

**PE45** - Cristian Gómez-Canela - *Liquid chromatography coupled to tandem mass spectrometry and Orbitrap mass spectrometry as analytical tools to characterize multi-class cytostatic compounds*

- PE46** - Jani Koponen - *Improved analytical tool for epidemiological studies and biomonitoring - simultaneous determination of PFAS and POPs from a low volume human serum samples*
- PE47** - Kelvin Sze-Yin Leung - *Probing the environmental fate of artificial sweeteners: occurrence and toxicity study*
- PE48** - Ivana Mihajlovic - *Assessment of air-soil exchange of chlorinated organophosphate flame retardants (OFR)*
- PE49** - Rubén Moreno-Gonzalez - *Seasonal input of pharmaceuticals through surface waters to a Mediterranean coastal lagoon (Mar Menor, SPAIN)*
- PE50** - Rubén Moreno-Gonzalez - *Seasonal occurrence and distribution of pharmaceuticals in surface waters from littoral watercourses*
- PE51** - Cristina Postigo - *Occurrence and toxicity of haloacetaldehydes in drinking waters: first evidence of iodo-acetaldehyde as a water disinfection byproduct.*
- PE52** - Iana Russkikh - *Determination of pharmaceuticals in waterbodies of North-Western Russia*
- PE53** - Oihana Ros - *Determination of persistent and emerging organic contaminants and their metabolites in fish bile*
- PE54** - Oihana Ros - *Assessment of commercially available low-cost polymeric materials for sorptive extraction of priority and emerging non-polar organic pollutants in environmental water samples*
- PE55** - Cancelled
- PE56** - Rosario Rodil - *Matrix solid-phase dispersion extraction of halogenated flame retardants from mollusk samples*
- PE57** - Rosario Rodil - *Low and high resolution liquid chromatography-mass spectrometry determination of ethyl sulfate in wastewater for alcohol consumption tracing*
- PE58** - Maria Isabel Beser - *Design of experiment approach (doe) for the optimization of polybrominated diphenyl ethers (pbdes) determination in fine airborne particulate matter (pm 2.5) by microwave-assisted extraction and gc-ms/ms*
- PE59** - Jesica Podlipsky-Sanchez - *Biomonitoring of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Fishes of Lake Constance, Germany*
- PE60** - Amalia Muñoz - *Measurements of selected pesticides in ambient air in the Valencia Region*



**PE61** - Gerard Bondoux - *Detection, identification and structural elucidation of unknown contaminants during a routine non targeted screening of river water samples using a new scientific information system.*

**PE62** - Giulio Pojana - *From basic to advanced characterization of engineered nanoparticles (NPs): the Nanotest project*

**PE63** - Laura Ferrando-Climent - *Incidence of chemotherapy drugs in the aquatic environment and their elimination by non conventional wastewater treatment by *Trametes Versicolor*.*

**PE64** - Ruben Reif - *Economic valuation of polishing WWTP effluents using ozonation to enhance PPCPs removal: environmental benefits*

**PE65** - Richard Bade - *Modern analytical methodology based on UHPLC-MS/MS for the sensitive determination of illicit drugs in urban wastewaters with emphasis in amphetamine and derivatives*

**PE66** - Wayne Civil - *Routine 'Trace level screening' for a broad range of volatile and semi-volatile organic pollutants in a range of Environmental waters using 'full scan' GC-MS with a 950 compound target screening database and deconvolution software*

## PLENARY LECTURE 1

### Optimizing the removal of trace organic contaminants in managed natural treatment systems

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Concerns associated with the presence of organic chemicals in wastewater effluent and urban runoff are necessitating the development of treatment technologies that are capable of removing trace concentrations of organic contaminants. Managed natural systems have the potential to provide cost-effective approach for achieving this objective. Engineered treatment wetlands have been used for decades as a means of removing nutrients from municipal wastewater effluent and urban runoff. Due to their low energy requirements and operational costs, as well as ancillary benefits, including the creation of aesthetically appealing spaces and wildlife habitat, they are an attractive option for treatment of trace organic contaminants. Despite the widespread enthusiasm for wetland treatment, concerns about variations in treatment efficacy coupled with an incomplete mechanistic understanding of contaminant removal in wetlands have hindered the widespread adoption of constructed wetlands for trace contaminant removal. Designing wetlands in a unit process manner, with individual wetland cells connected in series and optimized to enhance the removal of specific contaminants, could result in more efficient and reliable treatment of contaminants. For example, shallow, open-water treatment cells equipped with a liner to prevent the growth of rooted plants, can achieve excellent removal of a variety of trace organic compounds through a combination of photochemical reactions and biotransformation by microbes associated with a photosynthetic community lining the bottom of the basin. This type of unit process wetland cell can be included in a treatment train that includes vegetated surface flow wetlands and subsurface wetlands to achieve the simultaneous removal of a suite of contaminants. By considering the desired treatment objective and hydrology of the system, substantial improvements can be made in the performance of unit-process wetlands. This unit process approach can be used to improve water quality throughout the urban water cycle.

## PLENARY LECTURE 2

### Biomarker tools for abrupt climate change description in marine sediment cores

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Abrupt climate changes involve rapid climate oscillations expanding over short time intervals (millennial, centennial, decadal) which in some occasions are of comparable intensity (or even larger) than glacial-interglacial transitions. In marine sediments these events are recognized by changes in  $\delta^{18}\text{O}$  in foraminifera and sea surface temperature measurements (SSTs), generally based on the  $\text{C}_{37}$  alkenone composition or sometimes on Mg/Ca ratios in foraminifera. Obviously, these climate changes involve many other variations such as marine productivity, wind speed, vegetation type, marine surface currents, intensity of deep water currents, rain and snow regimes, and others that should be characterized for a complete understanding of their origin and impact.

Biomarkers take advantage of the wealth of information contained in the complexities of sedimentary organic constituents and may be useful for the description of both SST and these additional climate parameters. In this paper, several applications in the use of biomarkers for this purpose are summarized based on our on-going studies in the north Atlantic Ocean. The usefulness and range of application of  $\text{C}_{37}$  alkenones for the description of SST and displacements of the arctic front are considered (Grimalt et al., 2011; Martrat et al., 2004; 2007; Vautravers et al., 2004). This proxy is compared to the SST measurements obtained with isoprenoid glycerol dialkyl glycerol tetraethers ( $\text{TEX}^{\text{H}}_{86}$ ) in sequences recording abrupt changes (Huguet et al., 2011). The usefulness of odd carbon numbered  $\text{C}_{23}\text{-C}_{31}$  n-alkanes and even carbon numbered  $\text{C}_{22}\text{-C}_{30}$  n-alkan-1-ols for the measurement of wind intensity is also considered (Lopez-Martinez et al., 2006). Ratios between n-hexacosan-1-ol and n-nonadecane are also used for the measurement of the intensities of deep water currents (Martrat et al., 2007; Cacho et al., 2000). Examples of applications of all these proxies are shown. They records are compared with those obtained from the analysis of foraminifera, pollen and other proxies.

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## PLENARY LECTURE 3

### Sources, processes and impact of atmospheric aerosols

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Atmospheric aerosol particles are liquid or solid particles suspended in the atmosphere. Generally, the sizes of aerosol particles are in the range 0.001 - 100  $\mu\text{m}$ . Atmospheric aerosols are of interest mainly because of their effects on health and climate. Concerning health, many epidemiological studies have shown a link between increased mortality/morbidity and increased  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$  (particulate matter with an aerodynamic diameter smaller than 10 and 2.5  $\mu\text{m}$ , respectively). Concerning climate, aerosol particles scatter and absorb light (known as the direct effect on climate), and modify cloud properties (with a variety of effects known as indirect effects). These effects are influenced by the chemical and physical properties of the aerosol particles, which makes these properties important to be measured.

Atmospheric aerosol particles are produced by a large variety of sources, and are either emitted as primary particles (i.e., they are directly emitted as particles into the atmosphere) or formed by secondary processes (i.e., by transformation of emitted precursor gases). While the formation pathways of secondary inorganic aerosols such as nitrate and sulfate in general are reasonably well understood, the formation of secondary organic aerosol (SOA) is still an area of active research. A wide variety of gaseous precursors contribute to SOA, and their aerosol yields depend on a wide variety of conditions. In addition, it is still largely unknown to which extent and under which conditions oxidized organic molecules can contribute to nucleation, i.e., the formation of new particles.

This presentation will give an overview on recent laboratory experiments and field campaigns. The lab studies relate to SOA formation from a variety of precursors as well as the formation of new particles from gaseous sulfuric acid in combination with other precursor gases where the latter experiments have been performed in the CLOUD experiment at CERN. The field studies relate to the latest developments of source apportionment studies for the organic aerosol, which build on positive matrix factorization of aerosol mass spectrometer data.

## PLENARY LECTURE 4

### Toward a Better Understanding of the Fate, Behaviour and Risk of Fullerenes and other Carbon-Based Nanomaterials such as Carbon Nanotubes in the Total Environment

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Carbon based nanomaterials (NMs) of different kinds have been reported to occur in ordinary hydrocarbon flames [1, 2] and, emitted from common heat sources [1, 3]. It has been assessed that the amount of incidental nanoparticles (NPs) in the atmosphere due to human activity is more than 36% of the total particulate number concentrations. Fullerenes have attracted considerable interest in many fields of research and have found numerous applications which will be dramatically increased during the following years. Therefore, it is essential to determine the risk that these materials may pose to human health and the environment [4,5]. In addition, little is known about the bioavailability of NPs and NMs and their bioaccumulation potential. The heteroaggregation of NPs and NMs with organic colloidal particles may also alter the bioavailability of other environmental organic contaminants.

In this presentation different analytical approaches based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) will be introduced and environmental results of the investigation of the occurrence of fullerenes (C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub> and C<sub>84</sub> fullerene, C<sub>60</sub> pyrrolidine tris-acid ethyl ester, [6,6]-Phenyl-C<sub>61</sub> butyric acid butyl ester and [6,6]-Thienyl C<sub>61</sub> butyric acid methyl ester) in different environmental matrices [6-8] (suspended materials of wastewater and river water, air borne particulate, soils and sediments) will be discussed. First results on the characterization of NMs under real environmental scenarios of exposure and the toxicity of fullerene soot and other carbon based NMs, such as multiwall carbon nanotubes and graphene will be presented. In addition, synergistic/antagonistic effects with representative xenobiotics susceptible to be present in the same environmental compartments will be as well discussed in this presentation. Finally, the enhancement or limitation of the bioavailability of organic pollutants, such as brominated flame retardants, by the presence of NPs and NMs (Trojan effect) will be reported.

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## Green and Sustainable Chemistry: Methods and Metrics

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The trend towards what has become known as sustainable technology or green chemistry necessitates a paradigm shift from traditional concepts of process efficiency, that focus on chemical yield, to one that assigns economic value to replacing fossil resources with renewable raw materials, eliminating waste at source and avoiding the use of toxic and/or hazardous substances. The ultimate goal is technological sustainability and green chemistry is a means to achieving it.

Green chemistry is primary pollution prevention rather than end-of-pipe waste remediation. The need for a greening of chemicals manufacture is readily apparent from a consideration of the amounts of waste generated per kg of product in various segments of the chemical industry (see table), which we designated as the E factor. A primary source of waste is the use of (mainly inorganic) stoichiometric reagents resulting from the use of antiquated 'stoichiometric' technologies and a major challenge is to develop atom efficient catalytic processes.

### E Factors in the chemical industry

<u>Industry segment</u>	<u>Product tonnage</u>	<u>E ( kg waste/kg product)</u>
Bulk chemicals	$10^4 - 10^6$	< 1 - 5
Fine chemicals	$10^2 - 10^4$	5 - >50
Pharmaceuticals	10 - $10^3$	25 - >100

The above principles are illustrated by reference to the application of catalytic methods - homogeneous, heterogeneous, organocatalysis and biocatalysis - in industrial organic synthesis.

A prerequisite for progress is the ability to compare the greenness and sustainability of products and processes employing meaningful metrics. There is no absolute greenness, however, there are many shades of green. The most widely accepted measures of the environmental impact of chemical processes are, probably not coincidentally, the two most simple metrics: the *E factor* (see above) and the *atom economy* or *atom utilisation*. These and other green and sustainability metrics will be discussed and compared.

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## Characterisation and Behaviour of Nanoparticles from Road Traffic Exhaust

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Road traffic exhaust is the dominant source of nanoparticles in the urban atmosphere, with the only other source of appreciable magnitude being regional nucleation. An analysis of particle number count data from across Europe shows a clear influence of regional nucleation in southern Europe but a much smaller effect in northern Europe. The nanoparticle fraction of vehicle engine exhaust comprises two distinct particle types; one type is predominantly graphitic carbon with a typical modal diameter of around 70 nanometres whereas the other mode comprises condensed semi-volatile materials with a typical mode of around 20 nanometres resulting from nucleation during the dilution of exhaust emissions with ambient air. There is much evidence from laboratory studies that the latter component in diesel exhaust is sensitive to the sulphur content of the fuel, and atmospheric measurements indicate that the move to “zero sulphur” diesel fuel has had a substantial impact on the nanoparticle fraction in urban air.

There is relatively little information available on the chemical composition of the nucleated particle fraction of exhaust nanoparticles but the available studies indicate the predominant source being from semi-volatile compounds in lubricating oils. The most abundant individual species appear to be *n*-alkanes but there is little information on the other components as traditional gas chromatography is unable to resolve them.

Studies in the atmosphere have demonstrated the semi-volatility of the nucleated nanoparticle fraction and that such particles tend to evaporate on moving away from the traffic source. These studies will be reviewed and possible implications for human health will be considered. The evaporation process releases high molecular weight organic compounds which are then subject to oxidation, leading to a substantially increased mass of secondary particulate matter, as well as contributing to photooxidant formation.

### Universe of organics in drinking water treatment processes

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There are two types of organics relevant for drinking water treatment: natural organic matter (NOM) present in mg/l level and synthetic organic compounds (SOC) among which individual xenobiotics appear in a range of less than ng/l up to µg/l. Even though two classes have been dealt with separately, they belong to the same, but site-specific, galaxy of organic carbon family. Both groups of organics are relevant for water quality and affect process efficiency in either direct or indirect way. Over the last 50 years, both groups have been the subject to intensive research in the field of drinking water treatment (DWT) worldwide and are thus well-known to water professionals. The lecture will present a chronological overview of the main issues set in historical context. In pioneer days, the main driving forces for research were human health risks and optimisation of water treatment. In focus were the NOM structure, disinfection by-products (DBPs) formation, NOM removal with coagulation, adsorption, oxidation and development of most efficient water treatment trains. Surprisingly, after decades of research, rapid development of analytical techniques and progress in risk assessment, the same driving forces are still in the limelight - although the topics have changed a bit. The attention switched from trihalomethanes to a new generation of DBPs. The definition of hydrophilic/hydrophobic NOM depends on a technique used for characterisation (e.g. resin fractionation vs. LC/OCD analysis). Finally, the emerging xenobiotics are not the only emerging issue in water treatment. As far as processes are concerned, the application of membrane filtration is among the most prominent developments, where the mainstream research has been following three lines: fouling mechanisms related to NOM, potential of hybrid processes and interaction between membranes and xenobiotics. Related to xenobiotics, it has become evident that numerous organic compounds can threaten water supply sources. Some of them have been ignored or overlooked in the past but recently detected by advanced analytical tools even in drinking water. It was proven that priority pollutants are not always the key pollutants in European waterbodies – therefore, prioritisation becomes priority *per se*. From the water supply source to the tap, NOM is not a passive constituent that needs to be transformed and more or less removed. On the contrary, NOM interacts with xenobiotics as well as surfaces and generally determines the transport and fate of pollutants. The role of these interactions will be emphasised. The lecture will present an overview of the main DWT processes used for removal of organics, such as bank filtration, oxidation, coagulation, adsorption and membrane filtration with the emphasis on efficiency, main findings and research interests related to them. Although the state-of-the-art technologies seem to have an answer to each and every question raised, it is still necessary to deal with specific problems on case-by-case basis. Despite of decades of research and vast amount of information collected, there is a serious lack of simple tools to apply that knowledge, mainly due to unique nature of NOM and different xenobiotics, which may appear in various types of waters. In the end, human health risk, which derives from the presence/absence of organics, is only the tip of the iceberg – underneath lies the whole new universe – socio-economic aspect of water treatment and quality that deserves much more attention.



## Defining and Applying the Concept of Bioavailability- Techniques and Applications

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Although currently used within regulatory frameworks, a total measure of contaminants in the environment is a poor predictor of hazard and risk. The use of bioavailable or bioaccessible fractions offers a meaningful alternative. Current confusion in terminology and procedures negates its widespread adoption.

These are complex and dynamic terms influenced by a wide range of physical, chemical and biological factors. The terms are best defined by relating the response of a receptor to the particular chemicals of interest.

In the case of hydrocarbons and organic pollutants, the term bioavailability refers both to the fraction that may cause harm or be accumulated by a receptor but also the portion that may be in a form suitable for biodegradation. For elemental pollutants the term is applicable to trace nutrient assimilation and pollutant uptake.

To predict biodegradation, assays have been conducted that combine biotechnological interrogation with chemical analysis. This has enabled innovative applications in full scale trials.

For elemental contaminants, our research highlights the importance of a biological membrane and its interaction with external medium. Although our results show similarities between processes occurring in the aqueous environment and soil and sediment pore waters, the bioavailable fraction is larger than the dissolved pool of metal. The assays based on macro-organisms (plants, earthworms, infaunal organisms) demonstrate the affinity between the relative magnitude of the bioavailable fraction, physico-chemical parameters of the environment and the effect of time.

Bioaccessibility refers to a greater portion than the bioavailable fraction but enables an insight into human exposure pathways. In these applications, empirical measurements are integrated with human exposure models to derive protective limits.

Environmental protection and pollutant mitigation requires the adoption of these terms to derive innovative techniques for sustainable long term security.

## Emerging pollutants: of old compounds and new ones, of micrograms and tonnes, from the past to the future

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Some decades ago there were less different chemicals in use than nowadays. Often the tonnages produced were lower too. Concentrations in the environment, though, were often higher, i.e. in some cases in the mg/L-range. The progress of waste treatment and wastewater treatment as well as avoiding waste as a result from different production methods of chemicals has changed the situation. Still, in total there are more different chemicals on the market in a higher tonnage nowadays. In the EU about 100 000 chemicals are in use. It is estimated that up to 30 000 may be of environmental relevance. Nowadays the reason for their input into the environment is not improper handling of waste and wastewater but instead the proper use of products containing them. Typical examples for this are personal care products, pesticides, detergents, flame-retardants, textile chemicals to name just a few. Therefore nowadays there are many more different chemicals present in the environment, albeit often in lower concentrations. Although being in use even for decades in some cases, they have often not been analysed because of limitations of knowledge and analytical equipment. With the advent of the Internet on the one hand and the liquid chromatography coupled to mass spectrometry on the other hand, the situation has changed. It is now much easier to get information about chemicals constituting the products as well as to measure them. The on-going detection of compounds not measured before led to the expression of “emerging” pollutants or “micro-pollutants because of their concentrations in the  $\mu\text{g/L}$  or  $\text{ng/L}$ -range. Despite the low concentrations measured, such chemicals are often used in high tonnages. Therefore, they are present worldwide in a range of (aquatic) environments including big compartments such as lakes, rivers, freshwater, catchments, estuaries, reservoirs and marine waters. Therefore it is of high importance ( important )not only to keep in focus their low concentrations but also their total mass flows. Furthermore, only recently the fact gained more attention that these pollutants are often incompletely degraded. The challenge for the assessment of the parent chemicals that might be introduced into the environment already is a big one - if possible to master at all - because of numerous end points as well as limitations in time and financial resources. This holds even more for the myriads of possible transformation products.

Therefore chemicals of the future have to be designed in a manner that they fulfil the needs the consumer expects but at the same time that part of their functionality must be ready biodegradability at the end of their life before they enter the environment. As far as possible, knowledge gained by the analysis and assessment of emerging, i.e. micro-pollutants, is an important resource for this approach.

In summary, environmental chemists should not just go on to measure ever “new” compounds that at present are in low concentrations in the environment. They also have to think in terms of substance in order to set priorities and think about how to use the gained knowledge for improved emission treatment and improved, i.e. more sustainable, chemicals and contributing to sustainable chemistry. In other words we have to switch our view from the past to the future.

## **The Next Generation of Drinking Water Disinfection By-Products: Occurrence, Formation, Toxicity, and New Links With Human Epidemiology**

Susan D. Richardson

USA

Drinking water disinfection has been rightly hailed as a public health triumph of the 20<sup>th</sup> century. Millions of people worldwide receive quality drinking water every day from their public water systems. However, chemical disinfection has also produced an unintended health hazard: the potential for cancer and reproductive/developmental effects that are associated with chemical disinfection by-products (DBPs). Chemical disinfectants are effective for killing harmful pathogens in drinking water, but they are also powerful oxidants, oxidizing the organic matter, anthropogenic contaminants, and bromide/iodide naturally present in most source waters (rivers, lakes, and many groundwaters). Chlorine, ozone, chlorine dioxide, and chloramines are the most common disinfectants in use today, and each produces its own suite of DBPs in drinking water.

Of more than 600 DBPs known, only 11 are currently regulated in the United States. And, those that are regulated do not cause the primary type of cancer (bladder cancer) that is observed in the human epidemiologic studies. Recent research has identified 'emerging', unregulated DBPs that are more cytotoxic and genotoxic than those that are currently regulated, and the use of newer alternative disinfectants (chloramines, ozone, chlorine dioxide) can increase their formation. This is important because many drinking water utilities in the U.S. and throughout the world are changing from chlorine to alternative disinfectants to meet stricter regulations. Emerging DBPs include iodo-acids, iodo-trihalomethanes (Iodo-THMs), bromonitromethanes, haloamides, haloquinones, and nitrosamines (including nitrosodimethylamine, NDMA). In addition, new research has revealed that DBPs can be formed from pharmaceuticals and other anthropogenic contaminants introduced by wastewater inputs into drinking water supplies. To that end, the formation of toxicologically important DBPs from pharmaceuticals used for medical imaging (X-ray contrast media) will also be discussed. Finally, results from a new European epidemiologic study will be presented, which is the first study to integrate toxicology and chemistry data with human epidemiologic data for drinking water DBPs.

## Fate of PCB in aquatic ecosystems : cold case or hot topic ?

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Polychloro biphenyls (PCB) have been widely used in a variety of applications since their first industrial synthesis in 1929. Their use was banned in the 1970s in USA and in the 1980s in Europe because of their bioaccumulation and toxicity. However, significant quantities are still detected in all aquatic ecosystems because of the partial volatility and the strong persistence of these organic compounds<sup>1</sup>. Numerous papers in the literature are dealing with the quantification of PCB in the environmental systems but few of them deal with the fate of these pollutants. For example, the knowledge of their transfer from polluted river to lake, their repartition in the water bodies, their transfer from sediment to water, or the factors controlling their bioaccumulation in biota<sup>2</sup> are still poorly documented.

My talk will try to answer to some of these questions which are relevant because of the stepping up of the european regulation (setting maximum levels for PCB in fish<sup>3</sup>) but also because of the textbook case of a world wide contamination by a group of persistent organic congeners, having different physico-chemical (Koc, Koa, Sw...) or toxicological properties (dioxine-like PCB or non dioxin-like PCB).

The case of three peri-alpine lakes (Geneva, Bourget and Annecy) will be discussed in order to better understand how the catchment area planning can affect the contamination of the aquatic ecosystem. Whereas the contamination has clearly decreased in Geneva and Annecy lakes since 1980s, an important cleaning-up of an affluent of the Bourget lake is in process to achieve an acceptable ecological level. In this talk, a comparison with high altitude remote mountain lakes of the french Alps helps to quantify the atmospheric contribution to PCB contamination and lead to a better understanding of the factors governing the bioaccumulation in aquatic organisms. First results show that despite an homogeneous atmospheric deposition and a low water contamination, the PCB levels in the fish evolve differently between lakes and seasons.

From our point of view, the study of PCB in aquatic ecosystems is still a topic of great interest because of the widespread contamination by these persistent organic pollutants (POP) and because of the significant differences in physico-chemical properties of the congeners allowing to extend conclusions to other emerging POP.

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## Geochemistry of atmospheric particulate matter: from remote to urban environments

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Atmospheric suspended particles (or atmospheric aerosols) are ubiquitous in the atmosphere. Aerosols enter the atmosphere from a variety of sources, natural or anthropogenic, such as wind resuspension, industrial processes, fossil fuel burning, biomass burning and other biological sources such as pollen and viruses. Particles may be directly emitted as they are (primary particles) or may be formed in the atmosphere by chemical reactions from gaseous precursors or pre-existing particles (secondary particles). As a consequence of both the variety of sources and the complexity of atmospheric processes, the atmospheric particulate matter (PM) is a complex mixture of organic and inorganic components with a wide grain size distribution, showing a high spatial and temporal variation in concentration and composition.

Major components of the atmospheric aerosols are dust, sea spray, organic and elemental carbon, sulphate, nitrate, ammonium and a variety of metals. The concentrations, relative proportions and grain size distribution of these species will depend on nature and proximity of emissions, photochemical activity and meteorology. In remote continental areas, particulate matter is mainly composed of elements of a major crustal related origin, with different contributions of anthropogenic components transported from distant areas. In urban areas, contribution of a high variety of anthropogenic sources (mainly road transport, heating, construction, industrial activities, energy production, waste incineration...) result in high concentrations of carbonaceous compounds, secondary aerosols and metals (such as Fe, Cu, Zn, etc).

This paper synthesizes data on particulate matter (PM) chemical composition obtained over the past decade at around 40 natural background, rural, urban, and kerbside sites across Spain. Special attention is paid on the measurements obtained at a remote, a regional and an urban background sites located in Northeast Spain. A comparative assessment on the variability of major and trace PM components is carried out for the different environments. This kind of study permits to interpret the local and external contributions of natural and specific anthropogenic sources. Interpretation of the temporal and spatial variation of relative concentrations of specific airborne metals is carried out in order to identify a number of anthropogenic sources. Application of source apportionment models to the extensive chemical database available permits to quantify the contribution of PM sources.

## Effect-directed analytical approaches for the identification of contaminants of emerging concern

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There is increased focus on the presence of different chemicals in the environment that may have a detrimental effect on human health and/or the environment. Trying to establish those chemicals that may be exerting an effect is a difficult task due to the reliance of society on chemical products and their subsequent release into the environment. The European Chemicals Agency (ECHA) through its REACH (**R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemical substances) regulation has greatly improved how we in Europe evaluate the chemicals that we as a society are so heavily reliant upon. However, REACH and other regulatory mechanisms cannot be relied upon, no matter how effective they are, as a single approach to protect the environment and human health. Additional sources of information are needed to ensure that chemical threats are identified before any long term harm is caused. Targeted and broad-spectrum non-targeted analytical approaches can be used to inform on the presence of a specific chemical in a particular environmental compartment allowing the risks posed to be assessed. The challenges lie in identifying those specific chemicals that are exerting the greatest effect, including effects that may not necessarily be included in standard risk assessments. One such approach that has been proposed for the identification of chemicals demonstrating effects in the environment is effect-directed analysis (EDA). Effect-directed analysis is typically steered by a biological response(s) and in combination with isolation techniques, such as chromatographic fractionation based upon physico-chemical properties, and non-target mass spectrometric analysis. The technique has been widely employed with varying degrees of success as a research tool to identify contaminants of emerging concern in the environment and a number of examples will be presented. A number of key questions arise concerning the applicability of EDA as an approach, in particular regarding its success rate and whether it can develop from a specialized research tool to a hazard identification technique that is commonly applied. Examples of successful EDA studies will be provided along with the most recent developments as well discussion of where next for an approach that directly integrates bioassays with analytical chemistry.

## Sustainable Chemistry: from renewable resources to chemicals via catalysis

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Increasing demand of liquid fuels, chemicals; diminishing of petroleum amounts and growing instabilities in some production fields are strong arguments to find replacement from renewables. But if the use of renewable raw materials opens a wide spectrum of synthesis methods and end-products, some of which are quite different from those accessible by petrochemical routes. As mentioned in a recent paper (Chemical and Engineering News, December 3, 2012), Mitch Jacoby told that 'suitable catalysts for converting biomass to chemicals and fuels at low cost are not generally available today'. Moreover he added further that 'transforming biomass-derived compounds, such as carbohydrates and other highly oxygenated compounds generally calls conditions which may ruin porous oxide catalysts and which make petroleum refining catalysts unsuitable for biomass refining'.

To overcome these problems, even if catalysis is expected to play a pivotal role the prerequisite of the chemists is to find innovative catalytic chemistries to process these biopolymers into useful products. Indeed these raw materials are in most cases polyfunctional and their transformations require a close control of the selectivity.

Starting from oils, fats, sugars, cellulose, hemicelluloses, lignin, their conversion into higher added-value products (chemicals) require numerous and very different chemical steps including consecutive separation and purification and wastes treatment. Recent studies clearly showed that multifunctional catalysts based on porous inorganic or organic solid supports can directly and positively impact on the reaction rate and selectivity. The development of such new catalysts with a controlled distribution of different and dedicated active sites is probably one of the most fascinating examples. Moreover a control of the hydrophilicity of catalytic surfaces is also an important parameter and playing with the hydrophilic properties of a material surface can also significantly change the selectivity.

In this lecture, it will be showed that from the design of new catalysts surfaces it is possible to limit a lot of secondary reactions allowing us to transform carbohydrates, glycerol, hydroxylated fatty acids, unsaturated esters, ... with a high selectivity and yield. Moreover when possible the use of a solvent was avoided but for specific reactions and/or when starting from lignocellulosic compounds it is also a priority to search either new cheap and safe solvents capable of replacing the traditional volatile organic solvents or specific ones to perform new reactions. Finally it will be also demonstrated that 'catalysis' can be strongly improved when assisted by a physical technique such as a non thermal plasma, microwave, ...

## **Advances in software system for supporting environmental decision making**

Andrea Rizzoli

Understanding the complex relationships between humans and the environment is becoming more and more important. The efficient and sustainable management of environmental systems is essential to provide essential services such as water, for drinking and irrigation, preserving ecosystem diversity, guaranteeing food security, and an acceptable air quality, to name a few. As the scale of the challenge is rising, the need for sound methodological approaches to assist environmental managers is strong as ever, and environmental decision support systems (EDSS) can package and deliver such approaches.

Software systems have made huge progress in the last decade, and EDSSs are taking advantage of that progress. Here we want to discuss, appreciate and evaluate the impact of software engineering methods and computing tools in the implementation and delivery of modern EDSS. Topics include distributed and cloud computing, social computing, crowdsourcing, the semantic web and ontologies, open linked data, big data and non-SQL databases, GPU and parallel computing, advanced visualization techniques, agile programming and domain-specific languages, and their use in environmental software applications



## Removal of Pollutants in Water and Wastewater by Solar Advanced Oxidation Processes

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Conventional wastewater treatment plants, which make use of activated sludge systems to reduce biodegradable chemical oxygen demand (COD), are not effective when industrial wastewaters have to be treated due to the high COD load and the presence of recalcitrant compounds. This drawback becomes particularly critical when a significant concentration of non biodegradable toxic compounds is also present rendering the wastewater itself toxic to the microorganisms responsible for the biodegradation. In such instances, environmental regulatory requirements can be achieved by chemical oxidation pre- or post-treatments. Post-treatments can be used as polishing step after a biological treatment in the case of wastewaters containing large amounts of biodegradable organics and small concentrations of recalcitrant compounds. Pre-treatments can be advisable in the opposite case. The key is to minimize residence time and reagent consumption during the expensive chemical oxidation stage by applying an optimised coupling strategy.

The development of new analytical techniques like chromatography coupled with mass spectrometry, which push the limit of quantification/detection further into the low nano-gram range, permitted the detection and analysis of new contaminants and its metabolites in environmental samples, in extremely low concentrations. The so called “emerging contaminants” (ECs) are defined as a group of organic substances which are not subject to restrictions of any kind, but may be candidates for future regulations. The principal characteristic of these contaminants is that they do not have to be persistent in the environment to cause negative effects on life forms, as their possible high degradation and/or elimination are compensated through the constant release into the environment.

This work will overview several different advanced processes for treating water pollutants with emphasis on solar AOPs (TiO<sub>2</sub> photocatalysis and photo-Fenton) and their application in the treatment of wastewaters containing conventional contaminants, micro-pollutants and ECs.

**Oxidative Transformation of Cyanotoxins and other Contaminants of  
Emerging Concern in Water  
Using Advanced Oxidation Processes**

***Prof. Dionysios (Dion) D. Dionysiou***

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In modern treatment processes for water treatment and reuse, Advanced Oxidation Processes (AOPs) are gaining popularity for the removal of contaminants of emerging concern. Both homogeneous and heterogeneous AOPs are currently intensively explored for their beneficial use in a variety of types of unit operation treatment “train” in water treatment plants. In this presentation, Professor Dionysiou will overview mechanistic transformation pathways of treatment of cyanotoxins using AOPs. Emphasis will be given on UV and Solar-based Advanced Oxidation Processes such as TiO<sub>2</sub> photocatalysis (UV and visible) (i.e., a heterogeneous AOP) and UV/H<sub>2</sub>O<sub>2</sub> process (i.e., a homogeneous AOP). Details will be presented on the degradation of cyanotoxins like microcystin-LR (MC-LR), microcystin-YR (MC-YR), other microcystin isoforms, and cylindrospermopsin (CYN). Transformation kinetic rates and reaction intermediates formed by OH radical attack on specific sites of the target contaminants will be presented and the detailed reaction pathways will be discussed. Discussion will also be provided when oxidation takes place by other radicals like sulfate radicals and superoxide anion radicals under certain modification of the processes described above. The role of water quality parameters such as natural organic matter, alkalinity and pH will be discussed. The presentation will also highlight selective results of the transformation of some other contaminants of emerging concern like antibiotics, steroids, and hormones using these AOPs as well as combined biological-AOP processes.

## Novel strategies for the analysis of fullerenes in environmental samples

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Emerging contaminants have appeared in the last years as an issue of interest in environmental chemistry. These contaminants comprise products which are used in large amounts in everyday life, such as plasticizers, surfactants, human and veterinary pharmaceuticals and personal care products. Although most of these compounds are not persistent they can cause negative effects on the environment because of their continuous use and release. In this context, the important development of nanotechnology that has dramatically increased in the last ten years has led to the emergence of a new class of contaminants, the engineered nanoparticles. These compounds are used in various consumer products since their nanoscale and large surface to volume ratio gives them special physicochemical properties, with potential application in different areas such as pharmacy, food, energy and water. An important group of carbon engineered nanoparticles is the fullerenes. Since the discovery in 1985 of the remarkable stable carbon cluster  $C_{60}$  by Harald Kroto, this family of compounds have been used in a wide range of applications from drug delivery systems and anti-aging formulations to sensors, photonic devices and electronic products. As a result of the growing application of these fullerene-based nanomaterials in consumer products, considerably concern about their presence in the environment and health and ecological effects has raised. Although the hydrophobicity of fullerenes is well known, they can form aqueous colloidal suspensions that increase their effective solubility in water and have implications in their transport, transformation and biological effects. In addition,  $C_{60}$  is being used in a variety of personal care products, which might contain organic ligands that affect its solubility allowing their entrance into wastewater and other aquatic environments.

Measuring fullerene nanomaterial concentrations in natural environments is not straightforward because they exhibit a duality of physical and chemical characteristics as they change from hydrophobic to polar forms upon exposure to water. The analytical procedures must account for the potentially transitory nature of fullerenes in natural environments providing chemical information about molecular weight and the identity of surface functional groups. In this presentation the state-of-the-art analytical methods for quantifying fullerenes and their derivatives, the analytical challenges to overcome and how the analytical methodologies are playing an essential role in understanding the occurrence of fullerenes in the environment are discussed. Although in the past few years significant advances have been made in the analytical quantification of fullerenes, there is still a need to develop effective, sensitive and reliable methods for their determination in environmental samples. Some of the recent results obtained in our research group will be presented and the advantage of using high resolution mass spectrometry and new ionization sources such as atmospheric pressure photoionization will be commented.

## Development of in-vitro bioassays for the assessment of reprotoxicity in fish

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There is now clear evidence that numerous xenobiotic compounds act as endocrine disruptors (EDs) in fish by affecting reproductive functions. Some of these compounds exert their action by binding to steroid receptors, and several well established in-vitro methods can assess this mode of action. However, few methods are available to detect non-genomic mechanisms of action. The developed bioassays targeted specific enzymatic pathways that play a key physiological role in fish reproduction, such as: (a) testicular synthesis of oxy-androgens, (b) ovarian synthesis of estradiol, (c) ovarian synthesis of maturation inducing hormones, and (d) sulfation and glucuronidation of active hormones. The methods are based on the use of gonad –different stages of sexual maturation- and liver subcellular fractions from different fish species, viz. carp –*Cyprinus carpio*– and sea bass –*Dicentrarchus labrax*–, and allow a first screening of those compounds with a high potential to alter fish reproduction by inhibiting the synthesis and metabolism of active androgens and estrogens. A wide range of environmental pollutants, including pharmaceuticals, synthetic musks, organotin compounds, alkylphenols and polycyclic aromatic hydrocarbons (PAHs) have been investigated. Regarding the synthesis of oxy-androgens, in-vitro assays are performed by incubating testes mitochondrial fractions with labelled precursors (17 $\alpha$ -hydroxyprogesterone and androstenedione) in order to assess the activity of the CYP17 and CYP11 $\beta$  enzymes, involved in the synthesis of androstenedione and 11 $\beta$ -hydroxy-androstenedione, respectively. Among the tested xenobiotics, the pharmaceuticals, drospirenone and norethindrone, had the strongest inhibitory effect on both enzymes (IC50s: 0.4-3.8  $\mu$ M) followed by the PAH metabolite, 9-hydroxy-phenanthrene (IC50s: 10-31  $\mu$ M), nonylphenol, the polycyclic musks, galaxolide and tonalide, and the pharmaceuticals, fluvoxamine and fluoxetine. Interestingly, 9-hydroxy-phenanthrene also inhibited ovarian P450 aromatase (CYP19) activity (IC50: 4.3  $\mu$ M). Triphenyltin, tributyltin and nonylphenol inhibited the sulfation of estradiol (IC50s: 17, 18 and 41  $\mu$ M) and the glucuronidation of testosterone and estradiol. These bioassays allow the detection of selected chemicals that by interfering with key enzymatic pathways might finally affect physiological processes, such as gamete growth and maturation in fish. They can also be used to assess the effect of mixtures of individual compounds and environmental samples, and they may become useful tools for a more rational design of chemicals with reduced aquatic reprotoxicity.

## **Decisions in wastewater systems: different tools for different decisions' levels**

Manel Poch

Understanding the complex relationships between humans and the environment is becoming more and more important. The efficient and sustainable management of environmental systems is essential to provide essential services such as water, for drinking and irrigation, preserving ecosystem diversity, guaranteeing food security, and an acceptable air quality, to name a few. As the scale of the challenge is rising, the need for sound methodological approaches to assist environmental managers is strong as ever, and environmental decision support systems (EDSS) can package and deliver such approaches.

Software systems have made huge progress in the last decade, and EDSSs are taking advantage of that progress. Here we want to discuss, appreciate and evaluate the impact of software engineering methods and computing tools in the implementation and delivery of modern EDSS. Topics include distributed and cloud computing, social computing, crowdsourcing, the semantic web and ontologies, open linked data, big data and non-SQL databases, GPU and parallel computing, advanced visualization techniques, agile programming and domain-specific languages, and their use in environmental software applications

## Atmospheric plasma. A new technology to remove recalcitrant organic microcontaminants from water

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Water reuse and reclamation are viewed as strategic technologies in a context of population increase and global warming that will drastically increase the pressure on the water resources particularly in arid and semiarid countries. Therefore, sustainable technologies to remove contaminants from water are of great interest. In this regard, a large variety of advanced oxidation processes (AOPs) have been developed to remove recalcitrant contaminants from wastewater but most of them are energy intensive, are using strong oxidants or low pHs that limit their widespread use particularly when the reclaimed water needs to be reused in agriculture.

In this presentation, two-bench scale atmospheric dielectric barrier discharge (DBD) namely batch and continuous flow plasma reactors have been developed. A glow discharge plasma is generated between two electrodes at high voltage (~20kV) under different atmospheres (He, O<sub>2</sub>, Ar) where several reactive oxygen species, free radicals and free electrons are generated and as consequence the dissolved organic contaminants are removed from water. In this regard, the removal kinetics and energy efficiency have been calculated for a variety of organic microcontaminants (priority and emerging pollutants) in a batch and continuous flow reactors. Moreover, the continuous flow has been scaled up to pilot plant and it has been evaluated to industrial wastewater as secondary treatment. Although the obtained results are highly promising further development is needed for real wastewater application.

### ACKNOWLEDGEMENTS.

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# **Atmospheric Chemistry and Aerosols**

**Oral presentations: OA1-OA11**

**Poster presentations: PA1-PA39**

## Modelling the chemically speciated PM<sub>2.5</sub> over the French Northern region using the WRF-Chem system coupled to EMEP and regional emission inventories.

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The lack of information about aerosol chemical and physical properties in modelling systems is a critical step to enhance the emission reduction policies and the knowledge about aerosol impacts over radiative forcing and health. A data processing system, the European Emission Adaptation SYstem for WRF-Chem model (EASYWRF-Chem) has been developed to generate chemical information compatible with the WRF-Chem requirements from any emission inventory based on CORINAIR. EASYWRF-Chem created allows the use of low (EMEP) and highly (Regional) detailed emission inventories and has been tested on the WRF-Chem model.

Using the RADM2 or RACM mechanism, we converted “emission species” into “model species” using the SAPRC methodology. An aerosol chemical speciation profile processing completes EASYWRF-Chem. Coming from the adaptation of US EPA PM<sub>2.5</sub> profiles (Borge et al., 2008), those data separate the unspiciated PM<sub>2.5</sub> emission into five chemical families: sulphate, nitrate, elemental carbon, organic aerosol and unspiciated aerosol.

The WRF-Chem has been implemented on a European area with high resolution domains. Since PM<sub>2.5</sub> speciation modelling has never been evaluated over Europe with detailed emission inventories and with a high resolution modelling system, we statistically compared the simulated values with measurements. The aerosol composition has been quantified during four measurements campaigns in two sites over the French northern region using a High Resolution – Time of Flight – Aerosol Mass Spectrometer (HR-ToF-AMS) which provides hourly resolved speciated PM<sub>1</sub> concentrations. Meteorology, gas phase chemistry and particle phase composition has been evaluated simultaneously. Finally, it reveals that EASYWRF-Chem simulations respectively overestimate the PM<sub>10</sub> concentrations of +30% and +4% for summer and winter periods. The statistical analysis of PM<sub>2.5</sub> concentrations shows that, in summer, WRF-Chem overestimates them of +1% while, in winter, the concentrations are underestimated of -14%. Particulate organic matter concentrations in PM<sub>2.5</sub> are underestimated but hourly variations are well simulated. Sulphates concentrations are not correlated to the observed concentrations, the average concentration is underestimated. Nitrates concentrations are overestimated but variations are fairly well represented. Ammonium particulate matter is well represented. Black Carbon (BC) measurements reveal that EASYWRF-Chem forecast performance is higher in winter than during summer when BC concentrations are very low.

Borge, R., Lumbreras, J., and Rodríguez, E., *Environmental Modelling & Software*, 23, 1026-1044, 10.1016/j.envsoft.2007.11.002, 2008.



## POPs and PAHs in Norway and the UK – levels and distribution in pine needles, litter, soils and air

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Persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) have been an object of concern due to their many emission sources and their widespread environmental distribution and potential damage to wildlife and humans. In the last decade, there has been an exponential growth of publications reporting the occurrence of these chemicals in several environmental matrices. Levels in sediments, air and water are often reported, but soils and especially vegetation, a privileged biomonitor for airborne POPs and PAHs, do not seem to have as much scrutiny.

Since the gaps in the understanding of sources, occurrence and fate of these and other pollutants are still evident, there is a need to continue to investigate inter-matrix and trans-national characteristics. Some modelling works have been reported, but the comparison with experimental data is still unsatisfactory in many topics, which also demands for more experimentally-based information. Multi-matrix data has the advantage of drawing a more complete picture of the pollutants distribution and/or cycles.

Consequently, the purpose of this study was to further enlighten the distribution and pathways of emergent pollutants as well as to assess their loads in several environmental media, namely pine needles, litter, air and soil, vegetation. The strategy meets the continuous urge to understand the life cycles of priority contaminants, to better control or eradicate their hazardous effects. Extraction and clean-up methodologies previously validated for the environmental matrices in question and involving Soxhlet, solid-phase extraction columns and gel-permeation chromatography were used in the analysis of the samples, prior to the quantification of the target compounds by GC/MS. Levels, patterns and sources of contamination were assessed and compared in samples collected from over 30 sites in Norway and the UK.

## Gas-particle partitioning and air-sea exchange of polycyclic aromatic hydrocarbons in the central and eastern Mediterranean

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The marine atmospheric environment is a receptor for polycyclic aromatic hydrocarbons (PAHs) which are advected from combustion sources on land (power plants, biomass burning, road transport). Marine sources may be significant near transport routes (ship exhaust). A number of PAHs are semivolatile (saturation vapour pressures at 298 K in the range  $10^{-6}$ - $10^{-2}$  Pa) and, hence partition between the phases of the atmospheric aerosol, influenced by temperature, particulate phase chemical composition and particle size. Upon deposition to surface water PAHs partition between the aqueous and particulate (colloidal and sinking) phases and may bioaccumulate in marine food chains. Semivolatile PAHs may be subject to re-volatilisation from the sea surface, although net-deposition seems to prevail wherever determined.

Samples were collected along a cruise of RV Urania in the central and eastern Mediterranean, 27 August – 11 September 2010. The gaseous and particulate phases were addressed separately by sorption to polyurethane foam and total high-volume filter or impaction, respectively. Analysis was by GC-MS. Field LOQs corresponded to  $<0.01$ - $0.33$  ng m<sup>-3</sup> for individual substances. Air masses analysed had been transported mostly crossing central Europe, partly crossing western Europe.

The total concentration of 27 3-6 ring PAHs, out of which 24 were positively determined was by average 1.7 ng m<sup>-3</sup> and varied between 0.3 to 6.4 ng m<sup>-3</sup>, with  $\approx 8\%$  in the particulate phase, i.e. particles  $<0.25$   $\mu\text{m}$  of aerodynamic diameter.

Levels were rather uniform throughout the cruise. Three gas-particle partitioning models are tested. Air-sea exchange could be quantified for few substances. It is found that while fluoranthene and pyrene were close to equilibrium, retene was net-volatilisational in most samples.

## Seasonal and spatial variation of PM<sub>1</sub> organic tracers in densely populated and highly insolated urban areas of humid and dry atmospheres

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A comprehensive PM<sub>1</sub> aerosol characterization was conducted within the AEROTRANS project. About 100 organic tracer compounds were analyzed in PM<sub>1</sub> filter extracts that were sampled from 2010 to 2012 in busy streets in the urban centers of Madrid (700 m.asl) and Barcelona (20 m.asl) (Spain), at ground-level and at 50 m.agl (N=57) representing dry and humid atmospheres. Both urban areas have intensive traffic and high insolation. Samples were collected in summer and winter, as well as in night- and daytime, in order to record possible seasonal and diurnal variation in organic tracer composition and concentrations.

Primary organic tracers for traffic and dust were 2 times higher at ground-level, with a daytime maximum, and generally 2 times higher concentrations in winter.

No significant differences were observed between ground-level and altitude measurements for secondary organic tracers, including those of both biogenic (isoprene and pinene) and anthropogenic origin. The biogenic SOC concentrations were about 10 times higher in summer than in winter. The largest differences were observed amongst isoprene SOC tracers.

Organic tracers for biomass burning increased by a factor of ~7 in both sites during winter. However, a 2012 summer-time PM-event in Barcelona was directly linked to the impact of a severe wild-fire that occurred at about 100 km to the north of the city. All biomass organic tracers increased a factor ~100 in the 12-hour sample, compared to the other samples collected during summer.

Despite their different air properties (dry vs. humid), Madrid and Barcelona exhibit very similar compositions and concentrations of organic tracers for biogenic and anthropogenic SOC as well as for biomass burning. The most significant differences were observed among primary organics, such as primary sugars and fatty acids.

### Acknowledgements

This work was supported by the scientific research projects AERO-TRANS (CTQ2009-14777-C02-01) and TEAPARTICLE (CGL2011-29621).

## PM<sub>2.5</sub> source apportionment by directional sampling and Positive Matrix Factorization (PMF)

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The objectives of this study are both to determine the pollution sources affecting the study area and to assess which is the prevailing origin direction of the input sources. Indeed, in order to reduce the amount of pollutants in atmosphere, it is important both to determine the contribution given by the different source<sup>1</sup> and to identify which is the pollutant load due to local sources compared to long-range transport. For this aim, PM<sub>2.5</sub> was collected with samplers coupled with a wind select sensor, in order to sample only the air masses influenced by specific emission sources. A previous study<sup>2</sup> demonstrated that this approach cannot give quantitative and complete responses on the causes of air pollution. Therefore, the implementation with source apportionment statistical tools was necessary to finally reach the aim. Chemometric methods are very spread and useful in data analysis of complex datasets, since they allow to colleague contaminants related to the same source. Positive Matrix Factorization (PMF) is a new approach compared to Principal Component Analysis (PCA); it is more powerful and provides quantitative information on source contributions<sup>3</sup>.

The sampling site is located in the suburban area of the coastal tourist town of Riccione (Italy). The two principal wind directions are southwest and northeast (land and sea breeze), roughly perpendicular to the coast line. The sampling campaign was design for an alternate sampling of the air masses downwind of the costal urban area and of the hinterland, which is mainly characterized by the presence of a Municipal Solid Waste Incinerator (MSWI) and a motorway. At the same time, another sampler collected PM<sub>2.5</sub> in calm wind condition. For each sample, soluble ions, OC, EC, levoglucosan, metals and PAHs were determined.

PMF analysis indicates that the main source of PM<sub>2.5</sub> in the area is secondary nitrate. This should be mainly due to regional contributions, since the secondary nature of the source itself and the higher concentration registered in inland air masses. The motor vehicle emission source contribution is also important. This source likely has a prevalent local origin. The most toxic determined components, i.e. PAHs, Cd, Pb and Ni, are mainly due to vehicular traffic. Even if this is not the main source in the study area, it is the one of greatest concern.

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## Association between metal concentration in pregnant women and atmospheric traffic pollution

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Road traffic can be an important source for human exposure to some metals. In previous studies regarding PM components, Sb and Cu presence in mineral fraction has been associated mainly to road traffic. Metals occur in the very fine and ultrafine particles, so they can reach pulmonary alveoli. Consequently, an important exposure to these metals occurs in people living in places with intense traffic. Cu is an essential element but also toxic at high levels, whereas Sb is a toxic metal with demonstrated harmful health effects due to occupational exposure. Exposure to air pollution during pregnancy has been studied regarding PM, NO<sub>2</sub> and benzene, but no studies attending to human exposure to metals and its association with traffic pollution have been performed.

In this context, Sb and Cu were analysed in urine from pregnant women living in Sabadell. Then, association between concentrations and exposure at home to road traffic was studied, taking into account different variables related to exposure to road traffic such as personal perception of road traffic at the street where they live or distance to an intense traffic street.

65% of women had detectable levels of Sb, whereas Cu was detected in all women. Sb had a geometric mean concentration of 0.28 µg/g creatinine, while geometric mean levels of Cu were 14 µg/g creatinine. Concentrations of both metals were approximately on the same range than those reported in previous studies from places without an important source of pollution. Attending to multivariate linear regression, personal perception of car density traffic at home was significantly associated with Sb but not with Cu. Women who reported living in streets with continuous and very frequent car traffic had significantly higher levels of Sb than those living in streets with practically no traffic ( $p < 0.01$ ). Nevertheless, women living more than 150 m away from a street with intense traffic had significantly higher levels of Cu ( $p < 0.05$ ) whereas no significant association was found for Sb. Finally, both metals presented higher levels during winter, consistent with previous findings in studies regarding PM.

As a conclusion, women exposed to higher car traffic density at home exhibit higher levels of Sb during pregnancy. Association with Cu was not clear. Sb from car brake wear has been recognized as the most important source for atmospheric presence of this metal and, according to these results, it can be confirmed as the main factor associated with human non-occupational exposure, while Cu may come from other sources such as diet. The low dispersion conditions occurring during winter lead to higher exposure to these metals due to resuspension of particles containing them. During pregnancy these metals pass through the placenta and prenatal exposure may have important effects on the newborn child, therefore metals coming from car traffic at home could have a negative influence on children's health and development.

## Photochemical formation of humic-like substances: Phenol di/oligomerisation sensitised by the triplet state of 1-nitronaphthalene

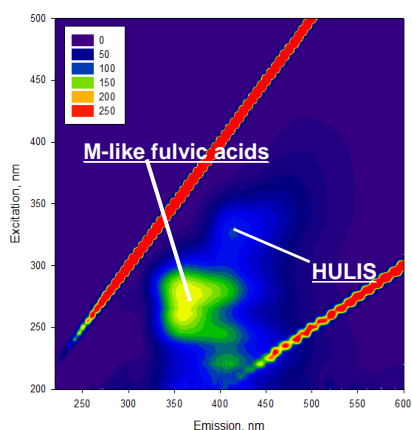
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Humic-like substances (HULIS) have recently gained interest in the field of atmospheric chemistry because they constitute a considerable fraction of the organic aerosol mass, significantly absorb sunlight and play an important role as cloud condensation nuclei.<sup>4,5,6</sup> Recent studies suggest that a possible pathway to HULIS formation involves phenolic compounds arising from biomass burning, in the presence of both photosensitisers and ozone.<sup>7</sup> Having recently shown that photosensitised phenol dimerisation does not require ozone,<sup>8</sup> we investigated the possibility of HULIS production by O<sub>3</sub>-independent processes. We used 1-nitronaphthalene (1NN) as photosensitiser, as nitroaromatics can be important in the photochemistry of atmospheric aerosols.<sup>9</sup> The UVA irradiation of an aqueous solution of 1NN and phenol causes transformation of both compounds, that of phenol being sensitised by the triplet state of 1NN (<sup>3</sup>1NN\*). Laser flash photolysis experiments indicated that <sup>3</sup>1NN\* reacts with phenol with second-order rate constant  $k = (4.5 \pm 0.1) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , producing the phenoxy radical and 1NN radical anion. Phenoxy radical should undergo dimerisation to give dihydroxybiphenyls and phenoxyphenols, which have been identified by GC-MS. Moreover, analysis of the irradiated system by fluorescence matrix spectroscopy indicated the formation of species analogous to “M-like” fulvic acids and, at longer irradiation times, of material with HULIS properties (see figure below). The photoprocessed material also produced <sup>1</sup>O<sub>2</sub> under irradiation, as shown by the degradation of furfuryl alcohol. These findings could shed new light on HULIS formation and on the photoactivity of organic material in atmospheric waters.



EEM (Emission-Excitation Matrix) fluorescence spectrum of an aqueous solution containing 0.1 mM 1-nitronaphthalene + 0.1 mM phenol, after 4 h of UVA irradiation. The two straight lines represent the Rayleigh scattering of water and its second harmonic.

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## Prediction, Identification, and Mutagenicity of Novel Nitro-PAHs Formed via Atmospheric Heterogeneous Reactions

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The heterogeneous reactions of five higher molecular weight polycyclic aromatic hydrocarbons (PAHs), benzo[a]pyrene-d<sub>12</sub> (BaP-d<sub>12</sub>), benzo(k)fluoranthene-d<sub>12</sub> (BkF-d<sub>12</sub>), benzo[g,h,i]perylene-d<sub>12</sub> (BghiP-d<sub>12</sub>), dibenzo(a,i)pyrene-d<sub>14</sub> (DBaiP-d<sub>14</sub>), and dibenzo[a,l]pyrene (DaIP), with NO<sub>2</sub>, NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub>, O<sub>3</sub>, and OH radicals were investigated in a 7000 L indoor Teflon chamber. Quartz fiber filters (QFF) were used as the reaction surface and substrate and the analyses of parent PAHs and Nitro-PAH (NPAH) products was conducted using electron impact gas chromatographic mass spectrometry (GC/MS) and negative chemical ionization GC/MS. In addition, the reacted and unreacted filter extracts were tested in the Ames assay, using *Salmonella* strains TA98 (with and without metabolic activation), to determine changes in mutagenic activities upon exposures. In parallel to the laboratory experiments, a theoretical study was conducted to assist in determining the formation of NPAH isomers based on the OH-radical initiated reaction. The thermodynamic stability of OH-PAH intermediates was used to indicate the position of highest electron density and the most stable NPAH products were synthesized to confirm their identity. NO<sub>2</sub> and NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> were the most effective oxidizing agents in transforming PAHs deposited on filters to NPAHs, under the experimental conditions. Reaction of BaP-d<sub>12</sub>, BkF-d<sub>12</sub> and BghiP-d<sub>12</sub> resulted in the formation of several mono-nitro PAH isomer product, while the reaction of DaIP and DaiP-d<sub>14</sub> resulted in the formation of only one mono-nitro PAH isomer product. The direct-acting mutagenicity of the products increased the most after NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> exposure, particularly for BkF-d<sub>12</sub> in which the formation of dinitro- PAHs was observed.

In addition, the degradation of particulate matter (PM)-bound PAHs by heterogeneous reaction with OH radicals, O<sub>3</sub>, NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> was also studied. Ambient PM samples collected from Beijing, China and Riverside, California were exposed in an indoor chamber under simulated trans-Pacific atmospheric transport conditions and the formation of NPAHs was studied. NPAHs were most effectively formed during the NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> exposure and, for all exposures, there was no significant formation of 2-nitrofluoranthene or 2-nitropyrene, suggesting that heterogeneous reactions predominated. In addition, the unexposed and exposed sample extracts were tested in the Ames Assay using TA98, with and without metabolic activation (S9). For the NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> exposure, the increase in direct-acting mutagenicity could be associated with the formation of mutagenic NPAHs. The importance of this research with respect to atmospheric long-range transport of PM-bound PAHs will be discussed.

## Dioxins, furans and dioxin-like PCBs in ambient air from Catalonia (Spain).

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Quality of ambient air and levels of pollutants in Catalonia are controlled through the Air Pollution Monitoring and Forecasting Network by Generalitat de Catalunya. In this framework, our study was focused on the characterization of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs).

PCDD/Fs and PCBs are chlorinated compounds catalogued under Stockholm Convention due to their properties: persistence, bioaccumulation, transboundary transport and toxicity. PCDD/Fs were never intentionally produced. However, they can be emitted to the atmosphere from a broad spectrum of processes, especially thermal ones. PCBs were industrially produced between 1929 and late 80s, when their production was banned in most European countries. Last years, the most frequent use was as dielectric fluid in condensers and capacitors.

Ambient air was sampled in 15 locations in Catalonia (Spain), grouped in three main zones: Camp de Tarragona (Zone 1), Barcelona-Vallès (Zone 2) and Plana de Vic-Catalunya Central (Zone 3). Active sampling was performed between 2005 and 2012 and in two seasons each year (autumn-winter and summer) in order to study possible seasonal variation.

Sampling devices consisted of high volume samplers equipped with a quartz-fibre filter, to retain particle phase, followed by polyurethane foam blocks for vapour phase absorption. Analytical procedure was based on international methods (US EPA 1613, UNE-EN 1948) and consisted of following steps: (1) pre-treatment of different parts of the sample, (2) spiking with <sup>13</sup>C<sub>12</sub>-labelled extraction standards, (3) Soxhlet extraction, (4) extract clean-up in multilayer silica column and pre-packed carbon tubes, (5) final concentration and <sup>13</sup>C<sub>12</sub>-labelled recovery standard addition, (6) instrumental analysis by HRGC-HRMS, (7) quantification by isotopic dilution method. Statistical methods were applied to the 124 samples analysed.

For most locations, levels of PCDD/Fs and DL-PCBs were medium-low compared to those published in literature. Some differences were observed between zones: Zone 1 showed the lowest levels of PCDD/Fs, while the highest were detected in Zone 3 (median concentration of PCDD/Fs: 10.4 fg TEQ/m<sup>3</sup> in Zone 1, 24.9 fg TEQ/m<sup>3</sup> in Zone 2, and 48.3 fg TEQ/m<sup>3</sup> in Zone 3) PCB concentration were lower than those of PCDD/Fs. They ranged from 3.2 fg TEQ/m<sup>3</sup> in Zone 1 to 7.7 fg TEQ/m<sup>3</sup> in Zone 3 (median values).

Seasonal variation was observed in all the zones. For PCDD/Fs, concentrations in autumn-winter were higher than in summer. This fact can be related to higher emissions and, also, to lower degradation rates in winter. For PCBs, the opposite was observed: concentrations in air were higher than in summer. This could indicate that main source of PCBs to air was evaporation from soils, increased with higher temperatures.



## Monitoring nitrogen-dioxide and benzene in air in the Central Transdaniubien Region, in the City of Veszprém

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### Abstract

The School of Environmental Engineering, University of Pannonia has been monitoring the air pollution - namely nitrogen-dioxide and benzene – over a period of one year with diffusive sampling (also called passive) method in the Central Transdanubien Region, in the City of Veszprém. The objective of the work was to follow the change in air pollutant concentrations and the possible impact of the air pollutants on environmental quality. The seasonal weather conditions were also taken into consideration during the study. Ten sampling sites were selected in order to monitor and follow up the impact of the traffic/transportation on the air pollutant concentrations with special emphasize on different traffic patterns at different locations and time within the city. The average concentrations measured for NO<sub>2</sub> and benzene were 26,54 µg/m<sup>3</sup> and 2,47 µg/m<sup>3</sup>. During the heating period in winter time the maximum values of NO<sub>2</sub> reached 82,4 µg/m<sup>3</sup> and benzene concentration was 7,7 µg/m<sup>3</sup>. The lowest concentrations were measured in the non-heating period during the summer when the concentration of NO<sub>2</sub> was 4,4 µg/m<sup>3</sup> and benzene was 0,2 µg/m<sup>3</sup>. The paper presents the change in nitrogen-dioxide and benzene concentrations and the results clearly show that both components are higher at those measuring points where the direct impact of traffic on the air pollutants is significant.

Keywords: air quality, passive sampling, air pollution monitoring, nitrogen dioxide, benzene

## Determination of N-nitrosamines and nicotine in particulate matter from air samples by pressurised liquid extraction and gas chromatography-ion trap tandem mass spectrometry

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N-nitrosamines are a group of organic compounds derived of amines which are produced by reaction of amines or their derivatives with nitrogen agents. These organic compounds are considered as potentially hazardous pollutants by the US Environmental Protection Agency (US EPA; 2009) and some of them are classified in Group B2 (probably carcinogenic effects on humans). Some studies demonstrate that this group of compounds are found in different kind of samples such as drinking water [1], wastewater [2], house dust [3], sewage sludge [4], in second-hand smoke ambient [5], among others.

The aim of this study is to develop a reliable method to determine nine N-nitrosamines and nicotine in particulate matter from air samples. The samples were taken using fibre quartz filters (PM10) to collect about 1000 m<sup>3</sup> of air with a high volume air sampler (TE-6070). The filters were extracted by pressurised liquid extraction with ethyl acetate and the extracts were analysed by gas chromatography-(chemical ionization) ion trap tandem mass spectrometry.

The method developed was enabled to determine this group of compounds in particulate matter from air samples from urban and harbour areas. N-nitrosomorpholine (NMor), N-nitrosopyrrolidine (NPyr), N-nitrosopiperidine (NPip) were found in most of the samples at similar concentration levels in both sites between <MQL (NNor) and 0.22 ng m<sup>-3</sup> (NPyr). However, the most abundant compound found was nicotine at average concentration level between 3.80 ng m<sup>-3</sup> (harbour area) and 12.5 ng m<sup>-3</sup> (urban area).

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## Comparison of water-soluble organic tracer compounds in fine aerosols in two cities: Los Angeles and Barcelona

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Water soluble organic compounds (WSOCs) make up an important fraction of the fine aerosol. Important sources for WSOCs are biomass burning and secondary organic aerosol (SOA) formation. Here, WSOCs from known biogenic and anthropogenic origin were analyzed in 103 PM<sub>1</sub> and 69 PM<sub>2.5</sub> filter samples collected in a background and road site in Barcelona (Spain) and in a background site in Los Angeles (USA), during one-month intensive sampling campaigns in 2010. Both locations have similar climates, characterized by relatively high solar radiation and anti-cyclonic conditions, and both locations are influenced by vehicle emissions.

For organic compound speciation the filter was extracted in dichloromethane and methanol (2:1), filtered and concentrated. Aliquots of the sample extracts were derivatized with bis(trimethylsilyl)trifluoroacetamide (BSFTA) and pyridine. The extracts were analyzed by GC-MS and the quantification was obtained with surrogate and internal standards applied in the extraction and injection respectively. The analyzed compounds were selected based on their relationship with emission sources or SOA formation. These compounds were monosaccharide anhydrides (levoglucosan, galactosan, mannosan), dicarboxylic acids (C<sub>3</sub>-C<sub>9</sub>, including hydroxy-diacids and aromatic-diacids), oxidated biogenic compounds (*cis*-pinonic acid, 3-hydroglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)) and oxidated isoprene compounds (2-methylglyceric acid and polyols).

Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) was used for source apportionment of WSOCs. MCR-ALS was originally developed for the resolution of multiple components in unresolved mixtures investigated by spectroscopic means but it has been proved its ability to resolve and model average temporal and geographical distribution profiles in environmental source apportionment studies.

Results of the application of MCR-ALS to the three different site data bases (separately and simultaneously) allowed distinguishing five consistent WSOC clusters, representing five sources, one biomass burning and four SOA. The abundance of these clusters was influenced by source strength and certain meteorological conditions that acted in similar ways in both geographical locations, suggesting that the organic aerosol is influenced by similar processes.

## The using of pine needles for long-term monitoring of air pollution

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This study is focused on outdoor air biomonitoring which uses pine needles as a form of passive sample. This plant is very suitable bio-indicator because of high content of wax in the structure of needles, accumulation of lipophilic substances and high availability. This matrix is suitable even for multi-year monitoring and thus, provides information on the long-term variability<sup>1</sup>.

We have decided to sample needles from two tree species (*Pinus nigra* a *Pinus sylvestris*) from the urban (Brno) and rural (Košetice) areas in Czech Republic. Samples were collecting continuously during three years every 28 days. Subsequently, samples were processed by the methodology developed in our centre. All analysis and evaluation of concentrations are concerned on polycyclic aromatic hydrocarbons (PAHs) in cut needles, uncut needles and dwarf shoot with scaly leaves.

The aim of this work is to compare the relative concentrations of different locations and species of pine in long-term scale. The study is unique because of large amounts of collecting samples (every 28 days during three years) and it can provide information about long-term deposition of polycyclic aromatic hydrocarbons in this matrix. We can compare these samples with air samples collected by active sampling (HiVol) and passive sampling (polyurethane foam) taken in the same time and place. The meteorological conditions are also the important factor.

In the case of comparing of locations values are quite clear and show large differences between urban and rural environment. Public transport and industrial sources influence concentration of PAHs in samples of needles therefore the city location has a much higher concentration of pollutants that samples collecting from Košetice.

As a result of this study, we managed to get a unique time scale of accumulative potential in samples of needles during three years of exposure.

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## The survey for tin in dust samples from apartments in Lublin area, Poland

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Nowadays people spent almost 90% of their time indoors, where the air creates a unique microclimate, with a composition different from the outdoor air and increased level of pollutants. Indoor air pollutions may be found in the form of gas molecules, aerosols and suspended particles. Particulate matter is one of major interests of researchers and analysts, although measurements were conducted mainly on the basis of particle size. Less attention was paid to the chemical composition of particles, as only information about SVOC sorbed on particles or alkali metals in aerosols have been published. But one gram of dust may contain 700 million particles of different components including heavy metals, *inter alia* tin. Different organic tin compounds have been used since 1920<sup>th</sup> as catalysts, fungicides, biocides and stabilizers of PVC and polyurethane foams. Some compounds were added to paints and other indoor finishing materials. An excess of tin inhibits cellular respiration processes and is toxic to the thymus, bile ducts and the nervous system. Tin compounds may also be absorbed into the body through the skin by the external contact, causing liver damage and chronic eczema.

Therefore, the survey to measure current levels of tin in the indoor settled dust was undertaken. Dust samples were collected in 2012 from apartments located in Lublin area, Poland, in the cities of Lublin, Chelm, Pulawy. These apartments are located both in the city centers, along major thoroughfares, as well as in suburban areas where traffic volume is significantly smaller. They are different in terms of the age of construction and indoor equipment. Dust samples were collected during vacuum cleaning. The material from vacuum cleaner bags was sieved into different fractions (20, 25, 50, 100, 100 - 125 microns) using vibratory and pneumatic sieve shakers, and then mineralized and analyzed with the use of chemical technique ICP-OES 3000 conducted on sequential spectrometer ISA Jobin Yvon - JY 238 ULTRACE. The resulting range of concentrations of tin ranged from 110 mg/kg of dust in the fraction 100 - 125 microns to 871 mg/kg in the fraction 20 microns. It was observed that the smaller the fraction, the concentration of that heavy metal in the apartments is higher. The highest tin concentration was found in the apartment build in the late 70<sup>th</sup> as well as located in the industrial neighborhood.

## Heavy metals in settled dust from educational institutions, Poland

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Biological and chemical pollutants are an integral part of the indoor environment in floor area. Human activities increase concentrations of chemical elements in the atmosphere, including heavy metals (Ba, Cu, Pb, Cr, Cd, Zn, Fe, Sn). The concentration exposure of these elements may have various health consequences depending on the time of the impact. In addition, children spend a lot of time in educational institution. Moreover, they are more vulnerable to pollution from dust because they often play on the floor.

The settled dust collected during the heating season in educational institutions such as schools and kindergartens in Lublin, Poland, was the object of the research. The presence of heavy metals was analyzed. The dust samples used in research came from vacuum bags. The resulting material was sieved into different fractions (20, 25, 50, 100, 100 - 125 microns) using vibratory and pneumatic sieve shakers, and then mineralized and analyzed with the use of chemical technique ICP-OES 3000 conducted on sequential spectrometer ISA Jobin Yvon - JY 238 ULTRACE. The highest concentration of barium was 16.31 mg/g of dust, and was found in the 100-125mm fraction, whereas the lowest recorded concentration of barium (5.86 mg/g of dust) was also in the dust with the particle size 100-125mm. The highest concentration of copper was noted on the level 6.25 mg/g of dust and the lowest was 1.84 mg/g. The content of zinc in the dust ranged from 7.6 mg/g to 87.8 mg/g. It turned out that for the majority of tested dust samples, the smaller size of the particles was, the zinc concentration was higher. The concentration of cadmium in the dust collected from educational institutions was within the range: 0,013-0,096 mg/g. The tin maximum level of dust was 1.098 mg/g and the minimum was 0.086 mg/g. Distribution of the tin concentration in samples was characterized by an upward trend with decreasing particle size distribution of the settled dust. Lead concentration of dust ranged from 2.43 mg/g to 6.0 mg/g. The content of iron of dust in the tested material was at the level 154.9 - 578.8 mg/g. In several samples, the concentration of iron increased with decreasing particle size distribution of analyzed dust. The largest recorded chromium concentration of dust was 3.01 mg/g, whereas the smallest concentration of this element was 0.63 mg/g. The concentration of chromium in the tested material is higher in smaller fractions. The dominant factor affecting the concentration of certain elements in the dust was traffic (Cd, Zn). Pollutant emissions from the combustion of fossil fuels influenced mainly the content of Cr, as well as Ba and Pb. Furnishings, carpets and artificial pigment used in dyed fabrics based on Cd as well as cigarette smoke could affect the concentration of this element. The release of organic compounds set in building materials used since the 20's of the twentieth century may contribute to the increase of Sn content in the tested material. Moreover, new window frames and old paint can be a source of Pb in the dust. While varnishes, paints and fungicides may increase the content of Zn.

## Trends of heavy metals levels in PM<sub>10</sub> and PM<sub>2.5</sub> in an industrialized area

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In the area of study, the main Spanish and second European industrial ceramic cluster, the main source of heavy metals in aerosols is related to the raw materials used in the ceramic process, mainly in pigment manufacturing. Concentrations of particulate matter and heavy metals (As, Ni, Cd, Pb) content in PM<sub>10</sub> and PM<sub>2.5</sub> have been measured and characterised by ICP-MS for the years 2005-2010 in two sampling sites: An industrial site and a urban site. Concentrations of PM<sub>10</sub> and arsenic, nickel, cadmium and lead ranges 27-46 µg/m<sup>3</sup>, 0.7-6.0 ng/m<sup>3</sup>, 0.3-57.2 ng/m<sup>3</sup>, 0.1-6.8 ng/m<sup>3</sup> and 0.0-470.0 ng/m<sup>3</sup> respectively in the industrial area and 25-40 µg/m<sup>3</sup>, 0.7-2.8 ng/m<sup>3</sup>, 0.2-39.4 ng/m<sup>3</sup>, 0.0-7.6 ng/m<sup>3</sup> and 0.0-210.0 ng/m<sup>3</sup> respectively in the urban area. Concentrations of PM<sub>2.5</sub> range 12 to 14 µg/m<sup>3</sup>, 0.5 to 1.4 ng/m<sup>3</sup>, 0.0-10.8 ng/m<sup>3</sup>, 0.0-6.6 ng/m<sup>3</sup> and 0.0-150.0 ng/m<sup>3</sup> respectively in the urban area. Most of the arsenic and other heavy metals are present in the fine fraction, with ratios of PM<sub>2.5</sub>/PM<sub>10</sub> in the range of 0.65 to 0.87 for arsenic. The PM<sub>10</sub>, PM<sub>2.5</sub> and its heavy metals content show a sharp decrease in recent years associated with the economic downturn, which hit severely the production of ceramic materials in the area under study. The production decrease due to the economic crisis combined with several technological improvements in recent years, such as substitution of boron which contains As impurities as raw material, have reduced the concentrations of PM<sub>10</sub>, PM<sub>2.5</sub> and As in air to a extent that currently met the existing European regulations. When the economy recovers and the ceramic production boost again, it is advisable that further technological improvements are considered to ensure that the particulate matter and heavy metal concentrations continue to meet the regulations.

## Organophosphate flame retardants in air and dust of German daycare centers and metabolite levels in urine (LUPE 3)

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Nowadays, different substances were used to prevent fire hazards by raising the ignition temperature of the polymer, reducing the rate of burning, reducing flame spread or reducing smoke generation. One class of them, the organophosphate flame retardants (OPFR) are responsible for nearly 20% of the yearly consumption of flame retardants in Europe. They are often used as a safer alternative for the banned brominated flame retardants.

Indoor air samples and settled dust from 22 daycare centers in Bavaria, Germany, were analyzed for the presence of 6 OPFR in our study. Moreover, urine samples of 103 children were collected after they attended the facilities and 5 metabolites were analyzed. The participants were between 3.0 and 6.7 years old (mean: 4.8 years) and weighed 11 to 30 kg.

Inhalable dust and gas phase were collected with a glass fiber filter and polyurethane foam over approximately 6 hours. Settled dust was collected by vacuuming the floor of the room using an ALK dust sampler. Indoor air, dust and OPFR metabolites were analyzed using a GC/MS method.

Tri-(2-butoxyethyl)-phosphate (TBEP), Tris-(2-chloroisopropyl) phosphate (TCPP), and Tri-n-butyl-phosphate (TnBP) were present in low concentrations in the room air with median values of 142 ng/m<sup>3</sup>, 3 ng/m<sup>3</sup>, and 2 ng/m<sup>3</sup>, respectively. In dust, median values of 442 mg/kg for TBEP, 2.4 mg/kg for TCPP, 1.0 mg/kg for 2-ethylhexyl diphenylphosphate (EHDPP), and 0.6 mg/kg for tri-phenyl-phosphate (TPhP) were found. We were able to quantify the metabolites of TBEP, TPhP and EHDPP, TnBP, TCEP, and TCPP in 72%, 83%, 79%, 53%, and 43% of the urine samples with medians (95th percentiles) of 3.1 µg/l (6.6 µg/l), 0.6 µg/l (2.7 µg/l), 0.2 µg/l (1.1 µg/l), 0.1 µg/l (1.4 µg/l), and 0.1 µg/l (0.4 µg/l), respectively.

Using only values above the LOQ, no significant correlations between the concentration of TBEP in air and the metabolite in urine were found. No significant correlation were found between the values in dust and the metabolite levels, except for the relation of the sum of the two phenyl phosphates in dust and their metabolite ( $r: 0.407, p < 0.001$ ).

Overall, we found low levels of OPFR in the air and settled dust of daycare centers. Compared with the literature our results in dust are comparable to that observed in Swedish daycare centers, whilst TnBP in our study is lower but TBEP higher as seen before in 10 facilities from Sweden.



## Reduction, Evaluation and Monitoring of Chemical Waste in Power Transformers Insulation Systems by Multivariate Image Analysis and Chemometrics

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Insulation system of power transformers consists of Kraft paper immersed on insulating mineral oil. The lifetime extension of power transformers depends directly on the stability of this insulation system. So that the more degraded the insulation system, the more likely to reduce its life, and that of the power transformer. During the power transformer operation, mineral oil and Kraft paper suffer a degradation process influenced by factors, such as temperature, humidity and oxygen. The major degradation products of paper's cellulose are furfurals, water and gases, such as H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>, which can be found in the insulating oil. These compounds dissolve into the oil changing its physicochemical and dielectric properties. Changes in the oil quality parameters should be accompanied by regular physicochemical testing, and chromatographic analysis. These analyses generate much waste and are highly time consuming. Interfacial tension is one of the physicochemical parameters most important used for evaluating the degradation of the insulation system. It corresponds to indirect measuring of polar substances, such as the furanic compounds and water, so the more the insulation system is degraded, the lower is the interfacial tension.

This work presents a method simple, rapid, non-destructive and which not generates chemical waste to evaluate indirectly the degradation in samples of insulating oils collected in power transformers. The objective is to determine their interfacial tension by using image analysis combined with a multivariate calibration method, PLS. Two hundred and sixty six insulating oil samples were obtained from CELG (Centrais Elétricas de Goiás S. A.), a state electrical power company, which is located in the center-west region of Brazil. Interfacial tension water/oil of these samples was measured by using a torsion Krüss K8 tensiometer, according to Brazilian norm NBR 6234. The measured values ranged from 14 to 46 dyn cm<sup>-1</sup>. Images were acquired using a simple table scanner Genius. Petri plates were filled with 15 ml of each oil sample and positioned under the scanner central region. Images were digitalized in RGB system and JPEG, PNG, TIFF and BMP, with resolution of 300 dpi. The images were processed using different linear *spatial filter* and then frequency histograms were extracted for each color channel R (red), G (green) and B (blue). PLS models were built for each format with mean centering data, with five latent variables and accounting for 42.25 and 82.18% of data variance in X and Y blocks, respectively. The best model was obtained in TIFF format with *spatial filter average* providing a RMSEP of 4.4 dyn cm<sup>-1</sup> and r=0.8829. This model provided prevision errors up to 13% and which were considered acceptable for the quality control laboratory of CELG company. The proposed method opens perspectives for implementing a non-invasive on-line assessment of conditions of insulating systems of transformers using a practical instrument of low cost, simple, rapid, non-destructive and environmentally friend.

## Investigation of contaminants filtration in metal fluid environments - laboratory evaluations

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Metalworking fluids (MWFs) may not be harmful in itself, whereas their mixture will show adverse effects. Thus, the basic contaminants emitted during machining, in particular of metals, include mineral oil mist and metal dust. High performance requires substantial machining speed, which, together with an increase in temperature leads to an increased secretion of oil mist consisting of the liquid phase (oil droplets) and the gas phase (oil vapor). Metalworking fluids can oxidize, contaminate the metal particles or products of combustion. It may also form a new, harmful substances, such as carcinogenic N-nitrosamines, polynuclear aromatic hydrocarbons (PAHs) including benzo[a]pyrene, which can also be a factor as the cause dangerous damage electronic equipment used in the machines.

Previous studies of exposure of machining workers were conducted mainly with the use of infrared absorption spectrophotometry, without taking into account the dimensions of the particles. Modern techniques using particle counting methods enable measurements of fractional concentrations of aerosols in a wide range of sizes, including nanometric dimensions.

Our Institute carries out work aimed at characterizing the dependence of the process of filtration of liquid and solids aerosols on the filtration parameters and the structural properties of nonwoven systems. Measurement of number concentrations and particle diameters were made using a Scanning Mobility Particle Sizer SMPS Model 3936 (TSI Inc) consisting of electrical mobility analyzer (LDMA, Model 3080L) and two condensation particle counters (CPCs, Model 3022 and 3775). In the studies were used ester bis (2-ethylhexyl) sebacic acid (DEHS) and ASHRAE 52.1 synthetic dust.

Description the relationship between filtration efficiency, flow resistance and size distribution of dust and liquid aerosol particles makes it possible to determine the optimum time of the use of filters in ventilation systems during machining. The determined filter utility factor should take into account the actual investment and operating cost borne by the users of ventilation systems in order to protect the environment by simultaneous reduce exposure to particles of liquid and solid aerosols.

This paper has been prepared on the basis of the results of research task I.B.11 carried out within the National Programme "Improvement of safety and working conditions" partly supported in 2011-2013 within the scope of research and development by the Ministry of Science and Higher Education. CIOP-PIB has been the Programme main coordinator.

## Legacy POPs and polybrominated diphenylethers in the central and eastern Mediterranean – levels in ambient air and gas-particle partitioning

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The marine atmospheric environment is a receptor for most legacy persistent organic pollutants (POPs) as no marine sources exist. In some sea regions, however, accumulation in surface waters due to atmospheric deposition in the past caused flux reversal. Polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs) are mostly emitted in urban areas. Most POPs are semivolatile (vapour pressures at 298 K in the range  $10^{-6}$ - $10^{-2}$  Pa) and, hence, partition between the phases of the atmospheric aerosol, influenced by temperature, particulate phase chemical composition and particle size. Due to significant lipophilicity ( $K_{ow} = 10^4$ - $10^7$ ) and bioaccumulation these substances pose a hazard for marine ecosystems.

Samples were collected along a cruise of RV Urania in the central and eastern Mediterranean, 27 August – 11 September 2010. The gaseous and particulate phases were addressed separately by sorption to polyurethane foam and total high-volume filter or impaction, respectively (e.g. [1]). Analysis was by GC-MS [2]. Field LOQs corresponded to <0.01-2.1  $\text{pg m}^{-3}$  for individual substances. Air masses analysed had been transported mostly crossing central Europe, partly crossing western Europe.

The concentration of DDT isomers and their metabolites, DDE and DDD, was by average 2.6 (0.4-7.7)  $\text{pg m}^{-3}$ . The metabolites accounted for only 51% by average and not more than 71% in individual samples. The concentration of penta- and hexachlorobenzene were on average 0.22 (<0.45-2.8)  $\text{pg m}^{-3}$  and 6.2 (2.5-24.1)  $\text{pg m}^{-3}$ , respectively, of PCBs (sum of 7 congeners) 3.5 (2.0-7.7)  $\text{pg m}^{-3}$  and of PBDEs (sum of 10 congeners) 7.5 (2.9-20.1)  $\text{pg m}^{-3}$ . On average 0.6%, 0.5% and 10%, respectively, of these species were associated with the particulate phase. The decabrominated ether accounted for 40% and congeners related to the pentaBDE for 59% of the PBDEs. The mean concentration of chlordane isomers and one metabolite (oxychlordane) in the particulate phase was 4.8  $\text{pg m}^{-3}$  and of endosulfan isomers and its metabolite (endosulfan sulfate) 5.1  $\text{pg m}^{-3}$ . The degradation products accounted for 0% and 72%, respectively, of these groups of compounds.

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## Cor-Ten exposed to a urban-coastal environment: preliminary study on metal release

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Cor-Ten is a low-alloyed steel that, thanks to small amounts of alloying elements, such as chromium, nickel, phosphorus and copper, exhibits the characteristic ability to self-protect from atmospheric corrosion, by the development of a stable and adherent protective layer. Resistance to atmospheric corrosion and aesthetic features allowed Cor-Ten to assume an increasing role in architectural, artistic and infrastructural applications.

After environmental exposure, many factors can determine the Cor-Ten behaviour. In particular environmental parameters, such as humidity, presence and amount of pollutants and precipitation events, and exposure conditions, such as geometry and orientation, can influence the growth of the superficial patina and may adversely affect its protective performances. In fact, the exposure to quite aggressive environments, like urban and industrial areas (with high pollutants concentrations) or coastal areas (with large amounts of chloride, which inhibits the creation of a compact patina) leads Cor-Ten to be susceptible to corrosion and wash-out processes. As a consequence of these processes, Cor-Ten releases a certain quantity of alloying metals that could disperse in surrounding areas (soil or water) or accumulate near the structures. Considering the nature and the potential toxicity of some of the alloying elements, it is very interesting to evaluate the extent of metal release with respect to the exposure time, the exposure conditions and the form in which they leave the surface, for example, as water-soluble compounds or non-adherent corrosion products.

Therefore, the present work focuses on the corrosion behaviour of Cor-Ten steel through environmental exposure of commercial specimens at a coastal urban site (Rimini, Italy), both in sheltered and run-off conditions. This location allows us to examine the effect of a critical environmental condition for this material; so, atmospheric depositions, climatic data and information about gaseous pollutants are constantly monitored. In addition, the influence of different kinds of surface finish was examined, testing commercial samples of bare and pre-patinated (with or without a beeswax covering) Cor-Ten A.

The release of the main alloying metals (Fe, Cu, Cr, Mn e Ni) is periodically monitored through Atomic Absorption Spectroscopy. Furthermore, the evolution and the behaviour of the alloy patina are followed by surface investigations (SEM-EDS and Raman Spectroscopy).

Here, an estimate of metal release during the initial stage of atmospheric exposure of Cor-Ten is given and the results are then compared to the information previously obtained from accelerated ageing tests, reproducing the behaviour of the alloy exposed to rain run-off and water stagnation, respectively.

## Comprehensive evaluation of the patterns of air pollution by PAHs over Europe by combining modelling and observational data under a climatic perspective

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The impact of climate change on air pollution is an issue of vital importance. Changes in climate for the past decades can affect the patterns of polycyclic aromatic hydrocarbons (PAHs) by changing the dispersion (wind speed, mixing layer height, convective fronts), deposition by precipitation, dry deposition, photochemistry, natural emissions and concentrations background (e.g. Jiménez-Guerrero et al., 2012). Hence, evolution and trends of these pollutants should be studied with a multi-scale system through chemistry transport models, allowing the characterization of transport patterns and distribution of PAHs.

This work relies mainly on the combination of MM5/CHIMERE models, with the addition of the modified EMEP (European Monitoring and Evaluation Programme) emissions. Experiments span the period 1989-2010 and cover the European continent, particularly the areas under EMEP assessment. The atmospheric simulations have a horizontal resolution of 25 km and 23 vertical layers up to 100 hPa, and were driven by the ERA-Interim reanalysis.

In order to understand the spatial patterns of PAHs, modelled concentrations of benzo- $\alpha$ -pyrene (BaP) will be evaluated against observations at the monitoring stations belonging to the EMEP network. A number of metrics will be used to examine the model performance. For example, the mean bias (B) is a common metric used to quantify the departure between modelled and observed quantities, while the mean normalized bias (MNB) represents a useful measure of the overall over- or under-estimation by the model of the monitored concentrations. These parameters will provide information on the skill of the model to reproduce accurately the dynamics of PAHs over the target area. Moreover, the trends and processes affecting the levels of PAHs over the Mediterranean basin will be characterised and defined.

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## The Atmospheric Chemistry of Three Common Gases

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Carbon dioxide, water vapour, and methane are reactants in a variety of processes. Carbon dioxide and water vapour react photochemically to produce oxalic acid. Carbon dioxide and methane react photochemically to produce formic and acetic acids. Ozone is a probable by product of the oxalic acid reaction as there is a direct correlation between oxalic acid and ozone concentrations. The production of ozone fits a model involving temperature, absolute humidity, and solar radiation. Ozone decomposition is also a function of absolute humidity.

## The sea salts contribution on inorganic ions in wet deposition of the central Balkans

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Rainfall samples were collected over of 10 years period from 2001 to 2010 at seven sampling stations in central part of Balkans peninsula (Serbia) and analyzed to assess the inorganic ionic composition. Ion concentrations were determined by ion chromatography.

Most parts of Serbia have a temperate continental climate. With respect to this basic feature of climate over Serbia, precipitation regime is such that the maximum usually occur during the summer and minimum during the colder part of the year. Exception is southeast part of country where precipitation regime is more like Mediterranean type. During the colder part of the year, precipitation is generally associated with the penetration of low pressure systems from the west (extra-tropical cyclones coming from the Atlantic Ocean). During the summer most of the precipitation is convective type, conditioned by the emergence of local instability and thunderstorm systems. The sea salts contribution on total wet deposition calculated by: sea salt =  $1.47 \times ss[\text{Na}^+] + [\text{Cl}^-]$  [1].

Table 1 Wet deposition of the ionic constituents in precipitation of Serbia

	Belgrade	Valjevo	Smederev. Palanka	Kraljevo	Kruševac	Čuprija	Niš
Number of samples	734	921	884	898	891	887	834
Total VWM (meq)							
SO <sub>4</sub> <sup>2-</sup>	1225.0	1433.4	1219.3	1252.8	1297.6	1024.9	1220.2
NO <sub>3</sub> <sup>-</sup>	192.5	265.5	215.3	213.6	131.0	182.9	154.1
NH <sub>4</sub> <sup>+</sup>	386.5	483.7	504.6	547.4	558.2	290.4	555.8
Na <sup>+</sup>	182.5	158.2	124.7	140.1	177.7	166.0	131.8
Mg <sup>2+</sup>	159.9	172.5	192.8	167.9	130.4	166.2	126.7
Ca <sup>2+</sup>	818.2	1023.5	680.0	737.6	864.2	831.8	631.3
Cl <sup>-</sup>	191.7	176.6	145.2	143.1	251.5	294.1	172.9
K <sup>+</sup>	88.2	89.1	62.8	82.2	106.2	77.6	117.7
Sea salt	131.9	53.2	54.4	89.6	152.7	170.1	123.3

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## Size distribution of particle-bound Currently Used Pesticides in the ambient air of a rural station in Centre Region (France)

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Currently Used Pesticides (CUPs) can reach the atmosphere during or after pesticide application in agricultural practices from three different emission sources such as spray drift [1], volatilization from soil and plants [2] and wind erosion of soil particles [3]. From these primary sources, pesticides can reach the atmosphere both as gas or aerosols. Moreover, the gas to particle distribution (G/P) and the particle transformation are other two processes than can explain the particle size distribution of pesticides.

Samples on 47-mm-diameter quartz fiber filters were collected from March to May during 2008-2009 in Centre Région (France) using a Gravimetric DLPI Impactor (Dekati, Tampere, Finland). Four different fractions with these size ranges 0.03-0.1 $\mu$ m (ultrafine), 0.1-1  $\mu$ m (fine), 1-10  $\mu$ m (coarse) and more than 10  $\mu$ m were collected. The total volume collected was approximately 720 m<sup>3</sup>.

Particle size distribution for some CUPs applied in agricultural practices were investigated. In general, pesticides presented a higher frequency of detection in the fine fraction (from 33 to 100%). No pesticides were detected in the size fraction > 10  $\mu$ m. Four out of eleven detected pesticides (ethofumesate, fenpropidin, fenpropimorph and spiroxamine) presented an unimodal distribution in the fine size fraction. On the other hand, acetochlor, alachlor, and metolachlor present a bimodal pesticide size distribution with peaks on the fine and ultrafine fractions. Likewise, a bimodal distribution was observed for pendimethalin and chlorothalonil but in this case with a higher concentrations on the ultrafine fraction.

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## Reactivity of chlorine radical on palmitic acid particles: kinetic measurements and products identification

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Recent studies have revealed that the concentration of organic matter in marine environments exhibits a seasonal behaviour, dominating the chemical composition of ultrafine particulate matter (PM<sub>1</sub>) during periods of high biological activity. Chemical analyses of organic compounds sampled from this interfacial layer have allowed to identify mostly fatty acid (C12-C18) compounds. In an attempt to better understand the heterogeneous oxidation of particulate organic compounds, reactions between Cl atoms and palmitic acid (PA) have been performed in our laboratory. We present here results coming from the study of heterogeneous reactivity between Cl and PA within an Aerosol Flow Tube (AFT) where fine particles generated by homogeneous condensation of PA vapours are introduced with Cl<sub>2</sub> as an oxidant precursor. Cl atoms are generated by photolysis of the molecular chlorine using UV lamps surrounding the reactor.

Uptake coefficient has been determined by monitoring the decay of PA by GC/MS analysis as a function of chlorine exposure. Experiments have been conducted with and without O<sub>2</sub>. Identification of the reaction products in the condensed phase have been performed by GC/MS analyses. The heterogeneous reactivity experiments performed without O<sub>2</sub> lead to the determination of  $\gamma = 14 \pm 5$  and reveal that: (1) an important secondary chemistry involves Cl<sub>2</sub>; (2) monochlorinated and polychlorinated compounds are formed (from PACl<sub>1</sub> to PACl<sub>4</sub> detected). Although, the PA particles are solid, the whole PA matter can notwithstanding be consumed. In the presence of oxygen, the reaction is still leaded by secondary chemistry but the propagation chain length is smaller than in absence of O<sub>2</sub> because there is no regeneration of Cl<sup>•</sup> and lead to an uptake coefficient  $\gamma = 3 \pm 1$ .

In the presence of oxygen, the reaction is still leaded by secondary chemistry but the propagation chain length is smaller than in absence of O<sub>2</sub> because there is no regeneration of Cl<sup>•</sup>. Results coming from experiments realized with O<sub>2</sub> allow us to observe products relevant with the detected compounds in the tropospheric particulate matter. We have observed the formation of HCl, CO and CO<sub>2</sub> in the gas-phase, while, in the particulate phase, oxocarboxylic acids (OXA) and dicarboxylic acids (DCA) are identified by GC/MS.

Finally, we have highlighted that there is a significant fragmentation and functionalization of the fatty acids by oxidation initiated by radicals. This leads to the volatilization of oxygenated low-molecular weighted organic compounds in the atmosphere and the formation of OXA and DCA in the condensed phase, species which have been identified in particulate matter sampled in a large number of environmental conditions (urban, coastal, remote marine, remote continental). Further research is needed to evaluate whether the functionalization of the primary organic matter and the formation of more polar compounds in the particle lead to the modification of the hygroscopicity of the particle.

## Comparison of two atmospheric aerosol samplers

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Atmospheric aerosol particles are always present in the environment, being often present at high levels in urban environments. At the Iberian Peninsula, in contrast with Northern European countries, PM levels frequently exceed Air Quality Directives from the European Commission. This trend is due to both the high temperatures and low precipitation levels that delay rain scavenging and promote dust re-suspension and associated to the intense insulation that enhances photochemistry and secondary aerosol formation.

Atmospheric aerosol sampling has specific problems due to the great variability of the particles' sizes and chemical properties. This diversity often requires the use of different types of samplers and filters, conveniently chosen according to the objectives of the studies, the analytical methodology that will be used and the flow rate used for active sampling.

The present study aimed at the comparison of the performance of two types of aerosol samplers, with aerodynamic diameter smaller than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ), a commercial Gent type sampler and a noncommercial one, made at the FCUL workshops. Several tests of active sampling of atmospheric aerosols took place in parallel with both samplers equipped with Nuclepore<sup>®</sup> 0.4  $\mu\text{m}$  pore filters, in an urban area of the city of Lisbon, specifically at Campo Grande. The cationic composition of the water-soluble fraction of atmospheric aerosols (sodium,  $\text{Na}^+$ , ammonium,  $\text{NH}_4^+$ , potassium,  $\text{K}^+$ , magnesium,  $\text{Mg}^{2+}$  and calcium  $\text{Ca}^{2+}$ ) was determined by ion chromatography (IC). The results of the parallel determinations were compared by a paired t-test for a confidence level of 99%. This study led to the conclusion that, for the studied cations present in the water-soluble fraction of the aerosols sampled from the studied urban air, both samplers produce metrologically compatible results.

## Determination of CO<sub>2</sub>-emission in the case of country houses heated by firewood

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The GHG-emission-calculations introduced by IPPC refer to the global emissions and necessarily contain average factors. The experts of IPPC also suggest that more accurate emission data can be obtained concerning national level or a smaller level, if we calculate the data which is typical of the area and of the fuel consumed. Data were found in the literature that during wood heating CH<sub>4</sub> is also produced in very small quantity (0.026%) besides CO<sub>2</sub>. At the end of our calculations, this is considered as a modifying factor because the heating potential of the methane is 23 times higher than that of the carbon dioxide.

During our work CO<sub>2</sub>-emissions of the houses (households) in a Hungarian rural village are calculated from the wood heating. The principle of our calculation is based on the chemical equation which describes the oxidation of the carbon content of the firewood used for heating considering the atomic mass of carbon and oxygen. For the calculation we had to know the water content of the Acacia wood used for heating and the carbon content of the dry material of wood. The former was determined with airing cupboard method in the case of all investigated households; the carbon content was obtained from literary sources. The amount of unburnt carbon, which remained in the ash, was determined by potassium dichromate method. With these data, we calculated the amount of CO<sub>2</sub> generated during the combustion of 1 kg dry firewood.

In a village in eastern Hungary 22 households were chosen by random walk method for the determination of CO<sub>2</sub>-emission. The households represent the building stocks and families of the village very well. Each house in the village is heated with wood acacia. In two heating seasons the amount of burnt firewood was measured with kg precision and the CO<sub>2</sub>-emission of the households was calculated in the manner described above and then the CO<sub>2</sub>-emission of the whole village was estimated by calculation. Finally, we investigated how much of the emitted CO<sub>2</sub> can be absorbed by the forest owned by the residents.

## Investigating the chemical components of aerosol from an urban, a rural and a remote site (North Italy) and their relation with the observed biological responses.

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Particulate matter (PM) exposure has been related to adverse health effects. PM is a complex and heterogeneous mixture of particles with different dimension, whose chemical composition changes with time and space. In accordance with the clearly emerging evidence that specific PM components, and/or PM source categories, can be associated with health effects (Kelly and Fussell, 2012; Lippmann and Chen, 2009), it is of great relevance to investigate how time and space variations in PM composition of certain area can potentially determine the health effects of exposed population. In the present study, we analysed the chemical composition of fine PM (PM<sub>2.5</sub> and PM<sub>1</sub>) collected during different seasons at three different sites in North Italy: an urban site (Milan, MI), a rural site (Oasi Le Bine, OB), and a remote mountain site (Alpe San Colombano, ASC, m. 2280 a.s.l.). The main chemical components of PM, that is elemental carbon (EC), organic carbon (OC) and inorganic ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), were investigated together with particle-phased trace compounds, such as metals (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn) and trace organic compounds deriving from primary source (PAHs, *n*-alkanes, levoglucosan) and secondary source (oxiPAH and carboxylic acids). Seasonal PM samples from sites were characterised for a total of 41 chemical compounds, and all concentrations were expressed relative to the particle mass ( $\text{ng mg}^{-1}$ ). In a recent paper (Perrone et al., 2013) we reported about the *in-vitro* biological effects of the same PM<sub>2.5</sub> and PM<sub>1</sub> samples, showing how they change with the season and sites, and such variation was related with the PM chemical components, and possibly the related source. Results indicated that the seasonal pattern of chemical components associated with secondary source (mainly  $\text{SO}_4^{2-}$  and oxalic acid), dust (Al), and the regional widespread biomass burning source (levoglucosan, PAHs) influence the biological effects produced by PM samples from both the urban and the rural site, while metals and EC from the traffic source are responsible for the observed genotoxic effects of urban PM. The biological responses induced by PM from the remote site at high altitude are associated with the high concentrations of metals and secondary species typical of the free tropospheric aerosol, influenced by long range transport and aging.

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## Experimental measurements of particulate matter DRH and CRH for the prevention of corrosion in Data Centers

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Data Centers (DC) accounts for about 27% of energy consumptions in Western Europe; up to 50% of these consumptions is due to the cooling process of the installed information technology (IT) via air conditioning (Shehabi et al., 2008). To reduce it, Direct Free-Cooling could be applied: outdoor air is used to directly cool the IT. However, this approach involves the risks of introducing atmospheric aerosol, which can become electrically conductive if the ambient air exceeds its Deliquescence Relative Humidity (DRH) and could provoke potentially dangerous electric bridging or corrosion phenomena. In previous work (Ferrero et al., 2013), the operating conditions of a new DC in the Po Valley were optimized considering aerosol properties (DRH) and meteorological parameters; DRHs were estimated from a thermodynamic model (E-AIM II, <http://www.aim.env.uea.ac.uk>, Clegg et al., 1998). In the design of the DC, a potential 81% energy saving was calculated. However, just mean seasonal DRHs were used for the aforementioned application.

In order to save more energy a daily controlled DFC cycle would be preferred. Thus a validation of modelled DRHs on a daily basis was conducted in this study by means of a specifically designed Aerosol Exposure Chamber (AEC). The AEC (1 m<sup>3</sup>, 1% steps of relative humidity) has been designed to measure particulate matter (PM) conductivity properties (monitored by Hewlett-Packard 3421A data acquisition module), in function of changes in relative humidity (monitored by DMA572.1 LSI-Lastem termohygrometer) inside the chamber itself. The aim was to experimentally determine Deliquescence Relative Humidity (DRH) and Crystallization Relative Humidity (CRH) of real samples collected in Milan (45°31'19"N, 9°12'46"E, PM<sub>2.5</sub>, 35 samples) and in Oasi Le Bine (45° 8'17.24"N, 10°26'10.99"E, PM<sub>2.5</sub>, 2 samples). These samples have also been analyzed by Ion Chromatography (Dionex IonPac AS14A-5µm and CS12A-5µm Analytical Columns) in order to quantify their principal inorganic fraction (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>). Ions concentrations were used as input for the model E-AIM II.

The AEC experimental data resulted in an average DRH of 59.47±0.76% and CRH of 47.83±0.64% while the E-AIM II calculated an average DRH of 64.00±0.77%. These results are significant in order to better estimate the safe thermodynamic working ranges for DCs.

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## Contribution of Barcelona metro train brake pads to atmospheric PM<sub>x</sub> levels in platforms

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High PM levels of a number of elements typically used in brake pads (especially Cu, Ba, and Sb) were found in air quality measurements in Barcelona metro in old Fontana Line 3 (F-L3) and new Sagrera line 9 (S-L9) platforms. F-L3 is also enriched in other potential brake pads-bearing elements such as Mn, Cr, As, Mo, and Zn with respect to the levels in Sagrera L9 (S-L9). The pneumatic braking systems are systems are frontal or lateral to the wheel in L3 (acting when breaking speed goes below 30km/h) and lateral in the L9 trains (when breaking speed goes below 10km/h). One sample of frontal and lateral brake pads from L3 and two samples of lateral brake pads from L9 were selected for chemical, mineralogical and textural characterization. Frontal L3 brake pad (the mostly used) shows two layers (reddish and dark layers) from the metallic support to the friction surface. The reddish layer is a periclase (MgO)-rich material while dark layer is a barite (BaSO<sub>4</sub>) and C-rich material. The L9 lateral brake pads show metallic Fe-Cu, stibnite and zincite (ZnO) as major mineral phases. S-L9 brake pads are enriched in e-Cu and stibnite (Sb<sub>2</sub>S<sub>3</sub>) with respect both lateral and frontal L3 brake pads. S-L9 brake pads are enriched in Cu, Sb, As, Zn, Pb, Ni, Cr, and S with respect F-L3 frontal brake pads. The later are enriched in Ba and Mo with respect S-L9 brake pads. The enrichment in Sb in S-L9 and in Ba and Mo in F-L3 brake pads is in agreement with the enrichment in atmospheric PM<sub>x</sub> levels in the corresponding platforms. Therefore brake pads are the major source of Sb (for lateral s-L9 brake pads) and Ba (or frontal F-L3 brake pads) in S-L9 and F-L3 atmospheric PM<sub>x</sub> levels in the corresponding platforms. Most probably, the steel and related materials used in the catenary (Cu-rich) and wheels are the major source for Cu, As, Zn, Pb, Ni, and Cr.

## Environmental Tobacco Smoke (ETS) in the outdoor urban area of Barcelona

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Environmental Tobacco Smoke (ETS), is the results of the diluted mixture of side-stream and exhaled mainstream smoke from combustion of tobacco products such as cigarettes and cigars. It contains thousands of chemical substances and many are carcinogenic, mutagenic, irritating, or toxic. For this reason indoor smoking is now forbidden in many countries, including Spain. Many compounds can be used as tracer for ETS, however, only nicotine is strictly related to the *Nicotiana* species, i.e. tobacco leaves, This compound is emitted in large quantities to be easily detected in ambient air (1).

During the aerosol sampling campaigns conducted in the past years in the urban area of Barcelona, nicotine was detected in relatively high concentrations in the outdoor air (2). The concentrations were correlated with socio-economic activities, presenting higher levels during weekday and daytime in comparison to weekends and nighttimes. Moreover, in the densely populated center of the city the concentrations were about 8 times higher than in an urban background site that was taken as reference. Similar differences were observed between the higher concentrations at street level and the lower concentrations at a roof-site, 50m above the street.

The results from this study showed that ETS is ubiquitous in the urban atmosphere. Nevertheless, the nicotine concentrations are about 2 orders of magnitude lower than those observed in bars and cafeterias when tobacco smoking was still allowed.

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## Chemical composition of organic atmospheric particulate matter in the Mediterranean Area

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A significant portion of atmospheric particulate matter (PM) corresponds to highly polar organic compounds containing oxygenated functional groups - hydroxyl, carbonyl and carboxyl - [1]. Regarding the determination of these polar organic compounds, generally used methods are based on analysis by gas chromatography - mass spectrometry, including prior derivatization of functional groups. In recent years, these photochemical degradation products have been investigated intensely, however, there are a large number of species at low concentrations and therefore it is necessary to improve the analytical techniques.

It has been developed and validated in EUPHORE simulation chambers, a methodology based on the derivatization of the functional groups of multi-oxygenated compounds, which has subsequently been applied to environmental samples of organic atmospheric PM. Environmental samples were analysed at different locations. Over 50 multi-oxygenated compounds were detected and some species have not been described previously in atmospheric samples.

The analysis of the data shows that seasonality is a factor where the maximum values were recorded in autumn when traffic activity and combustion of heating is higher, and with enough solar radiation to produce, by photochemical reaction, a higher concentration of long chain carboxylic acids. The proximity to an industrial area originated similar values in any season in some locations. The concentrations of the compounds identified were in the range of  $\text{ng m}^{-3}$  to  $\text{g m}^{-3}$ . These values agree with those obtained by other investigators compounds measured in urban areas [2]. The major species were short chain dicarboxylic acids - oxalic, malonic, succinic, glutaric and adipic acid, being attributable to the traffic relationship between the emission of aromatic hydrocarbons and their photo-oxidation reactions. Another important result is the high levels recorded for levoglucosan, compound directly related to biomass burning and wood combustion processes.

These results show that the application of the methodology developed is allowing mapping the chemical composition of atmospheric organic PM in the Mediterranean Area.

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## Time-resolved measurements of Particulate Matter ionic fraction: comparison between South and North Italy

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Time-resolved information about particulate matter (PM) ionic fraction and inorganic gases allow to study the chemical-physical processes occurring in atmosphere. Nowadays, the most important disadvantages regarding the chemical characterization of PM filters are the limited time resolution of the results and the inability to obtain simultaneously the information about inorganic gases concentrations. The AIM9000D provides time-resolved direct measurements of anion and cation both in particulate and gases phases and it is an useful tool that allow to investigate the chemical process leading to the formation of ionic fraction of PM<sub>2.5</sub> but also physical transformations and subsequent gas-particle partitioning of its semi-volatile inorganic constituents.

The main goal of this work is the study of PM formation processes that occur in atmosphere at Milan and Bari, using high time-resolved information about ions and inorganic gases concentrations. For this purpose, two high time resolved campaigns have been performed at the urban background stations in the Campus of University of Bari from 1<sup>st</sup> to 20<sup>th</sup> October 2011 and on the roof of the University of Milan from 6<sup>th</sup> June 2012 to 26<sup>th</sup> July 2012.

The preliminary results highlighted that the higher photoreactivity and atmospheric stability in Milan determined a photochemical production of HNO<sub>3</sub>. The hourly mean concentrations in Milan, in fact, showed a clear daytime peak when high ozone concentrations were registered. On the contrary, the hourly concentrations of HNO<sub>3</sub> in Bari were related to humidity percentage and NO<sub>x</sub> concentrations. In particular HNO<sub>3</sub> high concentrations were determined in the night hours between 3:00 and 6:00 a.m. This result suggested that the main formation process of HNO<sub>3</sub> in Bari was due to etereogenuos reaction occuring in the dark, between nitrate radical (NO<sub>3</sub><sup>·</sup>) and water on particle surface [2]. Moreover, the lower Sulphate Oxidation Rate (SOR) and the uncorrelated behaviors of sulphate and SO<sub>2</sub> concentrations for Bari data, suggested the negligible contribution of local sulphate in Bari unlike in Milan [3].

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## A study of the dioxin emission from energy facilities used liquid fuel in Korea

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We studied the current status of dioxin emitting facilities in Korea compare to the previous year and estimated national dioxin emissions based on the emission data measured in each facility. In the non-incineration sector, the contribution rate of dioxin in the emission from energy facilities has been on the rise—10.3% in 2007, 13.3% in 2009, and 20.4% in 2010. Therefore, in order to estimate dioxin emissions we have monitored PCDDs/PCDFs from energy facilities which use liquid fuel. In order to calculate dioxin emissions from energy facilities that use liquid fuel, samples were collected from five power plants, three times per facility, in the isokinetic sampling conditions of over 4 hours and over 3 Sm<sup>3</sup>. And The dioxin concentrations were analyzed using the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS: Micromass Co., Autospec Ultima) with the resolution of over 10,000.

The Average dioxin concentration in the emissions from the stacks of the five facilities was 0.1225 ng-I-TEQ/Sm<sup>3</sup>. Also the average dioxin concentration was 0.143 ng-I-TEQ/Sm<sup>3</sup> in fuel and 0.010 ng-I-TEQ/Sm<sup>3</sup> in the ash. Dioxin isomers emitted from each stack of the facilities were mostly HpCDF, HxCDF, PeCDF and OCDF, which was the same with the dioxin emission pattern (17 PCDD/Fs) of incineration. Based on these figures, the dioxin emission factor against energy production of the energy facilities was calculated to be 1-4 µg-I-TEQ/yr using the semi bottom-up approach. All the results of this study satisfied the air pollution emission standards in Korea. It is considered that management measures for dioxin emissions from energy facilities, even though the amount is relatively small compare to incineration facilities, need to be established taking into account annual energy production.

Keywords : Dioxin emission, liquid fuel, power plant, Dioxin emission factor

## Passenger exposure to PM while commuting in the Barcelona metro

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People living in urban areas usually spend a considerable amount of their daily time commuting, with underground rail being one of the public transport modes most used in cities worldwide. Despite the undoubted efficiency of subway travel, however, underground commuters are known to be exposed to high levels of particulate air pollution. Surveys of the concentrations and characteristics of inhalable particles existing in these indoor environments are of extreme interest since they have been shown to cause adverse health effects.

The metro system in the city of Barcelona (Transports Metropolitans de Barcelona: TMB) is one of the older underground transport systems in Europe, with its first line beginning operation in 1924. By the present decade, the TMB comprises 11 lines (3 of them are new, in operation over the last five years) with a total length of 102.6 km and including 140 train stations. Trains run from 5 a.m. until midnight everyday, with additional services on Friday nights (finishing at 2 a.m.) and Saturday nights (running all night long), with a frequency between 2 and 15 minutes, depending on the day (weekend or weekday) and time of day. The Barcelona metro absorbs around 50% of the urban commuting load, transporting around 1.25 million passengers on workdays. The most frequent average journey time is 35 minutes (approx 10.2 km) round trip.

The overall aim of the proposed study is to fully characterise passenger exposure to PM while commuting (including waiting time on the platform and travelling inside the trains) in the Barcelona subway system. Sampling campaigns both on platforms and inside trains and a comparison between the old and the new lines is currently ongoing. The platforms of four stations are equipped with a PM<sub>2.5</sub> high volume sampler; an optical particle sizer (TSI OPS 3330) monitoring real time TSP, PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>; and a real time CO<sub>2</sub> analyzer (TSI IAQ-Calc 7545). Additional measurements on platforms (from 24 stations from five subway lines) and inside the trains (during a one-way trip to and from the beginning of the line) are to be carried out using a portable Aerosol Spectrometer (TSI DustTrak 8533). Measurements are to be performed at each selected station for one hour, divided into periods of 15 minutes in 4 positions approximately equidistant along the platform for greater representativeness and to observe possible spatial differences depending on the position on the platform. A manual control of the exact arrival and departure times of each train is to be performed to assess possible correlations with the variability of the registered concentrations. In this contribution the detailed results of PM concentration variations on platforms and in trains obtained during the first months of the Barcelona campaign will be presented for the first time.

### Acknowledgements

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## Indoor and outdoor levels and composition of air pollutants in primary schools in Barcelona

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The study of health effects derived from the exposure to particulate matter (PM) is a research field of great concern. A major gap of knowledge is on the PM effects on brain neurodevelopment. Children constitute the main risk group due to their higher vulnerability and the importance of brain development in this period. Levels of outdoor PM and some of its chemical components are usual inputs in epidemiological studies, while indoors (where people spend most of their time) usually remain unknown.

Monitoring of different air pollutants during two campaigns of one week period was carried out from February 2012 to February 2013 in 39 schools in Barcelona within the framework of the ERC Advanced Grant BREATHE project. Using high-volume samplers, PM<sub>2.5</sub> was collected on quartz fibre filters to obtain mass concentration and a complete chemical characterisation of around 45 PM components: elemental (EC) and organic carbon (OC), soluble ions, metals and other major and trace elements. Sampling duration was 8h per day/filter during school time. In addition, real-time levels of black carbon (BC), PM<sub>2.5</sub>, ultrafine particles (UFP), and Lung-Deposited Surface Area (LDSA) were monitored, as well as weekly-averaged NO<sub>2</sub> concentration. All these parameters were simultaneously measured inside the classroom, in the school playground, and in one urban background (UB) air monitoring station at Barcelona for seasonal adjustment. The effect of factors such as traffic intensity, classroom ventilation and type of playground on indoor and outdoor levels of PM<sub>2.5</sub> and its chemical components was considered. Source apportionment analyses based on PM<sub>2.5</sub> composition were carried out to determine the main pollutant sources.

The schools showed high levels of air pollutants (particularly PM<sub>2.5</sub>) with concentration widely differing between them. PM<sub>2.5</sub> levels (both indoors and outdoors) were highly influenced by schools activities. An indoor source of OC and Ca in PM<sub>2.5</sub> has been identified. Cotton fibres from the clothes as well as skin cells and other organic emissions from children might be an important source for OC. Ca is related to the chalk used in the blackboards. Occasionally, high indoor levels of metals were found, due to some unknown activity. Sand playgrounds play a major role in PM<sub>2.5</sub> levels, resulting in large increases of mineral matter levels. Outdoor PM<sub>2.5</sub> levels were more than double the usual UB levels reported for Barcelona. However, for outdoor concentrations of N, EC, NO<sub>2</sub> (highly influenced by road-traffic) this factor diminishes to 1.2 – 1.6.

Therefore, PM<sub>2.5</sub> levels at schools were not an indicator of traffic but of school activities and playground characteristics. Traffic derived air pollutant levels found at playgrounds in schools are not equivalent to those measured in UB sites but intermediate between background and traffic sites.

## Monitoring of nitro-PAHs in Taranto (southern Italy)

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Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) are directly emitted in atmosphere from combustion sources or produced from gas-phase reactions of polycyclic aromatic hydrocarbons (PAHs) with oxides of nitrogen, with subsequent partitioning to the particulate phase. Primary sources include emissions from vehicles (mainly diesel vehicles), coke ovens, heating, smoking, certain types of food processing, and incomplete combustion in general. Once released into the atmosphere, many nitro-PAHs are highly persistent in the environment and can be transported long distances from their original source. The increased attention to nitro-PAHs is due to their persistence in the environment and higher mutagenic ( $2 \times 10^5$  times) and carcinogenic (10 times) properties of certain compounds compared to unsubstituted polycyclic aromatic hydrocarbons (PAHs). Although at lower concentrations compared to parent PAHs, in recent years it has become well-established that certain nitro-PAHs exhibit high direct-acting mutagenic potency in a microbial mutagenicity bioassays and in a forward mutation assay based on human cells. Furthermore, nitro-PAHs can be a significant fraction of direct-acting mutagenic compounds of atmosphere and can be a result of human exposure to respiration. These concerns have stimulated research into the primary sources, fate, and transport of these contaminants in the atmosphere. The present work shows the first results obtained from the analysis of particulate nitro-PAHs collected in 5 sampling sites of Taranto (southern Italy), 4 of which next to the biggest European steel manufacturing plants. The study of nitro-PAHs is part of a larger monitoring project organized by ARPA Puglia, which provided a monitoring campaign of atmospheric particulate matter (PM<sub>10</sub>), PAHs, and the main meteorological parameters in seven sampling sites for six months, from November 2010 to May 2011, in Taranto. The analysis of samples and meteorological data such as wind direction and speed allowed the study of the behaviour of nitro-PAHs in atmosphere and the impact of these pollutants on sensitive receptors as a function of the weather conditions, the type of emission sources and the distance and location of sampling sites from the emissive source. In particular it was found that high concentrations of nitro-PAHs were recorded when the wind direction is such as to allow the transport of these pollutants from the industrial area to the site in the direction of the wind. The comparison of the trend of the sum of PAHs and Nitro-PAH showed the presence of a primary source common to the two pollutants and that their monitored levels were comparable during some days of the campaign. Finally, the study of individual nitro-PAH concentrations allowed to identify the 2-nitro fluorene as a marker of the industrial emissions.

## NO<sub>x</sub> uptake on Ca-based absorbents

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Among the nitrogen oxides compounds, NO and NO<sub>2</sub> (NO<sub>x</sub>) are the most abundant pollutants in the gaseous emissions originated by the combustion of biomass and fossil fuels. Other relevant sources of NO<sub>x</sub> are storm-lightening, oxidation of NH<sub>3</sub> and volcanic activity. Nitrogen oxides (NO<sub>x</sub>) are the source of severe environmental problems such as acid rain, smog formation, global warming and ozone layer weakening. NO is mostly formed by the reaction between nitrogen and oxygen, whereas NO<sub>2</sub> is formed by oxidation of NO at low temperatures in the atmosphere according to the atmosphere.

In 2005, Li et al. <sup>(1)</sup> developed a new Ca-based material for the absorption of CO<sub>2</sub> in industrial processes: CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> was obtained by integrating solid CaO with a composite metal oxide, Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (Mayenite), acting as the binder. Mayenite is a nanoporous calcium aluminate prepared by calcination at about 1600 K of stoichiometric amount of calcium carbonate and alumina. Mayenite has an antizeolite-type structure with interconnected positively charged cages, which can host a variety of anionic species <sup>(2,3)</sup>.

Recently, we succeeded in using CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as a solid absorbent material in passive sampling devices for the determination of the atmospheric CO<sub>2</sub> <sup>(4)</sup>.

In order to obtain a class of calcium based sorbent materials for the quantification and possibly the removal of NO<sub>x</sub> from the atmosphere, we synthesized and characterized various CaO/Mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) substrates having different weight ratio (w/w) composition. Their reactivity towards NO and NO<sub>2</sub> was evaluated by means of several experimental techniques: FT-IR and XRD were used to characterize the species formed during the adsorption process, while IC and TGA analysis provided information about the dynamics of the adsorption process itself. The hydration reaction occurring on the substrate before NO<sub>x</sub> adsorption has also been considered in our investigation. We finally tested the performance and the reliability of the CaO/mayenite materials in field measurements by incorporating the substrate in a passive sampler device. The simultaneous absorption of atmospheric NO<sub>2</sub> and NO has been investigated and the role of the carbon dioxide in the NO<sub>x</sub> – CO<sub>2</sub> exchange reactions has been assessed. According to the data reported in this paper and thanks to the fairly low cost of production, CaO/Mayenite substrates represent a good class of inorganic alkaline adsorbents for NO<sub>x</sub> suitable for many applications in atmospheric sampling and remediation.

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## Aerosol studies in the Karst of Trieste (Italy)

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Regional air quality assessment and modeling of dynamics of gaseous and aerosol compounds can greatly benefit from experimental studies at sampling sites positioned in relative distance from intense sources of pollution; this is particularly valid in complex areas as the Karst, the limestone borderline plateau region extending in southwestern Slovenia and northeastern Italy, at some tens of kilometers from Trieste, a city of 210.000 inhabitants with an harbour, from the industrial town of Monfalcone with its 976 MW power plant and close to the Northern Adriatic Sea.

A sampling site for aerosol and organic gases was established in Spring 2012 in close proximity to the entrance of the cave called Grotta Gigante, where also a meteorological station is working since 1967. The site lays in a submediterranean deciduous forest classified as *Ostryo-Quercetum pubescentis*. A day-night campaign was conducted in late June 2012 where ions, OC/EC and secondary organic compounds were measured, showing that the site is adequate to study BSOA formation from terpenes and isoprene precursors. Contrasts between summer and winter were studied with a series of four days samples, where ions, OC/EC, n-alkanes and PAHs were detected; markers from biomass burning as well as MSA, signing marine biogenic contribution, highlight the plurality of sources contributing at formation of aereosols. Recent XRF powder analysis contribute to mass closure, with information about inorganic composition.

Experimental data are also compared with estimates from MEGAN model of emission of gas and aerosol from nature.

Chemistry of wet and dry depositions has also started to be studied, aiming at characterizing inorganic inputs to soils.

## **MONAIRNET - Monitoring network for persistent organic pollutants in ambient air of Czech Republic - Austria region**

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Persistent organic pollutants (POPs) are substances of very critical toxicity and the tendency to accumulate in the environment. Therefore, the UN has adopted the Stockholm Convention to meet this problem on an international level. POPs can cover large distances when transported in the air. This has been shown in previous monitoring programs like MONARPOP for the Alpine region and MONET ([www.genasis.cz](http://www.genasis.cz)). For a future joint action towards POP control, it is necessary to harmonize the different monitoring approaches currently used in the respective UN regions. At this point, the methods applied in Austria (part of the Western European and Others Group; WEOG region) and the Czech Republic (CEEC region; Central- and Eastern European Countries) are not fully comparable due to methodical differences.

The project aims to create a pilot monitoring network in the Austrian-Czech border region to assess the current POP-pollution in the air. The created monitoring network was connected to existing monitoring networks in the area (MONARPOP, MONET). This is to allow a consolidation of the currently applied methods and provide a comparability of the existing data. In the Austrian-Czech border regions was installed a new network of sampling points for active and passive air sampling as well collectors for atmospheric deposition. Samples were collected over a year and analyzed on several air-borne POPs (2011-2012). Additional to the technical part, the project results will be communicated to a larger public (publications, WEB portal: [www.genasis.cz](http://www.genasis.cz)).

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## Study of aldehydes in rainwater of the urban atmosphere

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Carbonyl compounds in ambient air originate from both primary and secondary sources. They are emitted directly into atmosphere as well as formed by photochemical oxidation of hydrocarbons emitted from anthropogenic sources (automobiles, thermal power plants, etc.) or natural biogenic sources. Different type and levels of these compounds could be related to their possible sources. Carbonyl compounds play a major role in urban photochemical smog and are precursors of free radicals and ozone in atmosphere. Several aldehydes such as formaldehyde and acetaldehyde have received significant attention as toxic air contaminants, mutagens, eye irritants and carcinogens. Aldehydes are water-soluble and hence wet deposition is an important removal mechanism for these compounds. Their concentration in rainwater depends on many factors such as air pollution level, the strength of rainfall, the amount of precipitation and origin of air masses.

The aim of this study was to investigate the levels of carbonyl compounds in rainwater of an urban area. For this purpose rain water samples were collected by automatic sampler in the area of Thessaloniki, Northern Greece for a period of six months (October 2012-March 2013). Samples have been analyzed for carbonyl compounds after derivatization to their corresponding pentafluorobenzyl oximes, extracted with n-hexane and analyzed by GC/ECD. Moreover, pH, conductivity, dissolved organic carbon, UV absorbance and fluorescence were also measured.

The most predominant carbonyl compounds in rainwater were formaldehyde, acetaldehyde, hexanale, glyoxal and methyl glyoxal. Results are discussed in relation to other parameters of rainwater (pH, EC, DOC, UV, Fluorescence) as well as to meteorological data (direction and velocity of wind, relative humidity, air temperature, amount of precipitation) and air masses trajectories.

## **Soil and Sediment Pollution, Wastes**

**Oral presentations: OS1-OS10**

**Poster presentation: PS1-PS51**

## **Analytical strategies to evaluate polycyclic aromatic hydrocarbons (PAHs) bioavailability in soils; correlation with their biodegradability**

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Polycyclic aromatic hydrocarbons (PAHs) are persistent and toxic pollutants which present geo-accumulation characteristics. Depending on their chemical form and soil characteristics, they are more or less strongly sequestered in soils, and the effectiveness of bioremediation processes is closely linked to their bioavailability for the soil degrading bacterial communities. The aim of this study was to develop a simple and rapid method to evaluate bioavailability of PAHs in soils and to show if a correlation exists with their biodegradability.

The extraction methods usually performed (Soxhlet, Microwave Assisted Extraction MAE, or Accelerated Solvent Extraction ASE) give pseudo-total content of PAHs in soil samples, but do not allow to access the labile and so bioavailable fraction of PAHs. Soft extraction methods, using solubilizing agents in aqueous phase, are more likely to give the labile fraction of PAHs in soils. Additives such as synthetic surfactants, emulsions and cyclodextrins were tested to extract PAHs from five dissimilar natural soils, with very different geochemical properties (nature and content of organic matter and clays, pH...). New cyclolipopeptidic biosurfactants, produced by bacteria, were also tested, as well as original additives such as micellar ionic liquids. The critical micelle concentration (CMC) of our synthesized ionic liquids could be determined by a novel method using capillary electrophoresis. The nature of soil organic matter was determined using RockEval 6 pyrolysis, and the nature of clays was assessed using X-ray diffraction.

Aqueous extraction capacities with these different additives were then compared to pseudo total extractions performed by MAE with organic solvents, in order to determine whether the ratio between labile PAHs and total PAHs was linked to the soil retention capacities. In parallel, we studied the degradation kinetics of 7 mixed PAHs, for three months, in the five soils. Thereafter, a principal component analysis (PCA) allowed us to correlate (or not) the biodegradation of low and high molecular weight PAHs to some characteristics of soils, to their bioavailability, but also to the total bacterial communities and to the number of cultivable bacteria degrading phenanthrene.

## Persistence of butyltin (BuT) compounds in the contaminated sediments from the Croatian Adriatic coast

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Since the biocidal properties of tributyltin (TBT) were discovered in the late 1950s, it found a wide application as an active biocide in the antifouling paints, and was directly introduced into the marine environment by this way. After it was established that TBT, acting as an endocrine disruptor, causes imposex and other adverse biological effects (already at levels of 1-2 ng L<sup>-1</sup>) it became clear that it is one of the most toxic anthropogenic compounds ever purposely introduced into the marine environment. TBT is included in the European list of priority pollutants and its use in antifouling paints was finally banned in 2008 in all European countries, including Croatia. However, first data on butyltin concentrations in marine samples (seawater and mussels) from the Croatian Adriatic coast performed in 2009 and 2010 showed widespread pollution of the coastal area with butyltin compounds and suggested that TBT-based antifouling paints were still in use in Croatia (Furdek et al., 2011).

Once introduced into the water column, TBT is subjected to microbial and photolytic degradation to less toxic dibutyltin (DBT) and monobutyltin (MBT) compounds, and finally to non toxic inorganic tin. All these compounds readily adsorb to settling particles and accumulate in the bottom sediment where their degradation continues, but at significantly slower rate. Due to their persistence in sediments and continuous release back into the water column, butyltins can cause problems long after their input.

The aim of this work is to present data on the distribution of butyltin compounds in sediment cores sampled at 26 polluted locations (marinas and ports) along the Croatian Adriatic coast and to study the factors that influence distribution and persistence of butyltin compounds in these sediments.

The results showed that tributyltin pollution is present at all investigated locations with total BuT concentrations ranging from 80 to 55000 ng(Sn)g<sup>-1</sup>, comprising 15 to 80 % of TBT. Butyltin degradation index [BDI=(MBT+DBT)/TBT] varied from 0.5 – 2 in the surface sediment and from 0.5 – 8 in the deeper sediment layers. The depth profiles of BDI and of BuT concentration showed very different patterns with depth, suggesting different degradation rates of BuT compounds in sediments from different locations. For better understanding of these unequal depth distributions we studied the influence of sediment characteristics (particle size distribution, specific surface area and organic carbon content) on the persistence of TBT in sediments. The assumption that sediment characteristics could affect TBT degradation in sediments was based on the results of our previous experiments which suggested that desorption from sediments into the porewater has a crucial role in BuT degradation in sediments, as the degradation of TBT and DBT in porewater was found to be a fast process, with the half-lives of  $t_{1/2} = 8.9 \text{ days}^{-1}$  and 2.9 - 9.1 days<sup>-1</sup>, respectively.

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## Food Crop Accumulation and Bioavailability Assessment for Antimony (Sb) compared with Arsenic (As) in contaminated soils.

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The metalloid antimony (Sb) is in the same group of the periodic table as arsenic (As) and has similar chemical properties. It has a range of common uses including as a flame retardant, and a hardener in lead shot but emissions to the environment have increased tenfold in the last decade. This is a result of a range of new applications, including in new memory devices in computers and USBs, mobile phones and LCD televisions. Arsenic is internationally recognized as a toxic element for which environmental protection guidelines have been established worldwide. This is not, however, the case for Sb, although exposure to Sb and its compounds can also result in acute toxicity and chronic effects<sup>1-2</sup>. Despite worldwide concerns about the increasing presence of Sb in our environment, regulation and management is severely limited by both poor understanding of its speciation in different environments and its bioavailability, plant uptake and accumulation through foodchains<sup>3</sup>. The aim of this study was to investigate and compare accumulation of Sb and As in foodcrops growing in soils with mining-derived contamination in the Macleay River Floodplain, Northern NSW, and, for the first time, test chemical extractants as predictors of the soil borne Sb and As bioavailability to plants and humans.

A nine week glasshouse growth trial was established using a range of common vegetable crops growing in contaminated soils collected from the Macleay River floodplain (Sb 8 – 15 mg kg<sup>-1</sup>; As 12 – 20 mg kg<sup>-1</sup>). The soils were extracted using i) EDTA as a potential predictive test for As and Sb accumulation in the vegetables<sup>4</sup> and ii) a simplified bioaccessibility extraction test (SBET)<sup>5</sup> to understand potential metalloid uptake in the human gut. Up to 10 µg L<sup>-1</sup> metalloid was detected in soil solution with Sb showing higher relative solubility than As in these soils. Antimony concentrations in the vegetable crops over the 9 week greenhouse trial, however, were less than the limit of detection. Accumulation of As was detected but at < 10 % total soil borne As. The results showed relative Sb accumulation in the vegetables to be lower than that of As, indicating different uptake mechanisms or greater inhibition of Sb uptake. The metalloid extracted by EDTA solution was < 3.5 % of the total soil concentration for all samples. EDTA was a poor predictor of metalloid accumulation in vegetables grown. Bioaccessibility as measured by SBET was < 7 % for both metalloids with Sb showing lower bioaccessibility than As.

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## **Sediment PAHs in the Rivers of Ammer (Germany) and Liangtan (China): Differences between Early- and Newly-Industrialized Countries**

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As a proxy to trace the impact of anthropogenic activity, sedimentary polycyclic aromatic hydrocarbons (PAHs) are compared between the early industrialized and newly industrialized countries of Germany and China, respectively. Surface sediment samples in the Ammer River of Germany and the Liangtan River of China were collected to compare concentration levels, distribution patterns, and diagnostic plots of sedimentary PAHs. Total concentrations of 16 PAHs in Ammer sediments were significantly higher by a factor of 4.5 than those in Liangtan. This contrast agrees with an extensive literature survey of PAH levels found in Chinese versus European sediments. Distribution patterns of PAHs were similar across sites in the Ammer River, whereas they were highly varied in the Liangtan River. Pyrogenic sources dominated in both cases. Strong correlations of the sum of 16 PAHs and PAH groups with TOC contents in the Liangtan River may indicate co-emission of PAHs and TOC. Poor correlations of PAHs with TOC in the Ammer River indicate that other factors exert stronger influences. Sedimentary PAHs in the Ammer River are primarily attributed to input of diffuse sources or legacy pollution, while sediments in the Liangtan River are probably affected by ongoing point source emissions. Providing further evidence of a more prolonged anthropogenic influence are the elevated black carbon fractions in sedimentary TOC in the Ammer compared to the Liangtan. This implies that the Liangtan River, like others in newly industrialized regions, still has a chance to avoid legacy pollution of sediment which is widespread in the Ammer River and other European waterways.

## Micropollutants as tracers of urbanization history of the Mingoa river watershed (Yaoundé, Cameroon)

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The aim of this study was to analyse the impact of urban dynamics on the receiving aquatic environment in tropical African conditions to better understand African environmental problems, often left aside by the research. As study site was chosen the upper part of the Mingoa watershed, one of the small and highly urbanized watersheds of Yaoundé city (Cameroon). The river watershed has a surface of 4 Km<sup>2</sup>, approximately 35000 inhabitants and ends with the Municipal Lake. The history of the impact was studied through the analysis of persistent and emerging pollutants in dated sediment cores (Cd, Cu, Pb, Zn, PCB, PAH, nonylphenol, parabens and triclosan), and the evolution of the watershed urban development.

The input of pollutants was traced from 1952, when the Municipal Lake was built, to 2010. Three periods were identified in sediment cores according to the mineral composition and contaminants levels:

- 1952-1964: contaminants concentrations were constant, and usually smaller than quantification limits. The watershed was not very urbanised during the last decade of the colonisation. The country independence was obtained in 1960.
- 1964-1991: contaminants concentrations increased. The post colonial period is characterised by population growth and infrastructures development.
- 1991-2010: concentrations of Cd, Pb, Zn and PCB stopped to increase after 1991 and remained constant until 2010. This period is characterized by the economic crisis (from the end of 80's to the end of 90's) with no investment in infrastructures. No correlation was observed between Pb levels and traffic development, despite its use in gasoline until 2005. Cu is different of other metals because its concentration increased from 1994 to 2010. PAH concentration remained constant between 1991 and 2000, and increased until 2010. A change for wood and coal to petrol as energy source was observed. The highest concentrations of nonylphenol and methylparaben were observed after 2000 due to an increase of the house and personal care products market.

The presence of a marsh upstream the lake tempers the impact of the watershed on the lake ecosystem. Contaminants levels observed in the Municipal Lake sediments are lower than in Western countries, and often don't attain the limits set by Environmental protection agencies.

## Comparison of Triglycerides and Fatty acids patterns in burial leachate and raw oils(animal fats, fish oils, cooking oils)

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Korea, foot and mouth disease virus was a hot issue in 2010's winter season. Because lots of livestock were treated by burial method and some was buried by improper method, Underground water contamination was a big problem for people living near burial. For now, markers for carcasses leachate were BOD, NH<sub>4</sub>-N, TDS, chloride and etc. But it was hard to classify between effect of compost and leachate. Fats and oils are markers distributed in food product. Many publications have shown that fingerprints of fatty acids match 96% of correct classification. The objective of the present study was to consider that fatty acids can be the marker for leachate of carcasses and find out end of effect of burial by monitoring composition change.

Samples classified as carcasses leachate, livestock manure, swine fats, dairy cattle fats, cattle oils, chicken oils, fish oils, general food oils were treated by 10M KOH 1 mL and methanol 2 mL at 100°C 1 hour. and shook for 30 minutes with adding heneicosanoic acid(10 mg/L) 50  $\mu$ l and 5 mL of pentane. Distributed solvent layer, concentrated to 50  $\mu$ l by nitrogen was reacted at 80°C 30 minutes with adding 2 mL of 2M HCl in MeOH and shook for 30 minutes with adding 3 mL of pentane. Finally the distributed solvent layer was concentrated and analysed by GC/MS. Standard mixture composed of methyl myristate(C14:0), methyl palmitate(C16:0), methyl palmitoleate(C16:1), methyl stearate(C18:0), methyl oleate(C18:1), methyl Linoleate(C18:2), methyl arachidate(C20:0), methyl arachidonate(C20:4).

Eight different FAs were determined. As following S.M. van Ruth's paper, Animal fats were rich in C18:1 (40%), C16:0 (23%), C18:0 (13%), and C18:2 (11%). Fish oils were composed mainly of C18:1 (17%), C16:0 (16%), C22:6 (15%), C20:5 (9%), and recycled cooking oils of C18:1 (39%), C18:2 (37%), C16:0 (13%). In this study, composition of leachate from burial of cattle and swine were different. For leachate of cattle, the main components were C14:0> C16:0> C16:1 and for leachate of swine the main components were C14:0> C16:17> C16:07. There is a difference of composition between animal fats and leachate of animal. From results of lab scale experiments we monitored composition of leachate as times. We can figure out that concentration ratio of C14:0 was increased in cattle and swine leachate. But ratio of C16:1 was increased in 2.3 times in 4 weeks only at the case of cattle. Concentration of C14:0 was increased 1.4 folds(cattle) and 2.1 folds(swine). In additive experiments we can find the ending point of burial influence by observing the change of C14:0 and C16:1 concentration.



## Integrated monitoring of particle associated transport of PAHs in contrasting catchments

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Water quality of rivers depends often on the degree of urbanization and thus the population density in the catchment. This study shows results of a 2 years monitoring campaign of total concentration of polycyclic aromatic hydrocarbons (PAHs), turbidity and suspended sediment particles in water samples from adjacent catchments in Southern Germany with similar geology and climate but different degrees of urbanization (“contrasting catchments”). Defined linear relationships between total concentrations of PAHs in water and the amount of total suspended sediments (TSS) as well as with turbidity (NTU) were obtained indicating predominance of particle-facilitated transport for these pollutants. The slopes of the linear regressions correspond to the average contamination of suspended particles and thus comprise a very robust measure of sediment quality in an entire catchment. For the first time we demonstrate that the pollutant load on suspended sediments in different catchments correlates with the degree of urbanization represented by the number of inhabitants per total flux of suspended particles (e.g. the ratio of “polluted” urban to “clean” background particles). Such catchment specific relationships in principle can be determined by event sampling campaigns or a number of grab samples covering different elevated turbidities. The new methodology allows integrated assessment of pollutant fluxes by monitoring discharge and turbidity as a proxy for particle facilitated transport (e.g. online by optical backscattering methods).

## Geochemical Speciation and Potential Toxicity of Trace Elements in River Sediments

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Sediments act as a sink but they can release trapped metals as a result of slight environmental perturbations. The distribution, mobility, and hence the bioavailability of metals in the sediments not simply depend on their concentrations but, critically, on their chemical forms (i.e. speciation). Therefore, studies on metal speciation in sediments are of paramount importance. The study focuses on the speciation of Cr, Ni, Cu and Pb in the sediments of the Yamuna-an important river of India. The studies were conducted to evaluate the availability of metals to biota and the consequent risk. For the analysis of metals, sediment samples were digested following standard procedure of USEPA and analyzed by AAS (PerkinElmer, *AAnalyst 800*, USA). The chemical partitioning of metals in sediments was studied by following the modified BCR (mBCR) sequential extraction scheme. Certified reference materials, IAEA 405 (estuarine sediment) and BCR 701 (lake sediment), were analyzed to assure the accuracy ( $\pm 10\%$ ) of the methods employed for the determination of total metal and different fractions of metals by mBCR scheme. The availability of metals in sediments follows the sequence Pb>Cu>Ni>Cr. Data were subjected to multivariate statistical analysis. Significant spatial variations in physicochemical characteristics and different geochemical forms of metals in sediments, indicated by two-way ANOVA, are attributed to various anthropogenic activities at different sites. A similar source for all the four metals is indicated by principal component analysis (PCA). PCA also indicates towards some independent sources of Cu and Pb. The hot spots were identified using hierarchical cluster analysis using available forms of metals in sediments as objects and the sampling sites as variables. Risk assessment code (RAC) analysis indicates that metals generally pose medium to high risk at different sites. However, at a few spots either Ni or Pb crosses the level of very high ecological risk.

## Estimation of Health Risk from Indoor dust as a source of Exposure to Heavy Metals in Istanbul

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Indoor dust can be an important pathway in exposure of people to various environmental contaminants including heavy metals, persistent organic contaminants etc. Once the contaminants enter indoors, they become incorporated into house dusts. People spend a considerable amount of time indoors such as homes, offices and schools. Over the past decades, there has been increasing concern about exposure of people, especially of vulnerable groups such as children, to indoor contaminants in order to assess the health impacts.

In this study, levels of eight potentially toxic heavy metals in indoor dust from homes in Istanbul were investigated. The concentrations of heavy metals in indoor dust from homes ranged from 60-1800  $\mu\text{g g}^{-1}$  for Cu, 3-300  $\mu\text{g g}^{-1}$  for Pb, 0.4-20  $\mu\text{g g}^{-1}$  for Cd, 210-2800  $\mu\text{g g}^{-1}$  for Zn, 2.8-460  $\mu\text{g g}^{-1}$  for Cr, 8-1300  $\mu\text{g g}^{-1}$  for Mn, 2.4-25  $\mu\text{g g}^{-1}$  for Co, 120-2600  $\mu\text{g g}^{-1}$  for Ni. Considering only ingestion+inhalation, the carcinogenic risk level of Cr for adults and children in Istanbul was in the range of EPA's safe limits ( $1 \times 10^{-6}$  and  $1 \times 10^{-4}$ ). According to calculated Hazard Quotient (HQ), for non-cancer effects, the ingestion of indoor dust appears to be the major route of exposure to the indoor dust. Results of the current study highlight the importance of exposure through indoor dust and the good hygiene standards to limit intake of indoor dust. In conclusion, contaminants from the ingestion/inhalation/dermal contact might pose potential risk to the children and adults in Istanbul.

## The use of dendrochemistry to reveal pollution history

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Tree rings provide a record of environmental change within the biological requirements of tree survival. Dendrochemistry has successfully applied several analytical techniques for solid-state analysis (e.g., energy dispersive X-ray fluorescence (EDXRF), particle-induced X-ray emission), analysis of wood extracts or digests (e.g., inductively coupled plasma-mass spectroscopy (ICPMS), atomic emission spectroscopy (AES)). EDXRF methods tend to be favored largely because of the capacity for simultaneous analysis of 31 target or marker elements and compounds at a high spatial resolution (50 µm) across the tree-ring sample. In this study, we describe the dendrochemical investigation methods and results in known pollution cases, contaminations with PAH, HVO, PCB and BTEX or metallic compounds, within the course of an international project named PIT (pollution investigation by trees). Since PIT was to run over 40 cores for its dendrochemical investigations, and owing to the complexity of handling such large files combining serial entries, multiple compounds, (up to 200 000 data entries per tree core resulting from line scanning the cores every 50 µm and over 30 analytical data gained at each point) and a variety of computational operations needed, a Microsoft Excel template was developed and named SCANCHEM. This template eases data preparation and organization of dendrochemical analyses and data exchanges within the scientific team.

## Waste biomass to biochar and bio-oil: conversion of various biomass materials by slow pyrolysis

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Biochar can be made from various waste biomass sources and may include a wide variety of biomass such as wood chips or pellets, bark, crop residues such as rice husks or nut shells, and grass residues<sup>1</sup>. The present work aims to make a comparative study between the physico-chemical properties of five different types of biomasses: waterhyacinth (WH) aquatic plant used in the treatment of wastewater; crop residues of eucalyptus (CE) to the forestry waste product; bagasse from the sugarcane (BC), castor meal (CM) and coconut pericarp (CP) as by-products, which are obtained via slow pyrolysis in order to observe the influence of the parent material on the characteristics of biochars. An energy balance of biomass was carried from the determination of gross calorific value of biochar, bio-oil. The CM is an alternative energy and biochar (77.93%), while BC has potential in its bio-oil (21.46%). Produced chars and feedstock were further characterized by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT). It is found that bands in the region between 3400-3060 cm<sup>-1</sup>, relative to the cellulose and protein disappear completely after the carbonization process. Very strong absorption bands about 1060 cm<sup>-1</sup> shows the presence of lignin in the biomass, with decrease intensity in biochars. The absorption peaks around 1739 cm<sup>-1</sup>, related to C=O stretching of the ester bond, observed in biomass disappear in the spectra of biochars, and bands near 1602 cm<sup>-1</sup> related to C=C stretching in the aromatic ring are more intense in the spectra of biochars. These results agree with the H/C ratio, the pyrolysis progressed, H and O were depleted in the biochar and it became carbon-rich. Moreover, the CM DRIFT spectra show aliphatic groups that are in agreement with the data from elemental analysis. The technique of EPR (Electron Paramagnetic Resonance) showed the presence of organic free radical for all samples. The BC presents broad line between ~2700 and ~3700 gauss of trivalent iron in concentrated areas, while the CE and CP all these lines are less intense. In CM have the same thick line, the thin line superimposed OFR, also exhibits six signal lines centered at g = 2.0 attributed to the hyperfine structure (A ~ G 90) of Mn<sup>2+</sup> ions (S = 5/2), in outer sphere complex plus a large line of Fe<sup>3+</sup> in concentrated dominium in ~ 1500 gauss (~ g = 2,1). In WH biochar all these lines are less intense. It was also observed that the WH and MC samples present OFR linewidth of 6.6 and 6.2 G, and is higher than the other biochars from other biomass and possibly it is a material with lower recalcitrance. Greater density of spins is observed in the CP, this effect is possibly due to the greater number of phenolic groups, correlating with the technique <sup>13</sup>C NMR (Nuclear Magnetic Resonance), where peaks at 150 ppm indicative of a phenolic group on the NMR spectrum appeared of the CP, and with the study of ΔpH (net negative surface charge) with values of -1.53 ± 0.01, higher than the other biochars. Moreover, several peaks of carbohydrates were visible at 50-100 ppm in the <sup>13</sup>C NMR spectrum of CM. The dominant peak near 130 ppm was observed in all pyrolyzed materials and was attributed to aromatic carbon resonance.

<sup>1</sup>Lehmann J, Gaunt J, Rondon M. *Mitig Adapt Strat Gl*, 2006; 11:403.

## Environmental remedial activities in the Sardas landfill, Sabiñánigo, Huesca (Spain). The problem of HCH

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For over two decades the landfill of Sardas (Sabiñánigo, Spain) was used for municipal, construction and industrial wastes and these were deposited directly onto the ground, consisting of Eocene marls. The industrial waste contained residues derived from the manufacture of chlorine and waste originating from the manufacture of lindane that included various isomers of hexachlorocyclohexane both in powder form and in free phase (Dense Non Aqueous Phase Liquid, DNAPL). This DNAPL is currently leaking from the landfill as leachate.

The site was investigated through joint funding by the National and Regional environmental authorities. The work consisted in the drilling and construction of more than fifty monitoring and pumping wells and the environmental characterisation of both soil and groundwater.

The DNAPL possesses a high density of 1.5 t/m<sup>3</sup> and it has been discovered that the flow path is complex and takes place at various levels. After flowing through the waste and leaking through the base of the landfill, the DNAPL descends to depths of up to 40 metres through rock fractures within the marls. The principal receptor is the Río Gallego reservoir, located within 100 metres from the site.

The DNAPL is currently being extracted from pump wells and simultaneously a detailed hydrogeological survey is being undertaken in nearly all of the existing fifty monitoring points in order to optimize the control of the contamination and environmental risks.

It is proposed to extend the hydrogeological characterisation, to analyse for dioxins, to conduct tests on the reaction of HCH with the marl substrate and tests to check if an alkaline hydrolysis of the organochlorides takes place when interacting with basic leachate. All of these tests and analyses have the objective to stop the flow of the plume, to verify the environmental situation of the soil and groundwater and to increase the knowledge of this site's particular problem.

## Evaluating *in situ* thermal remediation of a chlorinated solvent source zone

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*In situ* thermal desorption (ISTD) is a remediation technique that increases the effectiveness of soil vapor extraction through the simultaneous application of heat and vacuum (Triplett Kingston et al., 2010). In this study ISTD was applied to remove a chlorinated solvent source from unsaturated soil beneath existing above-ground infrastructure.

During the pre-remediation investigations at the contaminated site it was revealed that up to 2500 mg m<sup>-3</sup> of chlorinated solvents are present in the soil vapour. In order to evaluate the effects of the *in situ* thermal desorption applied, we monitored the chlorinated solvent concentrations in both soil vapor and in groundwater throughout the remediation, and used these data together with measured chlorinated solvent concentrations in soil before the treatment for geostatistical and material flow analysis (MFA, Brunner & Rechberger, 2004). In this study MFA has, for the first time, been used to assess the effectiveness of ISTD for the remediation of soils contaminated with chlorinated solvents and to reveal the total emission of chlorinated solvents into the environment, both prior to and during remediation.

MFA was performed for the period prior to remediation and for the period covering the remediation time and subsequent soil cooling. The MFA for the period prior to remediation showed that 360±570 kg of chlorinated solvents (predominantly PCE) were released into the soil. The majority of contaminants were captured in soil (270±570 kg), while 85±45 kg were emitted into the atmosphere and hydrosphere. The mass removed during ISTD, as shown in the MFA, is similar to the mean chlorinated solvent mass estimated by ordinary kriging to have been in the soil initially. Furthermore, only a negligible amount of contaminants was released into the environment as a consequence of the remediation action. The MFA results have therefore shown that the ISTD technique has been effective in removing the majority of chlorinated solvents from the soils at this test site, which was supported by the low soil vapor concentrations by the end of the remediation. The target concentration in soil vapor (<10 mg m<sup>-3</sup>) was reached after nine months of remediation, indicating the time-efficiency of this remediation approach.

Our study has shown that material flow analysis is a suitable tool for assessing the effectiveness of a remediation practice by connecting and quantifying the sources, pathways, and the intermediate and final sinks of the contaminants.

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## Analysis of human impact intensity changes during last 300 years using sedimentary records

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Environmental pollution with trace elements is considered as one of the most important environmental problems. Analysis of trace element accumulation in sedimentary phases of lakes may reflect the overall regional pollution level, but analysis of trace element accumulation patterns in sediment profiles can help to reconstruct history of anthropogenic impacts. The aim of this study was to analyse trace element concentrations in the sediments of Lake Engure in Latvia and analyze factors influencing their availability. The metal concentrations in sediments of Lake Engure are at a background levels, especially of compared with metal concentrations in West European countries. However analysis of element concentration changes in sedimentary profiles gives information about trends of recent accumulation (within last 300 years) and balance between natural and human induced accumulation processes. To identify changes of the major and trace element accumulation character in lake sediments within last century a study of corresponding and dated lake sediment profile has been done. In very recent sediments Na concentrations are relatively lower than K concentrations, but in older sediments – K again prevail. Concentrations of Mg in sedimentary records seem to be little changing during last centuries, despite to character of changes from chemical and geological behavior similar element Ca. For both elements common are relatively high concentrations in deeper layers of sediment profile, but Ca concentrations have a significant variability also in recent sedimentary profiles, indicating high natural variability of sedimentation conditions and weathering of Ca containing minerals in the lake basin. In case of changes of Fe concentrations in Lake Engure sediment profiles a pattern can be observed indicating some decrease possibly related to changes in the oxygen conditions as far as only Fe (III) is tending to form stable sedimentary phases, but if anoxic events becomes frequent Fe (III) can be reduced to soluble forms of Fe (II) and the iron accumulation reduces. In recent decades Fe accumulation again is increasing.

Influences of geochemical processes are evident, if analyzing differences in metal concentrations, especially in case of Zn and Pb. Decrease of concentrations is remarkable for most of studied trace elements associated with human impacts during last 50 years. The only one element with an increasing tendency of values in sediments within last 50 years is mercury, still indicating recent human impacts. Concentrations of trace elements like Pb, Co, Ni, Cu and elements which presence might be associated with human activities (as Zn) may help to identify human caused pollution and help to follow human induced changes in the pollution loading. However present study indicates low recent increase of these contaminants in the sediments of Lake Engure.

Lake Engure sediment composition changes take place at conditions when traditional low-intensity agricultural activities in the lake basin were common (actually the lake basin is relatively sparsely settled and forests and natural meadows dominate). Thus the sedimentary records of their elemental composition can allow to follow the changes of human induced and natural loading coming from lake basin.



## Reduction of 4-nitrophenol to 4-aminophenol over $\text{Ag}^0$ and $\text{Au}^0$ nanoparticles immobilized in $\text{SiO}_2$ matrices prepared via the sol-gel synthesis

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Phenol and substituted phenols, especially 4-nitrophenol, are known to be present in natural and industrial wastes. The toxicity of these compounds has been well documented. Supported transition metal clusters are active in a wide variety of catalytic processes. The ability of supported transition metal nanoparticles to catalyze the reduction of 4-nitrophenol by sodium borohydride was studied. Silver and gold nanoparticles were embedded in  $\text{SiO}_2$  matrices prepared by the sol-gel method. The  $\text{M}^0$ -NPs were prepared by reduction of silver nitrate or gold (III) chloride trihydrate with  $\text{NaBH}_4$  during the sol-gel process. Different preparation procedures were examined in order to determine the preferred method for obtaining a suitable matrix for the catalysis. Catalytic activity was found in matrices containing both  $\text{Ag}^0$  and  $\text{Au}^0$  nanoparticles. The structure of the matrices prepared was studied by using SEM analysis and catalytic activity by UV-visible absorption spectroscopy.

## Use of exhausted Y-Faujasite from FCC wastes for the removal of heavy metals.

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The use of exhausted Y-Faujasite from wastes of the FCC (Fluid Catalytic Cracking) process in the British Petroleum factory in Castellón (Spain) has been checked for the removal of heavy metals (Cr, Mn, Fe, Co) from waste water by ion exchange. The ion exchange test was carried out using 500 mL of 0.5M concentrated solutions of the metals and 0.5 mol/L of zeolite waste continuously stirred. The obtained results show a weight ion exchange in Cr<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> ions of 40, 23 and 10.8% respectively, the associated change of pH associated to the zeolite acid sites exchange precipitates Fe(OH)<sub>3</sub> in the case of iron. The kinetic of exchange follow the Nernst model.

## Assessment of water and sediment contamination by mining activities in the Aries river, Romania

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The Aries basin in the Apuseni Mountains, Romania, has a high economic importance by the large reserves of gold and base metals and the outstanding tourism potential through numerous natural reservations and caves. The study evaluates the current status of surface water and sediment contamination with metals in the Aries river affected by historical mining and processing of non-ferrous ores. The results revealed large variations in the water quality parameters among sampling sites relative to the distance from the pollution sources. The ecological status of surface waters corresponded to class II – good quality for Zn ( $100-200 \mu\text{g L}^{-1}$ ), to class III-fair quality for Mn ( $100-300 \mu\text{g L}^{-1}$ ) and Fe ( $500-1000 \mu\text{g L}^{-1}$ ), and to class IV-poor quality ( $50-100 \mu\text{g L}^{-1}$ ) for Cu. Pollution with these elements was found especially near the mining facilities and only a slight improvement of the waters ecological status was observed downstream. Overall the Aries river water was found to belong to class IV-poor quality as established by the worst quality parameter. Analysis of sediments revealed a significant spatial variation of Cu and Zn content in the main stream. Sediments of the Aries river were found to be very high contaminated with Cd, Cu and As, considerable with Zn, moderately with Pb and Ni and low with Cr. Metals enrichment factors and contamination degree of sediments increased from upstream to downstream with local peaks, demonstrating that the river remained a collector for pollutants coming mostly through the mine-affected tributaries.

## Determination of free Zn<sup>2+</sup> concentration in root extracts of *Hordeum vulgare*

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Glutathione ( $\gamma$ -Glu-Cys-Gly) is a relevant tripeptide in biological and environmental systems [1]. Part of its importance stems from the capacity of its thiol group to complex metals such as zinc and cadmium, and, thus, glutathione participates in detoxification strategies. In phytoremediation, it is uncertain whether the metal taken up by the plant is all complexed by glutathione and other thiol-rich peptides such as phytochelatins. Since it is well known that the uncomplexed metal is the responsible for most toxic effects, it is necessary to develop appropriate techniques to study this fraction. The voltammetric technique Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) [2] was designed to determine free metal ion concentrations. AGNES has been successfully applied to synthetic and natural samples like sea [3] and river water [4], soil extracts [4] and nanoparticle dispersions [5].

The study of the complexation of Zn with glutathione has been performed with AGNES in synthetic systems at various pH values and different total ligand and metal concentrations. Among the different complexation constants reported in the literature, the modelled concentrations from Ferretti *et al.* [6] fit best the experimental determinations with AGNES.

Free Zn concentration has also been measured with AGNES in *Hordeum vulgare* root extracts. For this purpose, seedlings were hydroponically cultivated and, after collection, roots were ground in liquid nitrogen. Water extraction of roots was selected as the most convenient method for this analysis. Total glutathione and zinc concentrations in these water-soluble extracts have been quantified. Due to the specific characteristics of these samples, some modifications have been implemented to AGNES standard methodology. A purging system with N<sub>2</sub>/CO<sub>2</sub> has been used to keep the same pH of the sample without adding acid or base. A specific system where nitrogen is saturated with water before the arrival to the cell has been designed to minimize the evaporation of the very small volume of the sample.

The obtained results show that most of the Zn in the extract is complexed, rather than free, suggesting the potential phytoremediation capacity of *Hordeum vulgare*.

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## SORPTION BEHAVIOR OF PERFLUORINATED COMPOUNDS IN SEWAGE SLUDGES AND SOILS

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Recently, perfluorinated compounds (PFCs) have raised a great attention because of their high bioaccumulation, extreme persistence and toxic properties such as endocrine-disrupting activity and carcinogenesis [1]. Due to their wide industrial application, PFCs are ubiquitously detected in environmental compartments, such as water, sediment, soil and biota [2]. Moreover, sewage sludges, as final product of wastewater treatment, can also be a reservoir of PFCs, and thus their use as organic fertilizer in agricultural soils may represent an additional risk for soil contamination.

To evaluate the risk associated with the application of sewage sludge in soils, not only the total concentration of PFCs, but also their interaction with the solid phase, either sewage sludge or soil, must be considered. This interaction can be evaluated from sorption experiments aiming at quantifying the solid-liquid distribution coefficient ( $K_d$ ), and will depend on the physicochemical properties of the target compound, on its concentration and on the characteristics of the solid phase. Previous works in the literature show a high variability of  $K_d$  values of PFCs in sewage sludges and soils, even for similar matrices, showing a potential dependence on the organic matter content [3].

Therefore, in this work, the sorption behavior of three PFCs (perfluorooctane sulfonate, PFOS; perfluorooctanoate, PFOA; perfluorobutane sulfonate, PFBS) was studied in sewage sludge samples from Spanish wastewater treatment plants and in soils with contrasted characteristics, such as pH and organic carbon content.  $K_d$  values were obtained from batch experiments according to the OECD Guideline [4]. A wide concentration range for each PFC was assayed in parallel in order to obtain the corresponding sorption isotherm. The concentration of the target PFC in the resulting supernatants was determined by ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS). The effect of several experimental parameters (filtration of the supernatant, internal standard used for quantification) in the  $K_d$  value obtained was also evaluated.

Finally, the influence of the physicochemical characteristics of the target PFCs, such as hydrophobicity and solubility, in their sorption behavior in the two types of matrices studied was also assessed, as well as the role that organic matter might play in this sorption.

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## **Dynamics of fluoride and borate in soils exposed to the emission of the ceramic industry of tiles and glazes.**

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The emission of fluoride and borate pollutants are characteristic in the manufacture of tiles (due to clay degradation in tile firing at 1100-1200°C) and glazes (due to condensation of borate vapours released from the frit kilns at 1400-1600°C). In this communication the historical evolution (2000-2013) of the presence of fluoride and borate in soils exposed to the emission of the ceramic industry of tiles and glazes in the ceramic cluster of Castellón (Spain) is analyzed. The fluoride is associated to tile industry and borate to ceramic glaze factories. The concentration of soluble borates depends of the rainfall which lixiviates it to underground waters. Instead, the presence of fluoride shows a relative accumulation in exposed soils due to calcium fixation as fluorite.

## **Diuron mineralisation in soil affected by the use of hydroxypropyl- $\beta$ -cyclodextrin and different amendments.**

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Results on diuron mineralisation and adsorption-desorption on a soil artificially contaminated ( $50 \text{ mg kg}^{-1}$ ), to which two different composted organic amendments (sewage sludge mixed with pruning remains, LDD, and domestic wastes, RSU), an inorganic amendment (micronutrients) and a hydroxypropyl- $\beta$ -cyclodextrin (HPBCD) solution were applied, were obtained. Treatments were investigated at different amendment concentrations.

From initial studies, the incapability of the endogenous soil microorganisms to mineralise diuron was confirmed. However, after the inorganic amendment was applied, with the aim of supplying essential nutrients for soil flora activation, a 5% of diuron mineralisation was reached after 150 days, concluding that the soil has a potential capacity to mineralise the herbicide through biostimulation-assisted natural attenuation.

Diuron mineralisation was improved using a HPBCD solution at a very low concentration of only 10 times the diuron equimolar concentration in soil. This molecule is able to form diuron inclusion complexes, which provokes an increasing in its hydrosolubility, and hence, in the amount of the herbicide in the soil solution. With this strategy, a higher amount of diuron molecules will be more bioaccessible for the soil microorganisms. After HPBCD application mineralisation rate was increased 27 times regarding to the inorganic amendment application, and the extent of herbicide mineralisation reached a 31%.

Organic amendments from different origins were also applied on the contaminated soil at different concentrations (0.5, 2 and 4% w/soil dw). In general, as increasing amendment concentration diuron mineralisation rate was improved, regarding to the inorganic amendment application. 33% of the herbicide was mineralised after RSU amendment was applied at 4% w/soil dw.

Finally, the joint application of the three amendments investigated and at the best conditions tested was conducted in order to obtain the best diuron mineralisation results. In this case, the inorganic amendment plus RSU amendment at 4% w/soil dw plus HPBCD solution provoked an extent of diuron mineralisation of 54,30 %.

## Cyclodextrin enhanced extraction of PAHs from spiked and aged soils. Effect of co-contaminants

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Excessive inputs from anthropogenic activities have caused serious environmental contamination and threaten to adversely affect human health. To address the associated environmental concerns, innovative remediation technologies are urgently needed. It has been observed that as soil-pollutant contact time increases, pollutant bioavailability and extractability decreases. This phenomenon has been termed "aging". Cyclodextrins (CDs) appeared as promising complexing agents to mobilize hydrophobic aromatic pollutants in soils while minimizing environmental impact, due to their non-toxic character. The aim of this study was to investigate the feasibility of a cleanup strategy using hydroxypropyl- $\beta$ -cyclodextrin (HPBCD) solution to enhance soil washing for extracting PAHs. We examined the potential of HPBCD for assessing the extractable fractions of PAHs in single and co-contaminant spiked and aged soils.

Three soils with different properties were selected in order to assess the effect of aging according to the characteristics of the sorbent. The extractions were done using two different solutions, an aqueous electrolyte solution and a HPBCD solution, and were carried out at 1, 35, 70 and 100 days after spiking. The soils were spiked individually with fluorene, fluoranthene, pyrene or anthracene, and with a mix of the PAHs considered as priority pollutants by US-EPA.

The highest extraction percentages were obtained for 3- and 4-ring PAHs, because of the appropriate size and shape of these compounds relative to those of the hydrophobic cavity of HPBCD, especially 3-ring PAHs. The better the guest molecule fills the CD cavity, the stronger the hydrophobic and van der Waals interactions are. In contrast, in the case of the less voluminous PAHs such as naphthalene, acenaphthene and acenaphthylene, the complexes with HPBCD are formed, but the interaction with the CD is very low, and their extraction from the soil was less efficient, presenting no advantage relative to the use of the electrolyte solution. In the case of 5- and 6-ring PAHs the tendency to form complexes with HPBCD is extremely weak due to steric hindrance. The results indicate that the extractable fraction of PAH was inversely correlated to the number of benzene rings and their octanol-water partition coefficient. With increasing hydrophobicity, the affinity of PAHs to HPBCD did not increase to the same degree as to soil organic matter. Therefore, PAHs that were not extracted by HPBCD almost certainly are not bioavailable and, consequently, they are not potentially toxic to the environment. When the mix of PAHs was extracted, differences in the effectiveness of HPBCD depending on the aging were only appreciable for 2- and 3-ring PAHs. Differences depending on the soil used were appreciable only when individual PAHs were extracted. The effect of the presence of individual PAHs or a mix of PAHs in relation to their percentages of extraction is discussed.



## Identifying the sources of chemical contamination after the fact

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### *Exponent*

In many environmental contamination events, it is necessary to reconstruct the source term and differentiate this source from other potential sources, and the baseline condition, without the benefit of any analytical data for the source *per se*. Several presentational and statistical methods have been used in the past although the majority of these are qualitative. More recently, new approaches to unravelling the environmental history have been possible with such methods as polytopic vector analysis (PVA) coupled with self-organising maps (SOMs). These combined techniques have enabled the elucidation of the source chemical profile along with those of the other contributors. Environmental data including atmospheric particles have been analysed for oil derived hydrocarbons, river sediments have been investigated with regard to metals and soils have been analysed for both PCBs and PCDD/F.

PVA generates a model with an increasing number of end members (sources) that at some stage explain the environmental data. The chemical composition can then be determined for each end member and the contribution that each end member makes to each sample calculated. The results can be very instructive on their own although when coupled with SOMs, the underlying factors that control the composition can be seen. In many cases, one end member will be the ubiquitous baseline condition and this may be a sensible approach to reconstruct both the concentration and chemical profile in contaminated environments.

## Comparison of isolation techniques for analysis of cationic surfactants from solid samples

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Surface active agents with positive charge head are commonly used in during formulation different products such as softeners and antistatic agents, pharmaceuticals, disinfectants and cosmetics. In the aquatic ecosystems cationic surfactant are characterized by a high potential to adsorb to surfaces such as suspended solids, sediments or organism cells. It is important to investigate the levels of cationic surfactants after discharging into environment due to their toxicity to living organisms and potentially distribution of the ecosystems balance.

In presented study, the efficiency of different isolation techniques of cationic surfactants from model solid samples was investigated with use of solid-liquid extraction (LSE), Soxhlet extraction, ultrasound assisted solvent extraction (UAE) and accelerated solvent extraction (ASE). During investigation of condition of isolations analytes were checked: type and volume of solvent or mixture of them, temperature and time of processes and clean-up stage.

The research results confirmed that the highest recovery of cationic analytes (more than 87 %) was obtained with application of accelerated solvent extraction using a mixture of acetonitrile and water (3:2; v:v). Solid phase extraction techniques applied at clean-up stage allows to eliminate toxic chloroform from sample preparation stage. At final determination stage was applied liquid chromatography coupled with conductivity detection. Proposed isolation protocol was used to determination of levels individual cationic surface active agents in real river sediment.

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## Biofilm systems for the prevention of As (V) problematic concentrations in river environments

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Arsenic (As) is a metalloid widely distributed in the environment and was one of the first chemicals recognized as carcinogen [1]. It's estimated that 40 million people worldwide are at risk from drinking arsenic-contaminate water [2]. Consequently, the World Health Organization (WHO) has set a provisional guideline of  $10 \mu\text{g L}^{-1}$  for As in drinking water [3]. Taking into account these considerations, there is an increasing interest in developing new eco-friendly tools to mitigate As spread. The main aim of this study was to assess the behaviour of natural biofilms in river waters with presence of As (V) problematic concentrations. With this objective, a lab experiment was carried out. A complex sediment sample was collected from the middle reach of the Anllóns River, an Atlantic basin located in the NW of Spain. Total As of the sediment was of  $11.8 \pm 2.5$  ppm measured by X-ray fluorescence. A nutrient media prepared with NaCl  $25 \text{ mg l}^{-1}$ , glucose  $10 \text{ mg l}^{-1}$ ,  $\text{NaH}_2\text{PO}_4$   $20 \text{ mM}$  and  $\text{NaNO}_3$   $0.4 \text{ M}$  was employed as nutrient supplier to favor biofilm growth onto  $8 \text{ g}$  of riverbed sediment. Day-night cycles of  $12 \text{ h}$  were employed in the process with a light intensity of  $3,109 \text{ lux}$ . The optimum growth of the biofilm was reached in 2 days, determined by the measurement of chlorophyll-*a* and chlorophyll-*b* optimum following the method optimized by Devesa et al. [4]. Total phosphorous concentration in the media was followed through the biofilm growth and at 2<sup>nd</sup> day was of  $467.5 \text{ ppm}$  determined by an acid digestion followed by colorimetric determination with molybdenum blue. Once the biofilm was fully developed, the overlying water was removed, except  $5 \text{ mL}$  of the solution to preserve the biofilm structure. Subsequently,  $55 \text{ mL}$  of As (V) solutions were added to the systems to achieve final concentrations of  $0, 5, 25, 50, 100, 250$  and  $500 \mu\text{g/L}$  in the overlying water. All the systems were prepared by triplicate. As concentrations were measured by ICP-MS after  $24 \text{ h}$  of contact. Results obtained showed that the maximum adsorption of As was only of  $7.8 \%$  for the highest initial concentration, showing even desorption in the third first initial concentrations. So, the determined Equilibrium As Concentration value, for which neither adsorption nor desorption occurs, was significantly high ( $89.6 \mu\text{g/L}$ ) due to, jointly, the presence of biofilm and of  $39.0 \text{ ppm}$  of phosphorous in the overlying water. These results are in contrast with the results obtained for sediment samples without biofilms and P presence which adsorbed, in the whole range of concentrations analysed, a mean adsorption percentage of  $78.9 \%$  and for biofilm systems growing with river water as nutrient supplier which presented an adsorption percentage of  $96.9 \%$ . In conclusion, systems prepared with the aforementioned conditions significantly prevent the As adsorption onto sediments, decreasing significantly their contamination, whereas the others systems analysed act clearly as sink of As.

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## **$^{137}\text{Cs}$ and $^{40}\text{K}$ radionuclides activity and heavy metals concentrations in soil samples from East part of the Flysh Carpathian Mountains in Poland**

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Soil, being an active component of the environment, accumulates chemical contaminants and is considered as a useful medium for monitoring of long term human impact on it. In respect to radionuclides, some of them are natural and are constantly present and tolerated in the environment [1]. But also human activity may lead to the environment contamination with radionuclides.  $^{137}\text{Cs}$  gamma radionuclide was introduced into the European mountainous ecosystem through nuclear tests conducted in the middle of the 20-th century and in 1986 – as a result of the Chernobyl nuclear reactor failure [2,3].

In this work the results of gamma radionuclides (artificial  $^{137}\text{Cs}$  and for comparison natural  $^{40}\text{K}$ ) activities), as well as heavy metals concentrations in soil samples from East part of the Flysh Carpathian Mountains in Poland (in the region of Beskid Niski and Bieszczady Mts have been presented.

The soil samples were analyzed using low-background gamma spectrometer equipped with ORTEC HPGe detector (10% efficiency). The obtained results were calculated on surface deposition and presented as  $[\text{Bq}/\text{m}^2]$  (the total deposition of a given radionuclide in the first 10 cm layer of soil). Heavy metals concentrations were determined by means of atomic absorption spectrometry (flame and electrothermal techniques) using Perkin Elmer Model 3110 spectrometers with HGA 600 graphite furnace, after microwave wet digestion (Anton Paar Multiwave 3000 digestive system).

The maximum concentration of cesium has been observed in the places of the altitude over 500 m asl and accumulated usually in the organic surface layers (Ofh) or in the illuvial layers (Bhfe). Maximum deposition of  $^{137}\text{Cs}$  exceeds 8 times the average cesium concentration in soils in Poland. For Beskid Niski Mts  $^{137}\text{Cs}$  activity varies from 202.1 to 14755.9  $\text{Bq}/\text{m}^2$  and in the Bieszczady Mts from 9873.8 to 3505.3  $\text{Bq}/\text{m}^2$ . Although measured  $^{137}\text{Cs}$  level was high, it does not affect in a hazardous way neither human nor animals life. Also high variation in metals concentrations (Cu, Zn, Cd, Pb) were found for the soil samples.

Obtained results are discussed in respect to sampling places, soil type and sorptive properties using chemometric tools (Cluster Analysis and Principal Components Analysis).

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## General aspects of environmental analysis: choice of methods, methods compatibility, data processing

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In the environmental analysis, main point is to define the aim, and subsequently to formulate the analytical problem and choose adequate methods of solving it. Substantial amount of money and time is wasted by improper decisions. Basing on our personal research the use of sequential extraction procedure for the determination of the fate of metallic contaminants in the sediments of drinking water reservoir are presented. Also, conclusions referring to the early stages of diagenesis can be made basing on the obtained data. The question issued by the Municipal Water and Sewage Company in Kraków referred to contamination of the sediments in the Dobczyce water reservoir: Do metals accumulated in the sediments constitute a threat to water quality and in what circumstances? Sediments, deposited at the lake bottom undergo the process of diagenesis – the process usually considered in a geological scale of time i.e. thousands of years. Can physical and chemical processes change the elements speciation in much shorter time (dozens of years) and how can we observe these changes? It was found, although sequential extraction is usually used for determination of bio availability of metals accumulated in soil, sediments and spoil-heaps, that in the lake sediments in the course of about 30 years metals change their forms into more labile. In consequence, in case of flood metals from sediments may contaminate water substantially.

Another problem of environmental analysis is its low precision (attributed to samples inhomogeneity and diversity) and in some instances high uncertainty of the samples age assessment. On the example of the sediments core analysis of the thoroughly selected object (the Smreczyński Staw Lake in the Tatra mountains in Poland) it was proven that  $^{210}\text{Pb}$  radio isotopic dating, combined with  $^{137}\text{Cs}$  analysis and elemental quantitative analysis lead to precise definition of the core samples age. The obtained results found additional confirmation in available historical documents.

The third considered aspect of the environmental analysis appears when high amount of diverse experimental data has to be discussed and interpreted. The application of chosen chemometric tools is the answer. By means of cluster analysis (CA) and principal components analysis (PCA) of the set of data consisting of 17 sampling points and more than 30 variables (elemental and mineral composition of the sediments) was analysed. The results enabled draw out conclusions referring to: a) sampling points similarity, b) relations between variables, c) formation of distribution models.

## Analysis of trace pesticide contaminants in deposits from water networks

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Pesticides are chemical compounds, widely used in many agricultural areas, in the prevention and control of harmful organisms. The introduction of pesticides in agriculture was of great importance, because their utilisation led to the reduction of the adverse effects of diseases in crops and plants, which allowed an increase in the production [1]. On the other hand, pesticides pose a serious risk to the environment and human health. Due to their highly persistent properties, pesticide residues may appear in fruits and vegetables and may be often distributed into aqueous environments by leaching and runoff from soil into ground and surface water [2]; this way, they can enter into water networks. In water distribution systems, pesticides can adsorb to pipe walls and deposits attached to the inner walls. If these contaminated inorganic deposits detach from the pipes, trace amounts of pesticides may be introduced in drinking water systems. Owing to the toxicity of pesticides, the EU establishes maximum concentrations of  $0.1 \mu\text{g L}^{-1}$  for individual pesticides and  $0.5 \mu\text{g L}^{-1}$  for the sum of all pesticides in water destined to human consumption [3]. It is, therefore, of extreme importance to be able to detect the presence of pesticides in contaminated inorganic deposits.

This work aims to study the interaction between pesticides representative of two classes, carbofuran (carbamate) and chlorfenvinphos (organophosphate) with inorganic deposits from water distribution networks. Adsorption and desorption assays were performed with two real deposits and a “model” deposit (kaolin). Adsorption percentages are variable (15-80%), depending on the compound (or mix of compounds) and matrix (which deposit is used), as well as operating conditions. In order to extract the compounds from the solids, several solvents were tested (e.g. acetonitrile, hexane, water). As before, desorption percentages vary according to the compound and the deposit used (5-70%) and conditions adopted. Therefore, in order to have a HPLC-DAD method for the quantification of these pesticides in inorganic deposits, a matrix-matched calibration approach was used.

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## **Dynamics of lead, zinc, copper mobile form and their biological accessibility in tailings dams after processing molybdenite and sulfide-hubnerite ores**

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The wastes of sulfide ores processing are source of dangerous environmental pollution. Oxidation of sulfides under the influence of atmospheric moisture leads to acidulation of filtrate in tailings dams and to formation of mobile compositions of potentially toxic elements. As a result of acid mine drainage the surface and underground waters, soils become fouled, also the microelement balance in ecosystems trophic chains of adjacent territories was broken. The Dzhidinsky tungsten-molybdenum mining-concentrating complex (the South Western Transbaikalia) from 1934 to 1997 had been processed molybdenite and sulfide-hubnerite ores. More than 40m tons of the wastes are stored in the abandoned tailing dams. After interruption of production the territories which are directly adjacent to tailings dams and correspond to an emergency ecological zone have widely extended.

The samples of wastes from tailings dam were selected in 2006 and 2009, selection depth was no more than 10 cm. In the places of sampling technogenic sand also cereals (*Agrostis* L.) and poplar (*Populus suaveolens* Fisher) were selected. The mobile forms of Cu and Zn in soils were defined by using acetate ammonium buffer (Russian standard technique: GOST R 50683-94, GOST R 50686-94). The concentrations of Cu, Zn, Pb in each extract and also total concentrations after full dissolution of the sample were measured by atomic absorption spectrometry (AAS-1N) (Russian standard technique: Instruction №155-XC 1978). The analysis of the vegetable samples was made by the ICP-MS method.

During three years in the top layer of tailings dam the average content of all studied metals had been decreased while the maintenance of the mobile forms of copper and zinc had been increased.

The maintenance of chemical elements in the vegetable samples of 2009, in comparison with 2006, except a few probes, is significantly higher. It can be explained with increasing quantity of mobile and ion-exchange forms of metals in a substratum on which vegetable samples grow. Cereals concentrate metals mainly in roots, and poplars – in leaves. The exception – the lead, which contents in poplar roots is more, than in leaves.

The provided data show dynamics of distribution and bioavailability of heavy metals during long storage of wastes in the given tailings dam.

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## Monitoring lead in soils in Lisbon during the last decade

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In 1999 Portugal, like most other countries in Europe, switched from leaded to unleaded fuel. It is known that some of the lead in water and in the soil was from precipitation runoff of lead coming from the vehicles exhaust and the soil along roads. Since lead can cause problems in nervous system, including mental retardation in children, immune system impairment, cancer of the lung, as well as similar adverse effects on animals and plants, because it is not biodegradable and accumulates in the body and in food chains, it is best to eliminate the use of lead wherever possible [1].

Gasoline still includes a tiny amount of lead because of the natural processes under which oil is formed in the ground, but it is no longer added lead to fuels. Considering these circumstances, in 1998 some studies were done, in Lisbon, using leaves from poplar (*Populus*) tree as lead bioindicator. In order to evaluate if the lead content in the leaves of poplar and in soil would drop significantly in the years following the abolition of leaded fuel, both species were analyzed between 1998 and 2011. In this work results of lead content in leaves and soil, collected in the city center of Lisbon (Marquês de Pombal), in a for a period of nine years (2003 to 2011) are presented and discussed. Lead content was analyzed by graphite furnace atomic absorption spectrometry (GFAAS).

After almost one decade of analysis it was found that lead content decreased significantly in the first five years after the elimination of leaded fuel (1998-2003) but in soils, after that rapid drop it was observed a slight increase every year (2003 - 2011). This is the confirmation of the accumulation of lead in urban soils as a heritage from many years of burning leaded gasoline in the internal combustion vehicles.

The real knowledge of the state of pollution in Lisbon city through this indicator is important since it allows for better decision making towards its use and also for considering the implementation of remedial measures, if necessary [2].

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## As and Pb immobilisation in contaminated sediment using bentonite and kaolinite supported nano zero valent iron

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The objective of this study was to investigate the possibility of using supported nanoscale zero valent iron with bentonite (B-nZVI) and kaolinite (K-nZVI) for immobilization of As and Pb in contaminated sediment from the Nadela river basin (Serbia). The assessment of the sediment quality based on the pseudo-total metal (As and Pb) content according to the corresponding Serbian standards shows its severe contamination that requires disposal in special reservoirs and, if possible, remediation treatments. The hazardous potential can be minimized by converting the contaminants into forms which are less soluble, less mobile or less toxic. A microwave-assisted sequential extraction procedure was employed to assess Pb and As potential mobility and risk to the aquatic environment. According to the results of sequential extraction procedure As showed lower risk to the environment in comparison to the Pb which has higher risk to the environment. The contaminated sediment, irrespective of the different speciation of As and Pb, was subjected to the same treatment. Ultra-fine powder of nanoscaled zero valent iron has a strong tendency to agglomerate into larger particles, resulting in an adverse effect on both effective surface area and catalyst performance. To address this issue, supported nanoscale zero valent iron with bentonite (B-nZVI) and kaolinite (K-nZVI) were synthesized by the sodium borohydride reduction method and used for immobilisation of Pb and As in contaminated sediment. In order to determine the long-term behavior of sediment - BnZVI mixtures and sediment - KnZVI mixtures, leaching tests were done in accordance with ANS diffusion test (ANS, 1986) in the period of 90 days. Treatment efficiency was also evaluated by measuring the cumulative fractions of metals leached, effective diffusion coefficients -  $D_e$  and leachability indices - LX. For Pb the LX values were greater than 9, suggesting the sediment mixtures with BnZVI and KnZVI are acceptable for controlled utilization. From the aspect of As the LX values were around 8 and in that case according to this test, sediment mixtures with BnZVI and KnZVI can be disposed of in segregated or sanitary landfills. Based on effective diffusion coefficients –  $D_e$  metals showed low mobility ( $D_e$  in the range  $10^{-8}$  to  $10^{-11}$   $\text{cm}^2\text{s}^{-1}$ ) depending on the BnZVI and KnZVI content. The Standard Toxicity Characteristic Leaching Procedure (TCLP) and DIN 38414-S4 test were applied to evaluate the extraction potential of As and Pb from contaminated sediment. Generally, the test results indicated that applied immobilizing agents were effective in immobilizing As and Pb in contaminated sediment.

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## Heavy metals in the floodplain: a case study of the River Tisza, NE Hungary

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The Tisza is Hungary's second largest river, which the Hungarian rivers characteristically also take its rise on beyond this country, so the river's water quality especially depends on activities of water quality influencing of beyond a border.

The quality of the floodplain's soils influence directly the human activities, furthermore the pollutant of the Tisza causes indirectly load for the soils. The soils respond differently these negative effects, their answer largely depends on his puffer capacity.

The sample area, Vásárosnamény, is flooded regularly by River Tisza. On the occasion of floods the floodplain gets a lesser or greater amount of pollutants from a river that could be in two forms: dissolved condition or attached to suspended sediment. The pollutants catch on the surface of colloids (the smallest grain of sediment), these can far to deliver and can accumulate on the floodplain in different concentration, so thus it may be exceed the limit value relevant of the soils and sediments.

Aim of the research was to determine the heavy metal accumulation in the floodplain and to call the attention on the potential risks. We collected 87 soil samples from the topsoil (0-20 cm) and analysed the soil properties (granulometrical compound, humus content, humus quality, pH, hydrolytic acidity, exchangeable acidity, CaCO<sub>3</sub> content). Furthermore, we determined 19 metals (Ag, As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, P, Pb, S, Se, Sn, Sr, V, Zn, Hg). Results were evaluated with considering several aspects as land use, distance from rivers and the dependence of heavy metal concentrations on soil properties. Statistical analysis was performed with SPSS 17.

We found 7 metals exceeding the pollution level (As, Cd, Cu, Hg, Ni, Pb, Zn based on the Hungarian regulations, 6/2009 co-decree). Regarding the land use, heavy metal concentrations were significantly different only in soils of grasslands, while the concentrations forests and arable lands were similar. Particle size turned to fine as the distance grew from the river channel and it also influenced the heavy metal concentration: larger ratio of silt and clay caused larger concentration of heavy metals. Results reflect the measure (magnitude?) and distribution of metal sedimentation and help to identify the factors biasing their accumulation. Our findings can be important considering the agricultural utilization of the area since the toxic metals can be taken up by plants and possibly get into the food chain.

## Field scale remediation experiment for oil-contaminated soil

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There are over 22 000 contaminated soil areas in Finland and 76 % of these are polluted with petroleum hydrocarbons. Oil spills are one of the most common causes of soil pollution in Finland and also on a global scale. As a case example, in 2010 a fuel transportation traffic accident occurred near the city of Iisalmi in Finland. Due to rapid action, a large part of the spilled diesel and gasoline fuel was collected soon after the accident but enough of both oil fractions entered the deeper soil layers to form a threat to the soil ecosystem and the groundwater. In Finland, the restoration of contaminated sites is still based mostly on the excavation and replacement of the contaminated soil. *In situ* remediation methods are used relatively rarely. The aim of this study was to model a fuel accident similar to the Iisalmi case in natural conditions and to compare the cleaning effect of three *in situ* remediation methods: biostimulation, chemical oxidation and monitored natural attenuation.

An experimental research was commenced in June 2012 when a pilot scale experiment was set up in the Jokimaa Soil Research Centre in Lahti, Finland. Two by one meter (depth x width) lysimeters were filled with sandy soil and topped with a humus soil layer replicating the soil profile of the Iisalmi site. Diesel and gasoline were poured into the lysimeters to simulate the accident site conditions. Oil infiltration was monitored from the beginning of the experiment and the cleaning treatments were started a few months later. Biostimulation has been performed by increasing the nutrient and oxygen level of the soil with a sparged urea solution containing a phosphate buffer. The Fenton reaction has been utilised in chemical oxidation by adding 10 % hydrogen peroxide solution to soil. In the monitored natural attenuation, the natural cleaning process of the soil, without any treatments, has been monitored. The remediation effect of the cleaning treatments have been determined during the experiment by measuring concentrations of different oil fractions. Microbial qualitative and quantitative changes have been investigated by length-heterogeneity PCR (LH-PCR) and quantitative real-time PCR (qPCR). Ecotoxicity of soil and leaching water has been tested by exposing earthworm *Eisenia fetida* and luminescent bacteria *Vibrio fischeri* in a laboratory. The final results will be collected in the summer of 2013.

## Residue patterns of Antibiotics in leachate from carcasses

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In Korea, foot and mouth disease virus was a hot issue in 2010's winter season. Lots of livestock were treated by burial method and some was buried by improper method. It made odors and contamination of underground water. Especially underground water contamination was a big problem for people living near burial. Korea is a small country, so it is difficult to raise livestock without using antibiotics extensively for preventing and treating animal diseases. As stated by the WHO, the increasing emergence of antibiotic resistance in human pathogens is a special concern. We determined the residue levels and patterns of 27 pharmaceuticals from carcasses leachate using SPE and LS/MS/MS. Then we compare the antibiotics in leachates of cattle and swine.

Samples were collected and prepared 20 mL from leachate that were generated from carcasses of cattle and swine in lab-scale experiment. For Acidic compounds, the extracts adjusted to pH = 3, extracted by tandem solid phase extraction cartridges using Oasis HLB cartridges (200 mg, 6cc) and Oasis MCX cartridges (150 mg, 6cc) after adding internal standard. For Basic compounds, the extracts adjusted to pH = 6, extracted by SPE cartridges using Oasis HLB cartridges (60 mg, 6cc). The eluted cartridge was dried by nitrogen stream and eluted by 10 mM Ammonium Acetate (pH 6)/Acetonitril (50:50, v/v) 1 mL. An internal standard (0.25 mL) was added to the residue. LC/MS/MS was used for determine the pharmaceuticals.

In this study we analyzed 27 items which are Acetaminophen, Acetylsalicylic acid, Cefadroxil, Cephalexin, Cephadrine, Chlorotetracycline, Cimetidine, Ciprofloxacin, Clarithromycin, Enrofloxacin, Erythromycin, Fenbendazol, Florfenicol, Ivermectin, Lincomycin, Oxytetracycline, Penicilline G, Sulfachloropyridazine, Sulfadimethoxine, Sulfadimidine, Sulfamerazine, Sulfamethoxazole, Sulfathiazole, Trimethoprim, Tylosin, Vancomycin, Virginiamycin M1. 12 items of all 27 items were detected. These were Acetylsalicylic acid (0.6~11.9 ug/L), Acetaminophen (n.d.~0.3 ug/L), Sulfathiazole (n.d.~ 0.6ug/L), Sulfadimidine (n.d.~2.5 ug/L), Sulfachloropyridazine (n.d.~312.0 ug/L), Cephalexin (n.d.~0.8 ug/L), Cefadroxil (n.d.~2.5 ug/L), Penicilline G (n.d.~0.3 ug/L), Clarithromycin (n.d.~259.0 ug/L), Cimetidine (3.78~15.14 ug/L), Tylosin (n.d.~0.03 ug/L). In leachate of cattle, there was no time variation in major compounds like Cimetidine, Sulfachloropyridazine. In leachate of swine, Acetylsalicylic acid that is one of the main compound decreased as time but Cimetidine and Clarithromycin didn't show the time trend. For Cimetidine, both leachate of cattle and swine had similar concentration. Level of cimetidine in river water were 1.163 average (0.065~3.000) ug/L in Korea.

## Bacterial degradation and bioremediation of polycyclic aromatic hydrocarbons in the industrially polluted soil

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The fate of polycyclic aromatic hydrocarbons (PAHs) in soil is of great environmental concern due to their toxic, mutagenic, and carcinogenic properties. As a result of industrial emissions increment and an intensification of car traffic more and more combustion products are being released to the environment and precipitating in soil and water, gradually accumulating there. Generally, in a normal natural environment, soil is able to purify itself, however this process can be quite protracted, especially if there is a complex pollution. Several microorganisms, mainly from the genera *Pseudomonas* and *Mycobacterium*, were found to be capable of transforming and degrading PAHs. These abilities might be useful in removal of PAHs from the environment. The new complex biopreparation, used in the study, was combined from the three bacteria cultures – destructors of PAHs, originally selected from the industrial contaminated soil: *Rhodococcus qingshengii*, *Pusillimonas ginsegisoli*, *Shinella granuli*. New strains of bacteria capable of degradation of PAHs at low temperatures (+ 4 ° C), wide range of pH (4.5 to 8.5), high salinity (up to 7 %) and in the presence of heavy metals were isolated from contaminated soil. The investigated microorganisms showed hyperstability to heavy metals and they retain the capacity for PAHs degradation. The strains were identified by investigation of 16S rRNA. The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) and their oxidation products were analysed by GC/MS. In two months the concentration of such PAHs as naphthalene, fluorene, phenanthrene, fluoranthene, and pyrene decreased in about 10 times, and the concentration of the acenaphthene decreased below limit of detection. The total concentration of PAHs in aerated and nonaerated samples decreased 6 and 4 times respectively within two months, from 2139 ug/kg dw up to 363 ug/kg dw and 563 ug/kg dw. At the end of the bioremediation experiment – four months from the start – almost all of the initial PAHs were destructed, and the total concentrations were less than 80 ug/kg dw in nonaerated sample and less than 70 ug/kg dw in aerated one. The successful application of bacteria to the bioremediation of PAH-contaminated areas requires a deeper understanding of how microbial PAH degradation proceeds. In this study, the bacteria involved and the metabolic pathways, for the degradation of 16 priority PAHs, their degradation products are summarized and the biological aspects of PAH bioremediation are discussed.

## PENTABROMODIPHENYL ETHER IN WATER AND SEDIMENT SAMPLES FROM SAINT-PETERSBURG AREA

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Pentabromodiphenyl ether (pentaBDE) represents polybrominated flame-retardants. The commercial products of pentabromodiphenyl ether contain pentabromodiphenyl ether as a main component of the mixture (50-62%). Other components are tetrabromodiphenyl ether (24-38%), hexabromodiphenyl ether (4-12%) and tribromodiphenyl ether (0-1%). In aquatic environment PBDEs (polybrominated diphenyl ethers) tend to be associated with particulate matter and ultimately deposited in sediment, where they may persist for a long time. Due to their toxicity, persistence and widespread occurrence, PBDEs have been identified as priority hazardous substances specified in HELCOM BSAP. [1] The aim of this study was determination of pentaBDE in water and bottom sediment of the Neva River and Neva Estuary.

10 sediment samples and 5 water samples were collected in the Neva River and in the Neva Estuary (Gulf of Finland) in December 2011. Samples were analyzed for 13 congeners of PentaBDE (tri- to hexaBDEs) by HRGC/HRMS according to EPA-1614 analytical method. Amounts of native congeners were estimated quantitatively assuming equal response factors as <sup>13</sup>C-labelled congeners with similar retention time. Low levels of pentaBDE (sum of 13 congeners) were found in all samples. The water samples contain 0.05 ng/l (r.Neva, suburban area), 0.1 ng/l (r.Neva, urban area), 0.14 ng/l (Neva Estuary), 0.3 ng/l (Neva Estuary, bottom water). The detection limit was 0.02 ng/l. The levels of penta BDE in the bottom sediments are in the range of 0.09 – 1.7 ng/g d.w. Higher (1.0 – 1.7ng/g) concentrations have been observed in the urban zone samples (r. Neva and the tributaries), lower (0.09 - 0.3 ng/g) - in the samples from suburban area and Neva Estuary. 0.5 ng/g of penta BDE has been registered in the sea port of Saint-Petersburg. The detection limit for sediment samples was 0.01 ng/g. In the congener profiles BDE47 (tetraBDE) is the dominant congener in sediment samples, while BDE99 and BDE100 (pentaBDEs) are predominant in water. For comparison pentaBDE levels in other countries are (ng/g d.w.) : <0.02 – 2.1 (Danish coastal and open sea sediments), 0.02 – 0.2 (Finnish coastal sediments), <0.02 – 1.0 (Sweden open sea and coastal sediments). The estimated Predicted No-Effect Concentration (PNEC) for sediments is 62 ng/g of pentaBDE [1]. Therefore our results indicate that pentaBDE is not a factor of risk to the studied ecosystem.

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## Changes of the soil pollution in the vicinity of a metallurgical plant

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In the Free State of Thuringia in Germany, formerly belonging to the GDR, the iron and steel mill Unterwellenborn (now Stahlwerk Thüringen GmbH) is located. As part of the German reunification, former GDR-industry locations got remediated and restructured in the 1990s. In this study the change of the soil pollution in this area is of interest because soil analysis provides long-term pollution studies and changes of the heavy metal content in the soil can show an improvement or a degradation of the soil condition. Therefore, we collected about 60 soil samples during two sampling campaigns in 1993 and 2007. The content of twelve elements, heavy metals as well as main elements, in the aqua regia digestion was determined with spectroscopic methods. Whereas in 1993 Cd, Cr, Mn, Ni, Pb, and Zn contaminated the soil samples <sup>[1]</sup>, the samples taken in 2007 have a lower content of these heavy metals. Only for manganese the content increases. These results show an improvement of the soil condition, which indicates that the remediation was successful. Moreover, we evaluated the results with different statistical techniques. First, applying factor analysis separates elements responsible for the pollution from elements shaping the geogenic background of this area. These results are listed in table 1.

Table 1: Factor analysis of the two sampling campaigns

	1993		2007	
	Explained variance	Elements	Explained variance	Elements
1. Factor	39%	Cd, Cu, Fe, Ni, and Zn	40%	Cr, Cu, Fe, Mn, and Ni
2. Factor	22%	Ca, Mg, and Pb	23%	Ca and Mg
3. Factor	21%	Mn and Cr	26%	Cd, Pb, and Zn

Whereas in 1993 the separation is between elements emitted by the iron-smelting (factor 1) and elements used for steel alloys (factor 3), in 2007 these elements are grouped together in factor 1. In contrast, in 2007 the separation is between elements emitted by the steelwork (factor 1) and elements dropped off at the waste dump (factor 3). Factor 2 is in both cases characterized by the geogenic background.

Secondly, we examined the spatial distributions of the elements with geostatistics. The isoline plots of the spatial distribution show an improvement for almost all elements. Potassium is an exception. Due to the augmented usage of K as fertilizer for agriculturally cultivated fields, the content of this element has increased in the whole area. Furthermore, the distribution of Cu, Mg, and Mn has not changed from 1993 to 2007.

Summarizing it can be said, that the soil condition has improved considerably after the remediation in the late 1990s.

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## Leaching of mercury during phytoextraction assisted by compost

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Phytoremediation is a modern technique of making the soil and water environment non-toxic. Categories of phytoremediation include phytoextraction, which is used for heavy metals soil and water cleaning. The phytoextraction consists in using plants to remove contaminants from soil. The pollutants are taken up by plant roots and transformed from the roots to the above-ground parts of the plant. The contaminated plants are generally removed from the site by harvesting. Because of the low bioavailability of heavy metals in the soil, the process can be chemically enhanced.

Based on the previous results, the substances that increase the efficiency of mercury phytoextraction from soil, by changing its solubility, are EDTA, KI and citric acid. However, the use of these substances in assisted phytoextraction of mercury polluted soils has disadvantages including poor biodegradability (EDTA) and decreasing of plant growth (KI). Moreover, the application of chelators increases the risk of mercury leaching to groundwater, and therefore, does not solve the problem of environment contamination. The assisted phytoextraction can be enhanced by application of natural substances, like compost obtained from the municipal green wastes. Compost is rich in nutrients, therefore it is usually used as a fertilizer.

The aim of the study was to determine the leaching of mercury during assisted phytoextraction of Hg contaminated soil. Using pot experiments, the effect of the application of compost in different soil:compost ratio (1:1; 2:1, 4:1) on leaching of mercury was determined and the results were compared. The results of the study showed that leaching of mercury from soil during phytoextraction process was on the level of 31.2% of total mercury concentration in soil and increased over twice during the conducted experiment (14 days). The application of compost decreased the leaching of mercury. However, the Hg leaching was dependent on the soil:compost ratio. The lowest leaching was observed for the variant of experiment where soil:compost ratio was 1:1. The concentration of Hg in this variant of investigation was equal 14.6-21.4% of total Hg concentration in soil. For the variant of experiment where soil:compost ratio was 4:1, the leaching of Hg from contaminated soil was about 26.9-37.6% of total Hg concentration in soil and was also dependent on the time of conducted experiment.

The results of the study showed that application of compost during the phytoextraction of mercury contaminated soil decreased the leaching of mercury. Therefore, the use of compost from the municipal green wastes should be considered as a potential soil amendment during phytoextraction of mercury contaminated soil.



## What do spice plants synthesize in answer to heavy metal stress conditions?

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During normal vegetation plants are exposed to many environmental pollutants such as presence of heavy metal ions in the soil, chemical pesticides, excessive UV radiation or attack of pathogenic microorganisms [Kozłowska and Konieczny, 2003]. One of the first defense reactions of living cells is an increase in the concentration of reactive oxygen species [Maleck and Dietrich, 1999; Kozłowska and Konieczny, 2003]. To protect living cells plant synthesize a series of defensive secondary metabolites, among which the polyphenolic compounds and defensive proteins play the most important role. Defensive proteins known as pathogenesis related proteins (PR proteins) exhibit different antimicrobial activity [Vallad and Goodman, 2004; Michalak, 2006]. Some of these proteins have documented allergenic properties and can cause severe allergic reactions, including anaphylactic shock [Buczyłko, 2010; Bokszczanin i Przybyła 2012].

In our work we examined the concentrations of polyphenolic compounds in the tissues of popular spice plants, their antioxidant properties as well as the concentration and identification of defensive proteins. We compared the content of these secondary metabolites in control plants vs. plants under heavy metal stress condition. During our research we were trying to check dependence between plant breeding conditions and the actual contents of defensive metabolites. We were trying to answer the question if there is any correlation between concentration of antioxidant compounds and the content of pathogenesis related proteins, which are a source of potential allergens.

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## Temporal trends of POPs in sediments from a high mountain lake in the Tyrolean Alps

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The European high mountain lake systems are useful and sensitive environmental indicators of the overall continental quality, affording the identification of global environmental problems including speed and directions of change. Persistent organic pollutants (POP), among them the organochlorine compounds such HCB, PCBs and DDTs, are xenobiotic chemicals that were introduced into the environment in the second half of the 20<sup>th</sup> century. These toxic compounds arrive to the high mountains after long-range atmospheric transport and part of them are buried in lake sediments [1, 2]. Under the Stockholm Convention the production and use of most POPs were restricted and prohibited to reduce their environmental emissions [3].

The present study describes the temporal profile of POPs in a high mountain lake sediment from the Tyrolean Alps (Gossenköllesee, 2417 m.a.s.l; 47°13'N, 11°1'E) to evaluate whether the input of POPs has decreased in the most recent decade (2000-2010) in comparison to the period of free synthesis and use of these compounds. For this purpose, in summer 2010, a 15 cm sediment core was sampled and POPs were analysed at 0.25 cm intervals.

In the deeper layers (>3.5 cm depth; pre-1950s) baseline levels (~0.1 ng/g dw) were observed while the POP levels increased to maximum levels for 4,4'DDE (2 ng/g dw) and 4,4'DDD (0,7 ng/g dw) in the layer at 2 cm depth (~ 1980s), while PCBs ( $\Sigma$ PCB = 3,5 ng/g dw) peaked in the sediment layer at 1.5 cm depth (~ 1990s). For 4,4'DDE and 4,4'DDD a constant decrease of about 0.04 ng/g dw per year was observed over the past 25 years ( $r^2 = 0.9$ ), while no significant decrease was observed for the PCB congeners.

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## Results of Monitoring and Strategies for the Reduction of Household Food Waste in Korea

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In spite of the government's various efforts to reduce food waste, the food waste in Korea has increased about 3 % every year, mainly due to the growing population, number of households, and income. Food waste occurs in the processes of production, transportation, distribution, storage and cooking of food ingredients. However, there has been little reliable data about how households - a major food waste source - store and treat their food and how much food waste they produce.

In this regard, we thought it was important to understand the exact amount and characteristics of food waste from households in order to reduce the country's food waste, which is why we monitored kinds, storage periods, treatment, and waste of food consumed in 100 households in the Seoul metropolitan area. Households normally store their food ingredients in refrigerators - on average 34 kinds and 55 kg of food are stored - and some of them stayed there for up to 3 years. Moreover, not a small portion of the food is thrown away nearly untouched, mostly because people tend to purchase too much food at one time or they don't know or miss their expiration dates. The amounts of food waste by type were in the order of vegetable>side dish>frozen food>fruit>seasoning.

Also, we suggest effective and realistic measures to reduce food waste and promote a more desirable food consumption culture in Korea.

## **A Study on Analysis Methods of Heavy Metals and Concentration of Portland Cement in Korea**

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Since 2007 the National Assembly and the media of Korea arouse issues on the degradation in health and environments caused by heavy metals included in cement in addition to interests on the wastes used in cement kilns. Therefore, local residents, government and civilian organizations, experts, and cement production companies are gathered to form a committee for determining an autonomous guide for Chromium VI in portland cement. Also, they investigated the criteria and analysis methods and established an autonomous management system in 2006 for the concentration of such heavy metals included in cement products including Chromium VI. In Korea, in the analysis methods for Chromium VI, the quantitative method was established by KS L 5221 Dec., 2007 and an autonomous agreement guide (20 mg/kg) was determined between cement production companies. Then, the results of the analysis of heavy metals are to be published for every month, and the degree of pollution has been monitored. In Korea, because there are no test methods for such main and sub-materials and wastes, the concentrations of five major heavy metals, such as As, Cd, Cu, Pb, and Hg, which are determined in the autonomous committee, are managed according to the US EPA test method.

In this study a investigates some effective and reasonable test methods for establishing a guideline for the criteria of the heavy metal included in wastes applied to cement kilns. In addition, the concentrations of seven different heavy metals (Cr(VI), T-Cr, Cd, Cu, Pb, As, and Hg) in cement products collected from 11 factories of 9 manufacturers are verified for every month and changes in the concentrations are also compared with the cement products of Germany, USA, Japan and China.

## Study on the possible utilization of the red mud as catalyst

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The red mud studied was taken from the storage facility of MAL Zrt, Ajka, Hungary, where the red mud disaster occurred in autumn of 2010 leading to an extremely serious environmental situation. The research is focused on exploring ways for the utilization of disposed red mud originating from alum earth production from bauxite minerals. The amount of red mud only at the Ajka storage facility is estimated to about 35 MT. The red mud sample was taken from the dry storage facility (containing of caustic materials from 10 to 30%). The determination of main elements of the red mud was carried out by ICP-EOS techniques. The sample, before ICP analysis, was digested with using microwave method. The investigated red mud mainly contains a mixture of iron oxide (Fe~16.2%), calcium minerals (Ca~6.6%), alumina (Al~6.4%), sodium oxide (Na~4.1%). It contains magnesium (Mg~0.4%), titanium (Ti~0.9%), manganese (Mn~0.08%), zinc (Zn~0.01%) and silicon (Si~0.01) as well in smaller amounts. Due to this it can be considered as a potential alternative catalyst for decomposition/cracking reactions of different hydrocarbon residues exhibiting acidic character. The red mud contains iron in form of ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) and after appropriate treatment its surface area can be increased and become resistant to sintering and poisoning. Red mud can be considered as an attractive potential catalyst for many reactions including upgrading acidic bio-oils. Studies are focused on the possible utilization of residual bio-refinery oils/wastes, biomass waste such a wheat straw and red mud. Batch reactor was used in the temperature range of 250-450 °C under mild pressure. The bio-oils obtained by pyrolysis are complex mixtures of oxygenated compounds as determined by GC-MS technique. Since the high acidity (pH~2.5) of the residual bio-oils and agricultural originated bio-waste streams exhibit problems for further processing the bio-oils must be neutralized and pretreated/upgraded if they are considered for possible utilization. The red mud can be used for the neutralization of the acidic oil cuts due to its caustic nature and the iron and accompanying metals in red mud can catalyse the conversion processes. The experimental data support this notion, however, further studies should be carried out in order to identify the conversion reactions.

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## Determination of pesticides in soil and waters by DLLME/MEKC, QuEChERS/MEKC

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Micellar electrokinetic chromatography (MEKC) with ultraviolet detection (MEKC-UV) was used for analysis of a group of herbicides that have widespread use in agriculture of Russia. MEKC-UV was employed for simultaneous determination mix of 27 polar pesticides of the main classes most often used in agriculture (neonikotinoids, sim-triazines, organophosphorus compounds, carbamates, phenoxy-carboxylic acids, urea derivatives, triazoles, triazinones, imidazoles and benzimidazoles).

The analysis was performed using an uncoated fused silica column, in borate buffer containing sodium dodecyl sulfate (SDS), ion-pair reagent tetrabutylammonium phosphate (TBA) and 10% acetonitrile, and UV detection at 190 nm. The addition of TBA and acetonitrile to the buffer improved the separation and affected intrinsic migration of analytes. The working standard solutions were prepared in water. Herewith high sensitivity and effective separation of pesticides were obtained.

Satisfactory recovery of pesticides was obtained from natural water using dispersive liquid-liquid microextraction (DLLME) technique. The limits of quantitation (LOQs) at a signal-to-noise ratio of 10 ranged from 1.0 to 22.0  $\mu\text{g}\cdot\text{l}^{-1}$ . The recoveries of 27 polar pesticides for water samples at spiking levels of 40.0 and 80.0  $\mu\text{g}\cdot\text{l}^{-1}$  were 45.4–91.7 % and 44.5–91.4 %, respectively.

Extraction of polar pesticides in soil was performed with acetonitrile, applying QuEChERS methodology, and the extracts were analyzed without any further clean-up step, providing better results than solid phase extraction procedure. LOQs ranged from 0.01 to 0.4  $\text{mg}\cdot\text{kg}^{-1}$ . The recoveries of pesticides mix for soil samples at spiking levels of 0.045 and 0.090  $\text{mg}\cdot\text{kg}^{-1}$  were 30.8–105.8 % and 29.1–92.3 %, respectively.

The proposed methods have been successfully applied to the analysis of the target pesticides residues in water and soil samples with satisfactory results.

## Organotin compounds in lagooning treatment plant: occurrence and behaviour

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Tributyltin (TBT) is one of the most anthropogenic hazardous pollutants introduced in the marine environment. It is a cytotoxic, genotoxic and endocrine system disrupter causing growth disturbance, reproductions troubles, and the occurrence of imposex (masculinization of females) in marine organisms. The EU water framework directive has classified TBT as a “priority hazardous substance”, whose emission, discharges and losses are targeted for phasing out or complete removal. The Environmental Quality Standards established sub-ppt limits for TBT compounds expressed as total concentrations in the whole water sample (dissolved and particulate phases). Studies on pollution by butyltin compounds in aquatic bodies are generally limited to regions with high port activity, because of the direct emission of TBT from antifouling paints, used on the hulls of boats. Nevertheless, TBT and its derivate compounds as DBT and MBT are detected in inland surface waters, including rivers, lakes and artificial water bodies. Many studies have investigated organotin presence and behaviour in conventional wastewater treatment plant (activated sludge) but few studies were related to wastewater treatment by lagooning process.

The main objective of this work is to contribute to the understanding the fate of the organotins in management systems especially in wastewater treatment by lagooning process. The geographical framework chosen is the Vene (France), Mediterranean intermittent River, where the presence of the OTs has been demonstrated. Our study focused on Gigean wastewater treatment by lagooning (6000 Equ.H) including 5 basins and deversing treated water in the Vene. This work involves a speciation monitoring of organotins in the various phases (water, suspended solids and bottom sludge lagoon) in the influent and the 5 basins as well as studies of organotin sorption/desorption processes on the bottom sludge from the first lagoon. The results reveal the systematic presence of butyltins mono-, di- and tributyltin and monooctyltin in water, suspended solids and sludge of the five basins of WWTP. Sorption kinetic and equilibrium parameters are studied at lab-scale, in batch experiments, by varying the initial organotins concentration and measuring during time the partition between the liquid and solid phase of the sludge. Organotin sorption is a rapid phenomenon, with very high removal efficiency (higher than 95%). High affinity is found between organotins and the sludge solid phase. Solid-water partitioning coefficient  $K_d$  is measured, according to a linear modelling of the equilibrium data. This coefficient is in the same range of the one measured in the same conditions on activated sludge, which demonstrates the same sorption behaviour of these two types of sludge. Desorption experiments were carried on both enriched and native sludges. Kinetics are less rapid than sorption ones and depends strongly of the sludge organotins contain. Results demonstrate that hysteresis occurred between organotins sorption and desorption mechanisms.

## Geochemical Speciation and Potential Toxicity of Trace Elements in River Sediments

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Sediments act as a sink but they can release trapped metals as a result of slight environmental perturbations. The distribution, mobility, and hence the bioavailability of metals in the sediments not simply depend on their concentrations but, critically, on their chemical forms (i.e. speciation). Therefore, studies on metal speciation in sediments are of paramount importance. The study focuses on the speciation of Cr, Ni, Cu and Pb in the sediments of the Yamuna-an important river of India. The studies were conducted to evaluate the availability of metals to biota and the consequent risk. For the analysis of metals, sediment samples were digested following standard procedure of USEPA and analyzed by AAS (PerkinElmer, *AAnalyst 800*, USA). The chemical partitioning of metals in sediments was studied by following the modified BCR (mBCR) sequential extraction scheme. Certified reference materials, IAEA 405 (estuarine sediment) and BCR 701 (lake sediment), were analyzed to assure the accuracy ( $\pm 10\%$ ) of the methods employed for the determination of total metal and different fractions of metals by mBCR scheme. The availability of metals in sediments follows the sequence Pb>Cu>Ni>Cr. Data were subjected to multivariate statistical analysis. Significant spatial variations in physicochemical characteristics and different geochemical forms of metals in sediments, indicated by two-way ANOVA, are attributed to various anthropogenic activities at different sites. A similar source for all the four metals is indicated by principal component analysis (PCA). PCA also indicates towards some independent sources of Cu and Pb. The hot spots were identified using hierarchical cluster analysis using available forms of metals in sediments as objects and the sampling sites as variables. Risk assessment code (RAC) analysis indicates that metals generally pose medium to high risk at different sites. However, at a few spots either Ni or Pb crosses the level of very high ecological risk.



## Comparison of phosphonate and carboxylate chelating agents in the Pb extraction from WEEE glass

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Notwithstanding DIRECTIVE 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment, among which Pb, there are some applications which are exempted from the requirements, such as lead in glass of cathode ray tubes containing Pb in the range 15-20%. Thus, the management of this kind of WEEE (Waste Electrical and Electronic Equipment) both as matter recovery and landfill disposal become problematic. In the context of its detoxification and stabilization processes, the melting treatment could be useful, because lead atoms contained in lead glass are strongly fixed by the encapsulation in the cavity of the glass network and therefore a Pb extraction cannot be fulfilled under ordinary temperature and pressure conditions. Otherwise, melting is critical from the emission point of view (guidelines for the application of IPPC DIRECTIVE 1996/61/EC to the glass industry and frits production, issued by D.M. 01.29.2007) due to Pb volatilization. In the present study a method with low energy consumption is proposed: a comparison of different chelating agents capability to sequester lead. Phosphonate (HEDP, ATMP and EDTMP) and carboxylate (EDTA, NTA, and citric acid) chelating agents have been tested in different conditions: mechanochemical process (treatment of Pb-glass at 8 hours without or with pre-treatment in acetic acid at 70-80°C), temperature (treatment of Pb-glass at 70-80°C with complexing agents without or with pre-treatment in acetic acid at 70-80°C), pH (treatment of Pb-glass at 70-80°C with complexing agents at pH 4 and pH 10 by means of buffer solutions). The highest lead extraction has been reached using EDTA with the mechanochemical treatment of 8 hs, pre-treated in acetic acid. The lead removal was around 38% and the amount of Pb in the glass decreased up to 11.1%. For the treatments at 70°C with and without pre-treatment in acetic acid and at pH 4 the results were not significant compared to those obtained by mechanochemical process, confirming both that the acid environment is not the optimum for the glassy network weakening and the complexation capability of the different chelating agents for acidic pH is low. On the other hand, the behavior of the glass complexing in a basic conditions is noteworthy. In fact the results at pH 10 after 1h reached, and in sometimes exceed, the lead extraction obtained in the mechano-chemical treatment after 8h, despite the lower glass surface/ volume ratio. This is due to both the best extraction capability of the complexing agent at high pH values conditions, and the attack to the glass matrix made by the alkaline solution. In all treatments HEDP and citric acid have shown a weak extractive capability for lead indifferently by particle size, temperature, pH, and time of contact; while a strong extraction capacity for sodium and potassium that means their higher affinity for these ions than lead.

## Inertization of chromium liquid waste in inorganic polymers by alkali activation of metakaolin

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Inorganic polymers are obtained by chemical reaction of aluminosilicate powders with Na-silicate as binder under highly alkaline conditions. The mechanism of inorganic polymers setting and hardening consists of a dissolution, transportation or orientation, as well as a polycondensation step. Many parameters such as curing time, curing temperature, relative humidity etc. can influence the geopolymerization process and lead to a resistant matrix usable for inertization of hazardous wastes.

In the present work, the waste immobilized in the inorganic matrix is in the liquid state and contains high amount of chromium (6.5 wt%) in forms of metallorganic salts dissolved in water. In order to evaluate the matrix immobilization capability an amount of waste added to the aluminosilicate precursor ranging from 3 to 20 wt% was tested. The water contained in the liquid waste (67 wt%) was exploited in the mixing and forming steps of the geopolymeric gel. The evolution of the process from the precursors dissolution to final geopolymer matrix hardening has been followed by FT-IR and ss-NMR spectroscopies, scanning electron microscopy (SEM/EDS), leaching tests and DOC e COD parameters. The results show the formation of a stable matrix able to immobilize chromium cations. In particular, leachability was studied in water accordingly to EN 12457 regulation (leaching process was monitored for 7, 14, 28, 90 days, 12 and 18 months). For all the compositions, the leachable metals in the eluate, determined by ICP\_AES, fall within limit values set by Italian regulation for non-dangerous waste landfill disposal confirming the effectiveness of the matrix to fix chromium.

## **Advances in Atmospheric Pressure Gas Chromatography (APGC) for the analysis of persistent organic pollutants (POPs); background and applications.**

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Gas chromatography coupled to mass spectrometry (GC/MS) has been extensively applied for determination of volatile non-polar compounds in many applied fields including food safety and environmental analysis.

To date, the analysis of dioxins and dioxin-like compounds is most often performed on high resolution GC (HRGC) magnetic sector instruments as required by the various legislative bodies (USEPA, EU & MOE Japan). In the near future a change to the EU regulations is expected and this change will allow for a more diverse range of instruments to be used for the analysis, including the potential for GC tandem quadrupole MS.

One technique that has potential for GC amenable compounds is atmospheric pressure gas chromatography (APGC). A significant advantage of this technique is that it produces ionisation that is comparable to atmospheric pressure chemical ionisation (APCI). This means that APGC is a much softer ionisation technique compared to electron ionisation (EI) therefore, a considerably higher abundance of the molecular ion is detected. This has significant benefits for sensitivity and selectivity. Another advantage being that this technique can be also used on an electrospray instrument with UPLC. The changeover between techniques is simple and fast with no compromise in data quality.

An APGC source coupled to a Xevo TQ-S was used to analyse dioxins, polychlorinated biphenyls (PCBs) and brominated flame retardants (PDBEs). Data is shown including, linearity, sensitivity and repeatability. The advanced features of the XEVO TQ-S (RADAR) are also shown.

This data illustrates that the APGC is a highly sensitive, robust and flexible technique with significant advantages for the future of POPs analysis.

## Selective leaching of Mo and Ni from spent Ni-Mo catalysts using a two-stage microwave-assisted method

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Petroleum refining industries produce large quantities (120000 ton/year) of spent hydrodesulphurisation catalysts, classified as hazardous wastes [1]. Because these catalysts contain metals, such as Mo, Ni, Co and Al, their recycling and recovery is an economically and environmentally attractive option.

The aim of this work was to study metals recovery from a spent HDS catalyst. Selective metal leaching allows a simpler subsequent metal recovery; so, a two stage leaching process to remove Mo and Ni separately was studied, where conventional (thermostatic bath) and microwave heating were compared.

The samples of Ni-Mo spent catalyst were roasted in air, at 500°C, and characterized. The first leaching stage was performed in alkaline medium to dissolve Mo [2]. In conventional method, temperature and NaOH concentration were varied. We concluded that at 80°C, 0.5 M NaOH solution led to high recovery of Mo (92%) and Al (20%), while a solution of 0.25 M affected Mo yield (77%), but allowed a more selective leaching since Al removal decreased (7%). For microwave leaching, the number of cycles and NaOH concentration were varied. Each cycle consisted of 30s heating in a microwave followed by cooling. For NaOH 0.25 M, Mo dissolution was 89%, after 4 heating cycles, while only 6% of Al was leached from the catalyst. Microwave-assisted method allowed a more selective and enhanced leaching of Mo from the catalyst. Al present in solution was precipitated and separated at pH 8. Mo was recovered as SrMoO<sub>4</sub> with a high yield (96%) and purity (>99%) [3].

The second leaching stage was first tested using H<sub>2</sub>SO<sub>4</sub> solutions, for recovering Ni. Both conventional and microwave heating were performed, giving similar results: 90-95% of Ni and 60-68% of Al were leached from the catalyst. In order to achieve a more selective removal of Ni, EDTA solutions were studied [4]. Using the conventional method, maximum recovery of Ni was 40% (90°C). When microwave heating was applied, removal of Ni was enhanced and best results were obtained for 4 cycles (1 min heating each followed by cooling) and EDTA 0.1M: 80% of Ni and 2.8% of Al were removed.

The application of microwave heating in a two-stage leaching of metals from spent HDS catalysts allows higher recoveries of the target metals in a more selective way, using milder conditions and lower processing times.

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## A sustainable method of waste cathode ray tubes recycling

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The cathode ray tubes (CRTs) represent a real disposal problem because of their growing magnitude in the municipal solid waste (MSW) and their role as a major source of lead in MSW. The US-Environmental Protection Agency has indicated that the CRTs are hazardous waste (code D008/Federal Register for 40 CFR 261) due to the toxicity characteristic of lead content. The EU legislation tries to impose some restrictions regarding the use of lead in the electric and electronic equipment (EEE), for example, the new RoHS directive allows the use of lead in the glass of CRTs and in the glass of fluorescent tubes if the lead content is not over 0,2 w/w% . Therefore it is very important to devise recycling solutions in order to manage the significantly increasing CRTs glass waste. The present study is focused on a promising application regarding the CRTs recycling by incorporating CRTs waste in concrete, which could immobilize the metal ions (especially lead) content and could prevent leaching. This composite can be used as building material. An important advantage of the proposed material is that it is manufactured in an environmental friendly manner that produces far less carbon emissions than typical cement-based building materials and it has economic benefits by decreasing the economic and environmental costs compared with conventional recycling processes. In order to predict safe conditions and applications for the proposed CRTs composite, in the present study the leaching mechanisms of lead from the composite material was studied under different conditions: the effects of CRTs size on the structural properties of concrete, the effect of CRTs/concrete fraction, the effect of CRTs type (panel and funnel) and the effects of pH and temperature. The results showed that the lead lechability from the composite is strongly influenced by the pH conditions. Lower leachability (average level of 0.179 mg/kg) was observed under slightly acidic conditions ( $5.5 < \text{pH} < 6.5$ ). The leachability increased with pH value, having an average value of 0.527 mg/kg at  $\text{pH} = 12$ . In acidic media the leachability was considerably higher reaching a value of 2.62 mg/kg at  $\text{pH} = 1$ . The data summarized in the present study proved that the obtained composite, which incorporates waste CRTs glass can be a good alternative for CRTs recycling and it can be safely used as building material. Only under extreme environmental condition ( $\text{pH} < 1$  and  $\text{pH} > 12$ ), which represents the worst case scenarios, the lead leachability exceeds the maximum allowed concentration set by legislation (0.2 mg/kg). The results of this study provide useful information for developing policies for managing CRTs waste.

## Energy from waste: Using red mud and residual glycerol from biodiesel to produce syngas

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Red mud (RM), the main waste of the aluminium production process, has been investigated for different applications such as catalyst and hydrogen production [1]. Glycerol is a by-product of biodiesel synthesis, corresponding to 10 wt% of all products generated [2]. Together, these wastes can generate syngas, a mixture of CO and H<sub>2</sub>, an important input of fuels market, since it can be converted in liquid hydrocarbons by Fischer-Tropsch synthesis.

A new route to produce syngas from glycerol is presented in this work and the technology is based on a two-step process. First, RM, formed basically by iron oxide and alumina is reduced by carbon source (glycerol) generating a composite metal-carbon (M/C), that is oxidized by water in a Step 2, producing syngas. In the end of this cycle, the catalyst (RM) is recovered and it can be used several times.

The glycerol decomposition was carried out in a horizontal furnace under inert atmosphere. A mixture of glycerol (90%) in water were injected under a rate of 0,01 mL min<sup>-1</sup> and the system was heated from 25 to 800 °C. The gas fraction formed was analyzed by gas chromatography. During this reaction, it was observed production of CO (0,0084 mol) and H<sub>2</sub> (0,0046 mol), mainly from 800 °C. In addition, were produced hydrocarbons, as methane, and a M/C composite, which was characterized by several techniques. Thermogravimetric analysis for this solid showed deposited carbon formation (5%) and Raman spectroscopy confirmed the presence of carbonaceous structures through appearance of D and G bands. DRX analysis exhibited peaks of reduced iron phases, as magnetite (Fe<sub>3</sub>O<sub>4</sub>) and wüstite (Fe<sub>1-x</sub>O).

The oxidation reaction was conducted under water injection (0,01 mL min<sup>-1</sup>) carried out by an inert gas (N<sub>2</sub>). The M/C composite was heated from 25 to 900 °C and gas products were identified by GC analysis. During oxidation reaction it was verified formation of hydrocarbons, as CH<sub>4</sub> (0,0001985mol), and H<sub>2</sub> (0,0010145mol) from 400 °C and CO (0,001385mol) at higher temperature, 650 °C. The H<sub>2</sub>/CO ratio, an important parameter in Fischer-Tropsch synthesis, was 0,73, a low value when compared with the required one, equal a 2,0. This fact can be explained by occurrence of Fischer-Tropsch synthesis in situ, which was evidenced through hydrocarbon formation.

Therefore, the combination of red mud and residual glycerol from biodiesel was very efficient for energy generation.

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## APPLICATION OF QUENCHERS BASED METHODOLOGY FOR THE ANALYSIS OF PESTICIDES IN SEDIMENTS

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The analysis of micropollutants present in sediments generally requires to carry out a complex protocol including several successive steps for sample extraction and purification. The most popular method, the extraction by pressurised fluid, is very efficient for extracting the target analytes but also for all the other potentially interfering components that might be present within the matrix. Moreover, this technique is relatively expensive since dedicated equipment is needed.

The QuEChERS approach, developed initially for the analysis of pesticides in fruits and vegetables [1], can be regarded as an alternative technique to simplify this step. It is easy to handle, relatively cheap and with low solvent consumption. Therefore, this technique has been evaluated in this study for the analysis of pesticides in sediments.

The priority pesticides and the substances candidate to integrate the Water Framework Directive (2000/60/EC) list of pollutants were considered. Since the purification step of the QuEChERS technique is not intended to remove all interferents from the sample matrix, the analysis was performed by gas chromatography followed by a selective detection using tandem mass spectrometry.

A QuEChERS type method and purification protocol based on the approach generally carried out for fruits and vegetables was applied. Therefore, an extraction with vortex agitation using acetonitrile was performed followed by a purification step by dispersive solid phase extraction with sodium sulfate, C<sub>18</sub> or PSA.

Initial tests were carried out on dry sediments but addition of 10 to 20% of water (v/w) increased the recovery of most of the pesticides tested. With this approach, recoveries ranging from 80 to 120 % were obtained for most of tested compounds. Limit of quantification were determined around 10 ng/g with linearity range up to 500 ng/g. This protocol was tested on certified reference material which provided satisfying results in most cases.

Overall, the QuEChERS based approach appeared suitable for the analysis of pesticides in sediments.

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## Securing HCH deposits of a former Lindane production in Aragon (Spain)

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Hexachlorocyclohexane (HCH) isomers ( $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH [lindane]) were listed as persistent organic pollutants (POP) in the Stockholm Convention in 2009. Therefore the legacy of HCH/lindane production with the associated large HCH waste deposits has become recognized as an issue of global concern and is addressed in the implementation of the Stockholm Convention (Vijgen et al. 2011). Lindane has formerly been produced in Spain at four production sites. Two production facilities were located in the Basque country of Northern Spain (82,000 tonnes HCH disposed), a factory in Galicia (several thousand tonnes of HCH waste and several 100,000 tonnes of contaminated soil) and a factory in Sabiñánigo (Aragon) containing the largest POPs waste deposit (approx. 115,000 tonnes HCH disposed).

For the Sabiñánigo site, the Aragon Regional Government and the Spanish Environmental Ministry are taking action with a focus on the transfer of HCH/POP wastes from one former dump site to a new secured landfill and on the treatment of a large DNAPL phase (4000 tonnes) threatening the Gállego River a tributary of the Ebro river finally discharging to the Mediterranean Sea. The DNAPL phase and surface water has been analysed. The DNAPL contain in addition to HCH isomers also chlorobenzenes, tetrachloro- and pentachloro-cyclohexenes, hexachlorohexadiene in g/kg range as major pollutants resulting also in high ground water contamination. A range of laboratory tests has been performed (with persulfate, peroxide, and nanoparticles of zerovalent iron) in order to plan an aquifer remediation.

The groundwater plume from the deposits has already reached the Gállego River and peaks of 1  $\mu\text{g/L}$  of HCH have been measured 0.5 km downstream, with an average concentration of 0.57  $\mu\text{g/L}$  and therefore above the EU Water Framework Directive limit of 0.2  $\mu\text{g/L}$ . From the HCH surface water concentration and water flux of the river it was estimated that approximately 140 kg/year of HCH is released from the two major deposits to the Gállego River. Such releases from landfills/dumps are currently not included in the European Pollution Release Transfer Register (PRTR), where for POPs/HCH, levels above 1 kg/year release have to be reported for IPPC installations. This highlights that releases from landfills and other deposits might need to be considered in the PRTR as well. Also these HCH/POPs releases should be addressed in the frame of the Barcelona Convention considering that the receiving river finally discharge to the Mediterranean Sea.

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## Pesticides distribution in dust with different particle size collected from urban environments

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Structural pest control entails that many pesticides are applied on residential areas during the spring and summer seasons. Recent studies have demonstrated that an undesirable side-effect of this application is the contamination of dust present on impervious surfaces. As a consequence, dust particles constitute an important carrier to transfer hydrophobic pesticides into the aquatic environment through urban runoff. However, the runoff potential or transferability of pesticides accumulated on such particles is still unclear and might be influenced by a wide number of different factors.

In this study, dust samples were collected from different locations of a neighbourhood in southern California during December 2012, several months after the pesticides application period. Dust collected from a drivewalk was fractionated into 4 particle sizes ( $\mu\text{m}$ ) : >250; 105 to 250; 53 to 105 and <53. 8 pyrethroids of current use, 2 organophosphates (legacy pesticides), fipronil and 3 fipronil degradates were extracted and analysed in each fraction using a GC/MS method.

Pesticide residues were found in all the dust samples and fractions, showing the high persistence of these pollutants in urban environments. Considering the total number of samples analysed, the pesticides detected at higher concentrations were bifenthrin (maximum concentration of  $199 \text{ ng}\cdot\text{g}^{-1}$ ), permethrin ( $55 \text{ ng}\cdot\text{g}^{-1}$ ) and the fipronil sulfone degradate ( $15 \text{ ng}\cdot\text{g}^{-1}$ ). In general, higher amount of pesticides were found in one specific sampling spot (a drivewalk), confirming that pesticides distribution in an urban environment might vary strongly depending on the location sampled.

In the fractionated samples, the legacy pesticide chlorpyrifos showed lower concentrations in dust with particle size <53  $\mu\text{m}$ . The pyrethroid bifenthrin showed the opposite behaviour, with the lowest concentration measured at particle sizes above 250  $\mu\text{m}$ , and permethrin tended to distribute preferably in the smallest particle sizes. The degradate fipronil sulfone had fairly similar levels in the four fractions. Although these results need further confirmation using a larger data set, when the specific weight of each particle size fraction was introduced in the calculations to estimate the distribution of pesticides in urban dust, it was evident that the largest and smallest particle size fractions contribute with the higher amount of pesticides. For example, 77% of the total fipronil sulfone measured in a dust sample is found in those fractions. This factor is relevant to understand the transferability of pesticides from dust to runoff during different events such as rainfall or sprinkler irrigation. The presented data may have practical implications for the development of mitigation strategies and further modelling approaches.

## **Water Pollution and Treatment**

**Oral presentations: OW1-OW20**

**Poster presentations: PW1-PW88**

## Laccases: Potential treatment for removal of micropollutants in municipal wastewater?

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Relatively high concentrations of micropollutants such as pharmaceuticals and biocides in municipal wastewater treatment plants (WWTP) effluents underscore the necessity to develop new treatments. Organisms that produce oxidative enzymes such as laccases are a potential means to improve biodegradation of these compounds. Laccases are polyphenol oxidases widespread among plants, fungi and bacteria. They are able to catalyse the oxidation of various aromatic compounds, including several pharmaceuticals and biocides. The goals of this study were to evaluate the potential of four strains of *Streptomyces* bacteria (*S. cyaneus*, *S. ipomoea*, *S. griseus* and *S. psammoticus*) and the white-rot fungus *Trametes versicolor* for i) their ability to produce laccase in municipal wastewater with diverse growth substrates, ii) their laccase activity at different pH, temperature and salinity values, and iii) their ability to degrade selected micropollutants, especially diclofenac (DFC), mefenamic acid (MFA) and bisphenol A (BPA), in buffer solutions and in municipal wastewater. Among the *Streptomyces* strains evaluated, only *S. cyaneus* produced extracellular laccase in quantities sufficient to envisage its potential use in wastewater treatment. Laccase activity produced by *T. versicolor* was however more than 20 times higher, the highest activity being observed in wastewater with ash branches as the sole carbon source, a cheap and easily available substrate. *S. cyaneus* ( $L_{Sc}$ ) and *T. versicolor* ( $L_{Tv}$ ) laccases were mainly active for acidic pH conditions (optimal pH in the range < 4 to 6).  $L_{Tv}$  showed significant activity for wider pH and temperature ranges, especially for near-neutral pH and between 10-25°C, conditions found in municipal wastewater. Both laccases could oxidize the selected micropollutants in buffer solutions, with faster degradation observed with  $L_{Tv}$ , especially at pH 7. However, in municipal wastewater (pH 7.6-7.8), no significant removal of DFC and MFA was observed with  $L_{Tv}$  alone (in 12 h, 23°C, 1000 U l<sup>-1</sup>), unless the pH was decreased to 6.7-7 and mediator (ABTS) added. High removal (> 80%) of these two compounds was reached in less than 24 h when *T. versicolor* was present in the wastewater, even at an initial pH of 7.9. This suggests that, despite the potentially efficacious oxidative capacity of laccase, treatment of micropollutants in municipal wastewater without pH adjustment is only feasible with the presence of the whole organism. The ability of *T. versicolor* to degrade recalcitrant pollutants such as DFC in municipal wastewater is therefore very promising. New challenges have now to be faced to develop a treatment suitable for municipal WWTPs.

## Pharmaceuticals removal from wastewaters in constructed wetlands

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Presently, most wastewater treatment plants (WWTPs) are considered a major source of several different emerging micropollutants, namely pharmaceuticals and personal care products (PPCPs) to the aquatic bodies. Despite the low concentrations usually found (from ng/L to µg/L level), concerns regarding their presence in the environment are increasing. Therefore, development of innovative approaches that ensure an efficient removal of these contaminants is crucial.

Constructed wetlands (CWs) have been researched in the last years has alternative and/or additional treatment systems for PPCPs removal from effluents (1). However, CWs ability for pharmaceuticals removal has been accessed mainly for a small range of human pharmaceuticals, ibuprofen, carbamazepine, clofibric acid, atenolol, ketoprofen, naproxen, diclofenac, salicylic acid and carbamazepine, at both microcosm and full-scale level. Therefore, more research on this topic is in need to validate the use of this technology.

This communication intends to give an insight of the main achievements and current research perspectives on CWs application for PPCPs removal from wastewaters. A few case studies will be detailed, such as the potential of CWs microcosms to mitigate the release of the antibiotics enrofloxacin (a fluoroquinolone) and tetracycline (tetracyclines family) (2).

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## Biologically-based water reclamation systems: a sustainable alternative for removing pharmaceuticals and endocrine disrupting chemicals from wastewater

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Pharmaceuticals and endocrine disrupting chemicals are organic micropollutants found in aquatic environments at concentrations from  $\text{ng L}^{-1}$  to up to several  $\mu\text{g L}^{-1}$  as they are incompletely removed in conventional treatment at wastewater treatment plants (WWTP) [1]. Biologically-based water reclamation systems, such as constructed wetlands and polishing ponds may be almost as effective as advanced treatment systems with the advantage of generating ecologically rich effluents whilst eliminating certain pharmaceuticals [2]. In order to study the role of the presence of bacterial communities, organic matter and aquatic plants (*Spyrogira* sp., *Zannichellia* pallustris and *Lemna* sp.) in the removal of pharmaceutical and endocrine disruptors from secondary wastewater effluents and the main processes involved in their elimination, 2.5 L of secondary-treated wastewater were spiked at concentrations ranging from 100 to 200  $\mu\text{g L}^{-1}$  with a pollutants mixture (tetracycline, oxytetracycline, sulfathiazole, sulfapyridine, sulfamethazine, sulfamethoxazole, diclofenac, acetaminophen, ibuprofen, carbamazepine, clofibric acid, caffeine, propranolol, 17 $\alpha$ -ethynylestradiol, and bisphenol A). Different experiments (unplanted covered control, unplanted control and planted reactors) were carried out by triplicate. The results show that photodegradation is the most significant process associated to the elimination of tetracyclines ( $t_{1/2}$ =3-5d) and some sulfonamides ( $t_{1/2}$ =14-91d). The identification of a tetracycline photodegradation product supports this assumption [3]. Biodegradation and the presence of aquatic plants played an important role in the removal of acetaminophen ( $t_{1/2}$ =1-5d), caffeine ( $t_{1/2}$ =1-4d), propranolol ( $t_{1/2}$ =7-8d), ibuprofen ( $t_{1/2}$ =6-7d), bisphenol A ( $t_{1/2}$ =4d) and 17 $\alpha$ -ethynylestradiol ( $t_{1/2}$ =4-5d). The results obtained suggested that non-ionic compounds (acetaminophen, caffeine and propranolol) are uptaken by the plants, whereas this effect was not observable for ionic compounds (e.g. ibuprofen). Finally, carbamazepine, diclofenac and clofibric acid were poorly removed ( $t_{1/2}$ >20 d). These findings highlight that polishing ponds are a highly effective and cost efficient technology for treating polluted waters containing pharmaceuticals and EDCs.

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## Solar Water Detoxification Processes for the Removal of Estrogens, Antibiotics and other Contaminants of Emerging Concern

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Solar water detoxification is a feasible and potentially low-cost method for the removal of micropollutants and emerging contaminants (ECs) from the environment. These include sub-ppm levels of cyano-toxins, estrogens, pharmaceuticals, personal care products, pesticides and many other ECs. In this presentation we review solar water detoxification methods and highlight the importance of engineering and rational reactor design for the effective degradation of ECs. The design criteria of such reactors are based on the principles of photon transport and radiation absorption and are strongly dependent on the optical properties of the photocatalysts. We show that reactor geometry, photocatalyst concentration and contaminant concentration are interrelated quantities that cannot be separated and present rational criteria for the design, analysis and evaluation of photocatalytic processes.

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Colina-Márquez, J., Machuca-Martínez, F., Li Puma, G. Radiation absorption and optimization of solar photocatalytic reactors for environmental applications. *Environmental Science and Technology*, 44 (2010) 5112-5120.

## Removal of organic micro-contaminants from municipal waste water by an IBR system coupled to a solar photo-Fenton process as tertiary treatment

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Nowadays, one of the main sources of water for potential reuse comes from municipal wastewater treatment plants (MWWTPs). However, quality demands for reusable water not to contain the so called Emerging Contaminants (ECs): pharmaceuticals, pesticides, hormones and others organics that escape conventional wastewater treatment techniques. These, along with conventional pollutants, such as pesticides, have been found in MWWTP effluents at concentrations higher than 1 µg/L. Consequently, new technology must be applied to overcome this problem. This work presents an easy, handy and efficient alternative that combines an immobilized biomass reactor (IBR) with a solar photo-Fenton process. IBR technology presents several advantages against a conventional active sludge (CAS) treatment: high biomass concentration which decreases the required volume of bioreactor, and it is more robust as it presents a buffer effect to treat different wastewaters. On the other side, photo-Fenton process is a well know technology within the scientific community due to its observed efficiency to organic contaminant removal from water.

Real municipal waste waters were collected from the MWWTP located at El Ejido (Almería, Spain). They rigorously characterized, including biodegradability test based on the study of the chemical oxygen demand (COD) different fractions. They were then treat by a pilot plant scale IBR installed at Plataforma Solar de Almería (PSA), which consists in a 20L column with a 90% of volume filled with K1 (AnoxKaldnes) supports. Water treatment was performed in discontinuous and continuous mode. Fresh wastewater was collected from MWWTP every two days for keeping the reaction volume constant at 30L. To monitor IBR performance several samples were analyzed daily by total organic carbon (TOC) and total nitrogen (TN) analyzer (Shimadzu-TOC-V CSN), ionic chromatography was also applied (Dionex DX-120 and DX-600) to check the proper mineral load inside the reactor as well as to observe the nitrification process. In order to observe the micro-pollutants behavior (removal, absorption, persistence, etc) during biological treatment, an advanced analytical process was carried out, consisting in a pre-concentration of samples by solid phase extraction (SPE) followed by liquid chromatography coupled to mass spectrometry (3200 QTRAP MS/MS, Applied Biosystems). Results were compared with those observed at the MWWTP secondary CAS treatment.

Effluents from the IBR, operating at the maximum treatment capacity, were treated by a previously optimized photo-Fenton process at pilot plant scale as tertiary treatment to entirely remove remnant micro-pollutant. This process was carried out at PSA using the compound parabolic collector (CPC) photo-reactor specifically designed for photo-Fenton application (total volume of 75L and 4.16 m<sup>2</sup> of illuminated area).

## Utilization of diatomite modified by ionic liquids for uranium ions adsorption from aqueous solutions

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The uranium pollution of the environment is connected in considerable extent with development of nuclear technology as well as with utilization of coal (coal fly ash), uranium-containing phosphate rock and phosphate fertilizers. The release of uranium into the environment leads to pollution of surface and ground water with some health effects to humans reported.

Adsorption of uranium ions on the natural diatomite from Borownica deposit (Poland) modified by ionic liquid ( $C_6H_{11}ClN_2$ ) has been studied as a function of contact time, initial uranium concentration and pH values by using a batch adsorption technique. The first order kinetic models have been used to analyze the adsorption kinetic results, whereas the Freundlich, the Langmuir, the Sips and the BET isotherms have been used to model the equilibrium adsorption data. The concentration of uranium was determined by the inductively coupled plasma mass spectrometer ICP – MS. The amount of the ionic liquid cation concentrations on the modified diatomite (5.8%) was calculated from the organic carbon content determined using a Analyzer TOC-5000.

Adsorption of uranium onto the diatomite modified by 1-ethyl-3-methylimidazolium cations as a function of time was expressed by a kinetic curve with three different stages, namely: an initial rapid stage of uranium adsorption, a stage with the rippling effect of adsorption/desorption processes and the third stage of adsorption slowly approaching to equilibrium. About 87% of the uranium had been removed from solution by within the first 5 minutes. The rate constant of the first stage was determined as 0.392 min<sup>-1</sup>. The final equilibrium was established after 240 minutes of the adsorption process beginning. This time period was used in the batch study of adsorption isotherms

The adsorption capacity of the modified diatomite increased with the increase of the initial concentration in the solution. The maximum adsorption capacity toward uranium was determined as 88 mg/g at an initial concentration of 500 ppm. Over 85% of the uranium can be removed from the solution with initial concentration up to 20 ppm. The results demonstrated also that the adsorption of uranium wasn't significantly dependent on of pH values of the solution. The adsorption effectiveness toward uranium increased from 72% to 87% in the pH range of 2.4 to 7.0 and decrease to 68% at pH = 8.6.

The results obtained in this study clearly reveal that the diatomite modified by 1-ethyl-3-methylimidazolium chloride may be used as an efficient adsorbent for uranium ions removal from aqueous solutions. The high efficiency of adsorption of uranium on a modified diatomite with solutions at low pH values is a particularly interesting result of the study.



## Transformation of Organic Contaminants in Plants

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By agricultural reuse of treated municipal wastewater in crop irrigation, by manuring or by the use of sewage sludge for fertilization poorly degradable organic pollutants are introduced into the soil system and may enter the crops and its edible parts.

A number of studies have investigated the uptake of organic trace pollutants from water or soil into agricultural plants and models have been developed to assess the extent of uptake. In most cases the plants have been considered as sinks for the contaminants in the sense that once taken up the contaminant would remain in the plant. Considering the limited capacity of plants to excrete non-gaseous compounds this appeared reasonable.

After having studied the uptake of a suite of contaminants from contaminated soil into agricultural plants such as carrots [1] we further investigated whether contaminant transformation occurs in plants after uptake. These studies were performed with two structurally related bactericides, triclocarban and triclosan, and its soil metabolite methyl triclosan. Transformations were studied using carrot cell suspension cultures [2].

Triclosan disappeared completely from the culture medium within 24 h and was continuously reduced in the cell material to < 10% within five days. For triclocarban and methyl triclosan the total concentration (culture medium + cell material) remained constant. Using liquid chromatography with high resolution tandem mass spectrometry (LC-QqTOF-MS) we could determine eight metabolites of triclosan and elaborate structure proposals for them. Seven of these metabolites were glycoside conjugates coupled via the phenolic moiety of triclosan, while the eighth metabolite was a sulfate. Triclocarban and methyl triclosan, which do not possess a free phenolic group, were not transformed by the carrot cells.

All eight phase II metabolites of triclosan could then be determined also in carrot plants grown in contaminated soil by LC-QqQ-MS with MRM detection. The total quantity of the triclosan metabolites exceeded the triclosan concentration in whole plants by about a factor of 5.

These findings indicate that the plant uptake of organic contaminants can be severely underestimated if plant metabolism is not taken into account. Further studies will show to which extent also phase-I metabolism has to be taken into account. Transformation of organic contaminants in plants also questions their use as biomonitors of environmental contamination.

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## Palladium biorecovery using anaerobic bacterial communities

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Bio-recovery of Platinum Group Metals (PGM), such as palladium (Pd (II)), from dilute industrial wastes can be considered an economically and environmentally attractive alternative to the use of chemical or electrochemical approaches aiming at their recycling. The use of bacterial communities simply enriched from environmental samples can be a promising solution for bioremediation and/or biorecovery processes. In addition, the ability of some bacterial strains to produce metallic nanoparticles (NPs) with unique properties and a multitude of applications has been reported [1,2] and is very important for industrial production. The main objective of this research was to find Pd(II)-resistant bacterial communities able to recover this metal from aqueous solutions. For that purpose the screening of sludge samples from different municipal wastewater treatment plants located in Algarve, Portugal, was carried out. The sludge was initially enriched in nutrient media with and without sulphate, under anaerobic conditions. Then, the enriched consortia were inoculated in the same conditions using nutrient media with similar compositions but containing different palladium (II) concentrations. Most of the enriched consortia obtained exhibited palladium resistance, but only one showed ability to remove palladium (II) from the growth medium. This community was able to remove 97% of Pd (II) from an aqueous solution containing 70 mg/L of Pd(II) in the presence and in the absence of sulphate. The Pd (II) removal mechanism was also investigated and it was verified that with the consortium grown with sulphate, the removal occurs mainly through the action of metabolic products, while for the consortium grown in the absence of sulphate, live cells were mostly responsible for palladium removal. TEM-EDS analyses are being carried out to verify the size and location of the palladium deposits, as well as a phylogenetic analyses of the 16S rRNA gene to identify the composition of both bacterial communities.

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## Intensified photocatalytic slurry reactor with a multitude of low intensity UV-LEDs for removal of micropollutants

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Photocatalysis is a promising technology for removal of micropollutants from waste water. Ultraviolet light emitting diodes (UV-LEDs) are possibly the best suited artificial light sources for photocatalysis. Some advantages are the long lifetime, the wavelength of emitted light can be selected, robustness and no use of toxic materials. Different designs for photocatalytic oxidation reactors exist, however the problem is that the different reactor designs either have good photon transfer to the catalyst or good mass transfer of the reactant to the catalyst. One design of a photocatalytic oxidation reactor is the slurry reactor. In this reactor the photocatalyst is present in the reactor as a fine powder resulting in a very good mass transfer of the reactant from the bulk of the liquid to the surface of the catalyst. To start the oxidation reaction the catalyst has to be irradiated with photons with the right energy levels. Because of the highly absorbing and scattering nature of the fine catalyst powder the photon transfer is poor in slurry reactors.

This research suggests increasing the photon transfer by irradiating a high surface area with a multitude of UV-LEDs distributed throughout the reactor, each with a low intensity. The goal was to compare one high-intensity UV-LED with a radiant flux of 0.2 W to 25 low-intensity UV-LEDs with the same combined radiant flux of 0.2 W. In this research titanium dioxide (TiO<sub>2</sub>) P25 from Evonik was used as the photocatalyst. The photocatalyst was added to the water resulting in a slurry system. The first hypothesis was that when irradiating a large surface area of photocatalyst with a low light intensity the photocatalytic oxidation rate would be higher than irradiating a small surface with a high light intensity. Second hypothesis was that with a multitude of low intensity UV-LEDs the loading (g/l) of TiO<sub>2</sub> at which the reaction rate is highest has to be higher compared to the high intensity UV-LED.

The results show a 2.5 times higher reaction rate for the 25 low-intensity UV-LEDs as compared to the one high-intensity UV-LED. The optimal loading for the high-intensity UV-LED was 0.5 g/l TiO<sub>2</sub> and for the 25 low intensity UV-LEDs the optimal loading was 2 g/l TiO<sub>2</sub>. When the average dose (J/m<sup>2</sup>) was calculated for the two systems the dose at the optimal loading of the two systems was in the same order of magnitude.

Irradiating a larger surface area with a multitude of distributed UV-LEDs resulted in a significantly higher reaction rate in a photocatalytic slurry reactor. With low-intensity UV-LEDs higher loading of catalyst is needed. The higher reaction rate and the higher loading of the photocatalyst results in a more intensified photocatalytic reactor. These results show a promising possibility to intensify photocatalytic reactors resulting in a way forward for the development of a large scale photocatalytic reactor and becoming a large scale technology for the efficient removal of micropollutants.

## Application of electrochemical processes for water and wastewater treatment

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Electrochemical processes have been intensively investigated for the removal of organic and inorganic contaminants from aqueous waste streams [1]. The unique ability of electrochemical processes to oxidize and reduce the contaminants at controlled electrode potentials and using only electrons as reagents represents a great advantage over other physico-chemical technologies. In electrochemical oxidation, oxidant species (e.g.,  $\text{OH}^\cdot$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ) are generated in-situ without the need for chemical addition, which represents a compelling advantage over competing technologies such as advanced oxidation processes. On the other hand, electrochemical reduction is an emerging treatment option for selective dehalogenation of persistent pollutants through controlled potential and selection of cathode material [2, 3]. Yet, high variety and complexity of waste streams makes overall evaluation of electrochemical treatment rather difficult, and further research is needed to ensure safe application of electrochemical processes. Within our research group, we have investigated the application of electrochemical processes for various types of contaminated water, including concentrated brine streams, hospital wastewater and even drinking water. This presentation will be an overview of the most interested results achieved.

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## Rapid and Cost-Effective methods for Detection of Environmentally Harmful Compounds from Waste Waters (RACE)

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According to EU regulations industries must be aware of the quality of their wastewaters. This includes knowledge on elements or compounds whose environmental release is limited or forbidden by EU. The aim of this research is to develop rapid and cost-effective monitoring methods for toxic compounds from industrial waste waters and harmful substances from municipal waste waters and natural waters. The monitoring methods that are being developed are based on optical spectroscopy and biosensor technology.

An on-line optical measurement method based on optical parameters (transmission, fluorescence, scattering and reflection) is being developed for monitoring process waters and/or waste waters. The basic measurement system consist of sample/rinsing lines, flow cell and measurement devices. The sample is guided by pumps through the measurement system and afterwards back to the process or waste. The operation of the system can be monitored on-line by wireless data transfer. The measurements of different optical parameters, several as spectrum data, give valuable information of the process by taking samples from one or several points of the process. It is also possible to customize the system according to the process and needs. The developed electrochemical biosensor is based on an enzyme inhibition method. The advantage of using biosensor is speed, sensitivity and selectivity. These techniques can be applied economically to produce environmental analyses and impact studies.

Two standardized eco-toxicity tests will be used will be conducted to compare and evaluate the developed methods. These traditional standard methods are: photo-bacterial light emission test with *Vibrio fischeri* (ISO 21338:2010) and *Daphnia magna* acute immobilization test (OECD guideline 202). The *Daphnia magna* test is among the most used tests in ecotoxicology having immobilization of the test organisms as the measured toxicity end point. The used kinetic photobacterial test has quite recently been standardized and has some improvements to the original test, enabling also testing soil, sediment and for example wastes water samples with colour. The original test has shown to correlate well with acute fish toxicity test. The measured toxicity endpoint is the reduction of emitted light from the bacteria.

## Application of early-warning system to identify surface water pollution

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The Water Framework Directive (2000/60/EC) was created as the long-term water policy of the European Union. Aim of the Water Framework Directive (WFD) is that the quality surface water reaches the good ecological and chemical state by 2015. This WFD has a number of objectives, such as preventing and reducing pollution, promoting sustainable water usage, environmental protection, improving aquatic ecosystems and mitigating the effects of floods and droughts. Improve and expand monitoring and assessment tools to ensure a statistically robust and comprehensive picture of the status of the aquatic environment for the purpose of further planning.

The project reviews both existing standard techniques and new innovative technologies with the focus on the early warning monitoring and control. On-line monitoring systems have been tested order to determine water quality.

The advantage of the continuous monitoring of the Stream Torna with the Accredited Water Quality Telemetry System (AVITAR-Mobile Water Monitoring Station) is that the changes can easily be detected. The AVITAR System was measured parameters (temperature, pH-level, conductivity). New analytical measuring Electrolyte Cathode Atmospheric Glow Discharge Emission Spectroscopy (ELCAD) that is able to direct analysis of the wastewater for heavy metal (Cd, Zn, Ni, Cu, Cr, Pb, Hg) pollution level. The Robotic Water Analyser (RWA) developed was adjusted, which is suitable to carry out real time measurements on  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N,  $\text{PO}_4^{3-}$ -P concentrations in the treated waste water. The measurements of the parameters are carried out on the basis of photometry with use of minimum amount of chemicals.

The results of the investigated monitoring systems indicated that the unexpected pollution in the water can be identifying by extreme in time (etc. midnight and weekends).

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## EU-wide monitoring survey on wastewater treatment plant effluents

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In the year 2010, effluents from 90 European wastewater treatment plants (WWTPs) were analyzed for 156 polar organic chemical contaminants. The analyses were complemented by effect-based monitoring approaches aiming at estrogenicity and dioxin-like toxicity analyzed by *in vitro* reporter gene bioassays, and yeast and diatom culture acute toxicity optical bioassays. Analyses of organic substances were performed by solid-phase extraction (SPE) or liquid-liquid extraction (LLE) followed by liquid chromatography tandem mass spectrometry (LC-MS-MS) or gas chromatography high-resolution mass spectrometry (GC-HRMS). Target microcontaminants were pharmaceuticals and personal care products (PPCPs), veterinary (antibiotic) drugs, perfluoroalkyl substances (PFASs), organophosphate ester flame retardants, pesticides (and some metabolites) or other industrial chemicals such as benzotriazoles (corrosion inhibitors), iodinated x-ray contrast agents, Gadolinium magnetic resonance imaging agents, and biological endpoints.

The obtained results show the presence of 125 substances (80 % of the target compounds) in European wastewater effluents, in concentrations ranging from low nanograms to milligrams per liter. These results allow for an estimation to be made of a European median level for the chemicals investigated in WWTP effluents. The most relevant compounds in the effluent water samples in terms of frequency of detection, maximum, average and median concentration levels were several organophosphate ester flame retardants and plasticizers (e.g. Tris(2-chloroisopropyl)-phosphate; TCPP), perfluoroalkyl substances (such as PFOS and PFOA), pharmaceutical compounds such as Irbesartan, Tramadol, Risperidone, Venlafaxine, Codeine, Fluconazole, Flecainide, Bisoprolol, Trimethoprim, Telmisartan, Ciprofloxacin, Oxazepam, Carbamazepine, Diclofenac, the insect repellent N,N'-Diethyltoluamide (DEET), the artificial sweeteners Sucralose and Acesulfame, benzotriazoles (corrosion inhibitors), iodinated x-ray contrast media, Caffeine, and Gadolinium. In addition, in several samples estrogenic and dioxin-like activity was detected by specific *in vitro* biodetection assays, as well as significant toxicity induced by some of the tested WWTP effluents in two aquatic organisms.

It is being discussed in Europe to upgrade WWTPs with additional treatment steps such as ozonation and/or carbon adsorption for the removal of micropollutants. Under the view of escalating population growth, reuse of treated water is becoming a more important option for water supply. The European Commission has set up a "European Innovation Partnership on Water" which supports (amongst others) such abatement techniques for emerging pollutants.

## **Boron- Doped Diamond - Boron-Doped Diamond Electroanalytical Detectors for Environmental Monitoring of Pharmacologically Active Compounds and Other Emerging Contaminants**

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Pharmacologically active compounds (PAC's, e.g. anti-inflammatory drugs such as paracetamol, beta-blockers, antibiotics and illicit drugs) are recognised as emerging environmental micropollutants at trace levels. Until recently there was minimal understanding and lack of data regarding the occurrence, fate, transport and exposure for PAC's, due to the absence of suitable analytical methods capable of detecting low concentrations of polar compounds within complex environmental matrices. Analysis with LC-MS instrumentation provided a sought after technique for investigating PAC's within the environment and with an ever-increasing collection of data has further developed knowledge in this research area.

However, despite continuing advances in LC-MS methodologies, limitations with the technique (high cost, complex/time consuming sample preparation, need for transport and storage, requirement of highly trained staff, inability to provide real-time measurements) requires the introduction of new analytical systems, such as electrochemical sensors, that can overcome the above mentioned limitations.

Generator-Collector voltammetric analysis allows for the electroanalytical detection of sub-micromolar concentrations of analyte due to an enhanced current response from 'feedback' between the generator and the collector electrodes. Here we demonstrate the use of a novel boron-doped diamond – boron-doped diamond (BDD) generator-collector electrode as an analytical tool for trace analysis. This setup allows the redox species to be detected in real-time demonstrating the fast response time of this technique. BDD as an electrode material is beneficial for this application as it has a wider potential window than other more conventional materials enabling detection of contaminants which have very anodic redox potentials.

Hydroquinone, Caffeic Acid and Paracetamol were the target compounds used in this study due to their similarity in structure and redox behaviour. Paracetamol was chosen as a "model molecule" for the development of an electrochemical sensor and Hydroquinone is a well-known redox active species, therefore extremely useful for comparative data. Various electrochemical parameters were investigated to improve the sensitivity of the generator-collector (working) electrode; one of which was gap size as this is of key importance to the detection limit of the sensor where smaller gaps are desirable for greater sensitivity.

This research will lead to the development of an electrochemical sensor with possible applications in monitoring PAC's and other small organic compounds within the aqueous environment.



## Detection of heavy metals, organotins and their toxicity with bioluminescent bacteria

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Chemical pollutions include inorganic contaminants, primarily metals, metalloids and organic micropollutants. The former are naturally present in the earth's crust, they are limited to the elements of the periodic table, and thus the resulting pollution is due to an enrichment that will have more or less a toxic impact to organisms. Organic pollutants originate from human activities are unlimited. For example, the European Community in 2001 published in the Official Journal a list of 33 priority substances to be detected in the context of water policy (No. 2455/2001/EC). Among these substances, organotins, metals, polycyclic aromatic hydrocarbons (PAHs) and long chain alkanes found in different environments such as polluted marine waters are classified as "priority hazardous substances". Monitoring of the pollution remains a necessity for the assessment of environmental policy.

A special issue in 2011 on the use of microorganisms for analysis provides a comprehensive overview of the current knowledge on biosensor microorganisms (Thouand, 2011). Microbial biosensors are advantageously applied in environment because they are able to account for the toxicity of an effluent or a chemical molecule (non-specific biosensor) or act as a specific biosensor for the measurement of a particular pollutant (metals, organotins, pesticides, ...). In all cases the organisms are sensitive to the bioavailable part of the pollutant, that is to say, the pollutant concentration which acts on a specific mechanism of microorganisms (respiration, DNA synthesis, ...).

The orientation of our research is to develop biosensors and bioassays using bioluminescent bacteria for all the main priority substances listed in European Country legislation, so far work has been done on organotin compounds and for heavy metals and pesticide. The group is now exploring developments of biosensor chips and microarrays for the detection of an overall toxicity or specific targets.

For the detection of heavy metals, a lack of specificity of the bioreporters triggered a specific research leading to the association of 5 bioluminescent strains, a specific software and a new concept of biosensor using long term preservation of the bacteria and avoiding any encapsulation. It allowed to specifically quantify a mixture of four heavy metals in environmental samples during a long time prefiguring robust and easy to use systems for on line monitoring in water (Jouanneau et al 2011 and 2012).

Sea water contamination remains often an ecosystem that is seldom taken into account. We focused on the detection of the prohibited organotin compounds (tributyl tin and dibutyl tin) known to be highly toxic. Organotin compounds especially tributyltin (TBT) have been widely used as biocide to prevent biofouling on ship hull. Even if the major antifouling paint companies have decided to comply with this regulation there is no simple way to control the application of this regulation. We have developed a bioassay based on the use of a recombinant bioluminescent bacteria to detect tributyltin and dibutyltin, one of its major degradation product. The genetic construction and the localization of the *lux* genes in the chromosome of this bacteria have been studied (Durand et al, 2003; Gueuné et al, 2008). The bioassay was tested on different commercial paint containing or not TBT, chemical analysis was done in parallel. The results show that the bacteria could detect the presence of TBT and DBT in the paint without any extraction procedure in one hour and also in waste water from shipyards. Due to its simplicity this bioassay could be used to control the application of the legislation on antifouling paint. These two examples will be used to illustrate the approach, the limits as well as the future of the detection with microbial biosensors.

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## Screening of arsenic in groundwater: a novel and green detection method

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The presence of arsenic in groundwater is a major problem in different areas of the world and affects a large number of people. Arsenic can be measured either in laboratories or by *in-situ* commercial kits. Laboratory based assays are generally required to accurately measure arsenic in environmental samples down to  $\mu\text{g/L}$  or even  $\text{ng/L}$  levels. However, expensive instruments (e.g. ICP-MS, HG-AAS) are usually required for such measurements. For sample screening or site survey purposes, field assays are preferred since they are relatively inexpensive and can produce a large number of results in a short time.

Several kits, based on the colorimetric reaction (Gutzeit method), for *in-situ* arsenic screening are commercially available. This method involves quantitative conversion of arsenic present in the water sample to arsine which finally reacts with mercury bromide impregnated in a paper strip. Despite the fact that the sensitivity of this method is appropriate, it consumes hazardous reagents.

We have designed a new method which combines a preconcentration step followed by a colorimetric reaction (based on the molybdenum-blue method for arsenic). This method does not require expensive instrumentation and can be implemented even in the field. It avoids the use of toxic reagents and allows semi-quantitative determination of arsenic by the naked-eye and quantitative determination by using a spectrophotometer. The preconcentration is based on the transport of anionic arsenic species present in water through a polymer inclusion membrane (made of polyvinyl chloride as the base polymer and Aliquat 336 as a carrier) placed in-between the sample and the receiving solution (0.1 M NaCl) [1].

This method has been validated and used to analyze several water samples naturally containing arsenic at  $\mu\text{g/L}$  levels from the region of Girona (Spain). Very good agreement has been achieved between proposed method and ICP-MS.

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## Ice cores for the reconstruction of historical input and migration behavior of POPs in Alpine glaciers

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Persistent organic pollutants (POPs) represent a group of anthropogenic organic substances, including industrial chemicals, pesticides, as well as unintentional by-products of combustion processes and chemical reactions. During the phase of application they were released to the environment and mainly distributed by atmospheric transport. Today, these hazardous chemicals are banned worldwide by the Stockholm Convention. Nevertheless, because of their persistence and volatility, they are still found and even enriched in remote mountain areas, far away from their initial emission sources.

In earlier work we have shown that melting Alpine glaciers represent an important secondary source of POPs that were previously deposited to and stored in these glaciers. (Bogdal et al., 2009;). In the frame of a follow-up research project on the role of glaciers as sinks and sources of POPs are investigated in detail on Silvretta glacier and Silvretta proglacial lakes, located in Eastern Switzerland.

We measure contaminant profiles in ice cores that serve both as an archive for reconstructing past atmospheric pollution and as a basis for predictions on the future release of these contaminants. The selected target chemicals, polychlorinated biphenyls (PCBs), are ubiquitous in the environment, though present in only very low concentrations in snow and ice samples. This analytical challenge resulted in the development of a suitable extraction method based on trapping of the analytes in the polydimethylsiloxane coating of an open tubular fused silica capillary. The method is characterized by minimal use of organic solvents and low susceptibility to laboratory background contamination.

We hereby show first results including concentration profiles from a glacial ice core obtained applying the mentioned technique. The temporal trends derived from concentration profiles of POPs are used for the validation of a recently developed chemical fate model.

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## Towards Highly Efficient Heterogeneous Magnetic Fenton Catalysts for the Degradation and Mineralization of Aqueous Organic Pollutants

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Advanced oxidation processes (AOP) are increasingly developed for wastewater treatment, since they lead to the generation of strongly oxidative hydroxyl radicals (HO<sup>•</sup>) which can mineralize numerous classes of toxic or non-biodegradable organic pollutants.[1] Fenton-like reactions are based on the production of HO<sup>•</sup> from hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in presence of a catalyst. They are among the most studied AOP, because of their low cost, high efficiency and the low toxicity of the reagents.[2] Traditionally, homogeneous catalysts such as ferric (Fe<sup>2+</sup>) ions are required. However heterogeneous catalysts have been recently developed. In comparison to homogeneous systems, heterogeneous Fenton catalysts don't require acidic medium, and can be recovered and reused without the generation of iron oxide sludges. Various examples of heterogeneous catalysts such as iron oxide particles or composites can be found in literature.[3] Good catalytic activities have been generally obtained but some drawbacks were still encountered such as Fe-leaching, and difficulty to recover the catalyst.[3]

The aim of our work is to optimise the efficiency, the stability, and the recovery of some heterogeneous Fenton catalysts constituted by maghemite nanoparticles ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP) dispersed in porous silica microspheres. The strong magnetic susceptibility of these materials implies that they can be easily recovered by a simple application of an external magnetic field given by a magnet or an electromagnet. This can be used to remove the catalyst from the effluent, with a better efficiency than conventional methods such as filtration or settling.[4] These materials were synthesized by sol-gel polymerization of silica in water-in-oil emulsions in presence of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP previously prepared by coprecipitation.[5] To comply with the requirements of green chemistry, the organic solvents used in the synthesis were replaced by vegetable oils.[5] The catalysts were characterized by various methods (electronic microscopies, adsorption volumetry, XRD, magnetometry...). Finally we thoroughly studied the influence on the degradation efficiency of several pollutants (dyes, phenolic compounds) of the catalyst structure, and of the conditions of the catalytic tests. We have especially shown that the dispersion of small  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP on a silica support can favour a high catalytic activity and may avoid the loss of the NP during the recovery of the catalyst.[6] We have also demonstrated the beneficial effect of an increased porosity in the silica, and the dramatic increase of the mineralization efficiency when silica is doped with additional iron species. These promising results may lead to test these materials at larger scale on industrial wastewaters.

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## Modification of graphite electrodes for the degradation of halogenated organic compounds: coupling of an electrochemical process with a biological treatment

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During the past few decades, degradation of refractory organic compounds in surface waters, ground waters and wastewaters have become of a major concern. In order to provide alternative technologies to biological treatments, novel processes such as Advanced Oxidation Processes have been widely studied. Since the complete mineralization of pollutants can be difficult to achieve and is often expensive, coupling of processes have also become of a great interest to reduce operative costs. The biodegradability of the effluent to treat is being improved during the pre-treatment stage, even though a high mineralization yield is not required because of the subsequent biological treatment.

We thus studied a promising electrochemical process coupled with a biological treatment. Our electrochemical pre-treatment is based on a home-made flow cell using a porous graphite felt of high specific area as a working electrode. Biological treatments are carried out in aerobic conditions with activated sludge from a local WWTP.

Many organic compounds are electroactive in oxidation and can thus be directly degraded at the electrode surface in such an electrochemical flow-cell. The performance of the electrochemical process was first studied in oxidation (1.6 V/ECS) to degrade a halogenated herbicide (2,4-D).  $96 \pm 3\%$  of the initial 2,4-D were degraded after the pre-treatment stage and  $34 \pm 4\%$  of the dissolved organic carbon were mineralized. The following biological treatment led to an overall mineralization of 85% with no acclimation of the activated sludge [1,2]. Most of the persistent organic pollutants being halogenated compounds, the specific removal of halogen groups from the substrate should be considered. Carbon-halogen bond reduction occurs at very cathodic potential and is thus difficult to achieve in aqueous media on the graphite felt. However, this reduction can be performed using Nickel and Cobalt based organometallic mediators. The graphite felt is a cheap material that is easily derivatized by chemical or electrochemical methods. Nickel and Cobalt mediators were immobilized on the electrode surface, covalently linked to the electrode or entrapped in Nafion<sup>®</sup> films. We studied the electrocatalytic reduction of carbon-halogen bonds of several halogenated target compounds as well as the influence of the dehalogenation on the biodegradability of these compounds.

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## Effect-based screening assays for water pollutions with endocrine disrupters, POPs, obesity and other toxicants

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Traditionally, mainly chemical monitoring systems are utilized to determine the presence of high risk chemicals to protect wildlife and humans. However, this chemical-by-chemical approach has significant limitations, as it detects only a very limited number of (priority) chemicals/pharmaceuticals, which can only associate risk with compounds if toxicological information is available and does not address the complexity of mixtures. This lack of information, together with a lack of proper analysis tools to screen with the same laboratory equipment for a wide variety of relevant toxicity endpoints (such as cytotoxicity, genotoxicity, endocrine disruptors, POPs and obesity) makes it favourable to work with high-throughput robotics and effect-based human cell-based reporter gene assays.

Our overview presentation aims to give an overview about a panel of stable transfected human reporter cell lines that allows rapid effect-based screening of hazards of pollutants in water life cycle (WWTP effluents/influents; surface water; drinking water) on multiple toxicological pathways such as (anti)-estrogenicity (ER CALUX), -androgenicity (AR CALUX), -progestinicity (PR CALUX), glucocorticoid (GR), -thyroid activity (TR CALUX), oxidative stress (Nrf2, ESRE, AP1 CALUX), obesity (PPAR $\alpha$ , $\delta$ , $\gamma$  CALUX), cytotoxicity, genotoxicity (P53 CALUX) and POPs-like activity (DR/PAH-CALUX). A broad initial screening on the ca. 50 available CALUX cell lines with a variety of relevant compounds with known toxicological profiles allows us now to detect relevant toxic endpoints from several known environmental pollutants such as endocrine disruptors (e.g. bisphenol A, phthalates), POPs (dioxins/dl-PCBs), obesogens (PFOA/PFOS, TBT), oxidative stress (organometals) or genotoxic compounds (PAHs) in the life cycle of water and water pollution.

We here report the current status of human cell based assays for many kinds of health related endpoints applied on drinking water, surface water, waste water, sediments and wildlife.

Results will be shown that address the potential and drawbacks of using such a panel of human cell based reporter gene assays to monitor complex mixtures of all kinds of chemicals/pharmaceuticals present in water, water treatment and human health.

## A doubly functionalised mesoporous silica nanoscavenger for the analytical extraction of tributyltin from water

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Tributyltin (TBT) is a highly toxic pollutant that occurs in the marine environment exclusively as a result of human activity. Interest in TBT measurement has been increased after the ecotoxicological effects of organotin compounds to non-target species became known around the 1980's<sup>1</sup>. A new analytical procedure has been developed for the determination of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in water samples. The method is based on the use of dual functionalisation of mesoporous silicas with diol and C<sub>18</sub> alkane groups for the collection of TBT and its derivatives DBT and MBT from water samples, followed by hexylation of the target matrices using a Grignard reagent and quantification by gas chromatography with pulsed flame photometric detection. The nanoscavenger concept replaces conventional solid and liquid phase extractants with nano-sized particles that can be readily dispersed in aqueous samples. Analyte partitioning between the solid and liquid phases occurs as the solid moves through the sample as a colloidal sol. By tailoring the size of the particles to approximately 250 nm diameters, they can be readily recovered together with the analytes by simple filtration or centrifugation. Recoveries of tributyltin, dibutyltin and monobutyltin chloride spiked matrices ranged from 90.2 ± 2.1 — 96.6 ± 3.7 in natural water and from 91.3±3.2—98.1±1.7 in sea water samples (n= 9 in both samples). The detection limit (the lowest detectable TBT concentration that can be reliably distinguished from zero TBT concentration with 95% confidence) obtained was 1.5 ng TBT (as Sn)/l. Repeatability (determined by analysis of 0.02 TBT (as Sn) µg/ml six times consecutively) and reproducibility (determined by analysis of 0.02 TBT (as Sn) µg/ml six times on three different days) were well below 8 % when the instrument was in routine operation. The proposed method will be very efficient in environmental monitoring programs of contaminants.

**Keywords:** Tributyltin, dual functionalisation, nanoscavenger, mesoporous silicas

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## Determination of estrogens in different types of wastewaters and technologies for their removal

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Estrogens are steroid hormones that help to regulate the growth, differentiation and function of reproductive tissues, as well as those of other organs such as the bones, brain and cardiovascular system [1]. The occurrence of these substances in aquatic ecosystems may affect the endocrine system of humans and wildlife so it has emerged as a major concern for water quality [2]. The content of estrogens in influents and effluents from two different types of wastewater treatment plants (WWTPs) (conventional, i.e. biological-mechanical and root-zone method (RZM) wastewater treatment plants as the real samples) was investigated in this study.

In our study we measured the concentration levels of four natural steroids (estrone, E1, 17 $\alpha$ - and  $\beta$ -estradiol, E2, estriol, E3) and a synthetic estrogen (17 $\alpha$ -ethynylestradiol, EE2) which exhibits the strongest estrogenic effects. Because of very low concentration of estrogens in the environment (sub-ng levels), development of a sensitive method for their detection and determination in different matrices was necessary. We took into account the effects of matrix which often strongly influence the accuracy of quantification. Two SPE steps (Florisil and NH<sub>2</sub> sorbents) were used for clean-up of SPE extract (OASIS HLB). In order to analyse such low concentration levels we used precolumn derivatization with dansylchloride.

Removal efficiencies of steroids found in investigated WWTPs were insufficient (lower than 69% for E3, <84% for  $\beta$ -E2 and <94% for E1) therefore we applied two different technologies for improving their removal. The technology using nanoiron (nZVI) and ferrates FeO<sub>4</sub><sup>2-</sup> has been tested in water samples from root-zone method WWTPs. It was shown that zerovalent nanoiron was not able to remove majority of all estrogens even at highest concentrations (50 mg l<sup>-1</sup>), whereas ferrates removed more than 99% of all estrogens in concentrations lower than 10 mg l<sup>-1</sup>.

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## Influence of Surfactant Loading and Interlayer Arrangement on Contaminant Uptake by HDTMA-Modified Montmorillonite

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Organic contaminants, including industrial chemicals, pesticides, pharmaceuticals, and ingredients of personal care products are ubiquitous in surface and groundwaters. Surfactant-modified clay minerals (i.e., organoclays) are receiving increased attention for use in removing such organic contaminants from water. In this work, we modified the interlayer environment of a Na-homoionized montmorillonite using the cationic surfactant hexadecyl trimethyl ammonium (HDTMA) at various loadings (nominally 0.5, 1, 1.5, 2, and 3x the cation exchange capacity (CEC) of the clay) and examined the influence of surfactant loading on contaminant uptake. Comparison of organoclay %C with Na<sup>+</sup>-release data revealed that at HDTMA loadings ≤1x CEC, nearly 100% of the surfactant sorbed to the clay, and sorption was dominated by ion-exchange processes. At greater loadings, the relative uptake of HDTMA by the clay decreased, and hydrophobic uptake of the surfactant salt became important. Xray diffraction (XRD) on both dry and water-saturated organoclays revealed a dramatic expansion of the interlayer spacing (from 7.5 to 25 Å) upon hydration of the 2x CEC organoclay, consistent with a conversion of the interlayer HDTMA from a pseudo-trilayer to a paraffin arrangement. This rearrangement has potentially important implications for contaminant uptake. At lower and higher HDTMA loadings, hydration had either a small or negligible influence on interlayer spacing, consistent with hydration of remaining interlayer Na<sup>+</sup> and exclusion of water from the hydrophobic interlayer, respectively. Sorption isotherms for common aromatic contaminants (substituted benzenes and polyaromatic hydrocarbons) were measured and interpreted in light of the loading and interlayer arrangement of HDTMA.

## Adsorption of Cr(VI) Using Magnetite Nanoparticles

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Magnetite ( $\text{Fe}_3\text{O}_4$ ) have been used to remove toxic Cr(VI) without knowing the exact mechanism : physisorption or chemisorption. In this study, we find that the collision of Cr(VI) with  $\text{Fe}_3\text{O}_4$  and chemisorption of Cr(VI) to the Fe atoms are crucial to the adsorption mechanism. OH groups could not adsorb Cr(VI) at the OH group concentration of  $4.84 \times 10^{-3}$  M and pH 2.5. Fe atoms of  $4.12 \times 10^{-3}$  M adsorbed 4 % of Cr(VI) and 47 % at pH 8 and 2.5 respectively. The chemisorption by coordination bondings between Fe atoms and Cr(VI) is the major bonding to the adsorption. Interaction between  $\text{Fe}_3\text{O}_4$  particles and Cr(VI) ions affects the collision.

## Anodic oxidation of sanitary landfill leachates at a Ti/Pt/PbO<sub>2</sub> electrode

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Due to its properties and composition, sanitary landfill leachate is one of the major environmental problems concerning water pollution [1]. Biological and physical-chemical processes, commonly used to treat sanitary landfill leachates, have shown to be inefficient in the treatment of these wastewaters containing persistent pollutants. In the last years, electrochemical methods have proved to be very effective in the degradation of complex effluents, namely sanitary landfill leachates [2-5]. However, it is critical to develop electrodes with a high activity for the oxidation of the pollutants and that have a long life. In this work, the electrochemical treatment of leachate samples from an intermunicipal sanitary landfill, collected at three different stages of the in-situ treatment, before and after the biological treatment and at the permeate of a final ultrafiltration operation, was carried out. The samples were first subjected to electrocoagulation, with consumable anodes, to remove colloidal and suspended particles. After that, anodic oxidation with a Ti/Pt/PbO<sub>2</sub> electrode was performed, to eliminate the remaining dissolved persistent organic compounds.

Ti/Pt/PbO<sub>2</sub> electrodes were prepared by thermal electrochemical method [6] and characterized by X-ray diffraction and scanning electron microscopic. Assays were followed by chemical oxygen demand, total organic carbon, ammonia and Kjeldahl nitrogen and UV-Visible spectrophotometry.

In order to maximize current efficiency, assays were run at moderate current density, i.e., up to 30 mA cm<sup>-2</sup>. Although the samples collected before the biological treatment have presented a slightly lower COD removal rate, due to the applied current densities, all the assays led to very high % COD removal, up to 95 %. From the obtained results it was possible to conclude that the combined treatment, electrocoagulation plus anodic oxidation with a Ti/Pt/PbO<sub>2</sub> electrode, can be an alternative to the recalcitrant effluents such as the samples treated.

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**Cork boiling wastewater treatment at pilot plant scale: comparison of solar photo-Fenton and ozone ( $O_3$ ,  $O_3/H_2O_2$  at different initial pH values). Toxicity and biodegradability assessment.**

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Cork processing includes a stage in which slabs are immersed in boiling water during one hour in order to improve their physic-chemical characteristics, requiring great volumes of water (around 400L per ton of cork). The resulting wastewater contains undesirable corkwood extracts (phenolic acids, tannic fraction, 2,4,6-trichloroanisol, pentachlorophenol, etc.) which are not easily removed by conventional treatments. Despite of their characteristics, these effluents are usually discharged into the environment without any previous treatment or directly to municipal wastewater treatment plants (MWWTP) involving active sludge low efficiencies, along with real environmental impacts to superficial and underground aquatic/soil systems. Provided that conventional biological processes cannot satisfactorily deal with cork boiling wastewater, one feasible option is the use of Advanced Oxidation Processes (AOPs).

Remediation of cork boiling wastewater was carried out at pilot plant scale by means of different treatments: solar photo-Fenton process and ozonation alone and in combination with hydrogen peroxide (at two different pH values). Moreover, the convenience of a physic-chemical pre-treatment was studied along with the efficiency of two flocculants ( $Fe^{2+}$  and  $Fe^{3+}$ ). After pre-treatment with  $Fe^{3+}$ , good removals of chemical oxygen demand (COD), dissolved organic carbon (DOC) and total suspended solids (TSS) took place. However, raw wastewater exhibited the best results after the solar photo-Fenton process, given that it required lower energy and hydrogen peroxide consumption than the pre-treated fractions. Ozonation tests were applied only to raw wastewater and  $Fe^{3+}$ -pre-treated wastewater. In this case, physic-chemical step favoured ozonation treatment, but no remarkable improvements were obtained when initial pH was increased from 7 to 10 or when  $H_2O_2$  was added.

Finally, it is important to highlight the increase of toxicity values for the real wastewater after the physic-chemical pre-treatment while biodegradability remained constant. On one hand, solar photo-Fenton process was not able to decrease the toxicity for the pre-treated fractions below the 50% threshold although biodegradability slightly improved after the treatment. Zahn-Wellens test revealed that at the end of the solar photo-Fenton process, high biodegradability percentages were attained after an adaptation period of the biological system. On the other hand, after ozonation treatments performed at initial pH 7, without hydrogen peroxide, toxicity showed a significant decrease and a biodegradability enhancement was observed for raw wastewater and  $Fe^{3+}$ -pre-treated wastewater.

## **Divalent heavy metal removal using a natural lignocellulosic based ion exchanger in a continuous bed up-flow process: sorption behaviour and modelling in single and multimetal mixtures**

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In the present work the valorisation of grape stalks (GS), an industrial by-product of wine elaboration, as sorbent for the removal of Cu(II), Ni(II), Pb(II) and Cd(II) from aqueous effluents has been investigated. Experiments were carried out in continuous in a fixed bed up-flow column. Sorption behaviour in single and multimetal mixtures has been evaluated.

In real sorption scenarios, when more than one metal ion is present in solution, interactions between them can take place, leading to competition for the same sorbent active sites. This competitive process in sorbent packed-bed columns provokes overshoots, characterized by a sudden increase above the feeding concentration of the metal and a further decrease to reach the concentration of the feeding stream. The overshoot and its magnitude are dependent on the adsorption affinity of the sorbates and their concentrations in the feeding effluent; sorbates with lower sorption affinity are displaced by those with higher sorption affinity. A good understanding of the competitive interactions and the development of a model that describes the competitive sorption is helpful in the accuracy of prediction of sorbent behaviour in simultaneous removal of two or more sorbates.

Characteristic breakthrough curves were obtained in single and in binary mixtures. In the binary scenario it was observed that Pb(II) is not overshoot in the presence of either, Cu(II), Cd(II) or Ni(II); Cu(II) is only overshoot in binary mixtures with Pb(II); Ni(II) and Cd(II) suffer more than 60% of metal sorption loose in binary mixtures when Cu(II) or Pb(II) are present.

A model based on the Homogeneous Surface Diffusion Model (HSDM) was developed to describe breakthrough curves. Langmuir model and Extended Langmuir Model (MEL) have been incorporated into the kinetic HSDM for breakthrough curves prediction of single and binary systems, respectively. The proposed model provides an accurate fit of the breakthrough curves of metal sorption in both, single and binary mixtures. In binary mixtures, the model also describes satisfactorily the elution profile of the overshoot metal ion.

## Chemical precipitation and anodic oxidation integrated process to treat sanitary landfill leachates

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Sanitary landfill leachates are a very complex wastewater, with colour and odour, containing different heavy metals, organic and inorganic compounds, some of them refractory and toxic [1]. Biological or physical-chemical conventional treatments have shown to be inefficient in the treatment of this kind of wastewaters and thus, the application of advanced technologies is required. Due to their effectiveness and ease in operation, electrochemical methods have recently received significant attention for wastewater treatment and several studies have reported the application of these methods in wastewater treatment [2,3].

In this study, the treatment of leachate samples from an intermunicipal sanitary landfill, collected before any kind of treatment, was carried out using combined chemical precipitation/anodic oxidation processes. Chemical precipitation (CP) was used as a first step, in order to remove colloidal and suspended particles, and after that, anodic oxidation (AO) was applied to eliminate the remaining dissolved persistent organic compounds. CP experiments were performed using hydrated lime as precipitant. Different precipitant concentrations were assayed. AO experiments were conducted with the supernatant of CP assays, in an undivided electrochemical cell, operating in batch mode with stirring. A BDD anode and a stainless steel cathode were used and different applied current intensities were tested. Assays were followed by chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>), dissolved organic carbon (DOC), total nitrogen (TN), Kjeldahl nitrogen (TKN), ammonia nitrogen (AN) and UV-Visible spectrophotometry.

According to the obtained results, CP and AO combined process can be an alternative to treat leachates from sanitary landfills. COD removals higher than 90% were achieved and TKN and AN were almost completely removed.

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## **Point-of-use treatment for Arsenic removal based on Adsorbia™ As600 resin**

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Millions of people around the world are currently living under the threat of developing serious health problems owing to ingestion of dangerous concentrations of arsenic through their drinking water. In many places, treatment of arsenic-contaminated water is an urgent necessity owing to a lack of save alternative sources. Sustainable production of arsenic-safe from an arsenic-contaminated raw water source is currently a challenge.

Different technologies are applied to remediate arsenic polluted water such as oxidation/precipitation, coagulation/coprecipitation, sorption and ion-exchange or membrane technologies. However, centralized treatment is not always a feasible treatment alternative, especially in areas where each home has a private well or where the treatment costs are prohibitive. In such instances, point-of-use (POU) treatment alternatives are more attractive and feasible since they are easy to install and operate.

We have focused or study on the commercial sorbent Adsorbia™ As600, which is a titanium oxide based resin with strong affinity for arsenic, lead and other heavy metals. On one hand, several laboratory experiments have been conducted to explore the effect of water composition on arsenic sorption, as well as the possible regeneration of the sorbent. On the other hand, this sorbent has been used as POU treatment to remove arsenic from well water. Consistent removal of arsenic has been observed in treated water, where other parameters such as silica, hardness and sulphates were also monitored in addition to arsenic.

## On site determination of free Zn<sup>2+</sup> concentration in river water

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The free metal ion concentration, rather than the total one, is the key parameter for toxic effects. Thus, analytical methods to assess the free concentration of various heavy metals, such as Zn, Cd, Pb or Cu, in natural waters are needed. In this context, AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has been specifically applied<sup>1</sup> to systems like Mediterranean seawater<sup>2</sup>, river waters<sup>3</sup> or dispersions of ZnO nanoparticles<sup>4</sup>. Amongst the validations, the one against DMT (Donnan Membrane Technique) in soils extracts and Rhine river water can be highlighted<sup>5</sup>. Recently, AGNES has been implemented with screen printed electrodes (SPE)<sup>6</sup>, which exhibit several outstanding features –specially when implemented with stripping chronopotentiometry– such as the lowering of the limit of detection, resolution of interferences and easy transportation<sup>7</sup>.

In this work, we focus on the application of AGNES to pristine waters of the Pyrenees. These measurements face two challenges: i) the very low ionic strength of the systems requires a judicious selection of AGNES parameters such as deposition potentials and deposition times<sup>8</sup>; ii) avoiding the purging of the sample is essential for an on site measurement. With no purging, the reduction of oxygen leads to a surface pH which is usually much higher than the one in the bulk of the solution. This shift in pH (which can be modelled with simple expressions) changes the local speciation close to the electrode surface. The oxygen interference can be reduced with sufficiently large buffer concentrations and can be cancelled by calibration in suitable media.

The practical implementation of on site AGNES to river waters from the Pyrenees confirmed that the addition of a background electrolyte, up to 0.01 M, does not distort the Zn<sup>2+</sup> speciation. Regarding oxygen interference, this can be minimised by calibrating AGNES in synthetic river water, which has some buffering capacity while reproducing well the changes in speciation of the sample (given the very low content of dissolved organic matter in these waters).

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## Induced nitrate attenuation in an artificial recharge pilot pond in Sant Vicenç dels Horts, Catalonia

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The artificial recharge system of Sant Vicenç dels Horts (Catalonia, NE Spain) consists of a decantation and an infiltration pond, which are recharged by water coming from the Llobregat River and/or from treated waste water. Both ponds were installed in 2007, in the framework of the ENSAT Life+ project. At the bottom of the infiltration pond a vegetal compost layer was installed to create favorable conditions for contaminant biodegradation. Preliminary results showed that this compost layer might enhance degradation of some emerging organic micropollutants (Barbieri et al., 2012). An induced denitrification experiment of groundwater was planned in the same area. The aims of the experiment were to assess whether ethanol can be used as a stimulant for in situ denitrification and to apply isotopic tools to study denitrification processes in the area (either induced by the pond compost layer or by the ethanol injections). An ethanol solution was introduced in an injection well, located close to the pond and upstream of the observation well. The transit time between the injection and the control wells was 7 days. Groundwater sampled at the control well was chemical and isotopically ( $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta^{13}\text{C}$ ) characterised. The  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  during the artificial recharge of the ponds prior to any ethanol injection ranged from +15 to +23‰ and from +10 to +16‰, respectively indicating that denitrification was already taking place, probably linked to the compost layer. Daily ethanol injections were performed during 5 consecutive days. 11 days after the first ethanol injection no changes in the isotopic signature were detected, indicating that the ethanol injections did not significantly enhance denitrification. Longer-term experiments and/or an increase in the ethanol quantity are proposed in order to enhance denitrification. These results allowed confirming that the compost layer was inducing denitrification in the recharge ponds area, proving the usefulness of an isotopic approach to characterize water quality improvement occurring during artificial aquifer recharge.

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### Acknowledgments

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## Cloud point extraction of Zinc in biological samples and determination by UV-visible spectrophotometry

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Three main sources that (Zinc) Zn is accumulated are air, water and food. As a result of its high frequency, wide industrial applications have been spread out. From the clinical standpoint, Zn plays a leading role in the activity of about 200 enzymes in the body, supporting our healthy immune system and growth during adolescence. Thus lack of zinc may cause disease such as, growth retardation, diarrhea, hair loss, eye and skin lesions and anorexia etc. Till now, the widely used techniques for determination of Zn are graphite furnace atomic absorption spectrometry (GFAAS) and flame atomic absorption spectrometry (FAAS). However some advantages such as speed and accuracy of these techniques will make them attractive, but their sensitivity is not quite sufficient to determine low concentration of the elements and also different factors such as presence of matrix effect will cause much more difficulties in direct analysis, moreover there is a need for us to devote more attention in the use of UV-visible spectrophotometry because of its high precision and simple accessibility. So in order to overcome the problems mentioned above preconcentration steps are required prior to determination process. Recently, separation techniques based on the formation of soluble aqueous complexes for metal extraction (CPE) have been used widely in analytical chemistry. Simplicity, consuming less toxic solvents and high preconcentration of factors are main advantages of this method which is in agreement with the principles of "Green Chemistry".

In the present work a CPE procedure was successfully used for separation and preconcentration of ultra trace concentrations of Zn ions prior to determination by UV-Visible spectrophotometry. The objective of this paper was to investigate the applicability of CPE for determination of Zn in biological samples such as sheep's brain. In order to recognize the accuracy and precision of the technique, various concentrations of Zn solutions from  $10^{-7}$  mol.L<sup>-1</sup> to  $10^{-10}$  mol.L<sup>-1</sup> were prepared and complexed with 1-(2-pyridylazo)-2-naphthol (PAN). At the optimum pH=9, extraction process accomplished using proper concentration of the surfactant named octylphenoxy-polyethoxyethanol (Triton X-114). The main parameters affecting extraction process, such as pH, concentration of surfactant and chelating agent were optimized. Under the optimized conditions the limit of detection (LOD), limit of quantification (LOQ) and linearity dynamic range for Zn were 0.1ng.mL<sup>-1</sup>, 1 ng.mL<sup>-1</sup> and 1-100 ng.mL<sup>-1</sup> respectively. The validation of this method was carried out by using analysis of variance.

Keywords: cloud point extraction, zinc, ultra trace, green chemistry, brain, uv-visible spectrophotometry

## Separation and Preconcentration of Trace Aluminum in Biological and Water Samples using Cloud Point Extraction

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Long term exposure to Aluminum ions is toxic and known to be a leading cause of common diseases such as dementia and abnormalities of skeletal system. It is therefore vital to be able to trace Aluminum at ultra-fine concentrations in both biological and environmental samples to avoid its taking by the body. Conventional techniques that have been used for preconcentration and extraction of aluminum are, liquid-liquid extraction, solid-phase extraction, each of these face the same difficulty of matrix effects and low concentrations of analyte. A possible solution for this issue is the alternative method of cloud point extraction (CPE), which is also in agreement with the principles of "Green Chemistry", due to low consumption of toxic surfactants compare to organic solvents. These surfactants are also non-flammable and present low volatility which can minimize the risks of extraction process.

In this investigation we examined the possibility of using CPE as a preconcentration method by UV-visible spectrophotometry to determine trace concentration of aluminum. The objective of this paper was to investigate the concentration of Al in biological samples such as bone tissues and also water samples. We hypothesize that it is possible to use CPE as a suitable processing method for both preconcentration and separation step in UV-visible spectrophotometry. To be able to recognize the accuracy and precision of the technique, various concentrations of Al solutions from  $10^{-7}$  mol.L<sup>-1</sup> to  $10^{-13}$  mol.L<sup>-1</sup> were prepared and complexed with 1-(2-pyridylazo)-2-naphthol (PAN) at the pH=9. As a result, Aluminum ions were successfully extracted by the formation of non-ionic surfactant's micelles of octylphenoxy-polyethoxyethanol (Triton X-114). Under the optimized conditions the detection limits, limit of quantification and linearity dynamic range for Al were 0.6 ng.mL<sup>-1</sup>, 1 ng.mL<sup>-1</sup> and  $1^{-10}$  (ng.mL<sup>-1</sup>) respectively. It was concluded that UV-Visible spectrophotometry, which is already a method of choice in most laboratories, can be a practical approach in evaluating trace concentration of toxic elements What remains is the issue of laborious sample preparation and time consuming process of centrifugation, which is believed to be overcome by on-line CPE procedure.

Keywords: Aluminum; Green Chemistry; Cloud Point Extraction; Bone; UV-Visible spectrophotometry

## Removal of Cyanobacterial Toxin Cylindrospermopsin by UV-mediated Advanced Oxidation Processes

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With the increasing occurrence of cyanobacterial harmful algal bloom events worldwide, it is vital to develop an efficient process to remove toxins that could be produced and released into drinking water sources. Cylindrospermopsin (CYN), although not detected until recently, is considered as a highly toxic cyanobacterial toxin that presents a potential health risk to ecological and human health. In this study, the effective removal of CYN from sources of drinking water supply by UV-mediated advanced oxidation processes (AOPs) was investigated. It was found that there was negligible degradation of CYN at a UV-254 nm fluence as high as 640 mJ/cm<sup>2</sup>; however, when the AOPs were applied, a significant improvement was achieved, suggesting the important roles of radicals, i.e., hydroxyl radicals and sulfate radicals. The presence of dissolved organic matter, as presented by TOC, UV-254 nm absorbance and fluorescence index, and alkalinity showed an inhibition on the destruction of CYN by the AOPs. The formation of hydroxylated-CYN confirmed the successful transformation of CYN, which provides us a better understanding of the mechanisms of the AOPs.

## The Elimination of Hazardous Compound for Environmental Protection: Photocatalytic Treatment of 4-Chlorophenol

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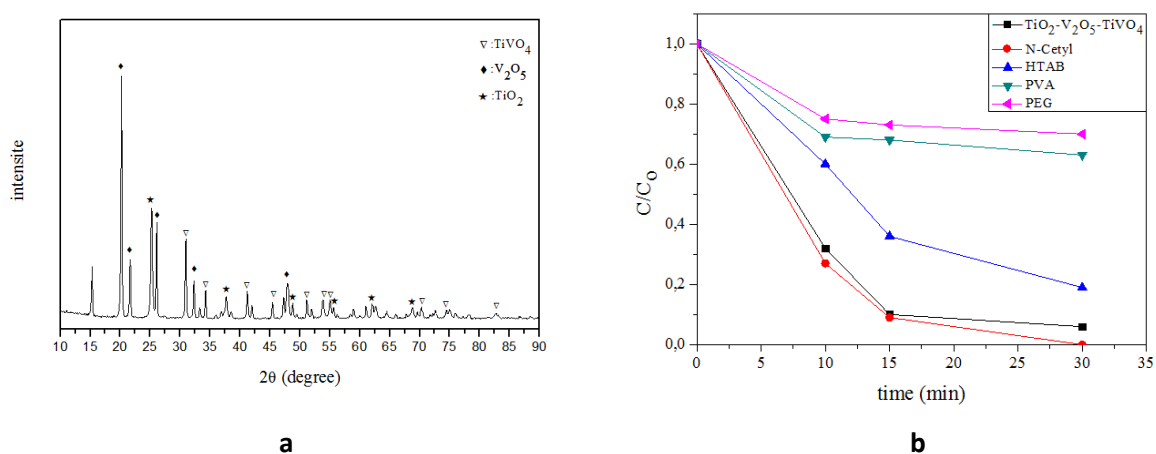
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Many studies have been conducted over the past few decades on semiconductor photocatalysts as sustainable material for environmental remediation. Titanium(IV) oxide (TiO<sub>2</sub>) is the most appropriate material for a photocatalyst because of its excellent properties, such as its high chemical stability, nontoxicity, and high oxidation ability. Therefore to date, TiO<sub>2</sub> and TiO<sub>2</sub>-based catalysts have been studied worldwide.

This study has been conducted for the purpose of reaching an ideal reaction conditions with using the most convenient photocatalysis. For this purpose, ternary metal oxides (TiVO<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>) are used that prepared by many different techniques and compared their activities for different light sources (UV-A, UV-B, visible, halogen lamps).

According to these results, under UV-A illumination, solid state mechanical mixing one attracts increasing attention due to its simplicity and effectiveness in terms of 4CP degradation in aqueous solution than TiO<sub>2</sub>. The catalysts were analyzed by various techniques (XRD, DRS, FT-IR, PL and SEM). The pattern of mixed metal oxide catalysts consists of TiVO<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> arrangements as depicted in Figure a and Figure b shows the concentration changes of 4 CP with time under various conditions



**Figure a)** X-ray diffraction of TiVO<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> ternary metal oxide photocatalyst.

**b)** Effect of light and surface-active substance for photocatalytic degradation of 4 CP.

The photodegradation process is completed within 90 min using a dose of 0.1 g/50 mL of the catalyst. To improve the photocatalytic activity of ternary photocatalysis, we added surface-active substances (CTAB, HTAB, PVA, PEG) by using solid-state dispersion method. CTAB showed a great deal of potential to improve photocatalytic activity to about 30 minutes under UV-A light irritation.

The present work describes that ternary metal oxide photocatalysts could be use to remove of phenolic substances from waste waters.

## APPLICATION OF SPME/GC/MS METHOD FOR DETERMINATION OF ORGANOARSENIC COMPOUNDS AND THEIR DEGRADATION PRODUCTS.

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Arsenic is present in various inorganic and organic chemical forms with different toxicities and mobilities in the environment. Many of these chemical species can be transformed due to biological activity or other changes in the environment, such as a change in oxidation-reduction potential and pH. This prospect of natural environmental changes creates the possibility that a wide variety of arsenic species are constantly transforming at any time. The main species of arsenic found in the environment are the arsenic (III) and arsenic (V) oxyacids. In many environments, the arsenic (V) is often deprotonated as an arsenic (V) or arsenate anion; in contrast the arsenic (III) oxyacid remains in its neutral form as arsenite. Groundwater and soil also contain organoarsenic species: monomethylarsenic acid, dimethylarsenic acid, trimethylarsine oxide, trimethyl arsine and other.

The paper presents method for methylarsonic acid (MMA), dimethylarsinic acid (DMA), phenylarsonic acid (PA), roxarsone and nitrasone determination. Solid phase microextraction with derivatization step was carried out and the species were analyzed by gas chromatography with mass detector. Analytes were derivatized with 1,3-propanedithiol (PDT) and then were extracted from the sample matrix by SPME with employed a 65  $\mu\text{m}$  polydimethylsiloxane divinylbenzene (PDMS-DVB) fiber. The limit detection and precision of the method was determined. The identification of photodegradation products of selected organoarsenic compounds in aquatic solution is presented in the paper, too.

## Photodegradation of estrogens in aqueous TiO<sub>2</sub> suspensions with UVA and UVC radiation

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There is growing concern over the potential risk posed by natural and synthetic chemicals that can produce adverse effects on human and wildlife by interacting with the endocrine system.

In this study the photodegradation of multicomponent mixtures of four powerful endocrine disrupting chemicals (estrogens) estrone (E1), 17 $\beta$ -estradiol (E2), 17 $\alpha$ -ethynylestradiol (EE2) and estriol (E3) was studied in the presence and in the absence of titania (Degussa P25) suspensions. Experiments were carried out with UVA and UVC radiation in a well characterized annular photoreactor. The results were analysed in terms of a simple first-order kinetic model, but including the explicit effect of photon absorption. This was accomplished by modelling the radiation field under heterogeneous (photocatalysis) conditions and by determining the spatial distribution of the local volumetric rate of photon absorption (LVRPA) in the reactor. The Six-Flux Absorption-Scattering Model (i.e., scattered photons follow the route of the six directions of the Cartesian coordinates) using optical parameters averaged across the spectrum of the incident radiation was used to determine the LVRPA. The intrinsic reaction kinetic constants, of E1, E2, EE2 and E3, independent of reactor geometry and level of radiation absorbed within the reactor were determined under each different oxidation conditions. The quantum yields (moles of estrogens degraded per Einstein of photons absorbed) were estimated. The quantum yields under UVC-TiO<sub>2</sub> photocatalysis were on average double the yields under UVA-TiO<sub>2</sub> photocatalysis. The established model was found to be appropriate to predict the time-dependent degradation profiles of the estrogens in multicomponent systems. Using this simple approach, intrinsic rate constants independent of reactor geometry and photon absorption can be obtained.

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**Comparative study regarding the treatment of contaminated groundwater from Căpuș area, Cluj region, Romania, by processes of adsorption on granular activated carbon and natural zeolite from Mirșid**

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The paper presents a comparative study regarding the performance of a natural zeolite and granular activated carbon (GAC) respectively, for treatment process of contaminated groundwater from Capuș, Cluj Region for nitrate removal. We showed that GAC presents higher adsorption efficiency than the natural zeolite from Mirsid. The equilibrium adsorption capacity of GAC and zeolite adsorbents for nitrate was determined. The adsorption isotherms were determined applying both Langmuir and Freundlich models. Based on the experimental data one established that the isotherms fits better Langmuir model in the case of GAC while in the case of zeolites Freundlich model was more appropriate.



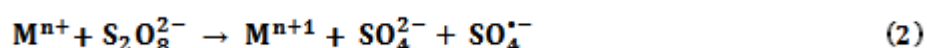
## Enhanced photo-Fenton oxidation of carbamazepine for water decontamination by using persulfate as an oxidant

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Pharmaceuticals have received increased attention as aquatic contaminants due to the occurrence of a large number of compounds at concentration levels in the ng.L<sup>-1</sup> to µg.L<sup>-1</sup> range in various water bodies. Therefore, it is very important to establish efficient treatment methods attaining for degradation and/or mineralization of these contaminants. Our work aims to establish an alternative for the well-known hydroxyl radical based advanced oxidation processes which are scavenged by various inorganic species and natural organic matter. Indeed, sulfate radical based advanced oxidation processes seem to be a promising alternative due to the higher selectivity of the sulfate radical anion (SRA) over hydroxyl radical (HR). Persulfate (PDS) was used to generate this highly oxidizing specie as illustrated in Eq (1) and Eq (2).



Carbamazepine (CBZ), an antiepileptic drug that resists to conventional treatment and persists in the environment, was chosen as a model contaminant. Different oxidation methods such as dark-Fenton and UV irradiation were tested. Photo-Fenton like techniques showed good efficiency and offered an environmental friendly source of radical species. Kinetic experiments in acidic solution (pH=3) were conducted in order to determine the optimal ratio for the pollutant removal with an initial concentration of 0.05 mM. A ratio of PDS:metal equal to 2:1 was found to totally remove CBZ in 30 minutes with an apparent kinetic rate constant of  $9.5 \times 10^{-3} \text{ mM}\cdot\text{s}^{-1}$ . Moreover, CBZ mineralization was achieved with a molar ratio CBZ: PDS equal to or over 1:40. CBZ removal is induced by the production of SRA in the early stage of the process and HR generation through ferric iron photo-reduction when the oxidant was totally consumed. Quenching studies with methanol and tert-butanol supported our hypothesis. During CBZ degradation, by-products were identified using a liquid chromatography coupled to high resolution mass spectrometry (with a mass error less than 3 ppm). The mechanism of degradation followed two distinctive routes. The ozonation-like pathway occurs through CBZ double bond attack and Criegee rearrangement. Two by-products (1-(2-benzaldehyde)-4-hydro-(1H, 3H)-quinazoline-2-one and 1-(2-benzoic acid)- (1H,3H)-quinazoline-2,4-dione) detected only in ozonation were identified in the early stage of the oxidation with a maximum at 5 min. HR-like pathway leads to the formation of hydroxylated intermediates such as epoxy-CBZ, acridine, hydroxy-CBZ, trihydroxy-CBZ, etc...The dual generation of HR and SRA has made Fe<sup>2+</sup>/PDS/UV process kinetically effective in removing CBZ both in distilled and wastewater without the accumulation of toxic intermediates.

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## Bioethanol production using water hyacinth grown in wastewater

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The ongoing depletion of fossil fuel reserves and the environmental pollution caused by such fuel raise the need for alternative sustainable fuels. Biomass-derived bioethanol may be implemented as a renewable source for transportation fuel and could become a good alternative to fossil fuels. Existing bioethanol sources are based on cultivation of agricultural that take up agricultural space designated for food production. Production of ethanol from lignocellulosic wastes has attracted much attention due to their availability, abundance and relatively low cost. The water hyacinth *Eichhornia crassipes*, a fast growing perennial aquatic plant which is widely spread around the world, is another source of lignocellulose. This plant has high hemicellulose content (30-55% of the dry weight) and may therefore serve as a source of sugars for bioconversion into bioethanol. In arid and semiarid areas, *Eichhornia crassipes* can be cultivated in reservoirs with partially treated wastewater, thus contributing not only to biofuel production, but also to a reduction in the wastewater organic load.

The production of soluble mono- or short oligo-sugars from hemicellulose can be performed by means of traditional multistage acid-base or enzymatic hydrolysis and, as proposed in this work, by a single-stage mechanochemical hydrolysis. The mechanochemical treatment was carried out by grinding the dry plant biomass in a ball planetary mill at various conditions. A 1.9 g/L concentration of the mono-sugar xylose was obtained from 1 g of air-dried biomass with the addition of 50  $\mu$ L of distilled water, which underwent mechanochemical treatment by milling with 10 mm balls for one hour at a 1/30 biomass to balls mass ratio. Transformation of the biomass paste into bioethanol was performed by fermentation with the yeast *Pichia stipitis*, which was chosen for its ability to efficiently consume xylose as a substrate. In further research, agricultural wastes may be added to the list of fermentation substrate sources and may lead to the elaboration of a conceptual scheme for the overall conversion of organic wastes and water plants into bioethanol.

## **Application of inorganic sorbents for removal of humic acids and heavy metals from water solutions**

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Humic substances belong to organic compounds widespread in soil and water environment. Main role in their origin play phenolic compounds being components of lignin and flavonoid compounds of plants. These are complex compounds, consisting of amino acids, heterocyclic forms of nitrogen and compounds containing alcohol, methoxy, carboxylic and quinone groups.

Depending on their structure, humic substances reveal various depending on pH solubility in water solutions. Fulvic acids are soluble in the whole pH range, but humic acids are soluble in alkaline solutions. Humic substance readily complex heavy metals.

The presented work is aimed at the development of effective method of bio-organic compounds and heavy metals removal from the sample water solution (pH 2-8) with the use of dedicated inorganic nano-powders as sorbents. The titanium, zirconium and yttrium nano-powders doped with rare earth elements were synthesized and tested. Nano-powders were applied either directly to the measuring system or prior to the measurements to the sample solution (and then centrifuged). The quantitative measurements applied for determination of organic compounds removal effectiveness were made using stripping voltammetry or by means of the differential double layer capacity measurements. The linear change of differential double layer capacity in relation of humic acids in wide concentration range was observed (up to 15ppm). The sorption effectiveness analysis of the used oxides was performed basing on heavy metals concentration measurements in solutions after sorbents centrifugation. The highest sorption effectiveness was found in solutions at pH value equal to 8.

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## Determination of organo-tin compounds with the renewable film mercury sensor

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Organo-metallic compounds due to their affinity to compounds present in living organisms and potential toxicity, are important and frequently monitored in the environment. Taking into account organo-tin compounds, they are of interest for over 150 years. About 800 of such compounds were identified, out of them methylated tin is especially dangerous for living organisms.

Potential toxicity and fate of the given compound depends on its solubility. Out of the methylated tin compounds (mono, di and three buthyl tin),  $Me_2SnCl_2$  is best soluble in water, and tri-buthyl tin is most toxic. In water environment, nM concentration of tri-buthyl tin leads to extinction of algae and animal constituents of plankton.

Two main aspects are presented herein. The first refers to the removal of organo-tin compounds (MBT, DBT and TBT) from aqueous solutions by applying titanium and zirconium nano-powders followed by their removal from the sample by centrifugation, and the second aspect consisting in speciation determination of remaining in the supernatant traces of organo tin compounds using highly sensitive sensor – renewable mercury film electrode  $/Hg(Ag)FE/$  - and differential pulse voltammetry (DPV) as measuring method.

### Acknowledgements:

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## Characterizing Water Quality for Photosynthesis Zone of Mosul Dam Lake, Northern Iraq by Means of Field Parameters

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### Abstract

The Mosul Dam Lake in Northern Iraq is one of the main reservoirs in Iraq with a surface area of 385 km<sup>2</sup> at the maximum operation level and a total storage volume of 11.13•10<sup>9</sup> m<sup>3</sup>. At five sites secchi disc visibility was read during July 2011 in a range between 0.9 and 6.1 m. The lower value (0.9 m) was at the outlet of Dohuk River where this outlet is located in the middle of the lake and transferring the pollutants to the lake. Simultaneously, 25 samples were collected from surface to 6 meter depth at the same sites. Water quality parameters included temperature, turbidity, chlorophyll-a, phosphorus, total inorganic carbon, dissolved organic carbon, total dissolved solids, electrical conductivity and pH. The pattern of vertical distribution of water quality showed variations with secchi disc visibility values for electrical conductivity, total dissolved solids, temperature, turbidity and phosphorus. The regression analysis gave us the significant empirical algorithms to calculate the turbidity depend on secchi disc values at the different depths ( $R^2 > 0.9$  and  $p < 0.001$ ). Also the signal regression analysis displayed significant correlation between the TDS and phosphorus concentration with secchi disc visibility at the most of the depths ( $R^2 > 0.7$ ). Furthermore, the multiple linear regression analysis was significant to calculate the turbidity, phosphorus concentration, and total inorganic carbon depending on simple routinely field parameters ( $R^2 > 0.5$  and  $p < 0.05$ ).

## Occurrence of ionic and non-ionic surface active agents in liquid samples collected in regions of varying intensity of anthropopression

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Surface active agents are group of specific organic compounds which are applied in different areas of human activity. After use they are discharged directly to surface waters or to wastewater-treatment plants (WWTPs), where surfactants can undergo numerous physical and chemical processes. Those aspects are potential sources of their emission to different ecosystems. Determination of surface active agents levels in environmental samples is important for the different parts of environment and the protection of human health.

This study examined the degree of contamination different liquid environmental samples (atmospheric deposits and precipitation, surface and run-off water collected in urban, rural and areas supposed to be free from contamination) caused by compounds from the group of cationic, anionic and non-ionic surfactants. Samples were collected in areas of varying intensity of anthropopression and capabilities of contamination with these compounds. Total concentration of analytes from mentioned groups was determined with application of modified standard methods (combination of liquid-liquid extraction and spectrophotometrical detection). All research data were analysed with use statistic methods (T-test, one factor analysis of variance, Pearson's correlation analysis) to estimate relationship between obtained results.

The average values of total concentration of cationic, anionic and non-ionic surfactants in samples collected at different geographical areas was ranged from  $0.070 \pm 0.049$  mg/L up to  $0.38 \pm 0.30$  mg/L,  $0.096 \pm 0.076$  mg/L up to  $0.60 \pm 0.44$  mg/L and from  $0.058 \pm 0.085$  mg/L up to  $1.3 \pm 1.2$  mg/L, respectively. Thus there is no statistic evidence to suggest a difference between concentration of every group of surfactants in samples collected in urban and rural regions (at the 5 % significance level). For results of samples collected in polar and air-port areas such differences were observed. To estimate strength and direction of association between two determined parameters (total concentration of anionic, cationic and non-ionic surfactants) were calculated Pearson's correlation coefficients. In presented study, there was a very high positive correlation between the variations of total concentration of ionic and non-ionic surfactants in atmospheric deposits (dew and hoarfrost) collected in urban and rural regions. For other types of samples, in most cases, no significant correlation between the degree of total concentration levels of determined surface active agents (except atmospheric precipitation from Arctic area).

### Acknowledgements

This work has been supported financially by the National Science Centre in Poland based on the decision DEC-2012/05/N/ST4 /01995. This research work was co-financed by the European Commission in the frame of the European Social Fund, by the European Social Fund, the State Budget and the Pomorskie Voivodeship Budget according to the Operational Programme Human Capital, Priority VIII, Action 8.2, Under-action 8.2.2: 'Regional Innovative Strategy' within the system project of the Pomorskie Voivodeship "InnoDoktorant – Scholarships for PhD students, V<sup>th</sup> edition".

## Occurrence and fate of ozonation by-products in Drinking Water Treatment Plant of Thessaloniki, Greece

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Over the last decades ozonation is applied increasingly in water treatment plants in order to remove organic micropollutants, disinfect efficiently and prevent the formation of chlorination by-products. However, several by-products such as carbonyl compounds, aldoketoacids, carboxylic acids and bromate are formed. The exact mechanism of their formation is not well known as well as their possible impact on human health.

The aim of this study was to investigate the occurrence and fate of carbonyl compounds as well as the concentration and characteristics of natural organic matter in the Drinking Water Treatment Plant of Thessaloniki, Greece. This plant receives surface water from Aliakmonas river and employs various treatment steps (pH correction, pre-ozonation, flocculation/coagulation, sand filtration, ozonation, filtration through activated carbon and chlorination) in order to provide 150000 m<sup>3</sup>/d of drinking water. Water samples have been collected after each treatment step every month for a period of one year. Samples have been analyzed for 14 carbonyl compounds after derivatization to their corresponding pentafluorobenzyl oximes, extracted with n-hexane and analyzed by GC/ECD, according to the EPA Method 556. Moreover, the dissolved organic carbon was measured as well as its characteristics including UV absorbance, fluorescence measurements, hydrophobic and hydrophilic fractions and biodegradable fraction.

The most predominant carbonyl compounds were formaldehyde, acetaldehyde, glyoxal and methyl glyoxal. The highest concentrations were observed after pre-ozonation treatment step mainly during spring. The relationships between the carbonyl compounds and the NOM characteristics were investigated.

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## Monitoring of Water Quality Using the Optical Cardiography of Shellfish

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One of the major environmental problems in megalopolises is the problem of water quality, first of all, in the water supply systems. In this respect it is very important to obviate the toxic effects on public health and to elaborate the new systems of monitoring of the water quality.

Whether water is biologically safe (a sum of non-additive factors) is determined by the response of a living organism (human, lab animals, cell cultures) to the water after it is consumed. Recently, with increasing frequency, the biological indication methods for water testing are used. An abrupt change in the behavior or physiological reactions of aquatic organisms is usually caused by certain water quality parameters. If this happens, delivery of drinking water from these sources must be discontinued until the reasons for change in behavior or physiological rhythms of the animals are found. Various living organisms serve as biological indicators: fish, crayfish and shellfish. Obviously, local species are preferred as they live in the same natural water which is used for water supply in the area, with the same temperature range and other physical and chemical factors.

Cardiac rhythm indicators have received considerable attention in biological indication studies and have been well-tested in practice. Using shellfish as bioindicators is related to their low mobility, which helps register their cardiac rhythm better and does not allow the shellfish to leave the affected area. In this study the abundant in the Moscow region ponds, swan mussels (*Anodonta cygnea*) were selected as an indicator material.

The experiments showed that if the toxic compounds are added to the water, the cardiac rhythm of the mussel changed, becoming considerably less regular. The twelve-channel optical cardiograph, which we have developed in this research (Fig.1), allowed displaying the cardiac rhythms, computing the cardiac rhythm periods, and carrying out long-term monitoring of cardiac rhythm changes.

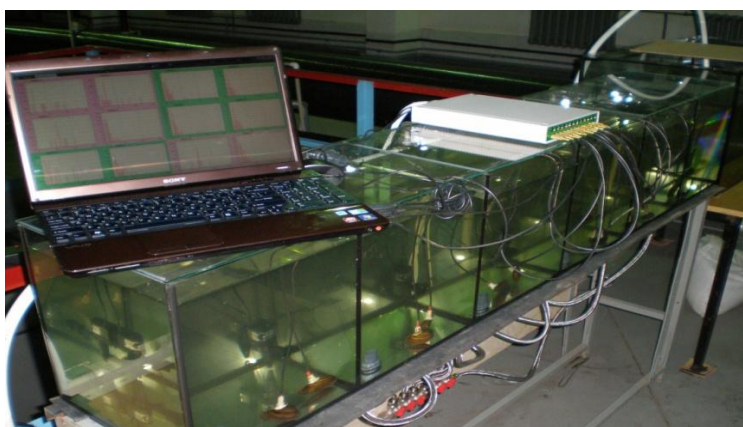


Fig.1. Optical cardiography system at one of the Moscow drinking water stations



## Pollutant Uptake from Water by Polycation-Clay Composites: an Experimental and Quantative Structural Activity Relationships (QSAR) Approach

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The clay mineral montmorillonite (MMT) is widely employed as an adsorbent in water treatment. In the current study the superior binding of hydrophobic and anionic pollutants to a MMT composite was achieved by adsorbing a hydrophobic polycation, polyvinyl-pyridine-co-styrene (PVPcoS) to the clay surface. The hypothesis is that specific chemical interactions between the pollutant and the polymer (such as electrostatic interactions, hydrogen and  $\pi$ - $\pi$  bonding) will yield higher removal efficiency in comparison with commonly applied sorbents. The PVPcoS-MMT composite has previously proved (experimentally) to have an advantage in pollutant uptake via column filtration methods in comparison to activated carbon. Adding a computational approach allows us to predict, compare and elucidate the removal capabilities of the composite.

The removal of 25 organic pollutants from various origins (PAHs, herbicides, pesticides, pharmaceuticals, fuel additives etc.) by the PVPcoS-MMT was tested. The resulting adsorption isotherms were fitted to the Freundlich adsorption model and  $k_d$  coefficients were extracted for a range of concentrations/activities. The adsorption trends evolved from S curves for relatively low adsorption through linear C curves to L and H- curves for the high affinity pollutants. Generally, pollutant affinity to the composite was high ( $\log k_d > 3$ ).

Quantative Structural Activity Relationships (QSAR) calculations were applied this group of pollutants. The adsorption coefficients were fitted to standard descriptors correlating to the classical Linear Free Energy Relationships (LFERs) descriptors (volume, excess molar refractivity, polarizability and hydrogen bonds acidity/basicity), and applied to three orders of concentrations /activities of the pollutants. Preliminary results show a moderate to strong dependence ( $R^2$  0.6-0.8) on hydrogen donor/acceptor properties and excess molar refractivity (which are indicative of bond formation through  $\pi$  and n electrons). Furthermore, a comparison with the available models (LFERs) applied to predict adsorption by activated carbon is carried out.

QSAR modeling gives an important insight into the governing adsorption mechanisms, enables comparing a wide range of sorbents and to predict the affinity of new pollutants to the polymer-clay composite.

## COD and heavy metal content variation during a combined electrocoagulation-electrooxidation treatment of a landfill leachate

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Solid wastes, some of them containing heavy metals, are disposed in municipal sanitary landfills. These heavy metals can remain trapped in landfills and eventually be released to the environment, due to generation of leachates caused by the water percolation through the solid waste. Many of the heavy metals present in leachates are problematic environmental pollutants, with well-known toxic effects on living beings. Thus, leachates have to be treated for removal of those heavy metals before they are discharged into surface waters [1]. The leachate treatments to reduce high contents in organic matter simultaneously with heavy metals represent a big challenge. In this field, several studies have proved the feasibility of electrochemical technologies, namely electrocoagulation (EC) and anodic oxidation (AO), for the treatment of these wastewaters [2,3].

In the present work, a synergistic combination of EC, using iron consumable anodes, followed by AO, with BBD anodes, was used and the COD and heavy metals (Fe, Zn and Cr) content removals were evaluated. COD and Fe, Zn and Cr determinations were performed according to standard methods procedures. The electrocoagulation experiments were performed at initial pH of 6 or natural pH (8.5), during 3 h, at an applied potential of 2.5 A. The electrocoagulation effluents were then submitted to anodic oxidation during 8 h, at a current intensity of 1 A. Both electrochemical methods were performed in batch mode.

After 3 h of EC, for initial pH of 6 and natural pH, COD removals were, respectively, 41% and 45%, and AO could further reduce COD above 77%, for both cases. In the EC assays, an initial increase in the iron content was observed due to the oxidation of the iron consumable anode. This initial increase was higher in the assay performed at lower pH, due to an extra dissolution of the anode by the acid effect. But for both initial pH tested, an iron content fluctuation occurs during EC, mainly due to the cycles of iron hydroxyl formation and precipitation. The Fe content further decreases during AO. The Cr was almost completely removed during EC and Zn is partially removed during EC, being the remaining part removed during AO.

In the coupled technique, electrocoagulation removes the colloidal and suspended particles, and diminishes the organic load and the heavy metal contents. After that, anodic oxidation oxidizes the remaining persistent organics and, simultaneously, heavy metal ions in solution are reduced to the metallic state at the cathode, being deposited over it.

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## New device for continuous measurement of trihalomethanes (TRIADEC)

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Trihalomethanes (chloroform, dibromochloromethane, bromodichloromethane and bromoform) are organic compounds generated as disinfection byproducts. Many trihalomethanes (THMs) are considered dangerous to health and the environment, even carcinogens. For this reason the World Health Organization recommends its control and regulation. The THMs formation is influenced by many external and environmental factors that can produce important fluctuations and exceed the legislation levels. For this reason it's necessary to continuously control THMs levels, which requires developing new continuous sampling devices to determine time average concentrations.

Labaqua has developed a device which consists of a small peristaltic pump controlled by an electronic board that governs its operation by pre-programming. A constant flow passes through a glass cell containing adsorbent material where the VOCs are retained. The adsorbent used, made in LABAQUA, is a mixture of alginic acid and activated carbon. Due to its high permeability it allows the passage and retention of THMs in a suitable way, thus solving many of the problems of other common adsorbents. After a sampling period of 7 days, the adsorbent is collected and analyzed in the laboratory to quantify the THMs average concentration. This device resolve some of the limitations of the classical sampling system (spot samples).

This study presents the results obtained by TRIADEC for quantifying the THMs. We present the validation of linearity over time and the limits of quantification, as well as the results of Sample Rate (Rs) obtained for each compound. The results demonstrate the high robustness and high sensitivity of the device. In addition the system TRIADEC has been validated in real drinking water samples, comparing the results obtained with this device with the values of classical spot sampling, obtaining excellent results.

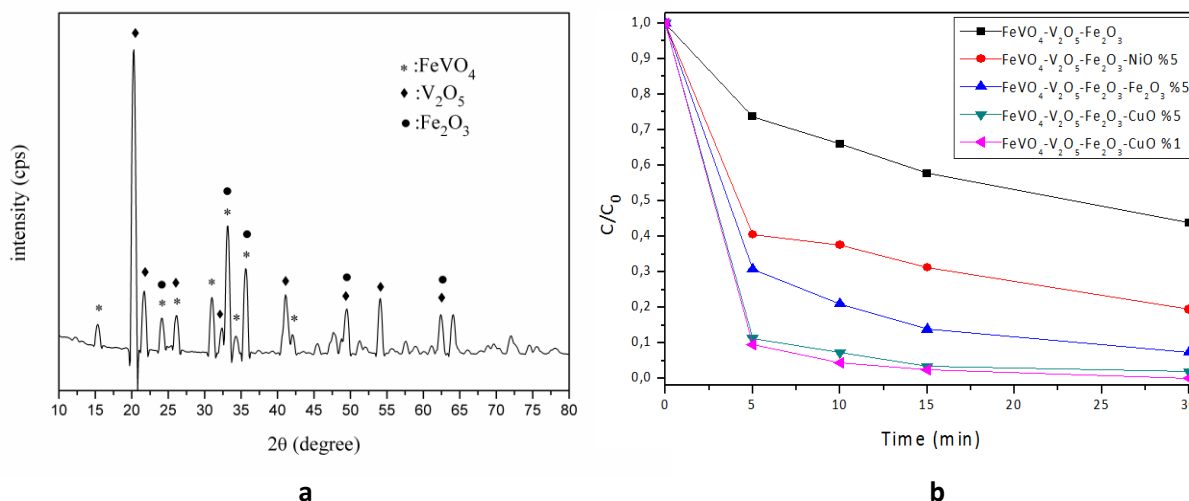
## Advances in the Environmental Applications: The Photocatalytic Removal of Organic Contaminant from Wastewater

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Chlorophenols represent an important class of environmental water pollutants. 2,4-dichlorophenol (2,4 DCP) is one of typical phenolic substances. The aim of this project is to study degradation of 2,4-dichlorophenol using inexpensive and nano-size photocatalysts by synthesizing simple method as soon as possible. Therefore, mixed metal oxide ( $\text{FeVO}_4\text{-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ ) photocatalysts are used that prepared by many different techniques (solid-state dispersion, solid-state mechanical mixing reaction, co-precipitation, hydrothermal treatment) and compared their activities. Under UV-A illumination, experimental results showed the mixed metal oxide complex that prepared by mechanical solid state mixing method have the higher photocatalytic activity in terms of 2,4-DCP degradation. The photodegradation process is completed within 90 min using a dose of 0.1 g/50 mL of the catalyst. Photocatalyst is improved with metal oxides that synthesized by microwave (CuO,  $\text{Fe}_2\text{O}_3$ , NiO) by using solid-state dispersion method. The catalyst doped CuO %1 showed a great deal of potential to improve photocatalytic activity to about 30 minutes under UV-A light. The reaction intermediates were identified by liquid chromatography (HPLC) technique. The catalysts were analyzed by various techniques (XRD, DRS, FT-IR, PL and SEM ).



**Figure a)** X-ray diffraction of  $\text{FeVO}_4\text{-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  ternary metal oxide photocatalyst.

**b)** Effect of metal oxide for photocatalytic degradation of 2,4-DCP.

Eventually, ternary metal oxide photocatalyst resulted in an enhanced efficiency for 2,4-dichlorophenol degradation. The catalytic activity was affected by the preparation method, light type and amount of metal oxides. The reaction results emphasize the achievement of the total mineralization. It is noteworthy to mention that, some structural features of catalyst play a significant role during the photocatalysis. These evidences also reveal that the system of mixed metal oxide catalytic materials can directly utilize sunlight and can be used to treat organic pollutants in practical wastewater treatment factories.

## Effect of pH on the photolysis and photocatalytic degradation of ciprofloxacin (kinetic and mechanism)

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Ciprofloxacin (CIP) is an antibiotic belongs to fluoroquinolone drugs, which has been widely used since 1987 for both humans and animals worldwide. CIP has been detected in hospital wastewater effluents<sup>1</sup> and also in the effluent of wastewater treatment plants (WWTPs).<sup>2</sup> This may lead to development of bacterial resistance resulting in toxic effects on fauna and flora.<sup>3</sup> Thus, the elimination of CIP from the wastewater is of main importance to meet the environmental and human protection. In this work, the influence of pH on the degradation kinetic of CIP in aqueous solution was investigated using two distinct methods: direct ultraviolet photolysis (UV-B irradiation) and photocatalysis (TiO<sub>2</sub>/UV-B system). A self-made lab scale batch reactor equipped with a 15 W UV-B lamp was used to investigate 500 ml of CIP with an initial concentration of 60 μM l<sup>-1</sup>. The degradation kinetic was evaluated at four different pH values (3, 5, 7 and 9) and the transformation products were also determined using liquid chromatography tandem mass spectrometry (QTRAP and QTOF LC/MS/MS). The kinetic study showed that the degradation of CIP for both photolytic and TiO<sub>2</sub>/UV-B photocatalytic process follow the first order kinetic with highest removal rates at pH 9 ( $K_{UV} = 3.6 \cdot 10^{-4} \text{ s}^{-1}$ ;  $K_{TiO_2/UV} = 4.1 \cdot 10^{-4} \text{ s}^{-1}$ ). The removal rate becomes slower when the pH value decrease ( $K_{UV} = 4.0 \cdot 10^{-5} \text{ s}^{-1}$ ;  $K_{TiO_2/UV} = 1.2 \cdot 10^{-4} \text{ s}^{-1}$  at pH 3). The transformation photoproducts proposed using the accurate mass, indicate that photolytic and photocatalytic degradation take place at the piperazine core including dealkylation (M-69,  $m/z = 263$  and M-28,  $m/z = 304$ ), formation of alcohols (M+30,  $m/z = 362$ ) and amides (M+14,  $m/z = 346$ , M+30,  $m/z = 362$  and M+2,  $m/z = 334$ ).

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## Electrochemical biosensor development for detection of eco-toxicological compounds in wastewater

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The aim is to develop an enzyme based biosensor for monitoring eco-toxicological compounds in industrial process wastewater streams. There is a need in many modern industrial processes to monitor the concentration of potentially toxic compounds at the end of a process line and in waste water to determine if their extraction processes have been effective and if the process water can be released into waste water reservoirs before being released to the natural environment. Environmentally harmful chemicals are often removed by liquid extraction, filtration and finally the process water is cleaned with activated carbon filtration. In order to ensure that this process is working at optimum capacity it is important to have a sensitive monitoring system that can detect if and when the activated carbon filter reaches full capacity and needs to be reactivate as to avoid the leaching of toxic chemicals.

The biosensor that is being developed is an amperometric sensor based on a neurotoxin enzyme inhibition format for the detection of multiple toxic compounds using cholinesterase enzymes. Butyrylcholinesterase (BChE) and Acetylcholinesterase (AChE) are important enzymes present in vertebrates and insects. These enzymes are inhibited by several toxic chemicals such as organophosphate and carbamate pesticides, heavy metals, nicotine, nerve gas and anatoxin-a(s).

In the development of the biosensor, different screen printed electrodes have been tested and Prussian blue and cobalt phthalocyanine electrochemical mediators have been compared. Sensor surface modification of the mediator on to the working electrode was made by either pipetting by hand or by printing with carbon ink using screen printing process.

Preliminary result of for the biosensor show that BChE inhibitor organophosphorous pesticide Paraoxon gives a good calibration linear range between 0.5 and 5 ppb and the detection limit is 0.5 ppb. Real industrial water samples and communal waste water samples are to be tested with developed biosensor and the results will be compared with standardized eco-toxicity tests.

## **Fast and 'green' multi-residue methods for the determination of emerging pesticides from various chemical groups in water samples by gas chromatography**

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The wide and large number of pesticides applications has resulted in an extension beyond agricultural applications into many other parts of the environment. These compounds pose a particular threat in natural waters and the various processes they undergo in the aquatic environment may cause them to be converted into substances of greater toxicity. Therefore, constant monitoring of these xenobiotics in the environment is needed.

Pesticides may be present in the environment at low concentrations, in complex matrices, meaning sample preparation and analysis is time-consuming. In addition to national guidelines, international legal regulations imposed by the EU concerning the permissible level of pesticide residues in water, have driven the development and improvement of novel analytical techniques towards multi-residue analysis, low limits of detection and the use of small sample volumes. The improvements of existing techniques are aimed at miniaturization, automation, and the use of solvent-free techniques at the sample preparation stage, that are consistent with Green Chemistry principles.

A simple and 'green' analytical methodologies to control and monitor the level of currently used pesticides from different chemical groups in aqueous samples will be presented. For extraction of analytes solid - phase microextraction (SPME) and dispersive liquid - liquid microextraction (DLLME) have been applied and compared. For the identification and quantitative determination gas chromatography coupled with mass spectrometry (GC-MS) was applied. The analytical procedures were validated and applied to natural water samples from river, lake, sea, canal and rain collected around Paisley region (Scotland, UK) and Tricity area (Poland). The developed analytical methods are simpler, lower costs and less labor intensive sample preparation techniques, than conventional techniques and can be used in monitoring studies to control the content of selected pesticides in water samples.

## Removal of priority pollutants from water by clay-vesicle complexes

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The occurrence of organic micropollutants in the sources for drinking water supply has been detected in the last few years. These micropollutants or emerging contaminants (ECs) have a great potential risk for drinking water supply because of their high water solubility and often poor degradability, which allow them to penetrate through all natural filtration steps and treatments for water purification. Moreover, they do not need to be persistent in the environment to cause negative effects due to continuous introduction (high fluxes). These organic emerging contaminants are suspected to cause in humans serious effects such as malformations of newborns, abnormal thyroid function, breast and prostate cancer... Therefore, drinking water industry is focusing on the development of new treatment processes for removal of POPs and ECs because of their ubiquity and adverse effects on humans and environment.

The main types of treatment processes for production of drinking water are: clarification/coagulation, filtration with granulated (GAC) or powdered (PAC) activated carbon, oxidation using chlorine or ozone, and membrane filtration. Filtration using GAC is widely-used and very effective in the removal of organic pollutants.

In this study, clay-based composites were designed for their use in filtration systems aimed at eliminating the presence of ECs such as the pharmaceutical ibuprofen, and the herbicide MCPA. The use of filters made of these materials can increase the effectiveness of other conventional processes in water purification processes or even be an alternative. The composites were based on the sorption of vesicles made of the organic cation didodecyldimethylammonium (DDAB) on the negatively charged clay mineral montmorillonite. The complexes were prepared in excess of positive charge and also presenting large hydrophobic domains. The performance of filters containing the clay-based composites was examined for removal of both pollutants and compared to those based on GAC. The initial concentration of IBF and MCPA was 100 mg/L. Saturation of the GAC filters was reached for IBF and MCPA after seepage of 67 and 133 pore volumes, respectively. On the contrary, clay-DDAB based filters were saturated after the seepage of 533 pore volumes. This larger efficiency was related not only to the larger sorption capacity of the clay-DDAB complex but also to its rapid kinetics for the sorption of both pollutants.

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## Photodynamic Disinfection of Wastewater Using Photosensitizers Immobilized in Polymers

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In the countries that have limited natural water resources, a use of treated wastewater for irrigation can become a solution for water shortage, but pathogenic wastewater microorganisms could pose a threat to the population. To avoid health and ecological hazards, the wastewater treatment should include a stage of disinfection. While the existing methods of eradication wastewater bacteria are based on a use of aggressive chemicals such as hypochlorites, chlorine dioxide and ozone, or power-consuming physical methods such as UV radiation, an alternative approach to disinfection of wastewater may involve photosensitizers immobilized in a solid phase. This approach includes excitation of photosensitizers by visible light followed by energy transfer from molecules of the photosensitizers to the dissolved in wastewater oxygen, producing reactive oxygen species, which cause direct and indirect irreversible damage to cellular components of bacteria and induce cell death. In our work the antimicrobial activity of immobilized in polymers photosensitizers was tested against sewage bacteria. As photosensitizers we chose two species soluble in both aqueous and organic solution - Rose Bengal and Methylene blue, and as polymer supports we used polystyrene, polycarbonate and polymethyl methacrylate. In a batch regime, the immobilized photosensitizers showed high antibacterial activity resulting in a 70-100% decrease in bacteria concentration. Photosensitizers immobilized in polystyrene and polycarbonate showed higher activity than those immobilized in polymethyl methacrylate.

## Synthesis of a novel octabrominated dimethoxydiphenyl ether (diMeO-octaBDE) and identification of its phenolic analogue in blue mussels from the Swedish west coast

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Hydroxylated (OH-), methoxylated (MeO-), diMeO-, OH-MeO-, and diOH-polybrominated diphenyl ethers (PBDEs) are compounds present in the marine environment and have been detected in e.g. marine sponges, algae and mussels.<sup>1,2,3</sup> All of these have been shown to be natural products, although OH- and diOH-PBDEs can also be metabolites of anthropogenic PBDEs and the former three have been shown to bioaccumulate in wildlife.<sup>1,4,5,3,6</sup>

In a previous study, an unknown compound was detected in the acidic fraction of blue mussel samples from Fladen and Väderöarna, on the Swedish west coast.<sup>2</sup> An octabrominated compound was of highest abundance in the mussel samples and was tentatively assigned as diMeO-octaBDE, identified as its methyl derivative based on its fragmentation pattern on GC/MS-ECNI.<sup>2</sup> In the present study, a synthesis method for 2,2',3,3',4,4',5,5'-octabromo-6,6'-dimethoxydiphenyl ether (6,6'-diMeO-BDE194) was developed and partly optimised with the purpose of serving as an authentic reference standard in order to identify this compound in blue mussel samples. The analyte was assumed to be of natural origin, wherefore 6,6'-diMeO-BDE194 was hypothesised as the congener of interest. The synthesis was conducted via the novel unsymmetrical diaryliodonium salt, 2,3,4,5-tetrabromo-6-methoxydiphenyliodonium triflate, which was coupled to 2,3,4,5-tetrabromo-6-methoxyphenol, similar to previously published methods.<sup>7,8,9</sup> 6,6'-DiMeO-BDE194 was identified as its methyl derivative in the Fladen mussel extract analysed by Löfstrand et al<sup>2</sup> and identified and quantified with an external standard in new mussel samples from the present study. Results showed mean concentrations of 4200 and 430 ng/g l.w. of 6,6'-diMeO-BDE194 in the mussels from Fladen and Väderöarna, respectively. Determining whether the octaBDE-analyte is diOH and/or OH-MeO also lies within the scope of this study.

### Acknowledgements

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## Physicochemical degradation of iodipamide – quantum yield calculation

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Iodipamide is one of the iodinated contrast media (ICM), which are detected in aquatic environment in wide range of concentrations. It is caused by their biological inertness and incomplete elimination in biological processes at wastewater treatment plants. The study concerns the possibility of iodipamide removal by means of UV light and calculation of quantum yield for investigated substance.

The photochemical pretreatment of the wastewater was carried out in a 350 mL glass reactor equipped with a medium-pressure mercury lamp, with the emission spectra from 255 nm to 579 nm (UVI LabP400, Vita Tech, Germany). Iodipamide in the aquatic samples was determined by means of high-performance liquid chromatography (HPLC - Ultimate UVD 3000; Dionex/Gynkotek). The Hypersil Gold Column (Thermo Scientific) was used as the HPLC column. The analysis were performed in a reversed-phase system. The mobile phase was composed of acetonitrile, Milli-Q-water and acetate buffer in a volumetric ratio of 50:40:10. A flow rate of the mobile phase was 0.6 mL/min. The detection wavelength was set at 238 nm. Under described condition, the retention time of iodipamide was equal to  $2.4 \pm 0.1$  min. An external standard method was used for its quantification.

The examination with photochemical processes lasted 60 minutes. The samples were grabbed in 0, 1, 2, 5, 10, 20, 30, 45 and 60 minutes of reaction.

During photochemical processes the maximum degradation efficiency exceeded 90%. The calculated quantum yield of iodipamide degradation was equal to 0,03.

## **The influence of sludge retention time on the efficiency of the iodinated X – ray contrast media removal in aerobic and anaerobic membrane bioreactors**

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A lot of studies have revealed that unmetabolised drugs enter the sewage system and, later, appear in the wastewater treatment plants. The treatment process in the plant usually fails to completely eliminate the drugs from wastewater. In consequence, the drugs, together with treated wastewater, are released into surface waters.

Iodinated contrast media (ICM), substances, which are used for imaging tissues, internal organs, etc., are commonly detected in aquatic environment in concentrations up to several milligrams (i.e. hospital wastewater).

The main aim of the study was to investigate the possibilities of the chosen ICMs (iohexol, diatrizoate, iodipamide) removal in aerobic and anaerobic membrane bioreactors (MBR). Five membrane bioreactors were operated at different sludge retention times (SRT) (from 24 days to 100 days) with the hydraulic retention time (HRT) of 67 hours. The synthetic wastewater (1100 mgCOD/L<sup>-1</sup>, 60 mgNH<sub>4</sub><sup>+</sup>-N/L<sup>-1</sup> and addition of ICMs) was used as a feed to bioreactors.

The results showed, that SRT seems to have relatively high influence on the efficiency of diatrizoate removal in aerobic (24% and 57% for SRT 24 and 40 days, respectively) and anaerobic conditions (72% and 89% for SRT 40 and 100 days, respectively). The SRT has also influence on the elimination of iodipamide in aerobic conditions (12% and 32%, respectively), however there is no such dependence in anaerobic conditions (around 40% in all bioreactors). In case of iohexol, the elimination was not dependent on the SRT in aerobic (around 30% in all bioreactors) as well as in anaerobic bioreactors (around 15% in all bioreactors).

## Water Purification by Photo-catalytic Destruction of Pollutants

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### Abstract

Many industrial processes (e.g. olive oil production and dye manufacture) produce water soluble organic pollutants including phenol. These need removing before the water can be actually discharged. Technologies use adsorption and filtration methods to counteract the release of such pollutants [1]. However, from an economic viewpoint, adsorption technologies usually require the use of activated carbons which are expensive to produce and regenerate. This has led to an unrivalled interest in the use of re-useable, cheap inorganic adsorbents such as natural clay materials (montmorillonites). These clays can be used as supports for heterogeneous catalysts for the destruction of phenols through photo catalytic processes, releasing carbon dioxide and water [2, 3]. These clays are often used in the presence of an environmentally benign oxidant such as hydrogen peroxide (Fenton processes) and they require light to enhance the photodecomposition (photo-Fenton) process; preferably in the visible region.

We have set out to develop a non-polluting, efficient, cheap and sustainable method for water treatment using magnetite clay nanocomposites (containing iron(II) as well as iron(III)), visible light and hydrogen peroxide as co-oxidant [4].

Herein we report the development of several different clay mineral magnetite clay nanocomposites that are effective in degrading phenol via hydroquinone, catechol, para-benzoquinone, maleic acid and oxalic acid to carbon dioxide and water. The time taken to remove the majority of the phenol pollutant has been reduced from several hours to much less than an hour at room temperature with visible light. However, small quantities of the penultimate degradation products, maleic acid and oxalic acid, still remain even after further addition of hydrogen peroxide. Future work will look to remove these low quantities of acids (<1 mol% of the starting phenol) and improve the use of oxygen (which appears to have an effect) in place of hydrogen peroxide in this promising water purification process.

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## Use of soluble bio-based substances isolated from urban biowastes as organic photocatalysts for the degradation of 4-chlorophenol.

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Natural organic matter (NOM) present in terrestrial waters and soil is known to contain light-absorbing species capable of promoting photochemical reactions that are considered as the major abiotic pathway for the removal of xenobiotics from natural waters. Recently it has been shown that soluble bio-based substances (SBO) isolated from urban biowastes (UBW) have similar chemical composition and photosensitizing properties as NOM. Since SBO may be obtained from easily available cost-effective sources, their performances as organic photocatalysts have been recently considered and encouraging results have been obtained [1,2]. Moreover the use of urban wastes as source of bio-based photocatalysts is rather appealing in the context of the current issues of waste management [3].

The present work aims to optimize the photodegradation promoted by SBO of 4-chlorophenol, a priority toxic and hardly biodegradable pollutant. Many aspects of the process have been investigated at the laboratory scale using simulated solar light: the effect of SBO concentration, the operative pH, the degradation mechanism, the main reactive species involved and the toxicity evolution. Moreover the effect of added hydrogen peroxide on 4-chlorophenol degradation rate has been considered, since the presence of iron inside SBO structure let envisage synergistic Fenton-like processes; at this purpose design of experiments (DOE) was chosen as methodologic approach to evaluate the influence of irradiation wavelength, hydrogen peroxide, substrate and SBO concentration on the degradation of 4-chlorophenol.

Finally the potential of the SBO-based photochemical process to be feasibly scaled up has been evaluated using a pilot plant working under real sunlight irradiation.

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## Organotin compounds in marine environment of the Eastern Part of the Gulf of Finland

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Organotin compounds belong to a large group of key marine contaminants. They had been widely used in the world industry as antifouling paints, fungicides and biocides until the middle of 1980s. Tributyltin (TBT) and triphenyltin (TPhT) are the most hazardous of all organotin compounds, causing such biological effects as shell deformation, endocrine disruption, imposex and intersex phenomena at the concentration of  $2 \text{ ng}\cdot\text{l}^{-1}$ . Most TBT and TPhT leach into the Baltic Sea from the ship hulls and contaminated harbour sediments. The use of TBT in antifouling paints was banned within EU in 2003 and in the Russian Federation in 2008.

The study is focused on surface marine water and bottom sediments, collected from the eastern part of the Gulf of Finland during the navigation season of 2012. Monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPhT) were analysed as ethyl derivatives using electron impact gas chromatography-mass spectrometry (GC-MS-EI) in single ion monitoring mode (SIM).

In contrast to many other hazardous organic substances, the distribution of TBT and TPhT is spatially very variable. The use of this group as an antifouling agent on ships and smaller vessels can be seen in the concentration gradient from harbours to coastal waters. TBT and TPhT were frequently found above MAC of  $1.5 \text{ ng}\cdot\text{l}^{-1}$  and  $2 \text{ ng}\cdot\text{g}^{-1}$  respectively in both water and bottom sediment samples collected from the Gulf of Finland water basin. Some concentrations are of high concern, such as  $140 \text{ ng}\cdot\text{l}^{-1}$  (TBT, Vyborgskiy Zaliv, yacht-club of Primorsk),  $670 \text{ ng}\cdot\text{l}^{-1}$  (TBT, St.-Petersburg, seaport),  $440 \text{ ng}\cdot\text{g}^{-1}\text{dw}$  (TBT, near Zelenogorsk),  $160 \text{ ng}\cdot\text{g}^{-1}\text{dw}$  (TPhT, Vyborgskiy Zaliv). The areas affected are mainly coastal areas with dense ship traffic.

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## Cyanotoxins in the Italian Deep Subalpine Lakes (DSL): distribution and controlling factors

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Toxic cyanobacteria blooms represent a serious threat for many aquatic ecosystems worldwide. The most common potentially toxic cyanobacteria in temperate waters belong to the genera *Microcystis*, *Planktothrix*, and *Dolichospermum*, which have the ability of producing microcystins and anatoxins. Toxins can produce severe effects on humans directly (contact or ingestion of contaminated water) or indirectly (consumption of contaminated food).

Deep Subalpine lakes Garda, Iseo, Como, Maggiore, and Lugano are important water resources in the Italian Northern district. We have conducted a sampling campaign in these lakes with the aim of compare the cyanotoxin diversity. We have applied advanced analytical techniques based on LC-MS/MS technologies. Two main classes of toxins have been found: microcystins (MCs) and anatoxins. A big variability in MC variants and concentrations has been found among the lakes. In the largest lake (Garda) we have also investigated in detail the temporal dynamics of the toxin production. The concentration of total MCs was strictly linked to the temporal dynamics of *Planktothrix rubescens* in the lake, irrespective of the season and vertical depth. These findings suggest a constitutive MC production relatively independent from environmental factors. It is stressed how the estimation of models linking MCs and cyanobacteria abundances should provide a greater reliability in the definition of management strategies aimed at minimising the risks due to cyanobacteria development.



## Liquid-liquid extraction studies for platinum recovery from chloride media using *N,N'*-dimethyl-*N,N'*-diphenyl succinamide

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Due to its high economic value and crescent utilization in jewellery, electronics and, mainly, as catalyst (e.g. in automotive catalytic converters), there is a great interest on the synthesis of efficient platinum extractants to be used in liquid-liquid extraction schemes. Amongst them, a few amide derivatives, namely *N,N'*-tetrasubstituted malonamides, such as *N,N'*-dimethyl-*N,N'*-dicyclohexyltetradecylmalonamide [1] and *N,N'*-dimethyl-*N,N'*-diphenyltetradecylmalonamide [2] have been effective for the solvent extraction of platinum from hydrochloric acid solutions. The research here reported presents some information about the platinum extraction capabilities of a new diamide derivative: a succinamide. The obtained results showed that Pt(IV) can be efficiently extracted from hydrochloric acid media by *N,N'*-dimethyl-*N,N'*-diphenylsuccinamide (DMDPHSA), and that the extraction increases with an increasing HCl concentration, from 1 to 8 M. Platinum extraction percentages of 80% and 90% were achieved for HCl concentrations of 6 M and 8 M, respectively. The stripping of the platinum loaded organic phase to a new purified aqueous phase was also evaluated. According to the results, the efficiency of the stripping stage is variable, depending on the stripping agent used: distilled water and 1 M HCl, which were generally effective for Pt stripping from *N,N'*-tetrasubstituted malonamides [1,2], were not efficient in this case. However, the use of several chloride salt solutions proved to be successful, since stripping percentages of about 80% were attained. The effect of some experimental parameters, such as equilibration time, diluent, and extractant and HCl concentrations, was also investigated. The overall data achieved until the present suggest that DMDPHSA is a promising extractant for Pt(IV) and thus it may be a good candidate for further studies concerning platinum separation from real solutions, such as those resulting from leaching of secondary sources, aiming at its recycling.

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## Education in Environmental Analysis – Leonardo da Vinci CHEMLAB II project

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CHEMLAB II is a European collaborative project aiming to educate young working people, without a University degree in Analytical technologies and to improve their skills in Chemical Analysis. The original concept of the program relies on the observation that recently, there has been a reduction in the number of experienced and qualified members of technical staff in analytical laboratories. This situation is partly due to the rapidly accelerating technological progress and increasing demands for knowledge, but also due to the insufficient level of training for graduates of basic education. Industries on the other are restricted to employ overqualified staff, which are capable of handling more efficient and less costly chemical analytical instruments in relation to technical staff.

The CHEMLAB II – Transfer of Innovation project aims at providing and fostering a “European Quality Standard in Chemical Vocational Education” for young apprentices in non-academic chemical training on-the-job. To that effect, an innovative VET-concept has been developed (and tested) based on a combined integrative approach of theoretical education and market-orientated training close to practice on chemical strategies and up-to-date methods of handling instrumental-technical, industrial or RTD challenges with special regard to analytical chemistry. As to the fields of application, the envisaged VET program is particularly on environmental analysis requirements. This individual practical module has been installed on one of the partner institutes (Environmental Pollution Control Laboratory, Thessaloniki, Greece), where in-firm trainees are educated in both theoretical and practical chemical techniques.

The overall training includes the development of specific training curricula with a detailed description of the theoretical and practical knowledge that is provided to learners. The development of the curriculum depended on the necessary theoretical courses and basic knowledge accepted in the Member States, but also it depends on business needs for environmental analysis. Finally a 30-day laboratory training exercise with simultaneous mobility of the trainees, on analytical techniques in environmental analysis, troubleshooting and real experimental challenges has been developed. It includes GC and LC-MS techniques, sample preparation and quality assurance.

Such knowledge will be certified with a European Certificate of Attendance, which ensures the quality and completeness of the knowledge of the learner.

## TOXIC EFFECTS OF NANO PARTICLES ON AQUATIC MICROORGANISMS

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### INTRODUCTION

The synthesis of engineered nano particles (ENPs) leads to an ambivalent situation: uncontrolled emission to the aquatic environment versus promising application for water treatment. In both cases the interaction of ENPs with micro organisms (MOs) plays a crucial role. Therefore experimental investigations are needed with the aim to reveal the toxicological effects involved.

### EXPERIMENTAL APPROACH

The detailed characterisation of the interactions were done with advanced methods for the determination of particle size, zeta potential, contact angle and growth curves in the low concentration range needed. Under defined conditions the MOs, E.coli, Pseudomonas putida, Saccharomyces cerevisiae, Lactobacillus plantarum were exposed to the ENPs, TiO<sub>2</sub>, Ag, FeOx and SiO<sub>2</sub> in the presence and absence of aquatic natural organic matter (NOM).

### RESULTS

The interactions and the toxic effects were highly dependent on the pH-value of the solution.

A sensitive toxicity method based on optically determined growth curves was developed and successfully applied. Ag turned out to be most toxic ( $\beta_0$  (Ag) > 0,1 mg/l). Positively charged SiO<sub>2</sub> was significantly more toxic against L. plantarum than the negatively charged species. FeOx (d=60 nm) showed the highest toxicity against E.coli at pH 4.0 and at pH 10. At both pH-values E.coli showed a negative charge whereas FeOx had a positive charge at pH 4 and a negative one at pH 10. The presence of NOM led to a mitigation of the toxic effects of ENPs on the MOs.

### CONCLUSIONS

NOM turns out to have a strong impact on the physical, chemical and toxicological properties of ENPs. This has severe consequences on the fate of ENPs in aquatic systems, on the water management and on a possible utilisation of ENPs in water treatment.

## Evaluation of the effect of sorbent morphology for SPE application

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Many approaches have been used for pesticides analysis and one of the critical steps is sample preparation. At this stage all errors will affect the final result of determination by loss or contamination. One of the most used pre-treatment procedures is the liquid-liquid extraction, due to its simplicity. However, it requires relatively large volumes of organic solvents, is time consuming, labor-intensive and hazardous to health and environment. Solid phase extraction (SPE) is becoming a popular technique due to its simplicity and is less time consuming. The selection of the appropriate extraction system is an important stage in the development of analytical procedure. In this work, a novel sorbent for pesticides extraction was fabricated, using the electrospray/electrospinning technique, for the pre-treatment of water samples with subsequent analysis by GC- $\mu$ ECD. The sorbent (particles, beaded fibers or fine fibers) was evaluated using SPE in the column and batch mode for three different groups of pesticides (organochlorine, organonitrogen and organophosphorous pesticides) in a water spiked sample, by recoveries studies. The results showed that recoveries for the sorbent in the particle form was about 60% and with the fine fibers and beaded fibers it was possible to achieve 100%, respectively. The study confirmed that electrospun fibers exhibit better properties for an SPE sorbent compared to beaded fibers or particles.

## Development of a novel Liquid Chromatography - tandem Mass Spectrometry method for the determination of rodenticides in wastewater

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Rodenticides are a type of pesticides that are used as pest control to eradicate rodents. In this study, we have developed a liquid-chromatography-tandem mass spectrometry (LC-MS/MS) method for the multiresidue determination of multi-class rodenticide compounds in wastewater. In a first step, ionization conditions were tested in positive electrospray mode and optimum fragmentation patterns were determined. Two Selected Reaction Monitoring (SRM) transitions were selected. Following, the chromatographic conditions were optimized considering that compounds analyzed have a very different chemical structure and chromatographic behaviour. The best performance was obtained with a Zorbax Eclipse XDB-C18 column, which permitted the separation of the 14 compounds in 18 min. This method provides good linearity, sensitivity, intra and inter- day precision. For the extraction of rodenticides in wastewater, different Solid Phase Extraction (SPE) cartridges were tested. Among various cartridges, OASIS HLB (200 mg, 6 cc) were chosen obtaining recoveries between 71 to 141% with relative standard deviation (RSD) between 1 and 25%, except for phenindione and fluindione which were not recovered successfully. Finally, 9 wastewater treatment plants (WWTP) were sampled around Catalonia where rodenticides were detected between 0.86 to 334 ng L<sup>-1</sup>. The main compound detected was warfarin with a concentration range between 1.17 to 334 ng L<sup>-1</sup>. Mass flows were estimated to determine the amount of rodenticides discharged to rivers and mean values were of 0.02 to 21.79 g day<sup>-1</sup>, being WWTP4 the wastewater treatment plant with higher discharge. In the other hand, the toxicity of the three of the most commonly used rodenticides to *Daphnia Magna* was evaluated and warfarin, bromodiolone and chlorophacinone presented LC<sub>50</sub> values of 170.19, 49.68 and 0.56 mg L<sup>-1</sup>, respectively. This means that the toxicity of rodenticides discharged to rivers is much below the EC<sub>50</sub> values and therefore, the risk they may pose to receiving waters is low.

## Treatment of cork processing wastewaters by anodic oxidation

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The wastewaters from cork processing industry are an environmental concern, since during cork cooking process natural lignocellulosic materials often originate effluents with phenolic compounds, in a concentration that inhibits the conventional biological treatments [1]. As alternative to the biological treatments, advanced oxidation processes were already tested in the degradation of these effluents, with good results [2]. In fact, these processes have in common the formation of a strong oxidant, hydroxyl radical, capable of the degradation of most of the organic molecules, namely phenolic compounds. One technology involving hydroxyl radicals that has proved to be very efficient in the degradation of complex organic molecules is anodic oxidation [3].

In this work, the degradation of cork processing wastewater by anodic oxidation was studied. As anode, a boron-doped diamond (BDD) electrode was used. Assays were run in batch with recirculation mode, with and without added electrolyte. Different electrolyte concentrations and applied current densities were tested. Assays were followed by chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub> and BOD<sub>20</sub>), dissolved organic carbon, total nitrogen, total phenols determinations and UV-Visible spectrophotometry.

According to the obtained results, anodic oxidation with a BDD anode can be a suitable alternative to reduce the organic load and to improve the biodegradability of these effluents. In the assays run with the highest concentration of added electrolyte, at the highest applied current density, removals higher than 90% were achieved for all the parameters used to follow the assays. Moreover, with anodic oxidation treatment it was possible to obtain a significant increase in the biodegradability from 0.15 to 0.75 and from 0.25 to 1.26 for the BOD<sub>5</sub>/COD and BOD<sub>20</sub>/COD ratios, respectively.

For the samples tested and for equal applied current density, the decrease in the electrolyte concentration has not shown any decrease in the organic load removal rate. On the other hand, the decrease in electrolyte concentration leads to higher applied potentials and, consequently, to higher energetic costs.

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## SIMULTANEOUS DETERMINATION OF DISINFECTION BY PRODUCTS IN WATER SAMPLES BY HEADSPACE SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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For decades, municipalities have utilized chlorine as a primary disinfectant for surface water sources, to inactivate microbial pathogen. While the benefits of chlorination are well documented [1, 2], a side effect of chlorination is that residual chlorine can react with naturally occurring organics in water to form disinfection by products (DBPs). These byproducts may lead to increased health risks if present at high ppb levels. These DBPs included trihalomethanes, haloacetonitriles, halonitromethanes, halo ketones and haloaldehydes. Nowadays they have begun to play an increasingly important role [3, 4], therefore the development of a highly sensitive method for their analysis has become a priority.

Natural organic matter (NOM) is of concern because it serves as precursor to the formation of disinfection by products. NOM consists of humic (non-polar, hydrophobic) and non-humic (polar, hydrophilic) substances, generally of terrestrial and biological origin, respectively.

The purpose of this study was to obtain quantitative occurrence information for new DBPs, beyond those currently regulated and/or studied. Therefore, a HS-SPME GC-MS method has been developed for the determination of 20 DBPs in water samples. Several variables affecting the chromatographic behaviour of the target compounds have been considered and investigated the experimental conditions affecting their extraction using HS-SPME. The variables considered in this study were: the type of fibre (PEG, PA, PDMS/DVB/CAR, PDMS/DVB) the time and extraction temperature, the ionic strength and the sample volume of the samples. Moreover, common analytical parameters, such as TOC, BOD, DO and UV254, have been analyzed and correlated with the concentration of DBPs.

The validated method has been used for the determination of the target DBPs in different kinds of aqueous samples, such as influents and effluents of reverse osmosis treatments, surface waters (Llobregat river, Barcelona), effluents of urban wastewater treatment plants (of WWTP Vila-Seca) and sea waters (Mediterranean Sea).

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## Impact of a tar contaminated site on an adjacent river – NSO-Heterocycles, PAHs, PAH-Derivatives and Phenols

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**Introduction:** The anthropogenic use of coal as an important resource for industrial products in the past century often caused a significant environmental pollution in soils and groundwater at manufacturing plant sites. Large amounts of pitch, tars and tar-oils were formed as byproducts of coking processes during town gas production in the 19<sup>th</sup> and 20<sup>th</sup> century and during production of metallurgical coke. Besides the well known PAHs and phenols, main contaminants found at these sites are the less investigated NSO-heterocycles (NSO-HET). Heterocyclic compounds are characterized by substitution of carbon by nitrogen (N-HET), oxygen (O-HET) or sulfur (S-HET) hetero-atoms within the hydrocarbon ring-system. In this study more than 100 aromatic compounds were investigated in the groundwater of a former coking-plant site and in an adjacent river course. The presented measurements were performed in order to identify predominant compounds and to quantify the impact of this potential point source on the river.

**Sampling and Methods:** The site investigated is a former steel-works site in Northern Germany, located adjacent to the river Fuhse in the city of Groß Ilsede. Besides 6 groundwater wells 5 spots within 4.6 km of the river course were sampled from May – December 2011. Aqueous samples were filtrated and extracted by solid phase extraction. Polystyrene-divinylbenzene cartridges (Lichrolut EN) were acidified to achieve a cationic bonding for the basic N-HET compounds. A first fraction containing PAHs and derivatives, phenols, S-HET and O-HET was eluted using 3 ml methylene chloride. A second fraction containing N-HET was eluted after rinsing with ammonia solution (5%) using 3 ml methylene chloride / acetone solution (2:1, v/v). Eluates were concentrated to 200 µl using rotary evaporation. Sample extracts were analyzed by GC-MS for fraction 1 and LC-MSMS for fraction 2. Volatile compounds were analyzed directly with headspace-GC/FID.

**Results:** Groundwater concentrations of up to 3.2 mg L<sup>-1</sup> in sum were found at the riverbank of the contaminated site. The mass fraction of NSO-HET in groundwater wells was found to be in a range between 5% and 30% with concentrations of up to 200 µg L<sup>-1</sup>. Recently established toxicological threshold values were exceeded for seven heterocyclic compounds. In all river samples analyzed a strong impact on concentrations of aromatic compounds was observed. Besides naphthalene, acenaphthene and 1-methylnaphthalene heterocycles such as benzothiophene (S-HET) and dibenzofuran (O-HET) are discharged from the contaminated site. Compared to background levels within the river Fuhse, sum concentrations of aromatic compounds were raised by 50%. Sum-mass flow of the point source into the river Fuhse was calculated to be 5 ± 2 kg/year. In contrast high N-HET concentrations (especially acridine) in the river Fuhse were related to a discharge from a wastewater-treatment plant. Results of this study emphasise the relevance of heterocyclic compounds at tar contaminated sites and in adjacent rivers.



## THE ANALYTICAL EXAMINATION OF THE MAGNETIC NANOPARTICLES

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Heavy metal industry reveals more importance, everyday. Nowadays, heavy metal industry is becoming more and more important. Besides; copper, nickel, mercury, arsenic, iron and chromium containing industrial waste is toxic and dangerous for all of the living organisms [1]. The toxic effect of the heavy metals threatens not only human health but also all of the organisms in the ecosystem. The water that contain these elements in trace amounts attends to the food chain in different ways.

For this reason, source of the pollution of heavy metal content must be purified before letting to the ground water and must be below the allowed values.

This study aims synthesize magnetic nanoparticles to remove the heavy metals from waste water. The motion of the magnetic nanoparticles under magnetic field gives some advantages for many applications. Coating the magnetic nanoparticles with the humic acid is designed to make complex under the magnetic field and create a synergic effect. For this purpose, quercetin and humic acid coated magnetic nanoparticles were synthesized with the co-precipitation method. The proposed method is selective, easy, cheap and environmentally friendly.

The usage of humic acid as the outer shell prevents the aggregation of iron and maintains a high capacity of complexing with metals as it carries functional groups (alkyl, aromatic, carboxylic acid groups) [2].

Quercetin, type of an antioxidant, prevents oxidation of the particles and gives anti-bacterial properties to the particles [3]. Thus, the newly synthesized magnetic nanoparticles not only remove heavy metals exceeding the limit values from the industrial waste water but also prevent possible growth of bacteria in water.

In this study, parameters such as pH, temperature, time and amount of nanoparticle were optimized after the appropriate amounts of quercetin and humic acid used during the synthesis procedure had been decided. For the characterization of the particles, UV-Visible spectrophotometer, molecular fluorescence spectrometer, IR and SEM equipments were used.

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## Clofibric acid degradation by heterogeneous Fenton-like process using Fe-zirconia catalysts

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The development of new catalytic oxidation technologies for the removal of organic pollutants at the point of origin is highly interesting. Advanced oxidation process (AOPs), defined as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification” represent a suitable tool to reduce environmental release of organic pollutants and they have been assigned an outstanding priority over other wastewater treatment method (e.g. adsorption and stripping), due to their ability to mineralize the organic pollutants [1]. Among all AOPs the conventional Fenton process is known as one of the most efficient advanced oxidation processes for the degradation of organic pollutants. However, it has some drawbacks such as the formation of sludge and required pH adjustments. Therefore efforts are mainly focused on the development of heterogeneous catalytic systems, which are active at ambient conditions and wide pH range and are easily separable and recovered from the treated wastewater [2]. In this work the degradation and mineralisation of clofibric acid (as a model compound of pharmaceutical wastewater) is studied using Fe-zirconia/sulfated zirconia materials as catalysts. Fe/ZrO<sub>2</sub> (1 and 5%) catalysts were prepared by impregnation method and also (1 and 5%) Fe/sulfated zirconia catalysts were prepared by sulfonation of zirconia followed by impregnation of Fe [3]. The reactions were carried out at ambient conditions in a magnetically stirred glass reactor with aqueous solution of CFA (100 mg/l), H<sub>2</sub>O<sub>2</sub> (500 mg/L) and catalyst (2g/L) at room temperature and free pH, and samples were periodically withdrawn and analyzed by HPLC and TOC. Catalysts were characterised by various techniques (XRD, ICP, N<sub>2</sub> physisorption, etc.). 100% of CFA conversion was obtained with both, 5%Fe/ZrO<sub>2</sub> and 5%Fe/sulfated-ZrO<sub>2</sub> catalysts in 6h of reaction. 40% of mineralization was obtained with 5%Fe/ZrO<sub>2</sub> with some leaching of Fe (0.5 mg/L) whereas 46% of mineralization was obtained with 5%Fe/sulfated-ZrO<sub>2</sub> catalysts without any leaching of Fe, in 6h of reaction. The effect of the amount of catalyst, H<sub>2</sub>O<sub>2</sub>, pH and T has also been studied.

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## Removal of pharmaceutical residues from wastewater by polymer-based spherical activated carbon (PBSAC)

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For several years, pharmaceutical residues and their metabolites have been detected in surface water, groundwater and even drinking water. These bioactive substances are suspected as potential risk for the environment and human health. Pharmaceuticals are mostly polar and hydrophilic compounds, which are removed incompletely from sewage by conventional wastewater treatment plants. Additional treatment technologies are needed to improve the elimination of the bioactive trace contaminants. The use of fixed bed adsorbers is one option to improve elimination of organic trace compounds from biologically treated wastewater.

A new polymer-based spherical activated carbon material (SARATECH<sup>®</sup>, Bluecher Company) was examined for its suitability as sorbent for waste water treatment (smoothing). The adsorption properties of the new sorbents with large surfaces, high weight load and a selective pore size distribution were studied for a set of polar pharmaceuticals and iodine containing diagnostic agents (Diatrizoic acid, Iopromide, Naproxen, Atenolol, Carbamazepine).

In batch experiments the sorbent was characterized by acquiring substance elimination curves and adsorption isotherms. To identify the influence of the wastewater matrix on contaminants adsorption behavior, purified water, DOC-containing water and wastewater solutions were compared.

The determination of the pharmaceuticals was performed by LC-MS/MS. Based on the data, the modified mass transfer coefficient of the respective film diffusion  $k_f a_v$  was calculated allowing conclusions on the adsorption rate and of the impact of diverse matrices.

It was found that the adsorption rates of all target substances decreased in the order of purified water, DOC-containing water to wastewater. However a complete elimination of more than 99 percent of all tested pharmaceuticals in the three matrices was achieved. These results are the basic information for further column studies and the construction of a pilot plant device feasible for smoothing treated wastewater.

## Biota monitoring of hexachlorobenzene and hexachlorobutadiene in *Silurus glanis* from a heavily polluted aquatic environment

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Biota monitoring is a crucial tool necessary to assess the quality of all EU waters (rivers, lakes, ground and coastal waters), as strongly suggested by the Water Framework Directive (WFD) [1]. Specific measures for pollution control and prevention that Member States need to implement are highlighted in the daughter Directive 2008/105/EC [2] which lays down the Environmental Quality Standards (EQSs) with the aim of achieving a *good chemical status* of surface waters. As foreseen, EU Member States that opt to apply EQS for biota, shall apply an EQS of 10 µg kg<sup>-1</sup> for hexachlorobenzene (HCB) and 55 µg kg<sup>-1</sup> for hexachlorobutadiene (HCBd), respectively, in prey tissue (i.e. wet weight), choosing the most appropriate indicator among fish, molluscs, crustaceans and/or other biota. In this study, the distribution and mass fraction of HCB and HCBd were determined in 29 Wels catfish (*Silurus glanis*) from the Flix reservoir, a heavily polluted artificial in-stream water body from the Ebro river basin (NE Spain). Despite the fact that top predators do not necessarily reflect site-specific bioavailability of chemicals, this benthic species was selected to check pollution level with the primary aim of producing a novel Certified Reference Material (CRM), available in the near future. The clean fillets were analysed dividing head and tail parts and an in-house fully validated method (ASE extraction, SPE cleanup and GC-IDMS) was applied. The results obtained show high variability in mass fraction levels among specimens, with tails showing the highest contamination level of about 1000 ng/g for both HCB and HCBd. EQSs were exceeded eighteen times for HCB and one time for HCBd in tail samples. On the other hand, the correspondent head parts showed lower pollution levels, sometimes below EQSs. In general, the most contaminated specimens were found among the oldest (judging by size) fishes, although it was not possible to establish a clear relation between fat content (interval in tails between 1.4 and 33.9 %) and pollution levels. These results confirm the already established heavy contamination degree from organic pollutants of the area [3] and point out the need for specific recommendations on how to exploit biota monitoring data for assessing water quality under the EU WFD requirements. *Silvia Lacorte (IDAEA-CSIC, Spain) is acknowledged for providing the catfishes.*

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## UV light-activated persulfate for the removal of erythromycin and antibiotic resistance from secondary wastewater

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Erythromycin (ERY) is widely used not only in humans, but also in food-producing animals to control bacterial diseases and promote animal growth. Pharmaceuticals are often partially metabolized in the organism and they are excreted as parent compounds or as metabolites into wastewaters [1]. Antibiotics are of high environmental significance because of their potential role in the development of antibiotic-resistant bacteria [2]. Most antibiotics tested to date are not fully biodegradable under aerobic conditions. ERY has been found at concentrations ranging from  $\text{ngL}^{-1}$  to  $\mu\text{gL}^{-1}$  in sewage treatment plant effluents, surface waters and groundwater [1,2]. Among various water treatment processes, non-biological methods such as advanced oxidation processes (AOPs) have also been employed to treat antibiotics [1]. Recently, sulfate radical based advanced oxidation processes have attracted great scientific interest due to their high efficiency in the degradation and mineralization of recalcitrant and/or toxic organic pollutants. Activation approaches of persulfate include thermal treatment, pH adjustment, UV radiation or the addition of transition metals to produce sulfate radicals. The scope of this work was the investigation of the destruction of ERY by UV-activated persulfate in real wastewater matrices. ERY degradation was assessed by measuring its concentration on an UPLC - MS/MS (Acquity) system, while UV-C irradiation was emitted by a 9 W Radium germicidal lamp. The degradation efficiency of the process showed a slight increase at pH 8, while TOC removal was near 15% at 90 min with  $10 \text{ mgL}^{-1}$  sodium persulfate. In addition, ERY removal was found to follow pseudo-first order decay kinetics with respect to initial concentration and the degradation decreased with increasing initial ERY concentration; for example after 60 min of treatment time with  $10 \text{ mgL}^{-1}$  sodium persulfate ERY degradation was 82%, 77% and 69% for ERY initial concentration of 50, 100 and  $200 \mu\text{gL}^{-1}$ , respectively. Moreover, ERY removal increased as the initial sodium persulfate concentration increased in the of range  $0\text{-}10 \text{ mgL}^{-1}$ . The results showed that the water matrix is a significant operating parameter for the photodegradation process. For example, the ERY degradation rate in double distilled water is higher than the degradation rates in bottled water and secondary treated effluents. Details on the degradation pathway and results on the antibiotic resistance removal will be also presented. Overall, it can be stated that UV/Persulfate is an effective technology for the removal of ERY from environmental samples at relative low concentration of sodium persulfate.

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## The effectiveness of sulfate radicals on the abatement of ethyl-paraben in aqueous media

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Parabens are widely used as preservative agents in many personal care products (PPCPs). This extensive use and recent studies that have suggested a possible relationship between them and breast cancer have awakened the concern about their potential long-term effects on human health [1]. These preservatives are continuously released in urban wastewater at relatively high concentration levels and, despite being considerably removed during conventional treatment through a combination of biodegradation processes and sorption onto microbial flocs, they have been still detected in surface water at ng to  $\mu\text{g L}^{-1}$  [2]. The main concern once they reach the environment is that they have proved to show oestrogenic activity [3].

Advanced oxidation processes based on the generation of hydroxyl radicals have gained considerable attention in recent years due to their high efficiency in degrading various organic compounds. Persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is a powerful oxidizing agent which can be decomposed to  $\text{SO}_4^{\bullet-}$  radical by UV radiation. The objective of this work was to investigate the  $\text{UVC}/\text{S}_2\text{O}_8^{2-}$  reactivity towards ethyl-paraben in various water matrices at a bench scale set-up in respect to the operating conditions, including the substrate concentration (50-300  $\mu\text{g L}^{-1}$ ), sodium persulfate concentration (0-10  $\text{mg L}^{-1}$ ), UV-C radiation (0-9 Watt), treatment time (0-90 min) and the type of water matrix (ultrapure water (UW), bottled water (BW), secondary wastewater (WW)). The evaluation of the process was performed by studying the removal of the substrate in solution by UPLC-MS/MS.

The degradation of ethyl-paraben follows pseudo-first-order kinetics while the (%) removal decreases with increasing the initial substrate concentration (100% at 50  $\mu\text{g L}^{-1}$  and 89% at 100  $\mu\text{g L}^{-1}$ ). The degradation rate of ethyl-paraben increases as the initial  $\text{Na}_2\text{S}_2\text{O}_8$  concentration increases. In addition it was observed that the pH has no significant influence on the degradation, while the efficiency of the process increases slightly at pH 8. The extent of degradation decreases in the order  $\text{UW} > \text{BW} > \text{WW}$ . The time needed for the complete degradation of the substrate was longer in the case of BW compared to UW; therefore the presence of bicarbonate and carbonate ions which may act as scavengers of the hydroxyl and sulfate radicals can be assumed. Moreover, it was found that the wastewater matrix has an adverse effect on the degradation rate; the time needed for complete substrate degradation in WW was found to be more than four times higher than that in UW. This is consistent with the fact that WW contains dissolved organic matter leading to extremely slow degradation.

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## Effects of ionic strength, oxygen level and humic acid concentration on photochemical degradation of fluoranthene in aqueous solution

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Polyaromatic hydrocarbons (PAHs) are widely distributed in natural water systems and marine sediments, and have been shown to be carcinogenic and mutagenic in animal models and human epidemiological studies. Photodegradation is determined as the primary abiotic pathway for degradation of PAHs in aquatic environments. Photolysis rates for fluoranthene were measured in aqueous solution as a function of ionic strength (salinity), oxygen levels, and humic acid concentrations over the range of conditions found in fresh to marine waters. Solutions were irradiated using a solar simulator and concentrations of PAH were measured as a function of time using steady state fluorescence detection or HPLC with fluorescence detection. 3D excitation-emission matrix (EEM) fluorescence spectroscopy was used to identify potential photolysis products. Photolysis of fluoranthene followed first order kinetics, with degradation taking place on the timescale of hours. The variations of photolysis rates as a function of natural water variables will be presented and discussed.

## Determination of inorganic and organic species of selenium in Iranian walnut by spectrophotometry after cloud point extraction

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Selenium is an essential, trace element in environmental and biological systems. It plays an antioxidant and chemo-preventive role in cancer and other illnesses like heart disease and arthritis. This element would exist in various samples such as vegetables, foods, biological matrixes in different chemical forms: inorganic species (selenite,  $SeO_3^{2-}$ ; selenate,  $SeO_4^{2-}$ ) or in the forms of organic species (selenoamino acids; selenomethionine and very complex selenoproteins). Inorganic forms are more toxic than organic forms and the toxicity of selenite is more than selenate for humans and most of other mammals. In fact, the measure of this element in human organism depends on its amount in the soil-plant system. Between the plants, walnuts are important source of selenium and specially selenomethionine.

Determination of selenium in walnuts needs a preconcentration step, due to the complexity of the sample matrix and its trace concentration. In order to solve this problem, was chosen cloud point extraction (CPE) as a preconcentration-separation technique instead of traditional extraction systems like: liquid-liquid extraction, liquid phase microextraction, solid phase extraction.

CPE is a rapid, safe, low cost method with high efficiency and a powerful tool for trace and ultra trace elemental analyses. In the case of selenium, CPE could also couple with different detection techniques such as gas chromatography, spectrofluorometry, electrothermal atomic absorption spectrometry.

In this work, selenium was reacted with 2,3-diaminonaphtalen (DAN) to form 4,5-benzopiazselenol, in an acidic medium. Using Triton X-114, as a surfactant, Se-DAN complex was extracted into surfactant-rich phase after centrifugation. Finally the absorption of walnut samples that had been selected from different region of Iran, were measured with UV-vis spectrophotometry. Affecting parameters on complexation and CPE: pH, temperature, the molar DAN/Se ratio and the concentration of Triton X-114 were optimised. The limite of detection was calculated  $0.017 \text{ ng/mL}$ .

Key words: Selenium; Walnut; Cloud point extraction; 2, 3-Diaminonaphtalen; Green Chemistry



## Effect of dissolved organic matter on micropollutants sorption by clays and oxides in aquatic system under strong urban pressure

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Sorption/desorption onto suspended matter and sediments is one of the major processes that affects the fate of hydrophobic organic compounds and trace metals in aquatic system. A good understanding of this process is crucial for predicting transport, distribution and bioavailability of contaminants in aquatic environment. The surface properties and reactivity of minerals in aquatic system (clays, oxides,...) can be modified by adsorption of dissolved organic matter (DOM). For example, adsorption of weak acid pesticide MCPA on the surface of humic-acid coated goethite decreased compared to the bare goethite (Iglesias et al., 2010) whereas phenanthrene sorbed better onto humic-acid coated clays (Feng et al., 2006).

Almost all published studies regarding the capacity of coated-organic matter to modify sorption properties of mineral surfaces pertain mainly to the so called “humic substances” or to natural organic matter which are mainly hydrophobic. Yet, in urbanized aquatic system, the hydrophobic characteristic of DOM is weaker as a result of various urban DOM discharges (Pernet-Coudrier et al., 2011). Very little information is available regarding the influence of urban DOM in micropollutants sorption/desorption onto mineral particles in receiving waters.

In this work, adsorption of DOM from waste water treatment plant effluents onto clays and oxides particles has been characterized and compared to those of natural and more hydrophobic DOM sampled in the Seine basin near Paris. After adsorption experiment, DOM remained in solution and coated particles have been characterised with UV-visible absorbance, 3D spectrofluorescence, <sup>13</sup>C NMR and IRTF. Strong sorption differences appeared in relation to the physico-chemical properties of each nature of DOM. Fractionation of DOM according to its polarity has been observed after sorption onto mineral particles. In a second step, we have studied the previously coated and uncoated particles to assess the influence of DOM onto the sorption of micropollutants with different properties (PAH, trace metals, metalloids). We observed strong influence of the organic matter coating onto sorption properties of particles. Some differences between natural organic matter and “urban” organic matter have been highlighted and are explained by their different properties.

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## **Alternative possibilities of the bio fraction handling of municipal solid waste**

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The directive 2008/98/EK of the European Parliament sets the criteria of the waste management in the community. According the directive the waste politics should aim on the reduction of the use of resources and should take into consideration the priorities of the waste hierarchy; landfill deposition should be repelled.

In connection with the above mentioned directive and the principle of the sustainable development network of regional waste-managements projects had been set in Hungary. One of these project is the North-Balaton waste management system that handles 120,000 ton/Year municipals solid waste (MSW) of app. 300,000 people by modern facilities. The biologically active waste is stabilized in 12 closed aerobe silos.

The aim of the research is a to investigate a possible technology of the biologically active fraction. The waste-analysis had been prepared for the input of the MSW in the North Balaton waste management system. The first procedure of the incoming waste is preshredding (to 300mm) and the removal of the ferrous content. Than 60mm sieve is used to separate the stream. The 0-60mm fraction contains mainly the biologically active parts that is 48% of the input waste.

For the research press is used to squeeze the leachate that is collected in barrels. The biologically active fraction could contain up to 40% leachate according to our measurements. The leachate was used for anaerobe fermentation to produce biogas. WTW OXITOP 100 manometric BOI, biogas meter was used for the fermentation and with it's analyzer the quantity of the biogas had been detected.

Beside the quantity of the biogas, we have led investigations of the effects of different additives in order to maximize the mass of the biogas. We have determined that the quantity can be raised by inoculating sludge and with additives with additives that contain Nitrogene in appropriate contain and form.

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## DEGRADATION OF PHENOLIC COMPOUNDS IN INDUSTRIAL EFFLUENTS BY IONIZING RADIATION

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The industrial growth and population increase have resulted in the release of different pollutants to the environment. Industrial wastewater without an efficient treatment is becoming a serious problem in industrialized areas [1]. Industrial wastewater is normally contaminated with very toxic compounds such as pesticides, detergents, dyes, phenolic compounds, chlorinated hydrocarbon, poly chlorinated biphenyl (PCBs) and polycyclic aromatic hydrocarbons (PAHs) which are highly resistance to degradation, very toxic and some of which are carcinogenic [2].

In this study, degradation percent of targeted phenolic compound (4-chloro-3-methyl phenol) at 100 ppm concentration increased with increase of irradiation dose up to 80 kGy (complete degradation). In this respect the removal percent reached 11, 29, 39, 51, 63, 73 and 100% with irradiation doses of 1, 5, 10, 20, 40, 60 and 80 kGy, respectively. The radiation dose of 80 kGy is sufficient to remove most of the targeted concentration residues of the phenolic compound in aqueous medium.

The results indicate the important role of phenolic compound type, chemical groups, presence of oxidizer and irradiation doses on the rate degradation of phenolic compounds. The amount of phenolic compound residues which have been degraded or removed as well as intermediate and final degradation products generated under irradiation were determined by Gas Chromatography-Mass Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC) and Ion Chromatography (IC). The removal efficiency of targeted pollutant was determined by calculating the proportion of degradation/removal based on the loss of initial concentration of compound irradiated by different irradiation doses. In addition, irradiation doses leading to the degradation of 50 and 90% of the initial concentration of 4-chloro-3-methyl phenol (D0.5 and D0.9) were calculated for data discussion.

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## Assessment of tritium activity in groundwater at Visaginas Nuclear Power Plant site, Lithuania

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Lithuania is planning to construct a new nuclear power plant (NPP) nearby the closed one. Groundwater characterization is an important issue in the setting process of new NPP. The most important component of groundwater is tritium as an indicator of radionuclide release from nuclear energy objects.

The activity of tritium in the groundwater was measured in many observation wells constructed new NPP. Water samples were taken from different layers (from 1.5 to 6.4 meters depth). Thus, the water samples of all observations points were measured several times and the average dose was calculated and recorded. Tritium activity was measured by the method of liquid scintillator beta – spectrometry. The tritium measurements in groundwater have been performed in other nuclear sites of Lithuania also (Fig. 1).

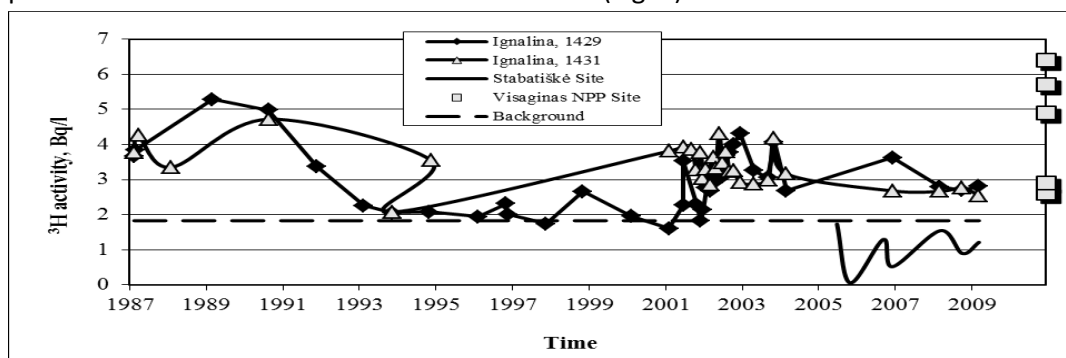


Fig. 1. Tritium distribution in groundwater of Ignalina NPP region

The obtained results of the tritium activity concentration at the new NNP sites show that the groundwater is not contaminated with artificial radionuclides. The evaluated tritium activities varied from 1.8 to 6.4 Bq/l at new NPP sites in Lithuania and it is coming to background level (1.83 Bq/l) and other nuclear object sites in Lithuania (from 0.1 to 5.3 Bq/l). Tritium activity concentration does not exceed the rate as regulated by the Lithuanian Hygiene Norm HN 24:2003 "Requirements for Safety and Quality of Drinking Water" with a value of 100 Bq/l.

## Water Purifying Using Waste of Electrical and Electronic Equipment (WEEE) as Fenton and Photo-Fenton Catalyst

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Over the last decades the amount of waste of electrical and electronic equipment (WEEE) has been increasing continuously and represents an important environmental problem.[1, 2] The complex composition of WEEE includes a wide number of metallic, ceramic and polymeric materials.[2, 3] This complexity makes the recycling of WEEE difficult and expensive, but it suggests the possibility of its application as catalyst for many different reactions.

In recent years, the advanced oxidation processes (AOP) have been studied to removal of organic contaminant from water, in special the Fenton process. This reaction uses hydrogen peroxide as oxidant agent and metals like iron or copper as catalyst. In the photo-Fenton light-sensitive materials are generally used to improve the Fenton reaction.[4]

In this work the application of WEEE as catalyst to heterogeneous Fenton and photo-Fenton reactions is presented. A dye contaminant (methylene blue) was used as molecule model.

The WEEE used in this work as obtained from printed circuit board (PCB) milled and was characterized by TGA-MS, SEM, ICP-AES, BET, XRF and UV-Vis. The material (30 mg) was used in Fenton and photo-Fenton reactions of degradation of 50 ppm (30 mL) methylene blue (MB) in presence of H<sub>2</sub>O<sub>2</sub> (50 vol.%, 0,3 mL), under dark (Fenton) and bright (photo-Fenton, incandescent light bulb of 60 W) conditions. The reactions were monitored by UV-Vis and TOC.

The WEEE showed small metallic particles (<1 µm) scattered over a high amount of polymeric and ceramic material, with small surface area and low density. The main elements observed were Cu (30 wt%), Si (20 wt%), Ca (11 wt%), Br (10 wt%) and Fe (8 wt%), as well smaller amounts of many other elements (*i.e.* Sn, Ti, Ni, Al, Mn, Ag, Nb, etc.). UV-Vis showed absorptions bands between 230 and 480 nm, indicating band gap energies of 2 to 5 eV, which is interesting for photo-catalytic reactions under visible region of the spectra.

The results of the reactions showed that the material was able to remove about 85 % of the MB in 150 min under photo-Fenton condition and 35 % for Fenton. After 270 min the colour removal was above 98 % for photo-Fenton and about 78 % for Fenton reaction. TOC analysis showed a removal of about 70 % and 20 % of the organic content after 270 min to photo-Fenton and Fenton reactions, respectively.

These results show that due to their composition, WEEE are promising materials for application as catalyst for AOP reactions and possible other catalytic reactions.

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## Use of Highly Oxygenated Biochar as Catalyst for Sulfide Oxidation

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Biochar is a carbonaceous material produced during the fast pyrolysis of biomass.(1) The high oxygen content present on the carbon surface as different functionalities produces several interesting properties for applications in adsorption and catalysis. In this work, we explored the redox properties of biochar for the oxidation of sulfide in aqueous medium. The effluents containing high concentration of sulfide cannot be discarded directly into the environment due to effects caused by the release of H<sub>2</sub>S, with unpleasant odor and high toxicity, even when present in low concentrations.(2) Sulfide oxidation has been investigated with different adsorbents, such as activated carbons that lead to the formation of species as polysulfides, thiosulfates, sulfites and sulphates.(2, 3) In this work, biochar obtained from the pyrolysis of sawdust and sugar cane straw was thermally treated at 400, 600 and 800°C under N<sub>2</sub> and characterized by different techniques (SEM, TG, IR, Raman and surface area BET).

SEM analysis showed that both biochar before and after heat treatment presents similar morphology. IR spectroscopy, Raman, TG and BET results showed that treatment at 600 and 800°C led to the decomposition of great part of functional groups with a strong increase in the surface area (1 m<sup>2</sup>g<sup>-1</sup> for pure biochar to 400 and 590 m<sup>2</sup>g<sup>-1</sup> after heat treatment at 600 and 800°C, respectively) with large volume of micropores.

The materials were tested in sulfide oxidation reactions in aqueous media. Kinetic studies monitored the formation of the primary product S<sub>2</sub><sup>2-</sup>. Biochar before heat treatment showed high activity for sulfide oxidation, likely related to the increased exposure of oxygenated functional groups. In contrast, the biochar subjected at high temperatures have low activity for oxidation reactions, which can be explained by the destruction of functional groups caused by heat treatment. The results were more satisfactory for pure biochar, but heat treated materials are also promising for other applications since there was a significant gain in the amount of surface area (-600%).

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## Efficient photocatalytic degradation of Methyl Tertiary Butyl Ether (MTBE) in aqueous suspension of Pt/WO<sub>3</sub> nanocomposite under sunlight-type excitation

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### Abstract

Visible-light-driven nanostructured WO<sub>3</sub> was synthesized using a hydrothermal method. The surface of photocatalyst was further modified with noble metals such as platinum (Pt) and Ruthenium (Ru) following photodeposition process. The photocatalytic removal of Methyl Tertiary Butyl Ether (MTBE) was investigated in the presence of these photocatalysts under sunlight-type excitation. Results indicated that the removal of MTBE could be rapidly achieved in presence of Pt-loaded synthesized nanostructured WO<sub>3</sub>. Pt/WO<sub>3</sub> showed better photocatalytic removal of MTBE than Ru/WO<sub>3</sub>, a pure nanostructured and commercial nano-WO<sub>3</sub>. Application of these catalyst were tested for the photocatalysis of MTBE in water samples and the reaction was monitored using solid-phase microextraction followed by gas chromatography/mass spectrometric analysis. The study revealed that the degradation of MTBE proceeds essentially via formation of formic acid 1, 1-dimethylethyl ester before its complete mineralization.

## Highly sensitive determination of polybrominated diphenyl ethers in surface water by gas chromatography coupled to high resolution mass spectrometry according to Directive 2008/105/EC

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Polybrominated diphenyl ethers (PBDEs) have become ubiquitous global environmental contaminants because of their widespread use as plasticizers in numerous household and commercial products. As a result analysis of these compounds has received increased interest due to their known toxicity.

Current EU Directive 2008/105/EC sets environmental quality standards (EQSs) for certain PBDEs at 0.5 and 0.2 ng L<sup>-1</sup> in inland surface water and other surface water, respectively. Therefore, according to this Directive, it is becoming necessary the development of highly sensitive and selective methods capable of determining PBDEs at low concentration levels (< 0.5 ng L<sup>-1</sup>).

In this work, a solid phase extraction (SPE) method was developed for the analysis of the 6 PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) specified by the aforementioned Directive in surface water samples. The final analyses were performed by gas chromatography coupled to magnetic sector high resolution mass spectrometry (GC-HRMS), which is one of the most sensitive and specific technique in the field of ultra-trace measurement of halogenated toxicants due to the instrument operates at a 10,000 resolution, and data are acquired in SIM mode for achieving the expected sensitivity and selectivity. GC-HRMS conditions were also optimized in order to detect the target compounds in water samples at concentrations below the EQSs established by European legislation. The validated method provided adequate linearity (determination coefficient,  $R \geq 0.9960$ ), recoveries (101-120%, except for BDE-47 at 5 ng L<sup>-1</sup>, which recovery was 127 %) and precision values (relative standard deviation, RSD < 20%) at the two fortification levels tested, 0.2 and 5 ng L<sup>-1</sup>. The method showed limits of detection (LODs) and quantification (LOQs) in the range 0.02-0.05 ngL<sup>-1</sup> and 0.05-0.1 ng L<sup>-1</sup>, respectively. The method was successfully applied to the analysis of PBDEs in surface water samples allowing the determination of these compounds at the restrictive EQSs established by current legislation.

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## Occurrence of organic contaminants in wastewater treatment plant effluents from the Mediterranean and Atlantic basins of Andalusia (Spain)

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The most characteristic feature of the Andalusian climate (South of Spain) is the shortage of rainfall, although there is a large difference between the Andalusian regions in term of precipitation. Therefore, Andalusia is a region with very different hydrographic need areas, and reusing reclaimed wastewater (WW) is emerging as an additional source of water.

Taking into account both the high probability that organic contaminants reach conventional wastewater treatment plants (WWTPs), which are not able to efficiently remove these micro-contaminants, and the subsequent reuse of the treated effluents, WW represent one of the main sources of environmental contamination. In this sense, a comprehensive survey of the occurrence of organic compounds in WWTP effluent samples from 21 urban WWTPs from both secondary and tertiary treatments was carried out in the Mediterranean and Atlantic basins of Andalusia region. For each sample, a total of 226 compounds including pesticides (and some of their transformation products, TPs), polycyclic aromatic hydrocarbons (PAHs), phenolic compounds and volatile organic compounds (VOCs) were monitored. Compounds belonging to each class were detected. Among pesticides, insecticides such as clorfenvinphos and diazinon as well as herbicides such as diuron, sebuthylazine, terbuthylazine and terbuthylazine desethyl, were the most frequently detected. The ubiquity of some compounds such as fluorene, phenanthrene and pyrene was also demonstrated. The compounds evaluated were detected at low concentrations (in general below  $1 \mu\text{g L}^{-1}$ ), except 4-tert-octylphenol, which was detected at extremely high concentrations (up to  $443 \mu\text{g L}^{-1}$ ). PAHs and VOCs were the compounds most frequently detected in the assayed samples, becoming the main sources of contamination in the WWTP effluents evaluated, as well as some herbicides and TPs.

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**(Eco-)Toxicology: Pollutants Exposure and effects  
on biota and ecosystems**

**Oral presentation: OT1-OT10**

**Poster presentation: PT1-PT39**

## Prioritisation of organic contaminants in the Sava River basin using chemical analyses and bioassays

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Region-specific contaminant prioritisation is an important prerequisite for sustainable and cost-effective monitoring due to the high number of different contaminants that may be present. This study represents the first comprehensive identification of hazardous chemical contamination in the Sava River watershed and provides a basis for their prioritisation. Three different matrices were analysed: sediment and surface water samples, collected at four Sava River locations, and wastewater effluents of the municipal wastewater treatment plant (WWTP) of the city of Zagreb. Before analysis, samples were enriched using large-volume solid phase extraction (SPE) for aqueous samples and accelerated solvent extraction (ASE) for river sediments. The analytical approach applied for chemical screening included a detailed analysis of organic contaminants using high resolution gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-QToF). In addition, the same samples were subjected to toxicity screening in a series of small scale or *in vitro* bioassays designed to characterise the biological response of hazardous contaminants having different modes of action. Cytotoxicity was determined by the MTT test; phase I induction potential measured as the ethoxyresorufin O-deethylase (EROD) activity; inhibition of the multixenobiotic resistance (MXR) by measuring P-glycoprotein transport activity; genotoxicity by the Ames bacterial test; and estrogenic potential using the Yeast Estrogen Screen (YES) assay. A large number of contaminants, belonging to different toxicant classes, were identified in all analysed matrices. Analyses of water samples showed that contaminants having polar character occurred in the highest concentrations, while in sediments, contributions from both non-polar and amphiphilic contaminants should be taken into account. Estimated contributions of individual contaminant classes to the overall toxicity indicated that, besides the classical pollutants, a number of emerging contaminants, including surfactants, pharmaceuticals, personal care products and plasticizers, should be taken into consideration in future monitoring activities. This work demonstrates the importance of the integrated chemical and bioanalytical approach for a systematic region-specific pollutant prioritisation. Finally, the results presented in this study confirm that hazard assessment in complex environmental matrices should be directed towards identification of key pollutants, rather than focusing on a priori selected contaminants alone.

## Toxic assessment of particle-bound PAHs: a novel environmental perspective.

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Air pollution is nowadays a recognized risk to human health, and a widespread threat to the ecosystems. Polycyclic aromatic hydrocarbons are Persistent Organic Pollutants (POPs) that have a high tendency to bind to particles. Indeed, they are constituents of ambient particular matter (PM). In this work, we used two complementary assays to evaluate the toxic effects of the organic fraction of urban PM samples. The AhR-based recombinant yeast assay (AhR-RYA) can detect and quantify the receptor-binding activity of dioxin-like compounds, such as PAHs. The zebrafish embryotoxicity test (ZET) is an *in vivo* method to assess toxic effects of chemical compounds in the early life stages of a vertebrate species. Air samples were collected from October 2008 to December 2009 in the city of Barcelona, Spain, using three different particle aerodynamic diameter cutoffs (i.e. PM<sub>1</sub>, 2.5 and 10). PM extracts with the highest PAH concentrations induced the highest response in both bioassays, with good correlation factors. Interestingly, data analysis linked the toxic effects to the abundance of heavier PAHs in the samples. No differences in PAHs concentration, AhR-RYA or ZET results were observed for samples collected at the same day with different PM size cutoffs. This indicates that the toxicity driven by the organic content of air samples corresponds to the sub-micron fraction of the PM (PM<sub><1</sub>). This work showed that both the AhR-RYA and ZET are sensitive assays to characterise the toxic potential of PM organic content in urban air samples. In addition, since the atmospheric deposition of PAHs is one of the major sources of contamination of the aquatic systems by those compounds, the ZET results gave new insights on the potential effects of the exposure of an aquatic organism to particle-bound PAHs. The PAH concentrations used in the ZET assay were in the ng l<sup>-1</sup> range, while the PAH levels reported for contaminated surface and coastal waters can easily reach µg l<sup>-1</sup>. This work emphasizes that the contamination of the aquatic systems by particle-bound PAHs might have an impact on aquatic vertebrates that has not been assessed and discussed until date. The authors thank the financial support of the Spanish Ministry through the project TEA-PARTICLE (CGL2011-29621; 2011-2013), and the Portuguese Foundation for Science and Technology for the doctoral grant of Sofia Mesquita (SFRH/BD/80710/2011) funded by the Programme POPH - QREN through the Portuguese Ministry of Education and Science and the European Social Fund.

## Ecotoxic and mutagenic effects of photolytic transformation products of pharmaceuticals: an experimental design for the investigation of mixtures

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The occurrence of active pharmaceutical ingredients in the environment has been well documented over the past decade. There is an emerging concern regarding the transformation products, apart from the parent compounds, which are present in wastewater. Photolytic transformation of active pharmaceutical ingredients is one of the most significant processes occurring in the environment and may be provoked by physical e.g. sunlight irradiation or technical e.g. UV irradiation processes. Conventional wastewater treatments often fail to eliminate these compounds, and as a result they remain present in treated wastewater, which can be then reused for agricultural and water replenishment purposes. Subsequently, potential adverse effects may be caused to organisms exposed through the wastewater reuse schemes applied.

In the present study, a four factor central composite design of 30 experiments was applied to investigate active pharmaceutical ingredients and their transformation products, which may be simultaneously present in solution, and in this way resemble real environmental conditions. Three common photolabile active pharmaceutical ingredients, diclofenac, ofloxacin and sulfamethoxazole were selected. Furthermore, their photo-transformation products after photolytic treatment were also investigated in this study. The irradiation time, the initial concentration and the combination effects versus the endpoints evaluated were intercorrelated. A battery assay with acute and chronic assays using *Vibrio fischeri*, *Daphnia magna*, *Pseudokirchneriella subcapitata* and a mutagenicity assay using mouse cells was applied. The parent compounds were quantified and the transformation products present were identified using UPLC-MS/MS analysis.

The main findings indicated that the initial concentration of the active pharmaceuticals was critical for the toxicity of both *P. subcapitata* (78%) and *V. fischeri* (10%); whereas, *D. magna* was not acutely affected by neither of the samples evaluated. The tk assay revealed low mutagenicity values for untreated and treated samples. In some cases however, the mutagenicity of the samples increased after photolytic treatment which will thoroughly presented. The UPLC-MS/MS analysis identified the main photo-transformation products of the mixtures of the active pharmaceutical ingredients.

## Exposure of breastfed newborn to DDT and metabolites from 1982 to 2009 in the Province of Vojvodina, Serbia

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Throughout 27 years (1982-2009), POPs were measured on seven occasions in early human milk collected from healthy mothers living in and around the city of Novi Sad (Serbia). p,p'-DDT, p,p'-DDD and p,p'-DDE were extracted from human milk with sulfuric acid using the Florisil column. Analytical determinations of DDTs in 3rd day human colostrums were performed using a GC-ECD (HP 5890) supplied with a 60 meter Quadrex fused silica column coated with 5% phenyl-95% methyl siloxane stationary phase with an ID of 320  $\mu\text{m}$  and a film thickness of 0.25  $\mu\text{m}$ . The following GC temperature program was used: 80  $^{\circ}\text{C}$ , 20  $^{\circ}\text{C min}^{-1}$  to 160  $^{\circ}\text{C}$ , 3  $^{\circ}\text{C min}^{-1}$  to 300  $^{\circ}\text{C}$ , 300  $^{\circ}\text{C}$  for 10 min. The first order rate equation was used to examine changes in concentration levels. Average daily intake of DDTs per kilogram body weight by newborns via milk was calculated assuming that the average weight of 3.5 kg newborn baby have an average intake of 60 ml/kg on the 3rd day of life.

DDTs level trends, were expressed with linear functions, showed decrease of p,p'-DDE. Linear decreasing correlation was observed for p,p'-DDT in the period 1982-1993, and an increasing from 1994 till 2009. The most consistent decline was for p,p'-DDE levels. Mean concentrations decreased from 69.39 to 2.52 ng/g w.w., and the  $t_{\text{dec}0.5}$  was 5.2 years. In contrast to p,p'-DDE, p,p'-DDT concentrations showed a slightly increasing trend from 1994. In the period 1982-1993, the  $t_{\text{dec}0.5}$  for p,p'-DDT was calculated to be 2.1 years. The body stores p,p'-DDE more tenaciously than other DDT metabolites, hence, the rise of p,p'-DDE is expected in future, as the consequence of this recent p,p'-DDT environmental influx. Mean concentrations of DDT decreased from 89.34 to 3.93 ng/g w.w. in period 1982-2009 and its half life was 6.3 years. These results are consistent with the declining trends of DDTs in other studies, with  $t_{\text{dec}0.5}$  of 5-7.5 years.

The estimated daily intake of DDT by 3.5 kg baby, on the 3rd day of life ranged from 5.36  $\mu\text{g/day}$  in 1982 to 0.24  $\mu\text{g/day}$  in 2009. A steep fall of DDTs average daily intake, comparing the first (1982) and the last (2009) year of the monitoring period in the Province of Vojvodina, was an expected finding, as a result of DDT use ban in Serbia since 1989. However, in the middle of this monitoring period, a small rise from 0.74  $\mu\text{g/day}$  to 1.18  $\mu\text{g/day}$  appeared between 1993 and 1994. The source of DDT influx in this period might have been the result of uncontrolled import to Serbia and use of chemicals of suspicious origin and quality. The estimated total DDT intake by a newborn on the 3rd day of life, throughout the whole period of monitoring was well below the maximum residue limit (MRL) of 0.01 mg/kg for pesticides in foods intended for infants and young children in Europe, hence there was no risk for breastfed babies in the region of monitoring.

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## Perfluorinated compounds: a cause for lipogenic disorder in JEG-3 cells?

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Perfluorinated compounds (PFCs) have emerged as global environmental pollutants widely distributed in wildlife and humans (Guilliland and Mandel, 1993). They are bioaccumulative, suspected to interfere in the lipid metabolism and to affect the oxidative metabolism of cells (Reistad et al., 2013). The present study investigated the toxicity of PFCs and the formation of reactive oxygen species (ROS) in human placental choriocarcinoma (JEG-3) cells, and further elucidated the differential uptake of PFCs by cells. Moreover, a comparative analysis of lipid profiles of non-exposed and exposed cells permitted to determine the effects of PFCs on JEG-3 cells lipidoma.

Eight PFCs were studied: perfluorobutanoate acid (PFBA), perfluorohexanoate acid (PFHxA), perfluorooctanoate acid (PFOA), perfluorononanoate acid (PFNA), perfluorododecanoate acid (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS) and perfluorooctanesulfonate (PFOS). Cell viability assay was conducted by applying Alamar Blue™ (AB) to monitor the metabolic activity and 5-carboxyfluorescein diacetate (CFDA-AM) to evaluate the membrane integrity. Cell toxicity was induced at relatively low concentrations of PFNA, PFDoA and PFOS with EC<sub>50</sub>-values of 220 ± 3.3, 219 ± 15.5 and 125 ± 6.4 µM, respectively. No significant cytotoxicity was observed for the other PFCs when tested at a concentration of 500 µM. The increase in ROS formation was assayed using the fluorescent probe 2,7-dichlorodihydrofluorescein diacetate (H<sub>2</sub>DCF-DA). However, no significant ROS formation was induced by any PFCs. To evaluate the amount of PFCs absorbed, cells were exposed to a mixture of PFCs at 0.6 and 6 µM and analyzed by UPLC-MS/MS after one, three, five, eight and twenty-four hours of exposure. Among the eight analytes studied, the highest uptake was observed for PFDoA, and in a lesser extends for PFNA, PFOS and PFHxA while the rest of PFCs remained mainly in the medium of culture. Moreover, the most toxic PFCs were those uptaken by cells which proved that cell toxicity was primarily due to its capacity to retain PFCs. Lipid profiles of exposed and non-exposed JEG-3 cells were obtained by HPLC-ToF-MS. The comparative study of lipid profiles was focused on phospholipids, sphingolipids, di- and triglycerides and cholesterol esters.

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## Influence of sulfamethoxazole on activated sludge bacterial community and removal efficiencies

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Antibiotics might be harmful for bacteria in the environment and natural elemental cycles. For this reason it is of major concern to get a deeper insight, from the microbiological point of view, on how the bacteria from wastewater treatment systems can cope with these substances. The sulphonamide sulfamethoxazole (SFX) is widely applied as a bacteriostatic drug and it is one of the top-selling antibiotics (Cavallucci 2007).

The bacterial community shifts on a 4-litres SBR lab scale reactor, together with the *sull* antibiotic resistance gene analyses, the biological nutrient and SFX removal performance, were studied before and after the addition of 50 µg/L SFX. Satisfactory biological nutrient removal was observed in terms of COD and Nitrogen. SFX removal efficiencies ranged between 20% and 50% with no evident signs of biomass acclimation, in terms of an increase in its removal.

Denaturing gradient gel electrophoresis was carried out (Miura et al., 2007). First, a loss in microbial population diversity was observed between the initial WWTP inoculation sludge and the next samples from the reactor, as a consequence of the bacteria adaptation to the new conditions established in the SBR. Afterwards, a further loss of richness occurred after the continuous SFX dosage. The class *Betaproteobacteria* remained generally stable along the study. On the other side, the classes *Sphingobacteria*, *Actinobacteria*, *Chloroflexi* and *Chlorobia* became weaker or even disappeared as a result of the antibiotic presence. Finally, *Thiotrix spp.*, belonging to the *Gammaproteobacteria* class, increased its presence after the exposure to SFX, likely due to its tolerance to the antibiotic.

The presence of antibiotic resistant bacteria was successfully identified over time the experimental period and the corresponding antibiotic resistance gene (*sull*) was quantified. Although the bacterial community changed significantly within the experiment, the resistance gene was present in a similar quantity over time. The obtained results verified that sulphonamide-resistant gene can remain stable in the media (Bean et al., 2005).

It can be concluded that the presence of SFX did provoke some important shifts in the studied bacterial community, even though the antibiotic removal efficiency or nutrient removal performance were not altered. Finally the bacterial community changes did not lead to any subsequent change in the antibiotic resistance gene presence.



## Development of oxidative stress biomarkers in developing zebra fish *Danio rerio* embryos.

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Oxidative stress reflects an imbalance between the systemic production of reactive oxygen species (ROS) and a biological system's ability to readily detoxify the reactive intermediates or to repair the resulting damage. In this study oxidative stress related responses were assessed in early life stages of *Danio rerio* (zebra fish). Measured responses include conventional biomarkers such as superoxide dismutase (SOD) and glutathione (GSH) levels, and a new tool to measure potential oxidative damage called senescence-associated  $\beta$ -galactosidase (SA- $\beta$ -gal).

In order to explore the underlying toxicity mechanisms of generated ROS, zebra fish embryos were exposed to model and non model prooxidants with and without UV radiance: a peroxide, tert-butyl hydroperoxide (BHP), the polycyclic aromatic hydrocarbon fluoranthene, three different TiO<sub>2</sub> nano-particles (NP 103, NP 104, NP 8- P-25) and one macro-TiO<sub>2</sub> (tiona). To account for transient antioxidant responses different exposure periods were studied. Zebra fish embryos exposed to 500 $\mu$ M of BHP showed increased SOD activity at 24 hours and GSH depletion from 48 to 192 hours. Elevated values of staining intensity for SA- $\beta$ -gal in exposed larvae indicated accelerating aging caused by oxidative stress. Photoinduced toxicity of 1.2 and 2 fold occurred respectively at 10 and 100 $\mu$ g/L of fluoranthene. GSH levels increased in embryos exposed to 100 $\mu$ g/L of fluoranthene under UV radiation. Enhanced SA- $\beta$ -gal staining levels occurred in individuals exposed to 100 $\mu$ g/L of fluoranthene with and without UV radiation. For TiO<sub>2</sub> particles, reduced growth and higher phototoxicity was registered in NP 103, NP 104 and NP 8-P-25 at 1000 $\mu$ g/L but not for tiona. SOD, GSH and SA- $\beta$ -gal were responsive to TiO<sub>2</sub> particles and varied across particle type and time of exposure. Only SOD activity changed under UV radiation. These results showed that the proposed method could be applied to evaluate oxidative stress in zebra fish early life stages.

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## The use of gene, biochemical and individual markers in transplanted *Daphnia magna* to characterize impacts in the field

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*Daphnia magna* individuals were transplanted across 12 sites from three Spanish river basins (Llobregat, Ebro, Jucar) known to have different sources of pollution. After being transplanted during 1 day in the field, feeding, biochemical and qPCR transcriptome responses were assessed and compared with those obtained in re-constituted water treatments spiked with solvent organic extracts obtained from water samples collected at the same locations and sampling periods. Feeding inhibition effects increased from up to downstream locations in Llobregat and Ebro rivers but not in Jucar. Cholinesterase enzyme activities of transplanted *D. magna* were affected in all river basins and in addition metabolic and biotransformation responses were also altered in those individuals caged in the Llobregat. The use of transcription patterns of up to 13 different genes encoding for general stress, metabolism and energy processes, reproduction and transporters corroborate phenotypic responses and allowed to differentiate sites within and across river basins. Furthermore, molecular responses obtained in transplanted individuals were similar to those obtained in individuals exposed to the re-constituted extractable organic contaminant fraction. These results, thus, indicate that the application of OMIC technology in the field is a promising subject in water management. This work was supported by the Spanish MEC grant CTM2011-30471-C02-01 and European Research Council project ERC-AdG-2012-320737. Claudia Rivetti was supported by a fellowship from the MEC, Spain (FPI BES-2012-053631).

## Uptake and clearance of non-toxic CdSe/ZnS quantum dots by the ciliated protozoa *Tetrahymena thermophila*

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The investigation of nanomaterial fate, behaviour and toxicity in the environment is a rapidly expanding area of research due to the mass production and, consequently, a crucial need for a complete environmental risk assessment. In the current study carboxyl functionalized CdSe/ZnS core shell quantum dots (QDs) were studied for their cellular uptake, localization and clearance in a unicellular eukaryote, freshwater protozoan *Tetrahymena thermophila*. Exposure to QDs at concentrations up to 80 nM induced no cytotoxic effects to *T. thermophila* nor elevations in intracellular reactive oxygen species or excessive lipid peroxidation as probed with fluorescent markers. The lack of toxicity could be explained by the low solubility of the studied QDs: the dissolved fraction of Cd in the exposure medium was negligible and the concentration of dissolved Zn remained below toxic concentrations to *T. thermophila*. The optical microscopy imaging showed that QDs, with an average hydrodynamic diameter of 12 nm, were readily phagocytosed by the protozoan upon the exposure to QDs in HEPES buffer. Flow cytometry analysis showed that the food vacuoles of *T. thermophila* became filled with QDs in time and dose dependent manner. The maximum filling of the food vacuoles with QDs was detected after 2-h exposure, while after 24-h exposure the tendency towards the clearance of the food vacuoles was detected. After replacing the QD-containing medium with the QD-free buffer about 50% of the protozoan cells had cleared their food vacuoles of QDs after 20 h. The confocal microscopy studies of QD-exposed *T. thermophila* revealed that phagocytosis was not the only pathway of entry for QD in the cell. In addition to larger aggregates of QDs in the food vacuoles also smaller-sized fluorescent particles were detected in the cells, suggesting QD internalization through cell membrane by alternative mechanisms (e.g. endocytosis). Inhibitors for phagocytosis and endocytosis were used to shed light on the QD internalization mechanisms in protozoa. Subcellular localization of QDs was studied with confocal microscope using cell organelle specific fluorescent markers. The current study provides insight into cellular trafficking of inherently nontoxic fluorescent nanoparticles that may pose possible risks by accumulating in the cells and becoming bioavailable for the organisms at higher trophic levels.

## The influence of bioaccumulated POP and metal levels on ecological water quality and fish communities

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Pollutants such as persistent organic pollutants (POPs) and metals, threaten the ecological quality of rivers, canals and lakes, and can cause adverse effects on local fish communities. Biotic indices, such as Flanders' Fish-based Index of Biotic Integrity (IBI), assess the ecological quality of a water body by evaluating different characteristics of the fish community. Well-balanced and adaptive fish assemblages can only be maintained by healthy ecosystems, hence fish community structure will reflect the ecosystem's health. The index is based on several metrics, including species distribution, trophic composition, reproduction success and their tolerance for disturbance. As the IBI reflects the overall quality of an aquatic ecosystem, it may also depict the potential impact of pollutants. From a governmental point of view, it would be very useful to know to what extent field levels of bioaccumulated pollutants show an effect on ecological quality of water bodies. This enables defining threshold values of bioaccumulated levels to allow better protection of the aquatic environment (as demanded by the Water Framework Directive). Nevertheless, visualisation of the direct negative correlation between the concentration of a pollutant and the biotic index is not always achievable, because the index is impacted by many other anthropogenic stressors, including modifications in the structure of the riverbed, presence of barriers or eutrophication.

The current study investigates a possible relationship between the presence of pollutants (PCBs, OCPs and metals) and the IBI score (expressed as an Ecological Quality Ratio (EQR), ranging between 0 "bad" and 1 "high status") in water bodies of Flanders (Belgium), based on concentrations in European eel (*Anguilla anguilla*). To this purpose, databases of long-term monitoring of pollution in eels and IBI have been combined and analysed (1156 fish and 185 locations). The main objectives of this study were to investigate if a decrease in ecological water quality, as indicated by IBI, was related with increasing pollution levels in the European eel, and if possible to formulate concentration thresholds above which a decrease in ecological water quality occurs. A generalized linear mixed model was used to determine which parameters (PCBs, metals, O<sub>2</sub>, water conductivity,...) significantly influenced the ecological status of Flemish water bodies.

For most pollutants, especially PCBs, arsenic, nickel, zinc and hexachlorobenzene (HCB) a clear decrease in IBI score was observed with increasing concentrations in European eel. This indicates that the presence of pollutants had a direct impact on the ecological quality. For these pollutants, a threshold concentration in eel tissue, above which a good ecological status (EQR $\geq$ 0.6) was never reached, could be formulated. Only for mercury, the observed levels didn't cause a decrease in EQR.

## Time trends of PCDD/Fs, PCBs, and PBDEs in Baltic herring in the Finnish coast of the Baltic Sea during 1978–2009

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In Finland, consumption of fatty fish from the Baltic Sea accounts for the majority of exposure to persistent organic pollutants (POPs). Long term biomonitoring is important in following the effects of emission reductions, and in estimating human exposure. Baltic herring is suitable for monitoring lipophilic PCDD/Fs, PCBs, and PBDEs, because the species is abundant all over the Baltic Sea. In this study, results from several studies are presented to illustrate the time trends of PCDD/Fs, PCBs, and PBDEs in the Finnish coast of the Baltic Sea during 1978–2009.

Altogether 344 composite and individual samples of Baltic herring (*Clupea harengus membras*) were collected across the Finnish coast of the Baltic Sea by random sampling in 1978–2009. The length, weight, and sex of the fish were determined during sampling. Age determination was based on microscopic examination of otoliths. 17 toxic PCDD/F, 37 PCB, and 14 PBDE congeners were analyzed at the National Institute for Health and Welfare, Chemical Exposure Unit (accredited by FINAS T077, SFS-EN ISO/IEC 17025:2005). The analytes were extracted with an organic solvent, cleaned, and quantitated against <sup>13</sup>C-labelled internal standards with high resolution gas chromatography mass spectrometry (GC-HRMS).

During the study period of 31 years, the concentrations of PCDD/Fs and PCBs in Baltic herring decreased 86–87%. In old herring (≥ 5 years), their levels decreased from approximately 50 to less than 10 pg/g fw and in young herring (< 5 years) from approximately 15 to less than 2 pg/g fw, expressed as WHO<sub>05</sub> TEQ. The temporal trend in PBDE levels was very different. During the study period, a 4–10 fold increase from 1–2 ng/g fw to 6–8 ng/g fw, followed by a corresponding decrease in PBDE load, with the maximum concentrations estimated throughout late 1980's–early 1990's. The temporal trends seem to reflect direct emissions from rivers rather than deposition from air. The POP levels depended strongly on the age of the herring. During 1978–2009, there were no substantial changes in the congener patterns of PCDD/Fs or PCBs, but BDE 47 proportion decreased significantly. The Finnish fish consumption guideline states that large herring over 17 cm (equals with age of 5 years) should only be eaten 1–2 times per month. In 2009, 94% of the young herring samples were below the EU maximum acceptable levels for PCDD/Fs, PCBs, and indicator PCBs.

The concentrations of PCDD/Fs, PCBs, and PBDEs in Baltic herring have decreased significantly during 1978–2009. Our results show that the efforts made by the EU, and other countries surrounding the Baltic Sea, have had a huge impact on the environmental levels of these pollutants. The exposure of the Finnish population to these compounds is expected to slowly continue to decrease.

**Transfer and accumulation of Cd, Cu, Ni, Pb and Zn in a soil – plant – snail food web and the effect of metal pollution on physiological and morphological biomarkers in *Cepaea nemoralis* (Gastropoda: Pulmonata).**

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Metal pollution cause environmental disturbances for both organisms and habitats by direct or indirect toxicity. Metals in soil can be taken up by plants and transferred to higher trophic levels by means of herbivory. Among possible candidates for assessing metal transfer within the food web, terrestrial snails are recognized as pertinent ecological indicators. Snails are saprophagous and phytophagous, while exchanges between snails and soil occur via soil ingestion and absorption through the pedal sole. Cylindrical field microcosms have been reported to be useful tools for assessing the response of biota under realistic exposure scenarios. Chemical analysis of organ tissue concentrations alone does not provide any indication of deleterious effects of contaminants on the biota and should therefore be supported by biomarker responses measured at different levels of biological organisation. This study aimed to investigate metal transfer in a soil-plant-snail food web taking into account soil physicochemical properties and to search for physiological and morphological responses to metal pollution.

A cross-transplantation experiment was performed by placing adult unexposed snails (*Cepaea nemoralis* (L.), Pulmonata, fam. Helicidae) in field microcosms along a metal polluted gradient in Antwerp (Belgium). Snails were removed and analyzed in intervals of 0, 2, 4, 8 and 16 weeks. Soil and *Urtica dioica* (L.) (Common nettle) samples were taken from the exact points where the snail microcosms were located. Soil and *U. dioica* metal concentrations plus soil physicochemical properties (pH, particle size and organic carbon content) were determined. Concentrations of the metals Cd, Cu, Ni, Pb, Zn and the metalloid As were measured in the digestive gland as well as the pedal sole. Physiological biomarkers (lipid, glycogen and protein reserves and glutathione S transferase (GST)) and morphological characteristics (shell volume, thickness and strength) were measured in the digestive gland.

The digestive gland accumulated significantly higher concentrations of As, Cd, Ni, Pb and Zn than the pedal sole. As, Ni, Pb and Zn concentrations in the digestive gland increased over time and along the pollution gradient while Cd and Cu concentrations stayed relatively constant along the pollution gradient and over time. Metal concentration in the digestive gland correlated significantly with the concentrations measured in soil and *U. dioica* while pH played an important role in the bioavailability of metals. Although significant differences in tissue concentrations between snails from polluted and control sites were observed, no real differences in biomarkers were observed between sites over time.

## Levels of selected pesticides in honey samples from Pomerania, Poland

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Honey produced by honey bees from pollen, plant nectars, and/or honeydew is composed of over 300 chemical substances which belong to different chemical compound groups. These are mainly carbohydrates, water, polysaccharides, fatty acids, proteins, minerals, dyes, fragrances, enzymes, hormones and vitamins in amounts depending on the plant from which the honey was made. Honey bees can bring many pollutants deposited on plants into the hive. Therefore, plant protection products used in agriculture can not only cause mass poisoning of bees but may also enter bee products, especially honey affecting its quality, properties and posing a particular threat to human health [1]. Pesticides are significant group of xenobiotics affecting the biota. Regulation 396/20 of the European Parliament and of the Council established values of the maximum residue levels (MRLs) of pesticides in products of plant and animal origin Regulation (EC), 2005. Since September 1st 2008, the European Commission set new MRLs of some pesticides in honey, which are in range of 10 and 50 ng/g [2].

In this work, analytical method employing liquid chromatography–tandem mass spectrometry (LC–MS/MS) with electrospray ionization (ESI) for the simultaneous determination of 30 pesticides in honey was optimized. Sample preparation approach based on acetonitrile extraction followed by dispersive solid-phase extraction (d-SPE) cleanup step was validated according to Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed (SANCO/10684/2009). The procedure involved homogenization of a 1 g sample with acetonitrile–water mixture followed by salting out with citrate buffer, magnesium sulphate and sodium chloride. Hereafter, d-SPE technique was carried out using primary secondary amine (PSA) and magnesium sulphate. This combination of cleanup steps ensured efficient extract purification. The recoveries were observed for most analytes and ranged between 70 and 120% (relative standard deviations <20% in most cases). Linearity of the calibration curves was studied in the concentration range between 2–500 ng/g. The method limits of quantification were ranged between 2.73–75 ng/g. Analytical procedure was used to analysis of real honey samples from Pomerania (Poland).

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## Determination of pesticide residues in honeybee samples with LC-MS/MS and GC-MS/MS

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Nowadays, pesticides are widely used in agricultural practices for pests and diseases control. The slow degradation of these compounds in the environment and extensive or inappropriate use by farmers can lead to the contamination of various ecosystems. The widespread distribution of pesticides is known to cause problems to apiculture industry. Bees may be contaminated by pesticide residues during harvesting. These contaminants can be transported on bee bodies or with the forages to the hive. The increased mortality of bee colonies has been noticed in recent years in the world. Most honey bee losses are attributable to pesticide exposure [1].

In this work, analytical method employing liquid chromatography–tandem mass spectrometry (LC–MS/MS) and gas chromatography–tandem mass spectrometry (GC–MS/MS) for the simultaneous determination of pesticide residues in honeybee samples was optimized. Sample preparation approach based on QuEChERS extraction was validated according to the Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed (SANCO/10684/2009). The recoveries were observed for most analytes and ranged between 70 and 120% (relative standard deviations <20% in most cases). The method limits of quantification provide the possibility to use this analytical procedure to the analysis of real samples.

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## Evaluation of environmental impact of silica-based nanoparticles

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Nanotechnologies are forecasted to rapidly expand and new nanomaterials will be incorporated in a wide range of products. However, the same properties of the nanomaterials that makes them so interesting for application can also provide them toxic effects to humans or ecosystems. At present, there is relatively little data regarding the extent to which nanomaterials might be released from products into the environment or how they are transported, transformed or accumulated in ecosystems. Hence, it is necessary to improve knowledge on the environmental fate and impact of these new materials. Above all, reliable data on the physico-chemical properties, toxicokinetics and degradability of nanoparticles are required to comprehend in which form and in what concentrations they can be expected to be found in the environment. Depending on physical and chemical conditions prevailing in aquatic systems, nanoparticles (NP) will occur in the environment either as aggregated or dispersed material. NP may sediment or otherwise become immobilized, or diffuse in aqueous environments and water columns, becoming more mobile, more bioavailable and thus more toxic. The aim of this work is to evaluate toxicity connected to these materials. We focus on silica and functionalized silica nanoparticles, often used as drug delivery systems or for core shell preparation. In particular, MCM-41 system, pristine or funzionalized with aminopropyl group (NH<sub>2</sub>-MCM41), was investigated. We have evaluated their acute toxicity by adopting a Microtox *Vibrio fischeri* assay and their citotoxicity performed on neuroblastoma cell line. In particular, since these materials are often used as drug deliver, we have also studied how their environmental impact may be modified by drug loading and release. For this, a key molecule, acid 5- aminolevulinic is studied. The choice of this molecule is due to its ability to act as pro-drug of protoporphirine, a photosensitizer widely used in the photodynamic therapy (PDT), employed in the treatment of actinic keratosis and some types of skin cancers. The toxicity of both aqueous and solid phases were considered and on the same cell line has been evaluated the cellular uptake of MCM-41, made fluorescent by impregnation with fluorescein.

## Priority and emerging brominated flame retardants in gull eggs (*Larus michahellis*) from Atlantic and Mediterranean colonies: trends and impact

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The present study was aimed to evaluate the geographical distribution and temporal trends of priority and emerging brominated flame retardants (FR) in yellow-legged gull eggs (*Larus michahellis*) collected from 3 National Parks from Spain. Compounds studied were polybrominated diphenyl ethers (PBDEs) and emerging flame retardants which included hexabromobenzene (HBB), pentabromoethyl benzene (PBEB), pentabromotoluene (PBT), 2,3-dibromopropyl 2,4,6 tribromophenyl ether (DPTE), 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (EHTBB), bis(2-ethyl-1-hexyl)tetrabromo phthalate (BEHTBP), 1,2 bis (2,4,6 tribromophenoxy)ethane (BTBPE), hexachloro cyclopentadienyl dibromooctane (HCDBCO) and decabromodiphenyl ethane (DBDPE). In a first step, we developed an analytical method based in liquid-solid extraction, Florisil clean up using solid phase extraction cartridges (10 g, WATERS) and analysis by gas chromatography coupled to mass spectrometry in negative chemical ionization (GC-NCI-MS) to determine PBDEs (including BDE 209) and gas chromatography coupled to tandem mass spectrometry in electron ionization (GC-MS/MS) to determine emerging flame retardants. In a second step, fresh gull eggs were collected from 5 National or Natural Parks which represent the most important gull colonies of the Iberian Peninsula: Medes Islands, Ebro Delta, Cabrera and Chafarinas, representing Mediterranean colonies and Islas Atlánticas de Galicia representing the Atlantic colony. In each colony, 12 eggs were randomly collected and pooled from 3 areas of the colony during the period 2009-2012. PBDEs were detected from 100 to 21444 pg/g ww, being BDE 209 the most ubiquitous compound. Mediterranean colonies had higher levels of PBDE than Atlantic, due to the more industrial and mass urbanization in this area compared to the open Atlantic environments. In addition, very small time variations were observed, indicating the pervasive presence of these compounds in the studied areas. For emerging FR, only BTBPE was detected and at very low concentrations. The effect of FR in eggs was studied in terms of egg shell biometry, development of the egg and survival rate and it was found that the presence of PBDEs did not affect any of these factors.

## The concentration of toxic metals in wild boars (*Sus scrofa ferus*) from industrial area in Poland

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Toxic metals, such as lead (Pb), cadmium (Cd) and mercury (Hg) are natural components of the earth's crust and their increased concentrations in the environment may result from anthropogenic activities, e.g. combustion of fossil fuels, mining and smelting of non-ferrous metals. These elements released to the environment by industrial activities can affect the food chain and accumulate in wildlife resulting in numerous health disorders and pose a potential threat to the consumers of venison. The aim of the study was to assess the accumulation of Cd, Pb and Hg in the tissues of wild boars (*Sus scrofa ferus*) inhabiting the area of Zinc Smelter "Miasteczko Slaskie" located in Upper Silesia Industrial Region (region A) and the Masurian District (region B) as reference site. The kidney, liver and muscle samples of 76 individuals were collected in the two regions from January to December 2012 in cooperation with local hunting authorities. The samples were homogenized, ashed in furnace at 450°C and digested in nitric acid. The concentrations of Cd and Pb were determined using a GF-AAS method. Hg concentrations were determined using an AMA-254 mercury analyzer. The quality control of analytical measurements was performed using the following certified reference materials: BCR-184, BCR-186 and BCR-151. The levels of Cd in kidneys, liver and muscles (in mg·kg<sup>-1</sup> of wet weight) in area A were as follows: 29.840; 2.947 and 0.023 respectively and were higher than in area B: 2.594; 0.196 and 0.004 (p≤0.01). The contents of Pb in the liver and kidneys in area A were: 0.700 and 0.269 and were higher than in area B: 0.083 and 0.085 (p≤0.01). Because the rifle bullets used by hunters are made of Pb, increased levels of this metal were found in the samples of the muscle tissue. For this reason, muscle cannot be considered a bioindicator of environmental pollution by Pb. The levels of Hg in the tissues (in mg·kg<sup>-1</sup> of wet weight) ranged from 0.004 to 0.052, but the differences between the mean concentration of this metal were insignificant. The results show that area A appears to be more contaminated with Cd and Pb than area B due to the industrial activities. Moreover, the majority of kidney and liver samples exceeded the tolerance limits for Cd and Pb for slaughter animals. This problem needs attention, considering the safety of the consumers of venison. The results presented in this paper are only a small part of research conducted in the main industrial regions in Poland. The concentrations of toxic metals in the hair of animals, rumen or gastric content, soil and plants from their habitat are also under investigation. This research will be continued in the next years.

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## INHIBITION EFFECT OF SOME PESTICIDES ON GLUTATHION REDUCTASE AND GLUTATHION PEROXIDASE

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Pesticides have become an increasingly serious source of chemical pollution of the environment due to their extensive usage in agriculture. In natural aquatic environments, alterations in the chemical composition, such as those caused by pesticide contamination, can affect the freshwater fauna, particularly fish. The fish plays an increasingly important role in the monitoring of water pollution because it responds with great sensitivity to changes in the aquatic environment. Recent studies indicate that pesticide toxicity in fish may be related to an increased production of reactive oxygen species, leading to oxidative damage. Antioxidant systems prevent the formation of reactive oxygen species (ROS), which can react with susceptible biological macromolecules and produce lipid hydroperoxidation, DNA damage, and protein carbonyls, resulting in oxidative stress. The biochemical function of glutathione peroxidase is to reduce lipid hydroperoxides to their corresponding alcohols and to reduce free hydrogen peroxide to water. Glutathione reductase is important in maintaining a critical ratio of GSH/GSSG (glutathione disulfide) under oxidative stress.

In this study, we searched enzyme activities of glutathione reductase (GR) and glutathione peroxidase (GSH-Px) which obtained from *Cyprinus carpio carpio* and also the effects of some pesticides (2,4-dichlorophenoxy acetic acid dimethylamine salt, fenprothrin, cypermethrin, lambda-cyhalothrin, deltamethrin) on antioxidant enzymes using UV-Visible spectrophotometer. Consequently, half of inhibition concentration values (IC<sub>50</sub>) of glutathione reductase are  $4.6 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $8.7 \times 10^{-4}$ ,  $8.3 \times 10^{-5}$  and  $1.72 \times 10^{-5}$  M and those of glutathione peroxidase are  $4.7 \times 10^{-4}$ ,  $1.33 \times 10^{-3}$ ,  $2.05 \times 10^{-5}$ ,  $3.11 \times 10^{-4}$  and  $1.2 \times 10^{-5}$  M, respectively.

**Key Words:** *Cyprinus carpio carpio*, Pesticides, Antioxidant, ROS, Glutathione reductase, Glutathione Peroxidase

## On the acute toxicity of polyphenols to freshwater alga *Chlorella vulgaris*

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The REACH legislation (Registration, Evaluation, Authorization and Restriction of Chemicals) obliges the submission of ecotoxicological information obtained from algal growth inhibition tests for compounds manufactured in or imported into the European Community above 1 ton/annum. Yet, the information on the algal toxicity of chemicals, in particular those eliciting toxicity through reactive mechanisms is seriously lacking. In this study, the toxicity of seven reactive polyphenols including pyrogallol (i.e., 1,2,3-trihydroxybenzene), three catechols and three hydroquinones to *Chlorella vulgaris* was determined in 96-hour static algal growth inhibition assays. Following range finding assays, the definitive tests were conducted in three parallels using five test concentrations and a control. The analytical concentrations were verified by gas chromatography.

The results revealed that the concentration that inhibits algal growth by 50% (i.e., IC<sub>50</sub>) as determined at the end of 48, 72 and 96 hours revealed no significant difference between the test durations as the IC<sub>50</sub> and the associated confidence intervals overlapped. Additionally, the toxicity of the tested compounds did not change significantly based on the toxicity calculation method (i.e., ICp, Weibull or polynomial regression)

From an organic chemistry perspective, *ortho*-dihydroxybenzenes (i.e., catechols) can be oxidized abiotically and enzymatically to *ortho*-quinones, which can act as Michael acceptor electrophiles. *Ortho*-quinones are much more reactive as Michael acceptors than the isomeric *para*-quinones (i.e., hydroquinones) because the carbon-oxygen-carbon-oxygen group (COCO) is more electronegative than the carbon-oxygen group. In line with the greater activating effect of the COCO group, catechol was found to be more toxic than hydroquinone to *C. vulgaris*. As for pyrogallol, this compound should be more toxic than catechol because the quinone form of 1,2,3-trihydroxybenzene should be more electrophilic than the *ortho* quinone from catechol. As expected, pyrogallol was found to be more toxic than catechol to *C. vulgaris*.

Of the seven polyphenols tested, six of them were classified as toxic according to the toxicity scheme provided by the European Union. Accordingly, strict measures should be warranted by regulators regarding the release of these compounds to freshwater environments to avoid the disruption of sensitive algal communities in these ecosystems.

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## Identification of neurotoxic compounds in produced water discharges from offshore oil production platforms by high-throughput effect-directed analysis

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Effect-directed analysis (EDA) is a powerful and promising technique to identify compounds responsible for a biological effect in a complex environmental mixture. EDA uses bioassays to guide chemical fractionation of the sample in order to reduce its matrix. Identification of the toxicants is done by non-targeted chemical analysis of the active fractions. In this study produced water samples from two offshore oil production platforms were used to identify neurotoxic compounds discharged into the North Sea.

Produced water is the largest volume waste in oil and gas production operations. Produced water is both the water trapped in the geological reservoir with the oil (or the gas), and the water injected in the reservoir with chemicals that leads to a higher recovery rate and safer operation. On offshore facilities, this water is directly discharge into the sea after a mechanical treatment. In Norway, more than 400 000 m<sup>3</sup> of produced water are discharged into the sea every day since 2000 and a wide range of compounds can be found in this water. Neurotoxicity can be measured by looking at the inhibition of Acetylcholine esterase (AChE). AChE is an essential enzyme for the neurotransmission because it hydrolyses the neurotransmitter acetylcholine at cholinergic synapses. An inhibition of AChE causes an over stimulation of muscarinic and nicotinic receptors which can cause various effects on the nervous central system.

After solid phase extraction, produced water samples were fractionated by high-performance liquid chromatography (HPLC) and neurotoxic potential was tested in each fraction. Biologically active fractions can be further fractionated in order to reduce the matrix of the active fractions. Following the fractionation steps, the biologically active fractions were analysed by gas chromatography coupled with high resolution time of flight mass spectrometry (GC-ToF-MS) in order to identify compounds present in these fractions. For this study an automated and high-throughput procedure was developed to directly link fractionation, biotesting, and chemical analysis steps. Every pipetting step and sample preparation between the fractionation, bioassay, and identification steps were automated by using a Biomek 3000 workstation. This allows a high-throughput EDA keeping human inputs as to a minimum.

## Human exposure to melamine from milk and related products – new molecularly imprinted polymer for melamine analysis

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The 1,3,5-triazine-2,4,6-triamine, also known as melamine, is a polar and hydrophilic compound with high content in nitrogen (about 66%), mainly used in plastic industry, because of its fire retardant properties. It has been detected in milk, as result of a fraudulent addition, with the purpose of increasing the apparent protein levels. Melamine, when combined with cyanuric acid (hydrolysis product) precipitates, leading to the formation of kidney stones, which can be lethal because of renal failure. On the other hand, migration from melamine-containing resins to food and beverages, as well as a result of the metabolization of cyromazine, an insecticide applied to crops, may occur. Therefore, efforts to detect melamine in various food products, particularly milk and dairy products is of utmost importance, aiming the estimation of the human exposure to this xenobiotic.

In the past, our research group has validated an analytical methodology by GC-MS, after sample derivatization, for the analysis of 20 milk and food samples derived from milk (cookies, biscuits, baby powder milk and soya powder) [1]. Even considering a high incidence of melamine detection (in 55% of the 20 samples tested), the maximum concentration was 2.3 mg/kg, which is not expected to be a significant hazardous for human health.

In this work a new, faster and more selective extraction methodology for HPLC-DAD analysis of melamine and a screening study of melamine in 50 food products are proposed, aiming the estimation of human daily intake. A new fit-for-purpose method, using a molecularly imprinted polymer (MIP)-based matrix solid-phase dispersion, prior to HPLC-DAD, was developed. The MIP was synthesized by suspension polymerization, using melamine as template, methacrylic acid as functional monomer, ethylene glycol dimethacrylate as cross-linker and chloroform as porogenic solvent. The resulting MEL-MIP was used as a dispersive extraction sorbent to extract melamine from 50 food samples, before HPLC-DAD, using matrix-matched calibration. The samples were from different origins, obtained either in supermarkets or in Chinese food stores.

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## Polycyclic aromatic hydrocarbon levels in octopuses from different geographical origins: inter- and intra-specific variability

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Cephalopods may act as bioindicator and sentinel species for ecological risk assessment and marine environment monitoring studies [1]. They are considered one of the most interesting ecological classes due to their capacity to accumulate contaminants and ability to grow and reproduce in polluted environments. Several contaminants exist in marine milieus. Particular attention should be given to polycyclic aromatic hydrocarbons (PAHs) since they are considered by the United Nations Economic Commission for Europe POPs protocol as persistent organic pollutants [2] and sixteen are regarded as priority pollutants by the U.S. EPA. The aim of this work was to characterize three commercially valuable octopus species (*Common*, *Mexican four-eyed* and *Curled octopus*), captured in distinct geographical origins (Northeast (NEA), Northwest (NWA), Eastern Central (ECA) and Western Central (WCA) Atlantic Ocean, Pacific Ocean (PO) and Mediterranean Sea (MS)) regarding their PAH levels in order to assess their status of contamination and their intra and inter-specific variability. Out of the 18 quantified PAHs (the 16 PAHs considered by U.S. EPA as priority pollutants, dibenzo(a,l)pyrene and benzo(j)fluoranthene) only Indeno(1,2,3-c,d)pyrene was not detected. PAH levels ranged from 4.45 (*Curled octopus* from NEA) to 87.3 (*Mexican four-eyed octopus* from WCA)  $\mu\text{g}/\text{kg}$  wet weight. Nine carcinogenic (probable/possible) PAHs accounted for 2 (*Mexican four eyed-octopus* from WCA) to 55% (*Curled octopus* from NEA) of the total PAHs content being the main contributors naphthalene and dibenzo(a,h)anthracene. PAHs source analysis indicated that all the capture zones of the different *octopus* species are significantly affected by both petrogenic and pyrolytic sources.

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## Monitoring the air quality in Venice-Mestre with *Tillandsia aeranthis*

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Air pollution is one of the main health risks humans are facing nowadays in the form of inorganic or organic compounds, emitted by natural and anthropogenic sources (Colbeck and Lazaridis, 2010). Humans as well as flora and fauna suffer from the unintentional uptake of a number of elements and compounds which have been demonstrated to produce mutagenic or even carcinogenic effects (IARC, 2013, Fischer et al., 2013). Therefore, investigating the air quality to prevent toxic effects is a first important step to increase humans' welfare. Monitoring can be carried out in different ways: with active or passive samplers or by biomonitoring. In this study, *Tillandsia aeranthis* (Loiseleur) L.B. Smith from the family of bromeliads has been used as a biomonitor for the air quality in Venice-Mestre (Italy). Plants were exposed in different emission scenarios throughout the study area, namely in an urban, industrial and harbour area. The peculiarity of these plants is their ability to uptake nutrients and water only from the atmosphere, as roots (when present) have the only function of anchoring the plant to the host. In South America, the home region of this plant, *T. aeranthis* lives on trees and telephone masts and it is transported by the wind from one place to another. To avoid removal, while exposing *T. aeranthis* to the ambient air in the three sampling stations in Venice-Mestre, it was anchored in holes in a piece of wood. In order to ensure that it was not exposed directly to the sunlight nor to the rainfall, it was kept in a tube with holes on both sides to ensure air circulation. Sampling started with six plants of *T. aeranthis*, and in periods of three weeks one of them was analyzed in terms of organic (Polycyclic Aromatic Hydrocarbons (PAHs)) and inorganic (metals) pollutants contained in the air particulate matter. Plant "blanks" were taken in the orchid greenhouse of the Botanical Garden in Padua and collected in the same time scales as the plants exposed outdoor. The amounts of 18 PAHs contained in the plants were analyzed by GC-MS, whereas metal determination was obtained with PIXE-analyses. The lipid content of *T. aeranthis* plants was also determined. Data obtained from plants' extracts were processed in comparison with pollutant values in airborne PM obtained by active air sampling on quartz fibre filters carried out by the regional agency for environmental protection of the Veneto region (ARPAV). The results established *T. aeranthis* as an encouraging biomonitor for the heavy metal and PAHs pollution of the ambient air of Venice-Mestre.

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## Human Exposure Assessment to Musks in the Metropolitan Area of Porto (Portugal)

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Synthetic musks are organic compounds commonly used in several cosmetics, personal care products and household products like perfumes, lotions, deodorants, soaps, shampoos, detergents, etc. According to their chemical structure, they can be divided into four major classes – nitromusks, polycyclic, macrocyclic and alicyclic musks [1]. When these personal care products are consumed, part of them is drained into the sewer system and reaches the wastewater treatment plants (WWTPs) and part is volatilized. Without complete removal, the effluents discharges can contaminate the ecosystems. Due to their extremely high incidence of utilization, lipophilic and persistent nature, these compounds tend to bioconcentrate and bioaccumulate in different matrices.

In the past decades, it was believed that musks were inert and had no toxic effects to humans and environment [2]. However, recent reports suggest that they can cause toxic effects, be carcinogenic (namely the nitromusks) and cause estrogen imbalance in aquatic animals [3]. Due to the lack of information, there are no certainties about the impact of these contaminants. Therefore, it is extremely important to carry out Environmental Risk Assessment (ERA) studies. In line with this idea, it is essential to examine the concentrations of synthetic musks in personal care products to enable a prediction of the human and environmental exposure by measuring its inputs.

In this work, a simple, fast and reliable analytical method (QuEChERS/GC-MS) was used to analyse musks in personal care products. The products were chosen according to the usage patterns of the population in the Metropolitan Area of Porto, Portugal. Synthetic musks were detected in most analysed samples in a wide range of concentrations. In general, detected musk amounts were higher in perfumes, lotions and deodorants. Galaxolide was the most frequently detected musk in the analysed products. The human daily exposure to musks was estimated, as well as the release rates of these compounds into the environment.

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## Recombinant yeast bioassay and strategies towards a ready-to-use alternative for detection of endocrine disruptive compounds

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Recombinant yeast bioassays constitute a suitable tool for environmental monitoring of compounds with endocrine disruption activities, notably estrogenic and androgenic activities. Compared to other more sensitive models, i. e. in vitro mammalian or fish cell lines, yeast-based assays are easy to perform, usually less time-consuming, show high sensitivity and reproducibility and represent relatively low costs. Despite all these advantages, to design a ready-to-use yeast-based assay with similar throughput to those including overnight culture incubation is one of the pending tasks. The rationale of this is making yeast bioassays more accessible to field studies and less equipped laboratories. During this project we aim to optimize yeast *Saccharomyces cerevisiae* based assays for the fast assessment namely of anti/estrogenic and anti/androgenic potencies of environmental samples and compare their applicability in comparison with more elaborate, expensive and equipment-demanding vertebrate-cell based models. The study includes detailed characterization and comparison of the sensitivity, robustness and reproducibility of the two types of models on a set of model compounds and comparison of their relative potencies. Also, suitability of different strategies with the aim to fulfill ready-to-use yeast bioassay is preliminarily evaluated. In summary, we consider new approaches to improve existing procedures with the aim to optimize and modified the assays for best sensitivity and applicability for field samples.

## Development of an obesogenic test in *Daphnia magna*

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The increasing concern on emerging contaminants has urged for the need of novel ecotoxicological procedures in Environmental Risk Assessment. Current toxicity assays such as those based on acute and chronic responses may not be sensitive enough to detect emerging effects at low doses. Here we include data on a new assay developed in *Daphnia magna* juveniles to test obesogenic effects of contaminants. The bioassay is based on short term *in vivo* exposures to the tested chemicals and *in vivo* visualization of lipid reserves using the fluorescent dye Nile Red. The test was validated with a model pollutant known to be obesogenic, such as tributyltin (TBT) and others that may be such as triphenyltin (TPT), 4-nonylphenol (NP), bisphenol A (BPA) and di-2-ethylhexyl phthalate (DEHP). The results obtained indicated that the Nile Red bioassay was able to reproduce lipid reserve dynamics in *Daphnia magna* within and between moulting, reproductive events, juvenile and adult stages. The *D. magna* Nile Red bioassay was also able to assess differences in lipids across low and high food ratio conditions. Tests performed with putative obesogenic compounds showed that TBT dramatically impaired lipid dynamics making organisms to increase their lipid reserves and delay moulting, and that food levels alter TBT effects. The other obesogenic compounds affect differently lipids dynamics. Obtained results will be discussed facing new evidences that state that in arthropods obesogenic compounds may act by disrupting retinoid X and ecdysone metabolic paths.

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## Pollution stress biomarkers in bryophytes and their composition

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Bryophytes are the second largest group in plant kingdom and there are around 15 000-25 000 bryophyte species. Bryophytes can be found in any location where photosynthesis is possible and they are divided in 3 divisions - mosses (*Bryophyta* - 14000 species), liverworts (*Marchantiophyta* - 6000 species) and hornworts (*Anthocerotophyta* - 300 species). Recent studies have found high amounts of terpenoids, phenolics, glycosides and lipids in bryophytes samples and bryophyte extracts have demonstrated antibacterial, antifungal, cytotoxic and many other kinds of biological activities and the number of studies of biologically active compounds in bryophytes is rapidly growing. Chemical composition of bryophytes may differ between species, growth environment and seasons. As relatively primitive organisms bryophytes demonstrate high tolerance in respect to naturally extreme environmental conditions, but also in respect to pollution. Relatively much has been studied metal accumulation in bryophytes and possibilities to use bryophytes as pollution bioindicators.

In higher organisms to study pollution impacts different biomarkers are widely used, however the pollution and environmental stress biomarkers in bryophytes are not studied. The aim of this study is to analyse bryophyte composition and its changes as a reaction on pollutant action. We have studied selected bryophyte basic chemical composition, UV, FTIR, <sup>13</sup>C NMR spectra, UV, fluorescence spectra of extracts as well as presence and concentration of polyphenolics in mosses, liverworts. There was significant variation in the elemental composition of bryophytes. The elemental compositions of the studied bryophytes were: C – 40-42%; H – 5.5-5.7%; N – 0.5-1.1%; S – ~0%. The dominant compounds judging by pyrolyses of bryophytes were: phenol, 4-ethenylphenol. Their origin is thought to be a tannin like polyphenolic biopolymer with 4-isoprenylphenol, being at least partially bound to it. We have analyzed not only total content of polyphenols in bryophyte extracts but also flavonoid content, as well as antiradical scavenging, antimicrobial and antitumor activity.

Under impact of stress factors (drought stress) and pollutants (heavy metals like Cu<sup>2+</sup>, Pb<sup>2+</sup>, NO<sub>2</sub>, phenol) the composition of bryophytes is changing and markers of oxidative stress appear. Integral indicators of pollution stress are polyphenols as bryophyte ingredients, but general ability to scavenge free radicals also is increasing.

## EFFECT OF SOME PESTICIDES ON ANTIOXIDANT ENZYMES OBTAINED FROM *CYPRINUS CARPIO CARPIO*

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Exposure to pesticides can cause oxidative stress in many aquatic organisms, since these contaminants can stimulate the formation of reactive oxygen species (ROS) or alter the antioxidant defenses. Pesticides may induce oxidative stress, leading to generation of free radicals and cause lipid peroxidation. Antioxidant enzymes are an important antioxidant defense in nearly all cells exposed to free radicals. It is shown that the antioxidants of fish may be useful biomarkers of exposure to aquatic pollutants. Superoxide dismutase is an important antioxidant enzymes are that catalyse the dismutation of superoxide into oxygen and hydrogen peroxide. Another important antioxidant enzyme is glucose-6-phosphate dehydrogenase a metabolic pathway that supplies reducing energy to cells (such as erythrocytes) by maintaining the level of the co-enzyme NADPH.

In our study, we investigated the effects of some pesticides on superoxide dismutase (SOD) and glucose-6-phosphate dehydrogenase (G6PDH) enzymes obtain from *Cyprinus carpio carpio*. For this study, today using at agriculture of five different pesticides (2,4-dichlorophenoxy acetic acid dimethylamine salt, fenprothrin, cypermethrin, lambda-cyhalothrin, deltamethrin) were selected. The pesticides effect on both of these enzymes showed inhibition impact to various degrees. As a result, we calculated half of inhibition concentre values ( $IC_{50}$ ) for superoxide dismutase are  $2.6 \times 10^{-4}$ ,  $4.1 \times 10^{-6}$ ,  $5.5 \times 10^{-4}$ ,  $3.5 \times 10^{-5}$ , and  $1.1 \times 10^{-6}$  M, and those for glucose-6-phosphate dehydrogenase are  $6.6 \times 10^{-5}$ ,  $7.1 \times 10^{-5}$ ,  $1.5 \times 10^{-3}$ ,  $6.1 \times 10^{-6}$  and  $1.1 \times 10^{-5}$  M, respectively.

**Key Words:** *Cyprinus carpio carpio*, Pesticides, Antioxidant, ROS, Glucose-6-phosphate, Superoxide dismutase.

## Persistent Organic Pollutants (PCDD/Fs, DL-PCBs) in Wild Fish from Two Polish Main Rivers

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Since of highly bioaccumulative ability, fish are frequently used as biomonitors for the aquatic environment. Several studies have been done recently regarding the contamination of Baltic Sea fish with polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/Fs) and dioxin-like PCBs (DL-PCBs). But contamination level of fresh water fish from Polish rivers by these persistent organic pollutants is unknown. Because of hydrophobic nature, the majority of these compounds released into aquatic systems ultimately become associated with the organic fraction of suspensions and/or sediments and the lipid-rich tissues of aquatic organisms. The aim of the present study was to define dioxins and DL-PCBs pollution status in fish of two main Polish rivers using fish muscles as biomarkers. Fish were collected from Vistula River close to the large urban agglomerations (Warsaw and Cracow) and from Odra River close to Wroclaw. Level of 29 PCDD/F and DL-PCB congeners was determined in common fish species such as bream (*Abramis brama*), white bream (*Blicca bjoerkna*), roach (*Rutilus rutilus*), and chub (*Squalius cephalus*). Altogether, 32 samples have been collected and evaluate. Fish muscles were analyzed by isotope dilution method using high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS). Hypothesis about high contamination level of fish from Odra River close to Wroclaw and Vistula nearby Warsaw were not confirmed. Concentrations were low (up to 30 % of established permit level which is 6.5 pg WHO-PCDD/F-PCB-TEQ g<sup>-1</sup>wet weight). In fish caught from Odra River average PCDD/F/DL-PCBs concentration were 0.69 ± 0.52 and from Vistula nearby Warsaw were 0.53 ± 0.10 pg WHO-TEQ g<sup>-1</sup> (w.w.). Much more contaminated were fish from Vistula River caught in central district of Cracow (Dabie). Mean concentration of 7.25 ± 1.88 pg WHO-PCDD/F/PCB-TEQ g<sup>-1</sup> (w.w.) was in 50 % due to PCDDs/Fs congeners, while before and after Cracow agglomeration (Laczany and Grabie) predominant congeners were DL-PCBs (70-85 %). High level of dioxins and DL-PCBs in Cracow central district indicates the presence of dioxins, furans and DL-PCBs sources in the area of Cracow. These result confirm well know observations and data concerning anthropogenic origin of pollution in Cracow. Mean concentration dioxin and DL-PCBs in fish caught before and behind Cracow central district were 1.67 ± 0.45 and 2.24 ± 1.50pg WHO-PCDD/F-PCB-TEQ g<sup>-1</sup> (w.w.). Congener profiles were similar in all analyzed samples and comparable with fish from Baltic Sea. The most abundant congeners of dioxins and furans were 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF. The dominant PCB congeners were PCB 118 and PCB 105. The study was performed in framework of research project financed by Polish National Centre for Research and Development (NCBiR) No 12-0127-10/2010.

## Occurrence and levels of organochlorine pesticides and polychlorinated biphenyls in freshwater fish species from Poland

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Environmental pollution caused by chlorinated hydrocarbons has been a serious global problem for over half a century. Aquatic biota are often contaminated by these compounds. The aim of this study was to assess the occurrence and to determine the levels of organochlorine pesticides (OCPs) and indicator PCB congeners in muscle tissue of freshwater fish species collected from different aquatic systems of the country during the fishing season in 2012. Sampling sites of fish did represent a range of contaminant sources (e.g. industry, agriculture, and urban areas). Seven sites were located on rivers of Poland: the Vistula River in vicinity of Cracow and Warsaw, the Oder around Wroclaw and at the Warta River estuary, the Wkra, the Brda, and the Dunajec. Fish were collected also from Rybnik Power Station Reservoir and from the Lake Maroz located in non-industrialized region of Mazury Lake District. A total of 134 fish samples were collected. Predatory species included pikeperch (*Stizostedion lucioperca*) and pike (*Esox lucius*). Omnivorous species included bream (*Abramis brama*) and roach (*Rutilus rutilus*). The determinations of HCH isomers ( $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH), HCB, DDTs (p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD) and PCBs (six indicator PCB congeners 28, 52, 101, 138, 153 and 180) were carried out using the capillary gas chromatography with electron capture detection.

The presence of DDTs and PCBs has been observed in all muscle samples of freshwater fish species. Residues of p, p'-DDE occurred in all samples, p,p'-DDD in 99%, p,p'-DDT in 54% and o,p'-DDT in 41% of the samples. The low contents of the isomers  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH were detected in about 30% of the samples and HCB in 47%, mainly in omnivorous species, with the mean concentrations from 0.5  $\mu\text{g}/\text{kg}$  to 2.7  $\mu\text{g}/\text{kg}$ .

The mean concentrations of DDTs expressed as  $\mu\text{g}/\text{kg}$  wet weight ranged from 7.2  $\mu\text{g}/\text{kg}$  (pike) to 175  $\mu\text{g}/\text{kg}$  (bream, median 25  $\mu\text{g}/\text{kg}$ ) and for PCBs from 1.3  $\mu\text{g}/\text{kg}$  to 29.9  $\mu\text{g}/\text{kg}$ . The highest levels of chlorinated hydrocarbons were detected in muscles of fish species from the Vistula River in vicinity of Cracow. PCB concentrations above 125  $\mu\text{g}/\text{kg}$  wet weight (maximum level acc. Com. Reg. 1259/2011) were found in four fish samples from that area. The lowest concentrations were found in the tissues of fish from the Lake Maroz, the Brda and the Wkra (DDTs  $\sim 10$   $\mu\text{g}/\text{kg}$ , and PCBs  $\sim 1$   $\mu\text{g}/\text{kg}$ ). The mean contribution of p,p'-DDE to DDTs and the sum of PCB 153, PCB 138 and PCB 180 to PCBs was 50% and 68% in all fish species studied, respectively. The differences in the levels of OCPs and PCBs in predatory and omnivorous fish species from studied aquatic ecosystems were observed.

The results indicate that freshwater fish species are rather low contaminated by the analyzed chlorinated hydrocarbons. Due to the environmental contamination marine and freshwater fish can contain higher levels of PCBs, OCPs and other chemical contaminants than farm animals.

The study was supported by the National Centre for Research and Development, project No. 12-0127-10.



## Environmental contamination of game animals by chlorinated hydrocarbons

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Studies of wild game are good indicators of environmental contamination by chlorinated hydrocarbons and the possible toxicological hazard to the game meat consumer. The aim of this study was to assess the occurrence and to determine the levels of organochlorine pesticides and indicator PCB congeners in adipose tissue of wild boars, roe deer and red deer from different regions of the country.

Samples of adipose tissue from 66 wild boar (*Sus scrofa*), 34 red deer (*Cervus elaphus*) and 56 roe deer (*Capreolus capreolus*) were collected during the hunting season from August 2011 to January 2012. Sex, age and weight were recorded for each animal. The studies were conducted in four industrial regions recognized as areas of significant environmental contamination, i.e. the Upper Silesian Industrial District, The Legnica-Glogow Copper District, The Belchatow Brown Coal Basin and The Turoszow Brown Coal Basin. As a reference area region of Warmia and Mazury Lake District was selected. The determination of organochlorine pesticides (HCB,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH, p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT) and six indicator PCB congeners (PCB IUPAC No. 28, 52, 101, 138, 153, 180) were carried out using capillary gas chromatography with electron capture detection.

The presence of DDT and its metabolites has been observed in all 156 samples of adipose tissue of game animals. Residues of p, p'-DDE occurred in all samples, p,p'-DDT in 48% and p,p'-DDD in 70% of the samples. The low concentrations of HCB were found in 43% of the animals. The isomers  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH were detected only in three samples. The occurrence of PCBs was detected in 99% samples.

The mean concentrations of DDTs expressed on the fat basis ranged from 0.033 mg/kg (roe deer) to 0.265 mg/kg (wild boar) and for PCBs from 0.015 mg/kg (roe deer) to 0.018 mg/kg (wild boar). The higher levels of DDTs and PCBs were detected in game animals origin from industrial regions. The levels of DDTs in wild boars were 10 to 20 times higher than in farm animals and were probably related with this species feeding habits and contamination of soils in forest. The mean contribution of p,p'-DDE to DDTs and PCB 153, PCB 138 and PCB 180 to PCBs exceeded 74% and 97% in all game animal samples studied, respectively.

The results of the present study indicate that game animals from different parts of Poland are rather low contaminated by the analyzed chlorinated hydrocarbons. Due to the environmental contamination wild living animals can contain higher levels of PCBs, organochlorine pesticides and other chemical contaminants than farm animals. Taking into account the consumption of venison in Poland, the levels of DDTs and PCBs in game meat are not a hazard and should be considered safe for consumers.

The study was supported by the National Centre for Research and Development, project No. 12-0127-10.

## Poorly Soluble Compounds in Cosmetics – an approach for a reliable environmental risk assessment (the ECOSM project)

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Personal Care Products (PCP) - often referred to as cosmetics - include a multitude of substances with various physico-chemical properties since they are designed for many different purposes. A lot of these compounds are poorly soluble in water with a water solubility below 1 mg/L. Due to the high production volumes of PCP, and their typical 'rinse off' application, substantial amounts of poorly soluble chemicals end up in waste-water treatment plants and may subsequently enter river systems with the effluent. This causes the need for a reliable assessment of their environmental behavior and toxicity to organisms, as requested by the European REACH-Regulation.

Standard ecotoxicity tests are not suitable for poorly soluble substances. Due to their high lipophilicity, extensive adsorption to surfaces like test vessels and organisms is expected. The lack of consistent, reliable results due to the difficulties in maintaining constant test concentrations may lead to improper assessment of possible environmental risks associated with these chemicals. A promising approach addressing this problem is the so called 'poorly solubles approach' making use of an 'ecotoxicological threshold concentration of no concern' (ETNC<sub>aqu</sub>) for inert substances with a narcotic mode of action. Below this threshold concentration, neither acute nor long-term adverse effects on aquatic organisms are expected to occur. The aim of the project ECOSM (ECOtoxicity investigations of COSMetic ingredients) is to develop pragmatic tools to test the ETNC<sub>aqu</sub> hypothesis in order to allow better environmental risk assessment of poorly soluble substances. Existing aquatic ecotoxicity tests will therefore be adapted to passive dosing techniques to obtain constant exposure conditions. Adaptation of the guidelines for the use of passive dosing techniques will be discussed.

The surfactant precursor Dodecylbenzene has been selected as a primary suitable model compound and already passed the first steps in evaluation. Different methods for chemical analysis using solid phase micro extraction and gas chromatography have been developed. With these techniques, the maximum solubility of the substance in distilled water and different standard media for selected test organisms as proposed by the OECD were exactly determined. The results specified the substance as a suitable testing compound for the ETNC<sub>aqu</sub> hypothesis. Furthermore, the results of various ecotoxicity tests adapted to passive dosing techniques with organisms of different trophic levels (e.g. algae, daphnids, fish eggs, and fish) will be presented.

## Toxic elements in free-living freshwater fish in Poland

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In the years 2011 and 2012 the analysis of toxic elements in different species of freshwater fish obtained from different fish living environment were conducted. The samples were taken from 9 areas, including the major rivers and lakes in Poland, with different sources of environmental pollution (industrial, municipal, and farming). The material consisted of omnivorous fish (mainly bream and roach) and predatory fish (mainly pike, zander and perch) which were taken from rivers and lakes (Lakes of Mazury - located in non-industrialized region, the Brda River – the impact of pig farms, the Wkra River – the impact of poultry farms, the Dunajec at the Roznowski Reservoir, the Vistula River at the height of Krakow and Warsaw, the Odra River at the height of Wroclaw and the Warta River estuary, and also from Rybnik Power Station Reservoir). Concentrations of lead, cadmium, mercury, arsenic and chromium were analysed in 390 samples of fish (muscle and liver) by using at atomic absorption spectrometry technique. The analytical procedures were covered by the quality assurance program.

The average concentration of lead in the muscles of examined fish (omnivorous and predatory) was at the similar level and amounted to 0.03 mg/kg. The highest value of this element was found in samples taken from the Vistula River at Krakow and the Warta River estuary, were the concentration of this element was twice times higher (0.060 mg/kg). Similarly, a high level of lead was found in the livers of fish examined, which in the Vistula at Krakow were: omnivorous – 0.106 mg/kg, predatory – 0.126 mg/kg. The average concentration of cadmium in the muscle of fish in all tested samples remained at low levels thousandths of mg/kg and was 0.004 mg/kg. The value of this element was determined in the muscle of fish taken from the Vistula River at Krakow, more than twice. In the muscle of omnivorous fish, mercury concentration was 0.111 mg/kg and was lower than that observed in the predatory fish – 0.170 mg/kg. A particularly high level of mercury was found in fish caught in the rivers near large urban areas. The average arsenic concentration in the muscle of omnivorous fish was 0.089 mg/kg and was twice higher of the value found in the muscle of predatory fish. The significantly higher values of this element were found in fish caught in the Vistula and the Odra River in comparison with the average detected in fish in the other examined regions. Concentrations of chromium found in the muscle of fishes at the level were hundredths and tenths mg/kg. The study indicated that the concentrations of toxic elements in free-living freshwater fish are rather low and safety. From the consumer's point of view, the studies have also shown that only a single fish samples exceeded a maximum limit for metals (mercury 0.50 mg/kg) - Commission Regulation (EC) No 1881/2006 of 19 December 2006.

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## Comparison of different methods to quantify POPs and emergent pollutants using pine needles

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Pine needles have been extensively used as passive biosamplers of emergent semivolatile pollutants like polycyclic aromatic hydrocarbons (PAHs) or pesticides [1,2] due to their waxy outer cuticle, which favours the entrapment of lipophilic contaminants.

In line with previous research, this work intends to compare different extraction methodologies to obtain the most suitable analytical method(s) for POPs and emergent pollutants biomonitoring. Five different chemical classes were analysed: brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), PAHs and synthetic fragrances (musks). While the first four are better known chemicals, musks only recently have raised concern, due to their high consumption and release into the environment, their bioaccumulation and their endocrine disrupting potential [3]. Musks have been detected in several environmental matrices (water, air) as well as biota (aquatic and terrestrial animals, humans), but to the authors' best knowledge no detection in vegetation has been attempted.

Two extraction procedures (Soxhlet and sonication), and two cleanup methods - solid phase extraction (SPE) and gel permeation chromatography (GPC) - were tested and compared. For SPE cleanup, glass columns employing silica, florisil and alumina with hexane, dichloromethane and a mixture of these two solvents were tested. GPC columns were prepared with different amounts of Biobeads S-X3 using dichloromethane/hexane 1:1 as eluent. Analysis was performed by GC-EI-MS using two different methods (one for BFRs+PCBs+OCPs and the other for PAHs+Musks) on a 60 m CP-Sil 8 CB column.

Sonication had comparable results to Soxhlet, showing slightly better recoveries for more volatile compounds. Therefore, it was chosen as the extraction method also because it saves time (30 min instead of 16 h) and solvents (100 mL instead of 300 mL). GPC is seemingly a feasible alternative to SPE, offering advantages of reusability, easier handling and possibility to set-up an automatic procedure.

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## Comparative performance of descriptors in a Multiple Linear and Kriging Models: A case study on the acute toxicity of organic chemicals to algae

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Quantitative-structure activity relationship (QSAR) studies are expected to reduce the cost and the number of organisms used for toxicity testing. They also fill the existing data gaps within the REACH (Registration, Evaluation, Authorization and restriction of CHemicals) regulatory framework in the European Union (EU). In this context, QSAR method relates the physicochemical properties of chemicals with their activity on the basis that similar compounds have similar activities. Many QSAR studies in ecotoxicology have been carried out with a multitude of descriptors using variety of methods. Among the modeling techniques, multiple linear regression (MLR) is the most attractive because of its simplicity. However, a linear relationship between a chemical and its activity may not always be the case. On the other hand, Kriging technique has found various application areas. Both MLR and Kriging derive a best linear unbiased estimator, based on assumptions on covariance. Kriging basically estimates the unobserved points via a weighted linear combination of observed values (dependent variables), where the weights are determined to minimize the variance of the error by using proximity between descriptors. It was first implemented in geostatistics for gold mining and it has also received some attention in the QSAR literature.

The aims of this study are to model the acute toxicity of organics to freshwater green algae using machine learning method Kriging and MLR with the same descriptors, and to compare the predictive performance of descriptors in both models. A structurally heterogeneous data set on acute toxicity of 91 organic compounds from different chemical classes to algae *Chlorella vulgaris* were taken from the literature. Descriptors obtained from DRAGON 6 and SPARTAN 10 software packages were approximately 3000. The data set was divided into two sets, training and test sets, for external validation. For model development, two significant descriptors were selected via all subset selection which is implemented in QSARINS. MLOGP representing the hydrophobicity and H\_Dz(Z) a 2D matrix-based descriptor weighted by atomic number were found to be important in modeling the toxicity of these compounds to algae. Models' applicability domains are defined via leverage approach, chemical class, and the ranges of the descriptors. The Kriging model performed better than the MLR model in terms of correlation coefficient and root mean squared error (RMSE) of the test set. Therefore, the Kriging model can be used to estimate the acute toxicity of untested organic chemicals, regarding its high external predictive ability, within the applicability domain of the model.

**Keywords:** *Chlorella vulgaris*, Kriging, QSAR

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## Honey significance as bio-monitor for the environment

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Honey is a sweet, sticky substance produced from the nectar of plants and flowers. Depending on the geographical conditions and the type of appearing flora, different types of honey can be distinguished. Each of them has a unique taste, color and crystallization properties. The main sugar component of honey of high water content (50-70%) plays saccharose, in opposition to honey with low water content (average 17%) where predominant sugars are glucose and fructose. In addition to beneficial organic compounds honey can be an important source of micro and macro elements (K, Na, Ca, Cu, Mg). Besides its nutritional and health properties, it is also an excellent source of information on contamination of the environment in which bees live. This is due to the fact that it is produced by the process of bioaccumulation. The area on which the bees collect pollen being in contact with air, water and soil is very big (over 7 km<sup>2</sup>). Thus, the content of elements (heavy metals) in honey reflects the contents of them in entire region. Analysis of changes in trace elements content in honey can be used as an indicator of environmental pollution. However, the analysis of honey, the samples of complex organic matrix and variable elemental composition, may be problematic [1-3].

The aim of this study was, by analyzing samples of honey from different regions of the world, development of appropriate analytical procedure (including both sample preparation and instrumental measurements) ensuring the reliability of the results, to assess pollution in the region. In the performed studies the samples were wet digested and metals concentrations were measured by means of atomic absorption spectrometry (flame and electrothermal techniques). Significant differences were found out in the content of metals in the analyzed samples of honey: K (460 - 2500 µg/g), Ca (76 - 700 µg/g), Zn (2,5 - 12 µg/g), Mn (0,1 - 30 µg/g). Analyses of other metals: Cr, Pb, Cd, Ni were also performed.

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## Toxic metals and trace elements in soil and fruiting bodies of selected mushroom species

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Mushrooms growing in nature contain many biologically active compounds such as polysaccharides, phenolic and indolic compounds, etc. [1]. Characteristic feature of fungal mycelium is absorption and accumulation of minerals (including trace elements like Zn, Mg, Cu, Fe, and also toxic like Cd, Cr, Pb from the surrounding environment [2,3]. Absorption of heavy metals by slow growing fungi depends on species, concentration of heavy metals in the environment and properties of the substrate on which they grow. In addition, fungi easily absorb more heavy metals than green plants [4]. This is due to the specific structure of mycelium, a high area of hypha and a large surface specific area of vegetative cells filaments. Accumulation of elements in mushrooms makes them good indicators of the environment they inhabit quality and reflect its degradation [5].

The aim of the study was to analyze samples of wild grown mushrooms (*Boletus badius*, *Lactarius deliciosus*, *Leccinum scabrum*, *Suillus luteus*, *Armillaria mellea*) from the Southern Poland. The analyzed material was wet digested and selected elements were analyzed quantitatively by means of atomic absorption spectrophotometry. The method is accurate and precise, that allows obtaining reliable results that will enable proper assessment of the environment pollution. The observed variations in the determined metals concentrations between fungal species were respectively Zn (34 - 685 mg/kg), Mn (6 - 280 mg/kg), Mg (211 - 1315 mg/kg), Fe (57 - 8104 mg/kg), Cu (8,3 - 53,2 mg/kg). In addition, a number of determinations were carried out for toxic metals including Cr (0,9 - 50 mg/kg) and Pb (0,003 - 0,630 mg/kg).

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## Alternative bioaccumulation test using zebrafish (*Danio rerio*) eleutheroembryos

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New legislation on chemical production and commerce has added new parameters and concepts for evaluation of hazard of a compound, especially in the environmental field. Apart from classical toxicity parameters, others such as environmental persistence and bioaccumulation capability are now recognised to play an important role in the evaluation of the hazard of a compound. Bioconcentration is defined as the accumulation of chemicals in an organism's tissues through any possible exposition route, including respiration, ingestion, or direct contact. Today, the OECD 305 guideline is the most used protocol for the evaluation of bioconcentration and it is also the suggested procedure in current legislations. This guideline established several experimental features that should be fulfilled, and establish that a representative set of animals, i.e. at least one hundred and ten adult fishes, should be involved in each compound evaluation. Apart from the huge analytical work required for such analytical determinations, the estimated cost for each bioconcentration test is around 100.000 euros. The interest of developing alternative less costly and faster procedures to this bioaccumulation test is consequently evident.

Here we present a test alternative to the OECD 305 guideline for the evaluation of the bioconcentration capabilities of selected pollutants of divergent nature. Zebrafish (*Danio Rerio*) was the chosen model due to the unique advantageous features over other vertebrate model systems, namely high homology genetic with the human and fast embryonic development. The proposed alternative test was optimized using polychlorinated biphenyls (PCBs) as target analytes and appropriated miniaturized analytical methodologies were developed for the determination of the test contaminants in embryos at different levels of development and their surrounding medium. The optimized protocol was subsequently applied to the evaluation of PAHs, pesticides, metals and nanoparticles and the results obtained were compared with values published in the literature involving the official procedure.



## Evaluation of toxicity and biodegradability of priority chlorinated compounds

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Volatile organic compounds (VOCs) are common contaminants in water, whose chemical characteristics make them cause of concern even at low concentrations due to their fate and impact on environment and human health. Halogenated organics are considered as priority pollutants by European authorities and are included in Directive 2008/105/EC, which establishes quality standards for those substances and other pollutants of concern. Possible sources of these compounds include industrial effluent and waste disposal, solvents, gasoline and refrigerants. In order to establish optimal cost-effective treatment strategies for VOCs removal, the toxicity and biodegradability of priority chlorinated compounds (dichloromethane, 1,2-dichloroethane, chloroform, 1,1,1-trichloroethane, trichloroethylene and carbon tetrachloride) were evaluated.

Toxicity was analyzed in term of  $EC_{50}$  by both respirometric (activated sludge) and Microtox® (*Vibrio fischeri*) bioassays. The Microtox  $EC_{50}$  values (19-596 mg/L) were lower than the respirometric ones (595-1962 mg/L) for all the analyzed compounds indicating that Microtox® test overestimates the potential negative effect on the activated sludge of a wastewater treatment plant. The effect of the number of carbon and chlorine atoms on the  $EC_{50}$  was also examined. Although none of the studied VOCs can be considered toxic, the higher number of chlorine atoms, the lower  $EC_{50}$  value with the exception of carbon tetrachloride. No significant differences of  $EC_{50}$  were found comparing the number of carbon atoms. Thus,  $EC_{50}$  value obtained by respirometry was near to 1800 mg/L for both dichloromethane and 1,2-dichloroethane and 50 mg/L by Microtox® assay. This behaviour was also observed in aliphatic compounds with three chloride atoms. Results of  $EC_{50}$  for trichloroethylene showed that the double bond reduces the toxicity of the chlorinated compounds.

Biodegradability was determined by an easy and fast respirometric method. When the response of the unacclimated sludge to the biodegradation of the target compound was negative, the Zahn-Wellens test was used to evaluate the inherent biodegradability. According to the fast biodegradability test none of the halogenated compound was biodegradable in 24 h. Inherent biodegradability calculated as percentage of TOC conversion showed that 1,1,1-trichloroethane is biodegradable (74%), dichloromethane is persistent and the rest of studied VOCs are partially degraded in 28 d with TOC conversion ranging from 17 to 35%. It can be concluded that toxicity and biodegradability measurements should be considered in order to use the most efficient treatment for VOCs removal.

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## Selective Bioaccumulation of PCDD/Fs and DL-PCBs in Wild Boars Tissue From Industrial and Agricultural Region of Poland

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Dioxins (PCDD/Fs) and dioxin-like PCBs (DL-PCBs) are ubiquitous, persistent toxic compounds highly bioaccumulative in nature. Air transfer from emission sources explains for their presence in terrestrial and aquatic ecosystems, poses a risk to humans and animals. Due to the toxicological danger a much of attention is paid to these compounds all over the world. PCDD/F and DL-PCB contaminations of food from farm animals have been monitored in Poland since 2006. However, but a complete of data on free-living animals, which are both indicators of environmental pollution and potential food sources derived from these animals. The aim of the study was to determine the status of contamination and bioaccumulation of 17 toxic dioxin congeners (2,3,7,8-PCDD/Fs) and 12 DL-PCBs in tissues of wild boars (*Sus scrofa*) from industrial and agricultural regions of Poland. The levels of individual congeners in muscles (32), adipose tissue (28) and liver (17) samples were determined. Wild boars were hunted in polluted industrial district located in south-east Poland (Lower Silesian Voivodeship) and from agricultural and tourist areas situated at north-east (Warmian-Masurian Voivodeship). The analysis of 29 congeners of PCDDs, PCDFs and dl-PCBs was made by isotope dilution technique using the high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS). Total PCDD/F and DL-PCB muscles content of wild boars from Lower Silesia was over 230% higher than from the agricultural area. The average concentration was respectively  $2.49 \pm 1.56$  and  $1.07 \pm 0.32$  pg WHO-TEQ/ g fat with predominant congeners PCDD/Fs (70%). There were minor differences in the concentrations of fat tissue ( $2.20 \pm 1.67$  and  $1.75 \pm 1.64$  pg/g) but the PCDD/ F content was 82% of the tested compounds. However, the level of sum of PDDD/F/DL-PCB was similar in the animal livers from both regions (average about 35pg/g) but the dioxins were count for about 90%. Congener's bioaccumulation was depended on the region type and specific congener. In particular, the differences were noted in the DL-PCB bioaccumulation regardless of the type of tissue examined which indicates the different source of these contaminants in the industrial and agricultural region. The dominant congeners were OCDD, HpCDD, PCB 156 and PCB 118. The results of this preliminary study suggest that wild boar livers bioaccumulate more PCDD/Fs than DL-PCBs. Dioxin levels in all tested tissues from industrial region animals contain higher dioxin levels than pigs and may pose some danger to the consumer's health often eat venison. This study was carried out in the framework of the research project of Polish National Centre for Research Development No 12-0127- 10/2010.

## **Evaluation of the mercury stress produced in plants by the analysis of phytochelatins and its Hg complexes induced in *Asparagus acutifolius* and *Retama sphaerocarpa* from the Almadén mining district**

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The development and growth of mining, metallurgy and industrial activities have increased the concentration of heavy metals into the environment causing the exposition of animals and plants to high concentrations of those contaminants. Plants absorb metals from soils, water and air. This property of plants is the basis of phytoremediation. Phytochelatins (PCs) are small, cysteine-rich peptides which are synthesised in plants in response to heavy metal stress. The general structure of this set of peptides is  $(\gamma\text{-Glu-Cys})_n\text{-Gly}$  ( $n=2$  to 5). PCs are assumed to be involved in the accumulation, detoxification and metabolism of heavy metal ions in plants.

The Almadén mining district (Spain) is known to put up the largest deposits of mercury of the world known to date. Because of this reason, the Almadén district can be regarded as one of the most Hg-contaminated places on Earth.

In order to evaluate plant response to Hg stress, soils and samples of *Asparagus acutifolius* grown in the Almadén mining district were analysed. These soils are highly Hg-contaminated, with some zones displaying values above  $4000 \mu\text{g Hg g}^{-1}$  soil. Although this extremely high concentration of mercury in soils, generally less than 2% is available for plants, as it is shown by different soil extractions which simulate bioavailability. In plants, Hg concentration increases depending on the content of Hg in soils, also Hg levels in roots are higher than in aerial parts as a strategy for protecting the more sensitive parts from the deleterious effects induced by metal stress. The content of phytochelatins and its complexes are in concordance with the amount of mercury in soils; more Hg in soils produces more PCs in plants as a response to metal toxicity. The comparison of PCs content between *Asparagus acutifolius* and *Retama sphaerocarpa*, another plant species growing in the Almadén mining district, shows that the second one synthesises more longer-chain PCs than wild asparagus in both roots and aerial parts.

All these facts highlight the important role that thiol compounds have on the capture and fixation of Hg from soils, giving plants the capacity to deal with heavy metals toxicity and the possibility to be used on phytoremediation studies of contaminated soils.

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## DETERMINATION OF TETRACYCLINE AND $\beta$ -LACTAM RESIDUES IN CHICKEN MEAT BY HPLC METHOD

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Beta-lactam antibiotics are the most widely used group of antibiotics due to their low side effects and bactericidal properties. Penicillin is the most important member among them. Tetracycline group of antibiotics are used widely in poultry breeding due to the fact that they are broad-spectrum and low toxic effects[1].

The aim of this study is to analyze the effect of tetracycline, oxytetracycline and penicillin G antibiotics in chicken meat samples by High Performance Liquid Chromatography (HPLC) method and compare the behavior of the two antibiotics related to heat. In this study, penicillin G and tetracycline, oxytetracycline are chosen for their common objectionable usage in animals and for the difficulties in the procedure of analysis. HPLC is chosen as the analytical instrument in order to obtain accurate results in a short period of time. Chromatographic conditions will be determined after the experiments with standard solutions of the chosen antibiotics were done. The most appropriate extraction method will be chosen before the analysis of chicken meat samples. The residual amount on samples will be determined and compared with the most residual levels (MRLs)[2].

In the second part of the study, the antibiotic residues in each of breast sample of the same chickens were treated under heat. The samples will be tested whether there is a change in amount of residue in sample or not. In general, effect of heat decreases the tetracycline residues however the type of heating process must be also evaluated. In this study, tetracycline and penicillin, which are two of the most commonly used antibiotics in chicken, can be compared in residues of chicken body. Also, studying on the degradation products of antibiotics, optimum time period before the slaughter of a chicken may be decided. We have to learn this because antibiotic residues may leave in human body after consumption. Therefore this event causes the proliferation of diseases, not to fight with the diseases. Consequently, the regulations regarding the usage of antibiotics in chickens may be evaluated as a result of this study.

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## Malodorous monocarboxylic acids in the neighbourhood of animal farms. Determination in the air and wastewater.

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Short-chain monocarboxylic acids (SCMAs) can be formed in the process of anaerobic biodegradation of organic matter such as carbohydrates, proteins and fats. They can be emitted from swine and cattle farms, food processing, agricultures etc.; they are responsible for unpleasant odors in the vicinity of waste water treatment plants, municipal waste landfills, etc. In the present study an analytical method was optimized for the determination of short-chain monocarboxylic acids (SCMA) in environmental aqueous samples using headspace-solid-phase microextraction (HS-SPME) followed by gas chromatography coupled with mass spectrometry (GC-MS). The various parameters including fiber coating, extraction time, extraction temperature, pH value, ion strength, sample volume, and desorption conditions of analytes isolation and introduction to GC column were investigated and optimized. The procedure developed was applied to determine SCMAs in real aqueous and air samples of very complex matrices such as cattle farm wastewater.

## Harmful algae and toxins in the Venice Lagoon and in the Po River Delta (northern Adriatic Sea, Italy)

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An integrated approach for the structural identification and quantification of algal toxins, in Northern Adriatic Sea, specifically in the Po river delta and in the Venice lagoon, by applying a combination of analytical techniques such as optical and scanning microscopy (OM, SEM), and Liquid Chromatography coupled with High Resolution Time of Flight Mass Spectrometry (HPLC-HR-TOF-MS), is presented. The proposed approach has been preliminary applied to the investigation of harmful algae occurrence and distribution in the above mentioned coastal areas.

The performed sampling sessions showed that potentially harmful algae such as *Dinophysis caudata*, *D. mitra* and *D. sacculus* were present during summer period in most of areas directly influenced by seawater, such as the Venice port entrances and the Po river delta, but not in the inner Venice lagoon parts. Nevertheless, quantitative observations demonstrated that their abundance were always significantly below the conventional limit (~200 cells/L) for which poisoning events could occur. The presence of Pectenotoxin2 (PTX2) in phytoplankton cells extract was anyway confirmed by HPLC-HR-TOF-MS at Venice lagoon port entrance, so indicating the potential release of toxins in detectable amounts even at such low cell concentration levels.

# **Modelling, Management and Risk Assessment**

**Oral presentation: OM1-OM9**

**Poster presentation: PM1-PM17**

## Resolution of Environmental Pollution Profiles in Polluted River Waters by Chemometric methods

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The densely populated river basins, usually, are subjected to intensive exploitation by both industrial and agricultural activities inputting the organic, inorganic and oxygen consuming waste in rivers. Usually, the concerned governments, research institutes and Non Governmental Organizations launch environmental programs to monitor the condition and quality of water resources over time. These monitoring programs result in large data reports comprising of a lot of data tables and figures, frequently rather cumbersome to interpret and conclude. Often, these large environmental datasets contain concentration information on multiple chemical compounds collected at different sampling periods from different sampling sites arranged in large tables, data matrices, or in more complex data arrays multi-dimensional (three or more dimensions) in nature, commonly referred to as multi-way or multimode data arrays. Multi-way data analysis methods can better summarize these huge environmental monitoring data sets providing a more in-depth interpretation of the relevant information contained in them.

Alternating least-squares is considered to be an efficient method for multi-way data decompositions and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) has emerged as a powerful tool to analyze multiset data arrays through matrix-augmentation fulfilling different model complexities [1-4]. The main advantage of MCR-ALS [5] in this context is that it is easily adapted to data sets of different complexity and structure, bilinear, trilinear or multilinear, providing optimal least squares solutions. Multivariate Curve Resolution Alternating Least Squares (MCR-ALS), a powerful chemometrics tool initially developed for the resolution of complex signals and spectra obtained through hyphenated analytical techniques [4,6], has also been extended and applied to explore three-way data [7] with trilinearity constraint. This study will focus on the extension of MCR-ALS with quadrilinear constraint to deal with four-way datasets. The applicability of the newly extended MCR-ALS method will be investigated to explore real and simulated environmental data. The results obtained with MCR-ALS will be compared with other methods based on factor analysis and used for the multi-way datasets.

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## Integrated Environmental Modelling with JAMS

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In order to deal with current pressures on environmental systems, adaptable tools and methods are needed to elaborate information, develop understanding and create strategies for their sustainable use and management. These tools should assist scientists, natural resource managers and decision makers by providing them with information about the current state of environmental systems, help them to identify suitable management strategies and quantify the impact of future development scenarios. These objectives are addressed by simulation models that can cope with the components and processes of environmental systems, e.g. the hydrological and nutrient cycles. Modelling frameworks that allow for an easy implementation and extension of component based simulation models have gained increasing attention from both model developers and users during the last decade.

The Jena Adaptable Modelling System (JAMS) (Kralisch & Fischer, 2012) is an open-source software framework that has been especially designed to cope with the challenges of environmental modelling. This is reflected by (i) a flexible approach for representing time and space, (ii) a strong separation of process simulation components from the declarative description of more complex models using domain specific XML, (iii) powerful analysis and visualization functions for spatial and temporal input and output data, and (iv) parameter optimization and uncertainty analysis functions commonly used in environmental modelling. Based on JAMS, different hydrological and nutrient transport simulation models have been implemented and successfully applied during the last years.

We will present the JAMS core concepts and give an overview of models, simulation components and support tools already available for that framework. Sample applications will be used to underline the advantages of component-based model designs and to show how JAMS can be used to address the challenges of integrated environmental modelling.

Kralisch, S. & Fischer, C. (2012). Model representation, parameter calibration and parallel computing – the JAMS approach. *Proc. Int. Congr. Environ. Model. Softw. Sixth Bienn. Meet.* (R. Seppelt, A. A. Voinov, S. Lange & D. Bankamp, eds.). Leipzig, Germany.

## MEMBRANE BIOREACTOR MODELLING: DETERMINISTIC VS DATA DRIVEN MODELS

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Membrane bioreactors (MBRs) –a combination of common bioreactors and membrane filtration units for biomass retention- are a rinsing wastewater treatment technology in the last decade due to their unique advantages such as high effluent quality and small footprint. However, fouling phenomenon and high operational energy requirements are the main drawbacks of this technology. A useful tool for optimisation of design and operation of wastewater treatment plants are mathematical models. Nevertheless, due to the complexity of the interacting biological and membrane filtration phenomena in MBRs there is not yet an accepted and general mathematical model able to cover the entire variables of the system. Deterministic models are most extended in this field, while data mining models are hardly found.

The objective of this work is to develop and evaluate two different models to describe the interaction between biological and filtration processes, using real data from two years of operation of a MBR industrial scale pilot plant. Specifically, the models aim to describe the most difficult variable to be predicted in MBRs (transmembrane pressure, TMP, the main indicator of fouling phenomenon) as a function of the other relevant variables and parameters. On the one hand, a deterministic model, based on series resistances, is developed using West<sup>(R)</sup> as a simulation tool. On the other hand, a regression tree, based on multiple regressions has been developed using WEKA<sup>(R)</sup>.

The oral presentation will show the accuracy on validation data for both models. The results will also illustrate the limitation of the deterministic model, since an important operational parameter in the fouling process has not been considered (membrane air-scouring), while data driven model seems to be able to capture the sensitivity of all the relevant parameters involved. Therefore, regression trees built upon long term historical data can be used to enhance the understanding of the system knowledge and to induce rules for the TMP prediction, which could complement the actual deterministic models.

## Modeling the Environmental legacy of technical HCH usage and Lindane production

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Technical hexachlorocyclohexane (a mixture of mostly  $\alpha$ -,  $\beta$ -,  $\gamma$ -HCH and  $\delta$ -HCH) has been one of the most used pesticides during the 20<sup>th</sup> century. Due to its detrimental effects on human health, it has been listed for elimination in the Stockholm Convention. Global production of technical HCH is thought to have ceased by the late 1990s, mostly replaced by Lindane, which is pure  $\gamma$ -HCH. In 2009, also Lindane has been added to the Stockholm Convention's list of chemicals to be eliminated.

In spite of the virtual elimination of HCH usage in any form, this persistent chemical is still ubiquitous in the environment. Atmospheric transport of  $\alpha$ -HCH from technical HCH usage has been shown to be a pathway for deposition in the Arctic [1-4].  $\beta$ -HCH has been suggested to reach the Arctic mainly via oceanic circulation, though different input pathways have been discussed, and current modelling studies still underestimate concentrations in the Arctic Ocean [4, 5]. Furthermore, Primary emissions of  $\alpha$ - and  $\beta$ -HCH may still take place in form of volatilization and leaching from waste-isomer stockpiles that remain at inappropriately managed former sites for Lindane production [6].

In this research, we exploit a new, highly-resolved version of *BETR Research*, a global chemical fate model, to address two remaining questions relating the occurrence of HCH in the global environment: a) Does the current emission inventory for technical HCH underestimate releases to rivers in Northern Russia, and therefore the transport of  $\beta$ -HCH along the North Atlantic current towards the Bering Strait? b) Will emissions of  $\alpha$ -HCH and  $\beta$ -HCH from stockpiles eventually dominate ambient levels of these POPs, if stockpiles are not remediated?

With regard to oceanic transport of HCH, we modelled  $\alpha$ - and  $\beta$ -HCH after their loading into the Kara-Sea during the 1990s [7]. Our model indicates that there is eastward oceanic transport, and that this leads to elevated concentrations in the Arctic Ocean, and in particular in the Bering Sea years after the first loading. Therefore, the discharge of HCH via rivers into the Russian Arctic Ocean is a potential cause of the elevated concentrations measured in the Bering Sea [5, 8]. Emissions estimates for HCHs from waste isomer stockpiles are highly uncertain. Using current best-estimates, we have modeled a range for past, present and future concentrations that can be attributed to evaporative emissions from stockpiles. For the Arctic, we forecast that stockpiles – if not remediated – may become the dominant source for  $\alpha$ -HCH between 2000 and 2020, and for  $\beta$ -HCH between 2020 and 2060.

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## Integrated assessment modelling to plan local optimal air quality policies harmonized with national and European actions

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Decision Support Systems (DSSs) should help public bodies, in charge of environmental management, to design sound and effective policies. In the field of air quality, DSSs should propose long-term emission reduction measures, to improve secondary pollution concentrations taking into account, at the same time, the cost of their implementation. The design of tools that can serve this purpose requires the formalization of a decision problem within which a model that links the proposed emissions to the resulting ambient concentration is necessary [1]. Current chemical-transport models (CTMs) that provide this link are too complex and time-consuming to be used within these tools. It is thus necessary to substitute them with a surrogate model, which closely replicates the CTM behaviour for specific meteorological and emission conditions. While most current approaches use a linear approximation, thus requiring a very large number of CTM simulations to replicate known non-linear relations, such as those between precursors and PM or Ozone, this work shows how the same result can be obtained using a limited number of simulations and a non-linear surrogate model [2].

This paper presents the methodology developed in OPERA (Operational Procedure for Emission Reduction Assessment) LIFE+ project (2010-2013, [www.operatool.eu](http://www.operatool.eu)) aiming to design and to implement an enhanced approach to identify efficient regional policies. Within such an approach, artificial neural networks (ANNs) have been extensively used by the authors to replicate CTM results over different regions in Italy and France and considering different pollutants (NO<sub>2</sub>, O<sub>3</sub>, PM). The presentation will concentrate on the method to design the experiments that provide the values for ANN training and on the performances of such surrogate models in different chemical atmospheric conditions.

It is important to underline that, while these surrogate models may constitute a reliable substitute of CTMs to solve a specific air pollution control problem, such a problem, and specifically the technical and non-technical emission abatement measures that can be considered and the indexes representative of air quality (AQIs), have to be defined precisely in advance and in accordance with the power and plans of the environmental agencies in charge.

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## Physicochemical properties of dimethylsiloxanes and their impact on the environmental fate

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The environmental research on organosilicon compounds has focused on three cyclic dimethylsiloxanes, namely octamethylcyclotetrasiloxane ( $D_4$ ), decamethylcyclopentasiloxane ( $D_5$ ) and dodecamethylcyclohexasiloxane ( $D_6$ ). However, the SPIN database (Substances in Preparations in Nordic Countries) currently lists 365 and 176 records containing the term “silox” and “silan”, respectively. Although a large fraction of the records are either polymers or hydrolyze quickly under environmental conditions, a number of compounds might be of environmental relevance. Lack or low quality of physicochemical data impedes the application of environmental fate models to these compounds and, more generally, is an obstacle to risk assessment.

We calculated physicochemical properties (vapour pressure, solubility, partition coefficients and OH radical reaction rate constant) of homologous series of cyclic and linear dimethylsiloxanes as well as a selection of silanols, i.e. their transformation products, using COSMOtherm, the SPARC On-Line Calculator and EPI Suite. The results were compared, both among the estimation methods and with the limited experimental data.

The three estimation methods show good qualitative, but limited quantitative agreement in estimated trends for the homologous series. In comparison to the group or bond additive methods used in EPI Suite and SPARC, COSMOtherm is the only surface-based method and able to comprise intramolecular interactions, resulting in higher accuracy of predictions for  $D_4$ – $D_6$ . The largest deviation for a single predicted value is a difference of ten orders of magnitude for the  $K_{OA}$  of 1,15-dihydroxy hexadecamethyl octasiloxane between COSMOtherm and the EPI Suite. This can be traced back to neglecting intramolecular hydrogen bonds by EPI Suite.

The values for  $K_{AW}$ ,  $K_{OW}$ ,  $K_{OA}$  and vapour pressure of  $D_4$ ,  $D_5$ ,  $D_6$  and dimethylsilanediol differ by 0.8–1.2, 0.0–1.1, 0.0–1.1 and 0.7–1.6 log units, respectively, between the COSMOtherm estimates and the best available experimental data.<sup>1–3</sup> The estimated OH radical reaction rate constants differ by 0.02–0.5 log units from experimental data.<sup>4</sup> These differences are low compared to ranges of reported empirical data on  $K_{AW}$  and  $K_{OW}$  of  $D_5$  which span two to three orders of magnitude; this shows the current challenges of studying siloxanes. Although associated with uncertainties, the property estimates for organosilicon compounds provide a valuable first basis for environmental fate modelling including consideration of e.g. joint persistence.

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## Integrating Near-field and Far-field Environmental Fate and Exposure Models for Screening-Level Exposure and Risk Assessment

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Various chemical management programs require the assessment of existing and new chemicals for risks to the environment and humans. Because conducting full assessments (e.g. biomonitoring) on a large number of chemicals is not feasible due to limited resources, screening-level assessments are used to prioritize chemicals for more comprehensive evaluation. A number of high-throughput modeling tools have been developed to screen chemicals for the potential to bioaccumulate and result in human exposure that is associated with harmful health effects. Because food intake is deemed the dominant exposure pathway for chemicals that tend to bioaccumulate, most screening tools focus on environmental processes in the far-field that govern dietary human exposure. However, increasingly studies indicate that human exposure in the indoor environment, via dust ingestion and dermal absorption, could contribute a large portion of total exposure. Thus, screening with models of human exposure that disregard indoor exposure may be insufficient and could possibly lead to false-negative results.

In this study, a screening-level indoor chemical fate and exposure mass balance model was developed by incorporating human bioaccumulation models for different age groups (i.e., adults, toddlers) into a previously developed multimedia model of the indoor environment. Pathways of chemical exposure via diffusion and particle advection include inhalation, dermal absorption from air, transdermal diffusion, and surface-hand-mouth transfer. Considering the potential roles of hands and skin in chemical exposure from the indoor environment, hand surface and skin surface were treated as unique compartments in the human bioaccumulation model. The model was parameterized based on a typical room inhabited by humans of different age groups. The model calculates intake fractions and internal concentrations (body burdens) from indoor exposure based on indoor emissions and allows for the identification of the factors that control human intake fractions and internal concentrations, including physical-chemical properties, biotransformation half-lives, environmental characteristics and activity patterns.

In order to assess the importance of near-field exposure pathways to chemicals primarily emitted indoors compared with far-field exposure pathways, the rates of chemical transfer from indoor to outdoor were used as emission input to an existing far-field environmental fate and exposure model. The relative contribution of near-field exposure and far-field exposure were compared. The relative importance of the two exposure pathways were found to be related to the chemical properties and human age groups (activity patterns). For illustrative purposes, a group of chemicals primarily emitted indoors were screened with this model linking near-field and far-field exposures. The screening/ranking results were compared with those from a model considering only far-field exposure.

## Will Persistent Organic Pollutants reach a global equilibrium distribution?

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Long-lived organic pollutants, such as Persistent Organic Pollutants (POPs) and chlorofluorocarbons (CFCs) have been found even in the most remote regions on earth. Their environmental fate has been intensely studied but is still only partially understood. A key hypothesis in the field of environmental fate says that persistent organic pollutants strive towards a fugacity-controlled global equilibrium state.<sup>1,2</sup>

Volatile persistent chemicals, such as CFCs and carbon tetrachloride, indeed show a fugacity-controlled multimedia distribution over large areas<sup>3</sup>, whereas others, such as polychlorinated biphenyls (PCBs), depend strongly on the historic emission patterns and seem not to approach a fugacity-controlled global distribution.<sup>4</sup> This means that there are chemicals that either have not or never will reach an equilibrium distribution.

At the same time, there is a conceptual gap that makes it difficult to test the hypothesis of a global thermodynamic equilibrium of chemicals in the environment. No attempts have been made to exactly specify the properties of global equilibria. Here we present a simple and transferable approach to defining global equilibrium states in Multimedia Box Models and employ it to characterize global multimedia distributions of pollutants.

We use CliMoChem, a global multimedia mass balance model, to characterize global equilibrium distributions and estimate the physicochemical prerequisites that enable a particular pollutant to reach a global equilibrium distribution. As most influential parameters the half-lives in air and water and the air-water, octanol-water and octanol-air partition coefficients  $K_{AW}$ ,  $K_{OW}$  and  $K_{OA}$  are identified. Chemicals with a  $\log(K_{OA}) < 4.5$  and a  $\log(K_{AW}) > 0.5$  can reach the equilibrium if their half-lives in air are longer than two months and longer than their half-lives in water. Chemicals with a  $\log(K_{AW}) > 2$  and a  $\log(K_{OW}) < 2$  need half-lives in water larger than one year and larger than the respective half life in air to reach equilibrium. Only a small fraction of typical chemicals of environmental concern actually exhibits these properties. Most pollutants will therefore never reach a global equilibrium distribution.

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## Assessing the impact of global change on micropollutants in aquatic ecosystems: Modelling the fate of nonylphenolic compounds in the Seine River

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This study aims at modelling the annual variability in concentrations of nonylphenolic compounds such as 4-nonylphenol (4-NP), nonylphenol monoethoxylate (NP<sub>1</sub>EO) and nonylphenoxy acetic acid (NP<sub>1</sub>EC) within the Seine River in the Paris metropolitan area. These compounds are of prime interest because the 4-NP is a well known endocrine disrupting chemical, while NP<sub>1</sub>EO and NP<sub>1</sub>EC are expected to be biodegraded into 4-NP in the environment (Giger *et al.* 2009). Thus the potential consequence of climatic change and urban evolution on the fate of these micropollutants is an actual issue for aquatic ecosystems. So far as we know, no study deals with the modelling of annual concentrations of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC in surface water and especially in a heavily urbanized area such as Paris.

Firstly, concentrations were simulated for 2010 and compared to monthly measured values downstream the Paris metropolitan area. To achieve this goal, the hydrodynamic and biogeochemical "ProSe" model (Even *et al.* 1998) was updated to simulate the fate of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC. Boundary conditions such as the upstream concentrations as well as the lateral inflows - wastewater treatment plant (WWTP) and the Oise River (tributary of the Seine River) - were estimated by using monthly sampling campaigns performed in 2010. The biodegradation kinetics of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC in the Seine River were deduced from a sampling campaign carried out on the same transect of the Seine River in September 2011. The Nash-Sutcliffe coefficient indicates, for year 2010, a good efficiency of the ProSe model to simulate the concentrations of 4-NP, NP<sub>1</sub>EC and NP<sub>1</sub>EO at the annual scale .

Secondly, 8 scenarios were built to forecast the impacts of global warming (Seine River flow), population growth (WWTP effluents flow) and optimization of wastewater treatments (quality of effluents) on annual concentrations of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC at Meulan in 2050 and 2100. A major assumption is to consider that the use of alkylphenols will remain constant during the 21<sup>st</sup> century. Based on these scenarios, the forecasts highlight that global warming and population growth may increase the concentrations of 4-NP, NP<sub>1</sub>EC and NP<sub>1</sub>EO especially during low-flow conditions, while the optimization of WWTP may balance the global changes by reducing inputs from WWTP.

Finally, this study is of prime interest to understand the long term behaviour of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC in surface water and may feed the decision making process to find what action should be taken to reach or maintain the good ecological state of water bodies in the future.

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## **Spatial vulnerability assessment and stochastic modelling of groundwater contamination in a transboundary watershed**

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Groundwater's contamination in fluvial environments shows high variability in space. Furthermore, it is also a non-stationary process because spatial variability depends strongly on the distance to pollution sources, the amount of precipitation and other climatologic variables.

Water's quality has an important role by being abundantly used in agriculture and livestock activities, one of the economic incomes for local communities. Characterization, monitoring and control of the impact due to several anthropogenic activities is of crucial importance.

The core of this work is the spatial characterization for contaminants distribution within the transboundary watershed – Portuguese and Spanish territory - of the Águeda river. Seventy four point-support data were sampled and monitored for a set of physical and chemical parameters.

The methodology presented herein deals in a first step with the achievement of a vulnerability map which allowed the subsequent overlap with the main risk focus and a better land use planning. In a second step a coupled multivariate statistics and geostatistics based methodology for the measured pollutants was used for pollution prediction in a generalized unknown space domain of the study area.

The used models showed to be suitable for evaluating the environmental impact of the considered contaminants (such as e.g. Electrical conductivity; Phosphates; Nitrates; Arsenic; Uranium and Manganese) and improved the local groundwater system's management.

The obtained results allowed further feasibility studies of different treatment schemes and the development of specific monitoring activities.

Key-words: Groundwater; Pollutants; Vulnerability mapping; Stochastic modelling; Geostatistics

## Micropollutant dynamics in Vidy Bay- a coupled photolysis-hydrodynamic model to assess the spatial extent of ecotoxicological risk

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The direct discharge of wastewater (WW) effluent into the Vidy Bay of Lake Geneva results in the seasonal formation of an effluent plume containing locally high concentrations of wastewater-derived micropollutants. A 10-month sampling campaign showed that the plume depth followed the thermocline, which moved to greater depths over the course of the warm seasons. In absence of thermal stratification, between November and January, the plume surfaced or was not detected due to enhanced mixing of the water column. The high concentrations of micropollutants near the wastewater treatment plant (WWTP) outfall present a potential ecotoxicological risk, yet the spatial extent of the risk zone remains unclear.

This work couples the two main processes affecting the spreading of the plume, namely water hydrodynamics and photolysis. The concentration of micropollutants around the wastewater outfall was predicted for typical wind scenarios and seasons relevant in Vidy Bay using a coupled hydrodynamic-photolysis model. Specifically, we experimentally determined the photolysis quantum yields and indirect photolysis rate constants for 24 wastewater-derived micropollutants (mainly pharmaceuticals), and implemented this data into a hydrodynamic particle tracking model, which tracked the movement of water parcels (“particles”) from the WWTP outfall through the Vidy Bay. Modeling results were validated with monthly field measurements collected in 2010.

Model results showed that the zone of potential ecotoxicological risk was generally larger under stratified (summer) conditions than under well-mixed (winter) conditions. This could be attributed to slower dilution, as well as decreased photodegradation due to the entrapment of the WW plume below the thermocline. The largest extent of the risk zone was observed under conditions of Bise (north-easterly wind) during the summer season, with a westward expansion of > 300m. Under Vent (south-westerly wind) conditions, the area of risk was generally smaller and extended mainly to the east (upstream) of the WWTP. As expected, photodegradation was an important removal mechanism for many compounds and thus contributed to a reduction in the ecotoxicological risk over time and distance from the WW outfall. The mixture toxicity near the outfall was dominated by five substances, mainly antibiotics. The coupled photolysis-hydrodynamic model revealed that the risk zone may affect a stretch of up to 600 m in proximity to the shore (ca. 300 m in east and west direction of the WW outfall). This zone should be targeted in future studies of the ecotoxicological effects of WW effluent in Vidy Bay.

## Emissions of cyclic volatile methylsiloxanes and polychlorinated biphenyls from Zurich, Switzerland

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The cyclic volatile methylsiloxanes decamethylcyclopentasiloxane (D<sub>5</sub>) and dodecamethylcyclohexasiloxane (D<sub>6</sub>) have been used widely and in increasing amounts in recent years, e.g. in personal care products. Polychlorinated biphenyls (PCBs), on the other hand, were extensively used as dielectric and coolant fluids, outdoor paints and many other applications, were banned several decades ago, but are still present in many materials. Both types of substances, although very different with respect to chemical properties and fields of application, are released from urban areas in relevant amounts. Here we report measurements of the urban source strength of these two substance classes from the city of Zurich, Switzerland.

The sampling for this study was performed in winter during a period with temperature inversion in order to exploit the accumulation of pollutants in a stable atmospheric boundary layer lasting for several days. The measurements were performed with a temporal resolution of 6–12 h over a period of eight days and at two sites, one in the city centre and one on a hill outside the city. A multimedia mass-balance model parameterized for the region of Zurich was used to interpret the levels and time trends in the measured concentrations and to back-calculate the rates of emission to urban air.

The emission rates obtained for D<sub>5</sub> and D<sub>6</sub> are 120 (68–270) and 14 (8–33) kg·d<sup>-1</sup>, respectively, which corresponds to per-capita emissions of 310 (170–690) and 36 (19–81) mg·capita<sup>-1</sup>·d<sup>-1</sup>. The emission rates of PCBs are approximately four orders of magnitude lower, 4.0 (2.3–8.5) g·d<sup>-1</sup> for PCB-28, 6.7 (2.8–10) g·d<sup>-1</sup> for PCB-52 and 0.3 (0.2–0.6) g·d<sup>-1</sup> for PCB-180. This corresponds to per-capita emissions of 0.01 (0.006–0.02), 0.02 (0.007–0.03) and 0.0009 (0.0005–0.002) mg·capita<sup>-1</sup>·d<sup>-1</sup> for PCB-28, PCB-52 and PCB-180, respectively.

The country-specific emissions of D<sub>5</sub> from deodorant products estimated for Switzerland that are incorporated in the estimate of 30,000 t·a<sup>-1</sup> for the Northern Hemisphere are 16–25 mg·capita<sup>-1</sup>·d<sup>-1</sup>.<sup>1</sup> Our estimate of the average per-capita emissions from the city of Zurich, which includes all emission sources, is higher by one order of magnitude. For PCBs, the estimates from Breivik's<sup>2</sup> emission scenarios for Switzerland for the year 2011 are 0.002 (0.00004–0.04), 0.001 (0.00002–0.02) and 0.0002 (<0.00001–0.004) mg·capita<sup>-1</sup>·d<sup>-1</sup> for PCB-28, PCB-52 and PCB-180, respectively. Our emission rates derived for Zurich are in good agreement with Breivik's maximum scenario, considering that the emissions of PCBs in winter are probably lower than the annual average.

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## Evaluating partial nitrification capability to degrade Sulfamethoxazole and their greenhouse gases emissions

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The sulphonamide antibiotic sulfamethoxazole (SFX) has been frequently found in wastewater treatment plants (WWTP) (Batt et al., 2007) and partial removal can be measured in some cases (Onesios et al., 2009; Larcher and Yargeau, 2012). Studies published in recent years have found higher removal of some pharmaceutical compounds in WWTP where nitrification is well established (Tran et al., 2009; Fernandez-Fontaina et al., 2012). This phenomena could be related to the metabolism of ammonia oxidizing bacteria (AOB) which are responsible for initiating the pathway of ammonia (NH<sub>3</sub>) oxidation by using the enzyme ammonioxygenase (AMO). It is known that AMO can catalyse the oxidation of a large group of compounds apart of NH<sub>3</sub> (Hyman and Wood, 1983; Keener and Arp, 1994) and it has been suggested to play a key role on the biodegradation of several micropollutants by AOB (Yi T & Harper W. 2007). On the other hand, AOB have been suggested to be the main contributors to nitrous oxide (N<sub>2</sub>O) emissions detected in WWTPs aerobic stages of performing biological nutrient removal. N<sub>2</sub>O is a potent greenhouse gas, 300 times stronger than carbon dioxide and therefore it is important to minimize its emissions. If the presence of pharmaceutical compounds into the wastewater has an effect on the N<sub>2</sub>O production by AOB remains unknown.

This study explored the SFX biodegradation by an enriched AOB culture (>80% of the microbial population belong to the AOB group) via several batch tests and compared it with the biodegradation detected using conventional activated sludge biomasses. Also, the effect of SFX on N<sub>2</sub>O emissions by an enriched AOB culture was assessed. Experiments were performed in aerobic conditions (2 mgL<sup>-1</sup> Oxygen set point; 0.5-0.6 Lmin<sup>-1</sup> constant gas flow), controlled pH at 7±0.05 and at 1 gTSSL<sup>-1</sup>. Reference tests were performed, without SFX (to calculate GHG emissions and NH<sub>4</sub><sup>+</sup> oxidation rate) and, without influent ammonia, to check AOB capability to degrade SFX in absence of their energy source. Afterwards, a unique pulse of 0.5 gN-NH<sub>4</sub>L<sup>-1</sup> at the beginning of the experiment guaranteed the AMO activity, with a maximum nitrite accumulation of 0.5 gN-NO<sub>2</sub><sup>-</sup> (not inhibitory for the considered AOBs). SFX doses were compared (10 µgL<sup>-1</sup>, 100 µgL<sup>-1</sup> and 1 mgL<sup>-1</sup>) evaluating the removal of SFX and of its two metabolites (4-Nitro-SFX and desamino-SFX), the nitrification rates and the GHG emissions.

The enriched partial nitrifier culture showed higher degradation of the target pharmaceutical (up to 90.2% at the highest tested concentration) than conventional activated sludge (29.9%) and different metabolites distribution. A N<sub>2</sub>O production of 1.38±0.22% (total emitted N<sub>2</sub>O/total NH<sub>4</sub> nitrified) was observed in reference tests as well as equivalent productions in the other tested conditions. The results suggest that enriched AOB culture can enhance the biotransformation of the antibiotic sulfamethoxazole, while achieving a stable nitrification, but no clear influence on N<sub>2</sub>O emissions was found.

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## Determination of *in-situ* biodegradation rate constants of nonylphenolic compounds in the Seine River

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Assessing the fate of endocrine disrupting compounds (EDC) in the environment is currently a key issue for determining their impacts on aquatic ecosystems. The 4-nonylphenol (4-NP) is a well known EDC. It results from the biodegradation of surfactant nonylphenol ethoxylates (NPEO). Biodegradation mechanisms of NPEO are well documented (Giger *et al.* 2009) but their rate constants have been mainly determined through laboratory experiments. To our knowledge only Jonkers *et al.* (2005) evaluate NPEO biodegradation rate constants according to field measurements. Their study was carried out in an estuary (salt water) and has to be confirmed for freshwater.

This study aims at evaluating the *in-situ* biodegradation of 4-NP, nonylphenol monoethoxylate (NP<sub>1</sub>EO) and nonylphenolic acetic acid (NP<sub>1</sub>EC). Two innovative sampling campaigns were carried out on the Seine River in July and September 2011, from Maisons-Laffitte to Triel-sur-Seine (along a 40km-transect downstream of Paris City). Their results were used for calibrating a sub-model of NPEO biodegradation of the hydrodynamic-biogeochemical model of the Seine River (PROSE, Even *et al.* 1998). Sampling times were estimated according to the Seine River velocity in order to follow the same volume of water. Simultaneously, during the September sampling campaign, small scale spatial and temporal variabilities of nonylphenolic compounds concentrations were assessed. Biodegradation rate constants of 4-NP, NP<sub>1</sub>EO and NP<sub>1</sub>EC between July and September varied greatly. Although the biodegradation rate constants in July were especially high (higher than 1 d<sup>-1</sup>), those obtained in September were smaller but consistent with the literature. This variability is probably linked to the biogeochemical behaviour of the Seine River. Indeed, the July sampling campaign took place at the end of an algal bloom leading to an unusual bacterial biomass while the September campaign was carried out during an "usual" biogeochemical state.

This study provides relevant information regarding biodegradation rate constants of alkylphenols in an aquatic environment. Such data may be very helpful in the future to better understand the fate and transfer of nonylphenolic compounds at the catchment basin scale.

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## Assessing Vapor Pressure Models of PAC Mixtures

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Thermodynamic models are often used to estimate the vapor pressures of contaminants for input into environmental fate and transport models, especially for coal tar mixtures comprised of polycyclic aromatic compounds (PAC). However, gaps in our thermodynamic understanding of the sublimation behavior of these mixtures raise questions as to the appropriateness of model application. Though there are a plethora of models available to predict the vaporization and bulk transport properties of PAC mixtures – from Raoult's law, to equations of state, to group contribution schemes – these models rely on pure component data with little to no experimental validation. The thermodynamics of a given contaminant mixture, especially its vapor pressure, are determining factors in the phase (solid, liquid, gas) and compartment (soil/sediment, water/NAPL, vapor/air) in which it will reside. By selecting the proper technique to model the vapor pressure of PAC mixtures, our fate and transport models and risk assessments will be more accurate and reliable.

By comparing experimental vapor pressure data on a series of binary and multi-component PAC mixtures to Raoult's law it is apparent that small, systematic deviations from ideal behavior occur. Overall, binary mixtures of low molecular weight PAC see fewer deviations from Raoult's law than those with molecular weights greater than 200 g/mol. Mixtures containing one or more five-carbon rings appear to deviate less from ideality than those composed only of six-carbon rings. Vapor pressures of mixtures without strong intermolecular interactions (such as acid-base interactions) tend towards the behavior of the more volatile component at lower temperatures, while at a specific temperature for each mixture, a transition to ideal behavior occurs, in which the experimental mixture data on a Clausius-Clapeyron plot are well-predicted by Raoult's law. The somewhat variable deviations from ideality result from simultaneous enthalpic and entropic effects. This implies a limiting value of mixture activity coefficients, which is often true of mixtures that experience strong hydrogen bonding.

To evaluate the appropriateness of using Raoult's law over other common vapor pressure prediction schemes, we modeled the vapor pressures of PAC mixtures using UNIFAC, Peng-Robinson and van Laar Equations of State (EOS) using ASPEN v.6. On the whole, it appears as though the Peng-Robinson EOS has a tendency to under-predict vapor pressures at lower temperatures, though at higher temperatures it often offers a better prediction than UNIFAC or the Wilson and van Laar equations. Within the ambient temperature region, the Wilson, van Laar and UNIFAC predictions are fairly accurate, with UNIFAC having a slight edge in mixtures containing heavier compounds. However, in terms of estimating vapor pressures of these compounds, especially for routine environmental calculations, Raoult's law is more consistently accurate across a range of environmental conditions.

## Evidence of the return of past organic pollution in the ocean – a model study

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Persistent organic pollutants are of great concern because of their long residence time and long-range transport potential in the environment and because they are readily bioaccumulated along food chains and toxic for wildlife and humans.

Recovery of the environment from exposure to widespread and persistent chemical pollution is determined by the spatiotemporal emission pattern and storage capacity and transports in environmental compartments.

We studied the 3D exposure of the global ocean changing over time in response to historic emissions of polychlorinated biphenyls (PCB) and dichlorodiphenyltrichloromethane (DDT), 1950-2010 using the multicompartment chemistry-transport model MPI-MCTM, which encompasses atmosphere (ECHAM5) and ocean general circulation models (MPIOM), dynamic sub-models for atmospheric aerosols and the marine biogeochemistry, two-dimensional surface compartments (topsoil, vegetation surfaces, ice, and temporal snow cover) and intercompartmental mass exchange process parameterisations [1-3].

The pollution wave received by the surface waters through atmospheric deposition is propagating downward. Besides considerable time lags with respect to the year of peak emission, temporal bimodal exposure to the pollutants is found in mid level and deep waters (200-1500 m) in some areas, e.g. in the western and eastern North Atlantic. This is a consequence of the combination of downward pollution transport by advection, diffusion, and particle settling. [4]

It is suggested that the combination of the same processes will lead to re-rise of pollutant concentrations in seawater in other regions in the future.

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## Prediction of water sources contribution in Barcelona supply system by real time UV-Vis spectrophotometry

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The basic physico-chemical characteristics of drinking water depend on the raw water source. The mineral content and the occurrence of water organic constituents change with the geographical location and seasons. Natural organic matter (NOM) content varies with water sources and it is affected by the vegetation cover and the soil content. NOM influences the aesthetic qualities of drinking water such as taste, colour and odour. NOM is a complex mixture of different heterogeneous compounds, hard to identify them individually, but its profile can be used as a possible fingerprint of its water source. The absorbance record at 254 nm is a typical quality parameter for organic matter, whilst the entire UV/VIS spectrum of a water sample can be used to obtain more comprehensive information about its nature.

In a previous study (Platikanov et al. 2011), a new methodology was developed to combine UV measurements (190–230 nm) with multivariate data analysis and Partial Least Squares (PLS) for water source determination and mixtures apportionment. This method was able to determine the two main river sources in tap drinking waters of Barcelona area and to predict their relative amounts in mixtures.

This study continues the previous work, using in this case, a submersible spectrophotometer UV/VIS probe (200–730 nm) to test its possible on-line or in-line application in a water distribution network. More than 200 drinking water samples have been collected during one year from the Barcelona metropolitan network, with monitoring sites distributed along the whole system to cover the different possible blending and seasonal changes. Also, laboratory analyses were performed to obtain 81 parameters for their physico-chemical characterization.

Chemometric analysis of the results obtained using Principal Component Analysis (PCA) has allowed the discrimination among water samples according to their main river source or treatment by means of their UV/VIS spectra together with other physico-chemical parameters.

The models developed in this work are intended to be applied to the Barcelona drinking network to have real time information about the water origin at selected sites. This information will help plant operators dealing with unexpected alteration of water quality, usually influenced by changes on NOM content and the main source of water.

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## The anthropogenic aluminium cycle through integration of MFA and LCA

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Material Flow Analysis (MFA) and Life Cycle Assessment (LCA) methodologies were applied to analyse the anthropogenic aluminium cycle in Italy with a focus on the historical evolution of stocks and flows of the metal, embodied GHG emissions, and potentials from recycling to provide key features to Italy for prioritizing industrial policy toward low-carbon technologies and materials.

Historical trend series were collected from 1947 to 2009 and balanced with data from production, manufacturing and waste management of aluminium-containing products, using a 'top-down' approach to quantify the contemporary in-use stock of the metal, and helping to identify 'applications where aluminium is not yet being recycled to its full potential and to identify present and future recycling flows'. The MFA results were used as a basis for the LCA aimed at evaluating the carbon footprint evolution, from primary and electrical energy, the smelting process and the transportation, embodied in the Italian aluminium. A discussion about how the main factors, according to the *Kaya Identity* equation, did influence the Italian GHG emissions pattern over time, and which are the levers to mitigate it, it has been also reported. The contemporary anthropogenic reservoirs of aluminium were estimated at about 320 kg per capita. Cumulative in-use stock represents approximately 11 years of supply at current usage rates (about 20 Mt versus 1.7 Mt/year) and about 90% is embedded in the transportation sector, building and construction, and machinery and equipment; recovery and recycling initiatives should hence focus on these markets. Moreover, collection of scrap is a key-issue in which Italy could act to decrease metal losses and consequently to increase the old scrap pool suitable for secondary production. Increasing support to separate collection and initiatives oriented to aluminium recovery specifically would allow Italy to increase its reliance on domestic material, and may also allow a decline of net-import of unwrought aluminium. This will be important to Italian industry and consumers, as on a worldwide scale, aluminium demand is expected to triple at least by 2050.

The analysis revealed high potential to enhance recycling activities for the country, based on dynamic quantification in-use stocks that will supply secondary resources and they would imply a potential of about 160 Mt of CO<sub>2</sub>eq emissions savings, providing support to the country for orienting industrial policy toward the goal of a low carbon society. The LCA results pointed out also the 'virtual' carbon emissions associated with international trade flows of aluminium are not negligible but they may cover up to two third of embedded leakage from a country's consumption, and the need of standardized procedures to properly account them in carbon markets. Finally, the analysis allowed to set historical indicators for the climate change category at national level, which does integrate and updates average scores generally published in international LCA-oriented databases. The research constitutes the first attempt of an integrated approach between MFA and LCA applied to the aluminium cycle in Italy.

## Poly- and perfluorinated compounds – global risks need global management

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Poly- and perfluorinated compounds (PFCs) are monitored all around the world, in environmental samples as well as in human blood samples. According to an OECD survey more than 600 known compounds belong to this group of PFCs. For one of the substances – PFOS – an international regulation has already been agreed on: As a persistent organic pollutant (POP) PFOS was included into Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2010.

Many industrialized countries have started to undertake regulatory action based on environmental concerns related to PFCs. In 2005, the United States of America implemented a stewardship program on PFCs with the goal to reduce the emissions of long chain PFCAs drastically. Eight fluoropolymer and -telomere manufacturers agreed to reduce the emissions of PFOA, its precursors, and related higher homologue chemicals by 95 % until 2010 using the emission data of the year 2000 as a baseline. Moreover an action plan has been implemented to reduce concentrations of long chain PFCs in consumer products.

Canada proposed a risk management scope for PFOA and long chain PFCAs and is working together with the fluorochemical industry on the elimination of PFOA residuals from products sold in Canada.

In 2012, the EU Member States agreed to consider certain long chain PFCAs as substances of very high concern according to the European chemicals regulation REACH. Additional risk management is in preparation.

However, manufacture and use of PFCs are distributed globally. Many consumer products using PFCs as components in their supply chains are manufactured in Asian countries. Monitoring data indicate that PFCA concentrations in Asian rivers are exceeding the concentrations in European and North American water bodies. Therefore, global risk management activities need to be considered to address the global issue of reducing PFC-emissions in the environment.

As early as 2006, the OECD established a group of interested member states to gather information on production, uses and releases of long chain PFCs worldwide. Together with UNEP, the group was later expanded to become the OECD/UNEP Global PFC Group and to contribute to SAICM's efforts in this area.

The objectives of the Global PFC Group are to provide scientific information via synthesis papers and webinars to interested countries. The transfer of knowledge seems to be the first step for a common understanding. This might be the basis for further international measures to reduce the emissions of PFCs successively.

## PM11

### Source-tracking of airborne dust by PLS modelling of spectrometric data

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For several years the EU limit values for ambient particle pollution have been exceeded on several occasions each winter in Reykjavík. It is of some importance to know the sources of the pollution and this is not a trivial problem. This lecture describes a project of chemical analysis and multivariate modelling which has successfully revealed the main sources of airborne dust in Reykjavík. As sources, samples from soil, asphalt, soot, brake lining and salt were selected. This involves collection of synthetic dust samples from the suspected sources onto filters using the same procedure as is used for the collection real dust samples. All samples are then analysed first in a non-destructive (NIR/Vis reflectance scans) then in a destructive manner (acid digestion followed by ICP-OES and ICP-MS detection) along with real dust samples. The resulting data are used to create a soft multivariate mathematical model (Partial Least Squares Regression) estimating the mass fraction of each source in the real dust samples. Collection of reflectance data is unusual in this context, but here it was included in hope of separating sources with suspected similarities in inorganic content i.e. minerals from asphalt vs. minerals from soil. The near infrared (NIR) spectral region contains a vast multiplicity of overlapping vibrational frequencies which are usually avoided in direct quantitative determinations. The region is however ideal for soft modelling work as spectra are likely have contributions from all major organic constituents and these can be utilized with multivariate techniques. The visible spectral region aids in separating sources by their colour, as Icelandic soils are of volcanic origin and thus often have strong red-brown colour. A problem with reflectance spectra is the background reflectance from the air filters used. This may be solved by introducing shielding factors and by using an iterative procedure of alternating rounds of multivariate modelling and reflectance shielding calculations. Individual sources are modelled individually and, as seen in the table below, the calculated mass fractions add up to numbers close to 100 percent for all samples, indicating that this is a valid methodology.

PM 10	Sample mg	Soil %	Asphalt %	Brake l. %	Exhaust %	Salt %	Total %
3069G	2,3	32	49	2	5	16	104
3392G	2,0	33	41	-10	23	16	102
3409G	2,6	33	58	-3	9	8	105
3371G	1,0		98				98
3388G	1,3	27	54	3	4	16	104
3578G	2,2	31	60	4	4	8	107
3581G	2,4	29	62	7	1	7	106
3593G	1,8	32	43	1	5	22	102
3594G	0,9	32	30	-8	19	28	101
3602G	0,8	33	53	-1	7	11	104
3603G	2,4	27	62	8	0	9	107
3604G	1,2	31	47	1	6	19	104
AVG		31	55	0	7	15	104

## Advanced quantitative environmental impact assessment for red mud disposal facility

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The environmental impact assessment has gained a very important role in the decision making regarding different projects, investments, actions and proposals. The environmental impact assessment is a systematic process which deals with the consequences of the future developments in advance. The methodology of the assessment includes several techniques. The quantitative methods focus on the evaluation of the impacts by assigning importance values to the environmental parameters and quality scores. The method devised by Robu was further developed and protocol for the determination of the complex environment state index was devised. This method is adapted for the red mud disposal facility of Ajka, Hungary where an extremely serious environmental disaster occurred in October 2010. Approximately 1 million m<sup>3</sup> of red mud sludge ruptured from the wet disposal facility resulting in loss of human lives and seriously damaging the surface waters, ecosystems and the soil as well as the social and economic conditions. For the evaluation of the environmental conditions after the emergency actions and rehabilitation and remediation in light of the baseline conditions a quantitative environmental impact assessment technique was devised on the basis of the environmental factors and parameters in different environmental elements. Conclusions are made on the environmental impacts of the activity of the company. The objective of the paper is to carry out an assessment on a red mud disposal facility in light of the legal stipulations and limit values to support the more efficient operation of the waste disposal system of the company with identification of the significant environmental impacts and making recommendations on the mitigation measures.

Key words: complex environmental index, environmental impact assessment

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## **Risk assessment of chemical accidents: Application of a screening model and a scoring method to a real accident case**

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Oil and chemical spills are one of the most common causes of soil pollution in Finland and on a global scale. Over 100 chemical accidents are registered yearly in Finland but fortunately most of them are relatively small. When chemical releases to the environment, managing authorities need to assess risks that chemical poses to human health, soil and water resources and ecosystems rapidly and decide right actions to manage the risks. The extent of the risk depends on many chemical- and site specific properties and conditions. Both qualitative and quantitative methods can be utilized in risk assessment. In this study, a screening level model to assess quantitatively the transport of fuels to groundwater was applied to a real accident case data in order to test the capability of the model to simulate the accident. Furthermore a scoring system to qualitative evaluation of transport, health and ecological risks of chemical accidents in Finnish conditions was developed and validated with case data.

A fuel transportation traffic accident occurred near the city of Iisalmi in Finland. Due to rapid action, a large part of the spilled diesel and gasoline fuel was collected soon after the accident. However, part of the both oil fractions entered the deeper soil layers, and form a threat to the soil ecosystem and the groundwater. Remediation process was started and will continue for years at the site. Screening level model (Hazardous Materials Transportation Environmental Consequence Model, HMTECM) gave a good estimation about the transport of gasoline and diesel as Non-Aqueous Phase Liquids (NAPL) in the soil. Modelled results were compared to the measured concentrations of oil fractions. Modelled and observed NAPL migration depths five days after the accident varied only about 1 meter. The scoring system was developed by choosing chemical- and site specific parameters and scaling and emphasizing them based on literature, expert opinions and modelled results. The scoring method allowed rapid mapping of the risks related to e.g. Iisalmi accident case without very specific site characterization data.

## Persistent Organic Pollutants' data in European Alps: A decade of multi-compartment monitoring

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Cold environments are affected by the transport of persistent organic pollutants (POPs). Moreover, they are identified as important "early warning" sites with respect to global and medium-range transport. Mountains have become good locations for monitoring activities to assess both regional and global contamination of POPs. Mountains have deserved a special attention as a "reservoirs", accordingly specific monitoring campaigns were planned, including air; mountain soils; lake water and sediments; vegetation; snowpack and glaciers; and alpine food chains both aquatic and terrestrial.

In Europe POPs emissions and deposition rates are monitored and modelled by the European Monitoring and Evaluation Programme (EMEP), reporting to the LRTAP Convention. Some EMEP stations are located in the Alps (Lago Maggiore); moreover, several other monitoring studies were conducted so far in the Alpine area, such as the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP). MOUNTAIN LAKES RESEARCH NETWORK that includes European monitoring programmes such as AL:PE, MOLAR, and other projects aimed at setting up a long-term monitoring programme regards to acidification and organic pollutants in a changing environment during the last 20 years.

We collected all the information related to POPs' concentrations in European Alps from year 1999 to year 2012 and organised this information in a database that will be released to the public. This database on POPs' concentrations in the Alps located in Austria, Germany, Switzerland, Slovenia, Italy and Czech Republic is aimed to close the gap between chemicals and environmental factors that govern POPs' environmental behaviour at high elevations and can help to identify the most vulnerable alpine zones and environmental compartments to exposure of high concentrations of POPs.

The called "PopsDB" includes six environmental compartments: air, soil, sediment, water, snow, vegetation and fauna. We have distinguished between active and passive air sampling and the monitored contaminants are those defined by the Stockholm Convention and Aarhus Protocol: DDTs (DDD, DDE, DDT), PAHs (34 species), PCBs (45 species), chlorinated paraffins, HCB, organochlorine pesticides (endosulfan, chlorophenol, chlordane, dieldrin, endrin, mirex, heptachlorine, aldrin, chlordane), HCH and PBDE.

In this communication we report on the use of the "PopsDB" database, as source and management tool of POPs monitoring data for the modelling of spatial and temporal trends of POPs according to changes in local climate.

## Monthly variation of geochemical parameters in the North Sea. From experimental to modelling

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In the framework of the project MICROMET (Microbial Diversity and Metal Fluxes in Contaminated North Sea Sediments), trace metal contamination in surface sediments was closely studied. High resolution profiles of trace metals were assessed monthly by DGT (Diffusive Gradient in Thin films) in muddy sediments of the station 130 (51°16.25 N - 02°54.30 E) of the North Sea. General parameters such as pH, redox potential, temperature, dissolved oxygen, sulfides and organic matter were also monthly measured in order to estimate the role and influence they have in the speciation of trace metals. Thermodynamic calculations with experimental data were undertaken in order to help to detail some major (geo)chemical processes of interest taking place and to predict the fate of trace metal in sediment in case of (physico-)chemical changes at the water sediment interface. The software VisualMinteq was used for calculation of metal chemical speciation of dissolved metals (Mn, Fe, Co, Ni, Cu, Pb and Cd) in overlying waters and sediment porewaters, and to predict the existence of solids associating trace metals. Experimental results obtained by DGT showed for Fe, Co, Ni and Cd the lowest metal concentration in summer, which can be explained by the highest sulfide concentration found in this period, since these metals have tendency to associate to sulfides. Cu and Pb behaviour was found to be less influenced by sulfides, since they are mostly associated to organic matter. The whole set of results clearly indicated that metal speciation in these sediments is controlled by sulfides and OM contents.

## Children exposure to pesticides in Valencia Region (Spain)

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Human biomonitoring (HBM) of pesticides can be used as indicator for exposure of children to the main non-persistent pesticides currently used in Spanish agriculture and residential settings. In a pilot study developed in Valencia Region, the second largest agricultural area in Spain, specific metabolites of organophosphate pesticides (OP), pyrethroids, herbicides and non-specific OP metabolites (dialkylphosphates) were analysed in 125 urine samples of children aged between 6-11 years and residing in an urban and a rural area. We also assessed the determinants of the variability in the urinary metabolite concentrations obtained using the detailed information collected in questionnaires.

Specific OP compounds were the most frequently detected metabolites (48%-86%), followed by dialkylphosphates (DAP) compounds (9%-79%). Pyrethroids and herbicides were detected at low frequencies (<26%) or were not detected in any sample. The geometric means calculated for major metabolites detected ranged from 0.46 to 3.05 µg/g creatinine. Factors associated with urinary levels of specific OP metabolites included age ( $p < 0.001$ ), residence ( $p < 0.05$ ), and vegetable consume ( $p < 0.0$ ). In other hand, factors associated with DAP concentration were the residence ( $p < 0.05$ ) and the parent educational level ( $p < 0.05$ ).

Levels of exposure obtained in this study were, in general, similar to these shown in other HBM studies in Europe and USA [1, 2]. Although the diet seems to be the main route of exposure to pesticides in humans [3], more in deep analysis of the results are necessary to establish other routes of exposure to pesticides in children population.

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## **Transformation and Fate of Pollutants**

**Oral presentation: OTF1-OTF10**

**Poster presentation: PTF1-PTF48**

## Direct photolysis of human metabolites of antibiotic sulfamethoxazole: Evidence for abiotic back-transformation

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The presence of potentially persistent and bioactive human metabolites in surface waters gives rise to concern; yet little is known to date about the environmental fate of these compounds. We investigated the direct photolysis of human metabolites of the antibiotic sulfamethoxazole (SMX). In particular, we determined photolysis kinetics and products, as well as their concentrations in lake water. SMX, N-acetyl sulfamethoxazole, sulfamethoxazole  $\beta$ -D-glucuronide, 4-nitroso sulfamethoxazole and 4-nitro sulfamethoxazole were irradiated under various light sources and pH conditions. All investigated metabolites, except SMX-glucuronide were found to be more photostable than SMX under environmentally relevant conditions. The products generated from the direct photolysis of SMX and its human metabolites were investigated using ultra-performance liquid chromatography/high-resolution mass spectrometry. Over 30 photoproducts were proposed and nine could be confirmed with analytical standards. A comparison of the conversion rates illustrates that the different ring substituents on the metabolites not only affect the direct photolysis reaction rate, but also the principal photolysis pathways. Among the confirmed products, cleavage reactions were predominant for SMX and N-acetyl SMX, whereas the nitro-group was very resistant to phototransformation and the nitroso group mainly underwent modifications of the substituent. Interestingly, photolytic back-transformation to SMX was observed for 4-nitroso-SMX, indicating that this metabolite may serve as an environmental source of SMX. This is the first evidence for photolytic back-transformation of a metabolite to its parent compound. Further studies show that yield of the back-transformation of 4-nitroso SMX to SMX is pH dependent, and increases if samples are stored in the dark after irradiation. The back-transformation reaction thus likely involves the hydrolysis of a yet unidentified, photo-generated intermediate product.

Additionally, sampling campaigns in Lake Geneva showed that human metabolites along with SMX were regularly detected. The knowledge that some metabolites retain biological activity, combined with their presence in the environment and their potential to retransform to the parent compound, underlines the importance of including human metabolites when assessing the effects of pharmaceuticals in the environment.

## A model approach to link indirect photochemistry in surface waters with climate change and human impact: the case of polymictic Lake Peipsi (Estonia/Russia) over the last three decades

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Over the last 3-4 decades, water of Lake Peipsi (sampling site A, middle part of the lake, and site B, northern part) has experienced a statistically significant increase of bicarbonate, pH, chemical oxygen demand, nitrate (and nitrite only in site B), most likely due to combination of climate change and eutrophication<sup>1,2,3</sup>. By use of a photochemical model<sup>4</sup>, we predicted a statistically significant decrease in steady-state concentrations of the radicals  $\cdot\text{OH}$  and  $\text{CO}_3^{\cdot-}$  (site A, by 45% and 35%, respectively) and an increase of the triplet states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ; site B, by about 25%). These species are involved in pollutant degradation<sup>5, 6</sup>, but formation of harmful by-products is definitely less likely with  $\cdot\text{OH}$  than with  $^3\text{CDOM}^*$ . Therefore, the natural ability of Lake Peipsi to photodegrade harmful xenobiotics probably underwent a decrease with time. This result would be linked to combined effects of climate change and eutrophication, while in other environments<sup>7</sup> the ecosystem restoration policies would produce the additional advantage of enhancing sunlight-driven detoxification.

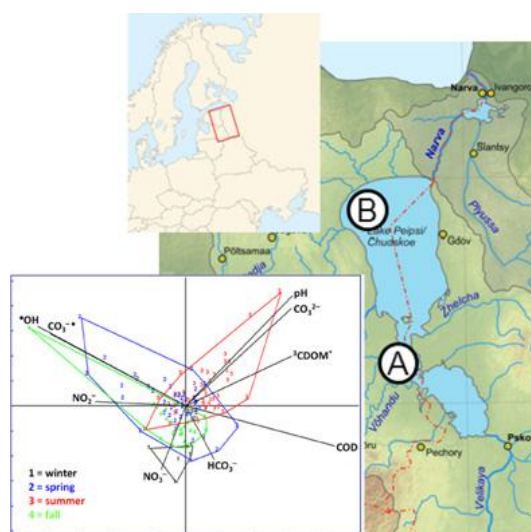


Fig. 1. Map showing the location of Lake Peipsi. The circles show the two sampling sites (A and B). Principal Components Analysis (PC1 vs. PC2) for site A.

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## Assessment of photochemical processes in marine oil spill fingerprinting

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Although the number of the accidental oil spills has decreased significantly during the past decades, catastrophic accidents such as the sinking of the *Prestige* tanker near the coast of Galicia (Spain) and the *Deepwater Horizon* platform blowout in the Gulf of Mexico, still pose an important threat to marine and coastal ecosystems. The source identification of these oil spills is the primary step in assessing their consequences and defining the response strategies.

The most consistent methodology for oil spill characterization is based on the chemical fingerprinting approach, where a series of molecular markers can be profiled by gas chromatography (GC) or comprehensive two-dimensional gas chromatography (GC×GC) coupled to flame ionization detector (FID) or mass spectrometry (MS). Characteristic distributions and ratios of selected 'diagnostic' compounds generate an oil 'fingerprint' which can be used to identify the source of the spilled oil.

A fundamental understanding of the weathering processes (evaporation, dissolution, microbial degradation and photooxidation) affecting oil spilled in marine environments is required for elucidating the recent history and predicting the future fate of the oil. This knowledge is essential in order to refine the diagnostic value of the source recognition indices and interpret the profiles in tracking oil sources.

We present laboratory and field data showing the compositional changes of oil spills by photochemical degradation. In this respect, PAH and biomarker diagnostic molecules in two different oils, *Macondo well* (MW) oil from the *Deepwater Horizon* spill, and oil from *Prestige* tanker spill were analyzed using GC×GC-FID and GC-MS fingerprinting methodologies. This included the analyses of weathered field samples from the Gulf of Mexico, and photooxidized samples of MW and *Prestige* oil, irradiated in two laboratory scale experiments, using natural sunlight and xenon lamp. Normalized peak areas of investigated compounds in raw and weathered oil samples were compared to calculate their losses, and commonly used fingerprinting ratios were calculated to test their consistency.

## Fluorouracil in the environment: analysis, occurrence and transformation

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5-Fluorouracil (5-FU) is a fluorinated pyrimidine analogue important in the treatment of cancer whose fate in the environment is yet to be fully addressed. Due to its high polarity 5-FU requires challenging sample preparation and therefore we thoroughly investigated different solid phase extraction mechanisms (ion pair, ion exchange, reversed phase), sorbents and derivatisation agents to enable trace-level analysis of 5-FU based on GC-MS/MS in natural and wastewaters. While ion pair and ion exchange retention mechanisms were shown inappropriate for complex environmental matrices, the reversed phase sorbent Isolute ENV+ gave the best extraction efficiencies (53% and 93% for wastewaters and surface waters, respectively). Further, alkylation was rejected in favour of silylation with MTBSTFA. The achieved LOQ for waste and surface waters were 1.6 ng/L and 0.54 ng/L, respectively. The method was used to analyse samples of hospital, wastewater treatment plant influent and effluent and surface waters. 5-FU was quantified in four out of the twelve samples of oncological ward wastewaters and municipal wastewater treatment plant influents in concentrations from 4.7 to 92 ng/L. This work is also the first to study the environmental transformation of 5-FU and its prodrug capecitabine (CAP). Their removal and transformation was simulated using a series of biodegradation and photodegradation experiments, where 5-FU proved more degradable in comparison to CAP. Transformation of 5-FU and CAP was studied by using ultra-performance liquid chromatography coupled to a quadrupole time-of-flight mass spectrometry (UPLC-QqTOF). Overall, six transformation products for 5-FU and ten for CAP are proposed; 13 of these are to our knowledge presented for the first time.

## DFT study on hydrolysis of polyhalogenated pollutants for estimation of environmental degradation rates

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High-level quantum chemistry methods have rarely been used for assessment of reactivity or persistence of pollutants. Such computations require careful selection of model chemistry and yet demand for extraordinary computation power, exceeding that of a personal computer. However, recent developments in soft- and hardware allow a non-expert in quantum chemistry perform meaningful *in silico* experiments at his/her desk.

This work describes experience in computations of the rates of hydrolysis of polyhalogenated aromatic pollutants (PCDDs, PCCDFs, PCBs, PBDEs, PCNs etc). Results are compared with limited experimental data and with hydrolysis rates obtained by correlation analysis methods of classic physical organic chemistry.

Geometry optimizations for studied compounds, reaction products, intermediates and transition states were performed with Gaussian 09, Revision B.01 at rb3lyp/6-31+g(d,p) level of theory. Single-point energies and frequencies were calculated at the same level or at rb3lyp/6-311+g(2df,p) level. Personal computer used was iMac with 2.8GHz Intel Core i5 processor with Mac OS X, version 10.6.8.

A good general correlation of computed and experimentally measured rates of hydrolysis (taken from literature and own data) of polychlorobenzenes and polybromodiphenyl ethers and with rates, calculated with “paper and pencil” using Hammett equation. However several cases of significant deviation were found. For instance, Decabromodiphenyl ether was found less reactive than Nonabromodiphenyl ether in all *in silico* experiments. This finding is in contradiction with experiment and with Hammett-based calculations.

Geometry optimization or frequency calculation at higher level of theory for each conformation of Decabromodiphenyl ether takes approximately 20 hours, while for compounds with smaller number of heavy atoms it takes just several hours or less; thus for those “lighter” compounds relative reactivities can be obtained in one working day or overnight.

With expected advances in personal computers DFT computation of environmental degradation rates should become a routine instrument of an environmental chemist.

## Formation of phototransformation products of iodinated contrast media; natural attenuation or disinfection process?

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Iodinated contrast media (ICM), a widely used imaging agent for organs or blood vessels during diagnostic tests, have been reported to occur in different water compartments including untreated and treated sewage, surface and ground waters. As consequence of the high dosages administered and the lack of human metabolism to metabolise it, ICM are frequently encountered in wastewaters at µg/L and ng/L to ug/L concentrations in river water. Apart from their abundance in the aquatic environment, these derivatives of 2,4,6-triiodobenzoic acid, are also susceptible to bio and photo-degradation.

Six ICM (Iohexol, Iopromide, Iopamidol, Diatrizoate, Iomeprol, Iodixanol) were degraded using Suntest (wavelength cut-off 290-900nm) and samples were collected over time. Samples were first run on a LC-UV with c18 column to see the chromatographic changes and subsequently on a UPLC-LTQ-Orbitrap-Velos to elucidate the structures of transformation products (TPs). Once the six structures were tentatively identified on a high resolution MS, semipreparative-LC-UV was used to separate newly transformed compounds in order to obtain standards for quantification methodology development and to additionally confirm the structures with NMR.

Once the six major TPs were identified and confirmed with NMR, a method was optimised for the extraction, separation and detection of six parent compounds and its six corresponding phototransformation products. Considering the high polarity of these compounds and its acidic/basic character, first a SPE method was chosen testing several different cartridges (mainly mix mode and polarity based). Chromatography method was also set to accommodate polarity issue and Hydrophilic Interaction Chromatography (HILIC) column was used, which in comparison to c18 column gave superior detection/quantification limits. Finally the optimised method using SPE-HILIC-LC-qTrap-MS was applied to the determination of the target analytes in real samples and in four matrices (influent and effluent wastewater, river and drinking water). Photoproducts were detected at concentrations of ng/L in river and drinking water. Influent and effluent wastewater samples were included in the present work in order to monitor the presence of the iodinated parent compounds in WWTP. Since all the samples were processed with the same methodology, traces of some TPs were detected in effluent water samples, tracing it back to the WWTP that uses UV treatment as disinfection step. Transformation of iodinated parent compounds in WWTP was evaluated with UV-photodegradation experiments simulating WWTP conditions where it was confirmed the formation of the six TPs in effluent samples. In conclusion, UV-disinfection and sunlight photolysis processes both contribute to the presence of ICM photoproducts in the aquatic environment.

## Evidence for Exposure to Chemical Contaminants in the Tropical Marine Snail *Telescopium telescopium* (Gastropoda:Potamididae)

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Wastewater effluent is a major source of endocrine disrupting compounds (EDCs) in aquatic environments due to the large number of man-made chemicals present in these effluents and their incomplete removal by conventional sewage treatment methods. Consequently, aquatic species exposed to wastewater effluent experience chronic exposure to a complex mixture of contaminants. Although many studies have documented the presence of EDCs in aquatic environments, and the adverse effects on aquatic organisms exposed to EDCs, few have been carried out in the tropics where the consequences of exposure still remain largely unknown. The objective of this study is to identify indicators of exposure to chemical contaminants in the marine gastropod *Telescopium telescopium*, commonly known as “Longbum”. Water, sediment and *Telescopium telescopium* were collected from estuarine sites impacted by secondary treated municipal wastewater and corresponding reference sites (those without wastewater outfalls present) located in Darwin Harbour, Northern Territory, Australia. *Telescopium telescopium* was used in this study as it lives naturally at potentially impacted sites, is widely distributed throughout tropical northern Australia, provides a food source for local Indigenous people, and has been demonstrated to accumulate organic contaminants from its surroundings. Water and sediment were screened for a wide range of contaminants comprising EDCs, pharmaceuticals and personal care products (PPCPs), herbicides, pesticides, PCBs, PAHs and heavy metals. In addition, the yeast estrogenic screen and yeast androgenic screen (YES and YAS) were used to assess (anti)estrogenic and (anti)androgenic activity. Tissues of *T. telescopium* were analysed for a selection of endocrine disrupting and heavy metal contaminants, along with nitrogen ( $\delta^{15}\text{N}$ ) and carbon ( $\delta^{13}\text{C}$ ) stable isotope analysis to obtain information on the biological uptake of nutrients from wastewater effluent. Histopathology was carried out to provide corresponding information on the health status of the animals with a view to providing ecologically-relevant biological end points of chronic contaminant exposure. A range of contaminants was detected in water and sediments together with (anti)estrogenic and (anti)androgenic activity confirming the presence of a complex chemical mixture of unknown toxicity in the tropical estuarine environment. Stable isotope and EDC analysis of *T. telescopium* tissue confirmed assimilation of sewage-derived nitrogen and bioaccumulation of EDCs, providing evidence for exposure to and interaction with these chemical contaminants. However, histopathological indicators of exposure to EDCs such as intersex and imposex were not observed. This paper presents the results of the study and discusses them in terms of levels of contaminants detected in each environmental compartment, and whether *T. telescopium* is a suitable bioindicator for future studies.



## Biodegradation of pharmaceuticals by the white rot fungus *Trametes versicolor* in hospital wastewaters; study of iopromide and ofloxacin as model compounds

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Pharmaceutically active compounds constitute a group of contaminants with one of the largest input into the environment. Hospital wastewaters are considered significant contributors of pharmaceutical residues in urban wastewaters. Even though in many countries hospital effluents are treated in urban Wastewater Treatment Plants, a pre-treatment of the effluent, before being discharged into public wastewaters is recommended. Due to the limited degradability of pharmaceuticals under conventional treatments applied in WWTPs, it is necessary to investigate on other possible treatment technologies. Ligninolytic fungi have proved to be an efficient group of microorganisms capable to remove a wide range of pharmaceuticals as well as other organic contaminants. In this context, the present work describes the degradation of the X-ray contrast agent iopromide (IOP) and the fluoroquinolone antibiotic ofloxacin (OFLOX) by the white-rot-fungus (WRF) *Trametes versicolor*. IOP and OFLOX were selected as model target compounds due to their ubiquity and high concentrations in hospital wastewaters as well as their low removal under conventional wastewater treatment processes. Degradation potential of WRF was first evaluated in Erlenmeyer flasks, in synthetic wastewater, and afterwards, it was studied in batch bioreactor fed with real hospital wastewaters under sterile conditions. In Erlenmeyer flasks, IOP and OFLOX, spiked at high concentration, were degraded between 60 and 70%. A significant number of transformation products were identified for IOP (seven) and for OFLOX (six) by means of on-line solid phase extraction-liquid chromatography-high resolution mass spectrometry (Qexactive Orbitrap™), confirming the degradation of both pharmaceuticals. The formation of iopromide transformation products was the result of gradual deiodination of the aromatic ring and N-dealkylation of the amide in the hydroxylated side chain of the molecule. Regarding ofloxacin, transformation products identified can be assigned mainly to the oxidation, hydroxylation and cleavage of the piperazinyl ring. Degradation of IOP and OFLOX in glass fluidized bed bioreactor, operated in batch, showed that almost 90% of IOP and nearly 98% of OFLOX were removed under sterile conditions. All seven IOP transformation products and three out of the six OFLOX transformation products identified in Erlenmeyer flask experiments were also detected in bioreactor samples. Acute toxicity tests (Microtox) indicated an important reduction in the toxicity of the final culture broth in both Erlenmeyer flasks and batch bioreactor, fact that strengthens the advantages and good performance of this degradation treatment.

## Biotransformation products of ibuprofen in soil - a new view on the relevance of non-extractable residues

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Ibuprofen is one of the most commonly consumed non-prescription drug. Although the removal efficiency of ibuprofen in wastewater treatment plants was reported to be high, this pharmaceutical is frequently detected in the biosolids. Application of biosolids in agriculture as fertiliser may introduce this pharmaceutical into soils. Up to date, it is still little known about the fate of ibuprofen in agricultural soils. Available few reports on turnover processes of this pharmaceutical in soil are limited to the general mass balances without any information about the chemical composition of non-extractable residues (NER).

NER formed during biodegradation of organic contaminants in soil are considered to be mainly composed of parent compounds or their primary metabolites with hazardous potential. However, in the case of easily biodegradable organic compounds, the soil NER may also contain microbial biomass components, for example fatty acids (FA) and amino acids (AA). After cell death, these biomolecules are subsequently incorporated into non-living soil organic matter (SOM) and are stabilised ultimately forming hardly extractable biogenic non-extractable residues (bioNER). We investigated the biodegradation of <sup>13</sup>C<sub>6</sub>-ibuprofen in sludge amended soil over 90 days with particular focus on the extent of biogenic residues formation. We analysed the labelled FA and AA in living and non-living SOM fractions.

<sup>13</sup>C-FA and <sup>13</sup>C-AA amounts in the living SOM fraction decreased in the time course, whereas the <sup>13</sup>C-FA and <sup>13</sup>C-AA in the non-living SOM remained surprisingly stable after 59 days. The results showed that, at the end, nearly all NER were of biogenic origin and contained only harmless biomass compounds. The presented data thus reveal that the formation of bioNER has to be taken into account in the case of readily biodegradable organic contaminants like ibuprofen for proper assessment of the potential environmental risks related to NER formation.

## Enantiomer distribution of chiral pesticides in traditional food from Arctic Greenland.

### Elucidation of selected up-take and distribution processes

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The determination of enantiomer distribution calculated as enantiomeric fractions (EF = E1/E1+E2) is considered a versatile scientific tool for the elucidation of selective biological distribution and uptake processes for chiral contaminants in environmental and biochemical research.

In the present study, we determined EFs for  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH), *trans*-, *cis*- and oxychlorane (TC, CC and OC, respectively) in Greenlandic traditional food items, such as fresh and smoked fish, whale, seal meat and narwhal mattak (skin and blubber). The EFs were non-racemic (EF $\neq$ 0.5) for all chiral pesticides except for  $\alpha$ -HCH in narwhal, TC in whale and smoked salmon and CC and OC in seal meat samples. The EF for  $\alpha$ -HCH was significantly below 0.5 for the fish samples, but above 0.5 for the marine mammal meat and blubber samples. This feature indicates clearly that different uptake and distribution mechanisms are resulting in the observed differences for mammal and fish samples. However considerable EF variation was found also within these groups. The narwhal samples were characterized by non-racemic EF values for all analysed chiral pesticides. These results indicate that a combination of species and individually characteristic enzymatic processes in combination with the stereochemistry of the respective chiral pesticide will result in specific transformation/ selective accumulation of the individual chiral chemical. Thus, the specific stereochemical structure of the chiral pesticides is a very important factor for biochemical transformation and selective internal enrichment processes.

In addition, all samples were analysed for polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE) and perfluorinated alkylated substances (PFAS) with standard quantitative analytical methods. The daily intake for the human consumers in Greenland was qualitatively assessed. As a general assumption, we concluded that the quantified levels of all analysed contaminants were below the tolerable daily intake (TDI) level.

## Fate and behaviour of erectile dysfunction drugs in wastewater treatment plants and receiving waters

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Phosphodiesterase type V (PDE-V) inhibitors are used for effective treatment of erectile dysfunction. Although only sildenafil (Viagra), tadalafil (Cialis), and vardenafil (Levitra) are approved, structurally closely related analogues of these PDE-V inhibitors have been detected in adulterated food supplements that are available through internet website markets. Recently, the presence of the three approved PDE-V inhibitors has been reported in wastewater streams at very low concentration (Nieto et al., *Wat Res.* 44:1607-1615), however, their biodegradability has not been yet evaluated. Moreover, no data about the presence of the analogues is reported in the scientific literature. Once in the environment, PDE-V inhibitors can undergo different processes such as photolysis which can be one of the dominant factors affecting the fate of these drugs. In this context, our research was focused on occurrence and transformation of PDE-V inhibitors in wastewater treatment plants (WWTPs) and surface waters. Therefore transformation products (TPs) were identified and new generic analytical methods for the screening of PDE-V inhibitors, analogues and their TPs in wastewater and river water were developed.

In order to simulate the biodegradation of PDE-V inhibitors under laboratory conditions, mixed liquor from a municipal WWTP was spiked with PDE-V inhibitors. The analysis of the samples of the batch reactor by UHPLC-Orbitrap MS system allowed to identify the two major TPs for sildenafil. The first peak at 3.01 min with  $[M+H]^+$  of  $m/z$  460 corresponded to N-demethyl SDF, previously reported as human metabolite of SDF; its identity was confirmed by an authentic standard. The second peak at 3.09 min with  $m/z$  491, was bearing one oxygen atom more, possibly arising from N-oxidation in the piperazine ring.

For the evaluation of the phototransformation of the PDE-V inhibitors, a Suntest sunlight simulator apparatus was used to irradiate different aqueous matrices. Accurate mass measurements and interpretation of characteristic fragmentation patterns on a UHPLC-Orbitrap instrument allowed to propose plausible chemical structures for 24 photoproducts. The mass spectral fragmentation confirmed stepwise destruction of the piperazine ring of all compounds which contain this ring.

A database containing the  $m/z$  and spectra of PDE-V inhibitors, analogues and TPs was built for performing suspect analysis in water samples collected from WWTPs and rivers. Detection of analytes was performed using Orbitrap Q-Exactive mass spectrometer. High resolution mass spectrometry (HRMS) was used for detection of targets and suspects, whereas HRMS with MS/MS fragmentation was used as a confirmatory step for proper identification of compounds. Sildenafil was detected in several wastewater samples.

## **Bio-Transformation Products of pharmaceuticals after biological wastewater treatment. A potential risk for the aquatic environment?**

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Since the first documentations about the occurrence of pharmaceutical residues in the aquatic environment a great number of research works have focused on that sector. Pharmaceuticals and their metabolites are mainly discharged with wastewater from household after human excretion. The large number of these compounds, observed in the municipal wastewater treatment plant effluents, proves the incomplete elimination during the state of the art of the biological treatment. As a result, these compounds have been detected in surface and ground waters from the ppb until the ppt level.

While pharmacokinetics of human medical compounds and their metabolites in the human body after application have been studied extensively, the degradation of such compounds by bacteria of the wastewater biocoenosis, their degradation pathways and the arising (bio)transformation products from biological wastewater treatment, have only hardly been investigated so far and therefore are predominantly unknown.

In this study, biodegradation tests were performed in laboratory scale to investigate the decomposition of three selected typical pharmaceuticals. Thus, closed-loop treatment experiments with immobilized biocoenosis for the degradation of Atenolol, Bisoprolol and Metoprolol were operated under wastewater treatment simulated circumstances. Some new transformation products were identified and determined via high performance liquid chromatography coupled with high resolution mass spectrometry (HPLC – (HR-MS<sub>n</sub>)). For the identification of the unknown bio-transformation products the use of the LTQ-Orbitrap enabled the designation of their exact molecular mass, so that a first proposal for the chemical structure was quite reliable. The confirmation of the structure formula was succeeded by a second spectroscopic method, the nuclear magnetic resonance (NMR). The substance amounts for these examinations were gained after applying a scale up preparative high performance liquid chromatography (prep. HPLC). Bio-tests were performed in order to gain knowledge about their ecotoxicological potential in the aquatic systems.

Some of the biological transformation products are identical to human metabolites, others, however, not before identified have a different yet unknown structure. Insights about the formation of stable transformation products obtained from drugs and their metabolites in the waste water treatment plants can help us detect these compounds in trace and ultra trace concentrations in water systems. In addition, from these results and additional computer simulations and we can get further important knowledge about the potential environmental risks of unknown compounds and also evidence for the strategies of advanced treatment methods.

## Sorption-desorption Behavior of Pesticides and their Degradation Products in Chilean Volcanic and Non-volcanic Ash-derived Soils

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Volcanic ash-derived soils are abundant and widespread in Central-Southern Chile accounting for 70% of the arable land. Soils from Andisol and Ultisol orders have a great importance in the agricultural economy and their main common characteristics are the variable surface charge and acidic pH (4.5-5.5). Andisols are rich in organic matter (OM) and allophane and present high specific surface area. Ultisols have lower OM than Andisols and contain Kaolinite type minerals and more crystalline iron oxides.

The aim of this research was to assess sorption-desorption behavior of Glyphosate (GPS), Atrazine (AT) and Metsulfuron-methyl (MSM) between herbicides, Chlorpyrifos (CPF) and Diazinon (DZN) between insecticides and Chlorothalonil (CHT) between fungicides which are the most consumed organic compounds in Chilean agriculture. Given the transport potential of the more polar transformation products from soils to surface and groundwater we also included amino-methyl phosphonic acid (AMPA) desethylatrazine (DEA) 3, 5, 6-trichloro-2-pyridinol (TCP), and 2-isopropyl-6-methyl-4-pyrimidol (IMHP). We selected three volcanic ash-derived soils, one Andisol and two Ultisols, sampled at two depths: 0-20 and 40-60 cm and four non-volcanic ash-derived soils sampled at 0-20 cm depth. Organic carbon content and pH ranged between 1.2 to 11.2 % and 4.7 to 7.7, respectively. All sorption and desorption isotherms were established through a batch system at  $30 \pm 1^\circ\text{C}$ . The concentration of compounds in solutions at equilibrium was determined by HPLC-DAD or HPLC-Fluorescence detection. Results were statistically analyzed using Origin Pro 8 and fitted to the Freundlich model.

A very high sorption capacity of GPS, AMPA and CPF was observed for the Andisol (both depths) with  $K_f$  values higher than  $600 \mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$ . The other parental compounds presented lower  $K_f$  values ranging from 1.6-93, belonging to MSM and DZN at the deeper and surface horizons respectively. The degradation products IMHP and DEA were scarcely adsorbed on this soil presenting a higher possibility of leaching in spite of its high organic matter content. AT, DEA, and MSM were weakly adsorbed on Ultisols (both depth) ( $K_f = 1.4-5.2, 1.0-3.0, 1.0-3.8 \mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$ , respectively) and sorbed amounts were easily desorbed ( $H$  coefficient  $\leq 1$ ). The non-volcanic ash-derived soils presented a very low sorption capacity, as expected, for the acidic compounds TCP and IMPH, with a null sorption for MSM. The permanent negative surface charge of this class of soils and the low  $\text{p}K_a$  value of these compounds allows electrostatic repulsion forces hindering the sorption process. From the global analysis a significant relationship between sorption capacity and organic matter content was established only for AT, DEA, DZN, IMHP, CPF and TCP ( $R^2 = 0.812-0.979$  for IMPH and CPF, respectively). The contribution of humic materials and phyllosilicates of soils in the sorption process of GPS, AMPA and CPF has been established in the literature. The variable  $K_{oc}$  values of CHT allow concluding that sorption is related also to mineral components. From this research we concluded that variable charge materials of volcanic ash-derived soils allow the retention of acidic compounds such as TCP and IMPH and that humic materials enhance sorption of AT and DEA, all compounds considered as highly mobile in most soils.

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## Evolution of toxicity in an effluent containing hormone, Estradiol, during mineralization processes by heterogeneous photocatalysis and photo-Fenton

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There is a growing interest in micropollutants present in the environment that can interfere with endocrine system affecting health, growth and reproduction of humans and animals. These substances are of great concern because they can produce deleterious effects in exposed organism also at extremely low concentrations close to ng/L. Natural and synthetic estrogens have been receiving special attention from the scientific community. Many studies show that these chemicals are the main cause for the observed estrogenic activities in effluents. Due to their incomplete removal in wastewater treatment plant, advanced oxidation processes offers an alternative for their removal and the reduction of their estrogenic activity toward aquatic organisms. In the present work we aimed at investigating photocatalytic degradation of 17- $\beta$ -estradiol, natural estrogens. Two processes were evaluated in term of performance, estrogenic activity reduction and identification of by products using high resolution mass spectrometry. Homogeneous photo-Fenton using monopersulfate as oxidant and heterogeneous photocatalysis using TiO<sub>2</sub> were activated using simulated solar light in a loop reactor. The reactor was a cylindrical borosilicate glass tube operated in a recirculation batch mode. With a total volume of 1L and equipped with radiation source (centred around 365 nm) corresponding to 35 W m<sup>-2</sup>. All the surface of the reactor was uniformly irradiated thanks to compound parabolic collector (CPC) positioned at the back side. Homogeneous photo-Fenton using persulfate as oxidant and heterogeneous photocatalysis using TiO<sub>2</sub> were high effective for E2 removal. Both processes were very fast because after 5 min, 95% of E2 was removed, but photo - Fenton processes was more efficiently than TiO<sub>2</sub> because the processes started immediately under dark condition. By-products identified during the oxidation of E2 correspond to those described in the literature. The first step is the formation of estrone followed by a polyhydroxylation and ring opening. Decrease of estrogenic activity test implies that the estrogenic activity inducing site have been destroyed. Hence advanced oxidation processes represent a powerful mean for the purification of aquatic bodies.

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## The fate of trace elements during the combustion of phytoremediation wood

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Because more than 3 millions sites within the EU are suspected of being contaminated by trace elements (TE), the management of TE-polluted soils is of major concern for most industrialized countries. There are potential economic opportunities for biomass production associated with phytoremediation, including bioenergy and traditional industrial products, such as paper, solid wood products and reconstituted products (i.e., paper, chipboard, laminated beams, extruded trim). However, when using contaminant enriched biomass crops for energy purposes, the impact of metals on conversion efficiency, as well as the energy needed to properly use or dispose the rest product after conversion need to be assessed. We investigated the fate of trace elements (TE) in poplar wood on the conversion of biomass to heat in a 0.2 MW combustion unit equipped with a fabric filter. The phytoremediation wood was harvested from a TE-contaminated agricultural site planted with a high-density poplar stand. The combustion technology used in the present experiment allows for an efficient separation of the various ash fractions. The combustion process concentrates Cu, Cr and Ni in the bottom ash, heat exchanger ash and cyclone ash fractions. Therefore, the impact of the fabric filter is negligible for these elements. Conversely, Cd, Pb and Zn are significantly recovered in the emission fraction in the absence of the fabric filter above the emission limits. The use of a fabric filter will allow the concentration of these three TEs in the ashes collected below the filter, thus complying with all regulatory thresholds, i.e., those from the large combustion plant EU directive. Because the TE concentrations in the different fractions differed significantly, it is recommended that these fractions be treated separately, especially when recycling of ashes from phytoremediation wood through application in agriculture is envisaged.



## Antiradical activity of sulforaphane, a phytochemical considered as a protector against ultraviolet radiation.

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Increasing level of UV radiation, one of the most prevalent carcinogen in our environment, is of great concern and this increase is caused mainly by the depletion of the stratospheric ozone and climate change [8]. It has been discovered, that some of phytochemicals, namely alkaloids (caffeine, sanguinarine), flavonoids (genistein, silibinin), carotenoids ( $\beta$ -carotene, lycopene) and isothiocyanates (sulforaphane) can protect against UV radiation-inflicted damage [2]. Their protective activity is partially due to ability to act as antioxidants [2].

Sulforaphane (1-isothiocyanato-4-methylsulfinylbutane, SFN, Figure 1) is a product of glucoraphanin hydrolysis, a compound naturally found in cruciferous vegetables, such as broccoli, kale and Brussels sprouts. SFN exhibits indirect antioxidant activity, and consequently, is considered as a protector against UV radiation [2-4].

On the other hand, there are some papers suggesting, that SFN scavenges free radicals, thus, it is able to act as direct antioxidant [5,6]. However, its antiradical mechanism has not been clearly recognized yet. The aim of this study was to answer which moiety is responsible for SFN direct antioxidant activity. In our work we studied SFN and its analogues (2-oxohexyl isothiocyanate, n-hexyl isothiocyanate and dibutyl sulfoxide) with model DPPH radical in different solvents (methanol, dioxane, acetonitrile). The progress of the reaction was measured by stopped-flow measurements at 517nm. Values of the bimolecular rate constants ( $k^s$ ) for the reaction with DPPH radical were calculated by the method described previously [7]. Obtained results will be discussed in this presentation.

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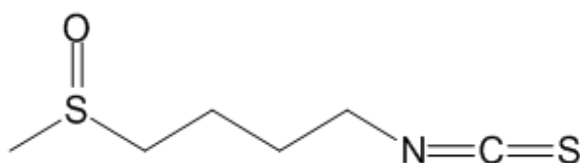


Figure 1. The structure of sulforaphane.

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## Simulation of the redox metabolism of antidepressant active compounds (emerging pollutants) by electrochemistry/mass spectrometry.

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Antidepressant pharmaceutical compounds have been raising environmental concerns, during the last years, due to their increasing and constant presence in wastewater and other environmental samples. They are considered to be emerging pollutants with various effects on the ecosystems.

In this work, the oxidative and reductive degradation pathways of selected antidepressants (fluoxetine, haloperidol) were studied. An apparatus was used to generate the oxidation/reduction by-products at various potentials. The electrochemical conversions were carried out using different types of electrode materials (magic diamond TM, glassy carbon, SS-reductive titanium), at various pH (4-10) and under different matrices (buffer solution, simulated wastewater, simulated groundwater). The by-products were determined directly, using electrospray ion-trap or ESI-TOF/MS instrumentation.

More than 7 different by-products were determined for each compound and they were linked to various potentials applied and the current density on the electrode. Possible degradation pathways are suggested based on the sequence of the by-product formation. The transformation sequence was pH and matrix-relevant. Higher TOC values inhibited the transformation, while reduction pathways showed little dependence on pH values rather than on electrode types. Magic diamond electrode demonstrated the widest range of capabilities and the lowest energy requirements. The capability of the system to recreate redox conditions that could take place under real environmental conditions is exhibited in this study showing the possible transformation pathways of these compounds.

## Assessment of the photoreactivity of surface freshwater in extreme ecosystems: lakes in Terra Nova Bay, Antarctica, as a case study.

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Antarctica is an extreme climatic region and its terrestrial ecosystems are among the most uncontaminated on Earth. Antarctic lake waters have been less extensively studied than other matrices, such as seawater or snow. Most available data on Antarctic lake waters derive from the McMurdo Dry Valleys area in southern Victoria Land<sup>9,10,11</sup>. In this work the photoproduction of excited triplet states of chromophoric dissolved organic matter (CDOM) and singlet oxygen were assessed upon irradiation of water samples, taken from shallow lakes and ponds located in the Terra Nova Bay area, Northern Victoria Land (Antarctica). Absorption spectral features, fluorescence emission and the chemical composition of samples were investigated, too. The fluorescence spectra suggested the absence of organic material such as humic and fulvic substances, usually correlated with highly photoactive waters. On the other hand, CDOM optical features and Total Organic Carbon (TOC) concentrations measured in the studied samples revealed the presence of relatively small organic compounds, probably due to marked photobleaching of CDOM as a consequence of intense UV irradiation<sup>12</sup>. All the samples showed an unexpectedly high photoreactivity, especially for the photoproduction of triplet states of chromophoric dissolved organic matter, despite the negligible presence of humic/fulvic acids that we have previously observed as the main photoreactive species in Alpine lakes<sup>13</sup>.

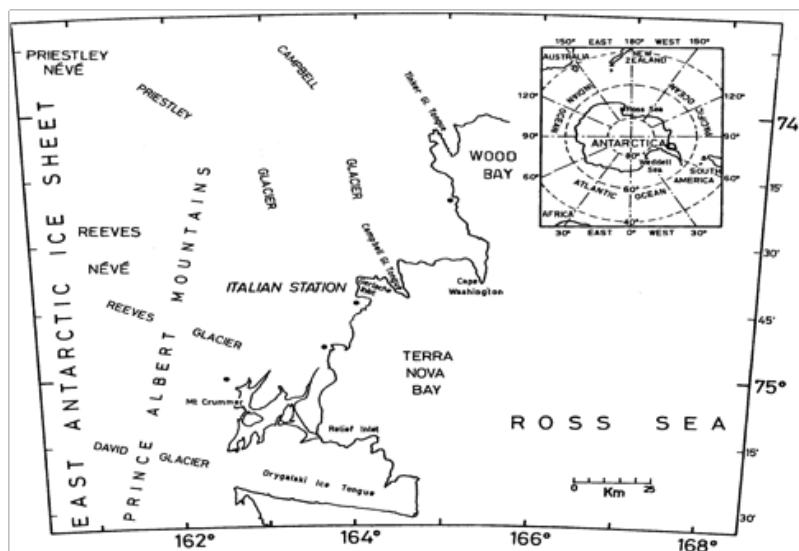


Fig. 1. Map showing the location of sampling sites.

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## Atrazine removal in municipal secondary effluents by Fenton and Photo-Fenton treatments

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Over the last decades, increasing attention has been focused on several types of compounds identified as contaminant of emerging concern (CECs). Concern related to “emerging contaminants” is due to their features of bioaccumulability and persistence as well as their potential effects on health. Due their resistance to conventional wastewater treatments, specific processes are required in order to make possible the use of reclaimed wastewater for several purposes especially in agriculture. CECs include a wide array of different compounds as pharmaceuticals, household chemicals, personal care products (PPCPs), insecticides, pesticides and herbicides, some of which are suspected endocrine disruptors. One of them is atrazine, an herbicide largely used in past that was banned from the European Union in 2004. Nevertheless, due its considerable use in the past, moderate solubility and good stability, atrazine has often been detected in atmosphere, surface water, groundwater and soil, leading to environmental problems.

In this study, advanced oxidation processes based on Fenton’s reaction were applied to remove atrazine from secondary effluents of a municipal wastewater treatment plant based on activated sludge in order to demonstrate their ability to attain the levels of reuse parameters required by legislation. The treatments tested were: Fenton, UV-A photo-Fenton and UV-C photo-Fenton.

Initial characterization of secondary effluent spiked with 0.1 mg L<sup>-1</sup> of atrazine showed an initial Total Organic Carbon between 11 and 18 mg L<sup>-1</sup>. Atrazine removal obtained was around 20% for Fenton treatment, 60% and 70% for UV-A and UV-C Photo-Fenton treatments, respectively. Organic matter mineralization by Fenton treatment was monitored and no significant reduction was observed. However, organic matter oxidation (in terms of COD reduction) around 30% and 40% were achieved by Fenton and Photo-Fenton processes, respectively. From the results it can be stated that Photo-Fenton process with UV-C is a useful technique for the atrazine degradation. The use of UV-C light allows to achieve higher yields of degradation than UV-A. Nevertheless, higher costs related to the use of UV-C light must be considered in order to perform an adequate cost-benefit analysis.

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## Assessing sources and sinks of hexachlorocyclohexane (HCH) isomers at contaminated field sites using stable carbon isotope analysis

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Hexachlorocyclohexane (HCH) isomers are pollutants of particular concern because of their widespread distribution in the environment, toxicity and persistence. Especially in former production sites, significant soil and groundwater pollutions have been detected. For cost-efficient and highly productive remediation strategies of these HCH-contaminated sites, it is necessary to investigate sources and sinks of HCHs. In recent years, compound-specific stable isotope analysis (CSIA) has gained more and more attention as a tool for characterizing and assessing contaminant sources and *in situ* biodegradation of organic pollutants. Analytical methods were established and verified for determining carbon isotope ratios of HCHs isomers using gas chromatography – stable isotope ratio mass spectrometry (GC-IRMS). In laboratory experiments, the carbon isotope fractionation associated with biodegradation of HCHs under oxic and anoxic conditions was investigated. Substantial microbial isotope fractionation was observed for the HCH-isomers allowing the analysis of HCH biodegradation in field studies. The potential of CSIA was tested at a contaminated aquifer and significant changes in carbon isotope ratios of HCH-isomers were observed comparing contaminant sources and the fringe of the plume indicating *in situ* HCH-biodegradation. Besides CSIA for HCH-isomers, a concept for enantiomer-selective stable isotope analysis (ESIA) for  $\alpha$ -HCH was developed in order to analyse sources and sinks of  $\alpha$ -HCH in the environment. ESIA fingerprints of  $\alpha$ -HCH allow combining enantiomer patterns and carbon isotope analysis which might give additional information to trace sources, transport and sinks of  $\alpha$ -HCH.

## **Fate of waterborne organic microcontaminants in the soil-plant system: Effect of biochar and nanoparticles**

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Worldwide freshwater resources are contaminated at a different extent with a myriad of organic microcontaminants (e.g. pharmaceuticals and personal care products (PPCPs)) coming from anthropogenic activities. The presence of these pollutants in water cycle may be hazardous to wildlife and human health. According to this, their determination in different environmental compartments and food products becomes necessary to evaluate their exposure for risk assessment studies.

The aim of the present study is to evaluate the uptake of selected PPCPs by vegetables from irrigation water in a greenhouse experiment. In addition, the effect of biochar and nanoparticles (e.g. silver nanoparticles and fullerenes) in soil on the microcontaminant bioavailability and soil mobility is evaluated in a 90 mesocosms study. Accordingly, leachates, soil and plants will be analyzed. In this regard, a new analytical method is developed and optimized for the evaluation of plant uptake based on in vivo solid-phase microextraction by using two types of fibers the C18 and SCX mixed mode. For the identification and quantification of contaminants, ultraperformance liquid chromatography (UPLC) or gas chromatography (GC) depending on the polarity of these analytes coupled to tandem mass spectrometry (MS/MS) will be used. Finally, statistical analysis of the obtained database will be performed and the behavior of microcontaminants correlated with their physico-chemical properties.

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## Thermal and Transition Metal Activation of Peroxides for the Destruction of Emerging Cyanobacterial Toxin Cylindrospermopsin in Water Environment

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Commonly found peroxides, hydrogen peroxide (HP), persulfate (PS) and peroxymonosulfate (PMS), could be activated by heat and transition metals to produce active radical species, such as hydroxyl and sulfate radicals, for the destruction of organic pollutants in the environment. In this study, when radical quenching agents, such as alcohol, natural organic matter (NOM) or alkalinity were added, a significant inhibition was observed to degrade nitrobenzene, para-nitrobenzoic acid, para-chlorobenzoic acid, and benzoic acid by PS and PMS, confirming the roles of radical compounds. As a result, when these peroxides were used for the degradation of cylindrospermopsin (CYN), a highly toxic cyanobacterial toxin which reacts very fast with both radical species, satisfactory removal efficiency was achieved. There was no significant removal of CYN by hydrogen peroxide. The presence of transition metals in natural water samples probably contributed to a significant improvement in destructing CYN. This provides a feasible field remediation to remove CYN as well as other organic contaminants from water resources.

## **Biotransformation of benzotriazoles: Insights from transformation product identification and compound-specific isotope analysis**

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The assessment of biological transformation processes of organic micropollutants is important to understand their fate in the environment. Transformation products of micropollutants that are formed by biodegradation, for example during wastewater treatment, can enter surface waters and hence contribute to the pollution of water resources.

Benzotriazoles are corrosion inhibitors used in many industrial and domestic applications and thus omnipresent organic micropollutants in the aquatic environment. In this study, biological transformation mechanisms of benzotriazoles were elucidated by identification of transformation products using liquid chromatography–high-resolution tandem mass spectrometry (LC-HR-MS/MS) and compound-specific isotope analysis (CSIA).

Aerobic degradation experiments with activated sludge led to biodegradation half-lives of 1.0 days for 1H-benzotriazole, 8.5 days for 4-methyl-1H-benzotriazole, and 0.9 days for 5-methyl-1H-benzotriazole. The co-metabolic transformation reactions included hydroxylation, methylation, and oxidation of methyl-groups. Major transformation products were identified as 4- and 5-hydroxy-1H-benzotriazole for the degradation of 1H-benzotriazole and 1H-benzotriazole-5-carboxylic acid for the degradation of 5-methyl-1H-benzotriazole. These compounds were also found in several wastewater effluent and surface water samples, showing their environmental relevance. The formation of many other candidate transformation products, which were tentatively identified by interpretation of MS/MS spectra indicate that several unspecific co-metabolic processes also occur. The biotransformation of 1H-benzotriazole exhibited significant carbon and nitrogen isotope fractionation, which suggests aromatic monohydroxylation as predominant isotope-sensitive step pertinent to the biotransformation of 1H-benzotriazole.



## Phototransformation of acidic pharmaceuticals in riverwater

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Large amounts of human pharmaceuticals are consumed each day and then enter the waste water system through urine and faeces. In waste water treatment plants (WWTPs) the compounds are partially removed or changed and then released into the recipient water body, where they are now commonly detected micropollutants. The occurrence of a wide variety of pharmaceuticals in locations around the world is well documented and the focus of research has now shifted toward the fate of these compounds once they have entered the recipient water bodies. One major route for transformation of chemicals in the aquatic environment is due to photochemical reactions. The energy of the UV light from the sun can be absorbed by some compounds that subsequently may undergo intramolecular reactions that give rise to new chemical entities. These might be of higher environmental concern than the original compounds. The aim of this study was to monitor the behavior of a complex mixture of pharmaceuticals in river water when irradiated with artificial sunlight in a laboratory photoreactor.

For the irradiation experiment 1.6 l of river water from the River Rakkolanjoki near Lappeenranta, Finland were spiked with 50 µg/l of the acidic pharmaceuticals diclofenac, ketoprofen, naproxen, ibuprofen, bezafibrate, warfarin, methylprednisolone and the illicit drug metabolite 9-carboxy-tetrahydrocannabinol. The water was then irradiated under deaerated conditions in a photoreactor for 60 minutes. Samples (50ml) were taken after 0, 1, 2, 5 and 60 min extracted by solidphase extraction and analyzed using a LC-MS/MS method.

After 60 minutes diclofenac and ketoprofen could not be detected in the water samples, while warfarin appeared to be very stable under the given conditions. All other compounds degraded to some extent, but were still present in the sample taken after 60 minutes. Ibuprofen, which is known to degrade very rapidly biologically showed a somewhat lower degree of phototransformation than bezafibrate and naproxen.

## Debromination of Polybrominated Diphenyl Ethers (PBDEs) by hepatic microsome of marine and freshwater fishes.

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**Introduction** BDE209 is dominant congener in DecaBDE product which is one of commercial products of PBDEs. BDE209 can be source of lower brominated congeners which has been banned due to their toxicity and bioaccumulability. Some studies demonstrated metabolic debromination of PBDEs using hepatic microsome<sup>1-5</sup>. In the present study, we conducted *in vitro* experiment using hepatic microsome to compare debromination of BDE209 of freshwater fish and marine fish. We also focused on relationships between debromination activity and level of PBDE contamination of fish.

**Materials and methods** Four species of freshwater fish and one species of marine fish were sacrificed for the experiments. Fresh water fish included common carp (*Cyprinus carpio*), rainbow trout (*Oncorhynchus mykiss*), Seema (*O. masou masou*) and Japanese trout (*Plecoglossus altivelis*, JT). Marine fish was Japanese sea bass (*Lateolabrax japonicas*, JSB). Two types of common carp, i.e., wild one (WCC) lived in sewage effluent in urban area and cultured one (CCC) bought from rural area of Japan were used in the study. The other freshwater fish were also cultured in clean water. JSB was caught in inner part of Tokyo Bay. Microsome fractions extracted from fresh livers of the fishes were used for metabolism incubation. The 24-hours incubation was conducted in triplicate. Muscle tissues of the fishes were used for chemical analysis for PBDE concentrations.

**Results and discussion** Debrominated congeners were generated by incubation of BDE209 with microsome of both of common carps, JT and JSB. Among these fish, decrease of BDE209 was also observed in WCC and JSB. In debromination of BDE209 by microsome of 5 species of fish, WCC was debrominated the most. PBDE concentrations in muscle tissues of WCC and JSB were higher than those of four cultured fish. Debromination activity (amount of debrominated congeners) in the incubation with microsome of WCC was the highest, whereas the amount of debrominated congeners of JSB was trace. Though debromination of BDE209 by CCC and JT was much more than that of JSB, PBDE concentrations in muscle tissues of CCC and JT were also low. The results indicated no consistent relationship between debromination activity and PBDE concentrations in the tissue. PBDE concentrations in muscle tissues of WCC were higher than that of CCC. Debromination activity by WCC was also much higher for the WCC than those of CCC. Because the WCC lived in sewage effluent, they would be exposed to higher concentrations of chemicals including PBDEs than CCC. In the case of other enzymic system high biomarker levels was observed because the enzyme would be induced by chemical exposure.<sup>6</sup> It is suggested that activity of some enzymes regarding debromination is affected by the conditions in habitats. In conclusion, debromination activity of BDE209 varied depending mainly on species of fish. Contamination level of PBDEs in the fish tissue could be secondary factor to control the enzymatic activity.

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## ***In-vitro* hydrolysis of asymmetric phthalates**

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Many phthalic acid diesters widely used as plasticizers and in particular those with a carbon chain length of C4-C6 (“critical chain length”) are known for causing toxic effects to organisms [1]. Owing to their reprotoxic properties and their ubiquitous presence in the environment, particularly symmetric phthalates such as dibutyl- and di-(2-ethylhexyl)phthalate are classified as reprotoxic 1B in accordance with Regulation EC No. 1272/2008 (CLP Regulation). Previous toxicological studies identified the respective phthalic acid monoesters as main metabolites responsible for the reprotoxic effects [2]. In case of asymmetric phthalic acid diesters, two different monoesters may be formed. For asymmetric phthalic acid diesters with a “critical” and an “uncritical” chain length concerning reprotoxicity, metabolism can lead to a monoester with either a “critical” chain length of C4-C6 or an “uncritical” monoester. Thus, for an adequate assessment of possible health risks of asymmetric phthalic acid esters it is essential to know, which of the monoesters are preferably formed by human metabolism.

For this reason we studied the chemical and *in-vitro* hydrolysis of 11 asymmetric phthalic acid diesters in comparison to their symmetric counterparts. Under acidic conditions and 5 day-treatment, chemical hydrolysis of all asymmetric phthalates formed preferably the mono ester with the shorter alkyl moiety. Asymmetric diesters containing a benzyl group always hydrolysed to benzyl alcohol and the respective alkyl monoesters.

In *in-vitro* experiments with rat liver S9 homogenate, the hydrolysis was much faster but less selective than the acidic chemical hydrolysis. Hence, mixtures of both possible monoesters were produced.

Using human liver S9 homogenate, the formation of phthalic acid monoesters from asymmetric diesters is even less selective than with rat liver S9 homogenate and, as a consequence, organisms are exposed to mixtures of different phthalic acid monoesters.

Based on these results, the risk assessment of asymmetric phthalic acid diesters seems to be more complex than that of symmetric phthalates because two different monoesters will be formed, which both require separate toxicological consideration dependent on the composition of the respective monoesters.

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## Efficient biodegradation of flumequine using ligninolytic fungi

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Flumequine is used as broad-spectrum antimicrobial agent commonly used in veterinary medicine. Flumequine and its metabolites are excreted after application via feces and urine and enter environment. In floodplain sediments flumequine was detected up till concentrations of 32 µg/kg [1]. Traces of antibiotics in the environment can induce resistance in pathogenic bacteria causing potential risks to human health [2,3].

In order to reduce flumequine in the environment several white rot fungal strains were examined for their potential to biodegrade this antimicrobial agent. The metabolites formed were elucidated and the antibacterial activity of the degradation mixture characterized.

Flumequine was degraded in a liquid malt extract medium within 14 days by three strains of ligninolytic fungi [4]. Residual antibacterial activity of the degradation mixtures were determined using Kirby-Bauer disk diffusion susceptibility test [5].

Within 6 days treatment, flumequine was very efficiently (98-100%) removed from the nutrient solution by *Irpex lacteus*, *Trametes versicolor* and *Dichomitus squalens*. 9 metabolites were recorded and identified by LC-MS. Tentative structures were provided by LC-TOF-MS and MS-MS experiments.

Particularly in case of *D. squalens*, the removal of flumequine was successful but the degradation mixture indicated remarkable residual antibacterial activity probably caused by the transformation products of flumequine.

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## Determination of clindamycin and its metabolite clindamycin sulfoxide in diverse sewage samples

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The use of pharmaceuticals and therefore their input into the aquatic environment after passing the sewer system and sewage treatment plants (STPs) is of increasing concern. Clinical and urban waste water as point sources of high amounts of pharmaceuticals play an important role in the assessment of environmental exposure and risk. The present study focuses on the antibiotic clindamycin, which is a widely prescribed drug and associated with an increasing risk of antibiotic resistance for humans and wildlife.

In the first part of this study clindamycin and twelve further antibiotics were determined in different sewage samples: clinical waste water, urban waste water as well as influent and effluent of the STP. In contrast to the other drugs an increase of the clindamycin concentration in the final effluent in comparison to the influent of the STP was observed. The reason of this effect has to be discussed. Errors in measurements and matrix effects could be excluded using two different HPLC systems (reversed phase and HILIC) and two different transitions in the tandem MS. Additionally, all samples were measured twice with and without standard addition.

Only a small part of administered clindamycin is excreted unchanged. The main part of the drug is excreted as the bioactive metabolite clindamycin sulfoxide into the waste water. To examine that a retransformation of clindamycin sulfoxide to clindamycin within the STP might explain the measured effect the following analysis was conducted: Clindamycin sulfoxide concentrations in the different sewage samples were measured additionally by the LC-MS/MS method. A separation with reversed phase chromatography and two different transitions in the tandem MS in each case ensure the specificity of the analytical method. Using 2.5 ml sample, solid phase extraction (SPE) and the LC-MS/MS-method the low limits of quantification of clindamycin and clindamycin sulfoxide were 20 ng/L. The concentration of clindamycin sulfoxide measured in the waste water samples was up to ten times higher than the concentration of the administered drug there. The metabolite concentration in the final effluent was similar to the concentration in the influent of the STP. The transformation of clindamycin sulfoxide back to clindamycin could neither be proved nor excluded up to now, therefore, long-term measurements were started.

The determination of clindamycin sulfoxide in sewage or surface water is important for the assessment of antibiotic input into the aquatic environment and the risk management of antibiotic resistance. The described method is the first to determine thirteen antibiotics and the bioactive metabolite of clindamycin in sewage samples.

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## Investigating the presence of phototransformation products of pharmaceuticals and their human metabolites in Lake Geneva

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In recent years, increasing evidence has pointed toward the importance of investigating the presence of both human metabolites of pharmaceuticals and photo-transformation products of pharmaceuticals in surface waters. Human metabolites of pharmaceuticals may potentially be as toxic and/or persistent as their parent compound and hence are of rising concern. On the other hand, assessing the presence of transformation products can help understand the fate of parent compounds in environments influenced by multiple mixing and degradation processes. In this study we assess the presence of selected pharmaceuticals, their photo-transformation products and human metabolites in Vidy Bay (Lake Geneva).

Firstly, the presence of 5 pharmaceuticals and 8 of their corresponding human metabolites were assessed in lake water samples taken at various depths and locations in the vicinity of a wastewater treatment plant (WWTP) discharge location in the Vidy Bay over a 10-month period. Among the targeted metabolites, six were detected with concentrations ranging from 5 to > 100 ng·L<sup>-1</sup>. The detected metabolites include trans-10,11-dihydro-10,11-dihydroxy carbamazepine, carbamazepine 10,11-epoxide, N-desmethyl clarithromycin, 4'-hydroxy diclofenac, sulfmethoxazole β-D glucuronide and N-acetyl sulfamethoxazole. The highest concentrations were detected above the WWTP outfall, supporting the assumption that wastewater represents the main source of human metabolites to the lake. Comparison of the metabolite to parent compound ratio at various locations in the Bay, indicate that the metabolites investigated here were less recalcitrant to environmental degradation than their parent. Nevertheless, their presence in the aquatic environment may lead to an increase of the ecotoxicological risk.

In parallel we investigated for the presence of photoproducts of 5 pharmaceuticals that had been regularly detected in the lake and were known to degrade rapidly by direct and/or indirect photodegradation processes: N-desmethyl azitromycin, N-(4-chlorobenzoyl)-tyramide, 6-hydroxy-6-defluoro ciprofloxacin, 3-ethylbenzophenone and 3-amino-5-methylisoxazole. Laboratory tests under a solar simulator confirmed their relative stability under prolonged irradiation, supporting the possibility of their presence in the lake. A preliminary sampling campaign in 2012 showed that three among the five targeted photoproducts were detected, but only in surface samples (0-1 m). The concentrations were always below that of the corresponding parent compound and the highest frequencies of detection were again observed above the WWTP outfall. The change in the photoproduct: parent ratio was furthermore examined as a function of distance from the WWTP outfall, in order to assess the contribution of photodegradation to pharmaceutical degradation in Lake Geneva.

## Identification and Characterization of New Disinfection By-products of Polycyclic Musks (AHTN and HHCB) in Swimming pool water

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The polycyclic musks 6-Acetyl-1,1,2,4,4,7-hexamethyltetraline (AHTN) and 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- $\gamma$ -2-benzopyran (HHCB) are widely used fragrances in cosmetics, products of daily care and cleaning products for households and industry. They are in the focus of interest due to their estrogenic potential. Both compounds can be found at low  $\mu\text{g/L}$  concentrations in surface water where they are introduced mainly by sewage treatment plants supplied by municipal wastewater. In order to disinfect wastewater in sewage treatment plants or water in swimming pools, chlorine can be added to water as gas or hypochlorite solution. This disinfectant has a high oxidation potential resulting in the formation of disinfection by-products, the estrogenicity and toxicity of which might differ from their precursor. In this work the behaviour of AHTN and HHCB upon treatment with sodium hypochlorite solution was investigated and chlorinated possible disinfection by-products could be identified as well as a carboxylic acids and lactones derived from AHTN and HHCB. The identified species were characterized by GC-MS, LC-MS<sup>n</sup> and <sup>1</sup>H-NMR. The elucidated structures of potential disinfection by-products are verified by X-ray crystallography.<sup>[1-4]</sup> Finally the estrogenicity between the parent analytes and generated transformation products were compared.<sup>[5]</sup> For that task, MCF-7 assay has been chosen for being most relevant to humans.

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## Occurrence, fate, and transformation of the antiepileptic Lamotrigine

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Studies have revealed that pharmaceuticals are present in influents and effluents from wastewater treatment plants (WWTP), and in lesser extent in the receiving waters. Examining the overall presence of pharmaceuticals in receiving waters, the patient use of prescription and over-the-counter drugs is the principal source of contamination. However, no more than 8 % of the marketed pharmaceuticals have been monitored in the environment among which is lamotrigine also known as Lamictal® (6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine). It was launched in 1991 and nowadays it is a widely prescribed drug for the effective treatment of epilepsy and bipolar disorder. This pharmaceutical is extensively metabolized in humans to produce predominantly the N<sup>2</sup>-glucuronide and to a minor degree the N<sup>2</sup>-methyl-lamotrigine [Hussein, Z. et al. *Br. J. Clin. Pharmacol.* 43 (1997)]. Currently there are no data describing the whereabouts of lamotrigine in WWTP or receiving waters. Only one U.S. study reported on the environmental occurrence of lamotrigine and its N<sup>2</sup>-glucuronide with mean concentrations in wastewater of 488 and 209 ng/L, respectively [Ferrer I., Thurman E. M. *Anal. Chem.* 82 (2010)]. Less frequent detection in surface waters went along with occasional positive findings in groundwater samples.

In order to investigate the biotic and abiotic transformations of lamotrigine, we designed two experiments: one for assessing its potential biodegradation by the bacterial community in mixed liquor from a municipal WWTP, and the other for evaluating its solar photolysis using a Suntest simulator. While the UPLC analysis of the samples from the aerated batch-reactors showed the formation of a single metabolite, the photolysis produced three transformation products (TP). High resolution mass spectrometry ((+)ESI-LTQ-Orbitrap) allowed to propose the structures of the four detected TPs with monoisotopic masses of 219.0312, 237.0417 and 273.0184 Da for photolysis and of 269.0235 for biodegradation. Their formation was the result of the following reactions: (a) dehydrochlorination, (b) replacement of one chlorine atom by a hydroxyl group and (c) hydration for photolysis, and (d) N<sup>2</sup>-methylation on the triazine ring for biodegradation.

In a retrospective data analysis of full scan chromatograms from Orbitrap mass spectrometry, samples from the river Rhine (Basel, Switzerland) and effluent samples from Swiss WWTP discharging into this river, revealed the presence of lamotrigine along with its human metabolites including the N<sup>2</sup>-methylated TP.

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## Oxidation of several pharmaceuticals with aqueous permanganate: reactivity, kinetics and transformation products.

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### Abstract

Pharmaceuticals have become one of the most important classes of environmental pollutants. Over sixty drugs have been found in the aquatic environment, from a variety of therapeutic groups, including but not limited to, non-steroidal anti-inflammatory drugs (NSAIDs),  $\beta$ -blockers and  $\beta$ -agonists. These compounds and their metabolites enter the environment primarily through domestic use to wastewater treatment plants, being detected in municipal wastewater samples in the  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  range. The incomplete removal of some of these pollutants during conventional wastewater treatment has permitted their spread through surface waters. Subsequently, some drugs are again not completely removed during drinking water production and thus, they have been identified in drinkable water at the  $\text{ng L}^{-1}$  level [1]. Yet, the study of transformation/degradation products produced during conventional treatment has received less attention, particularly with potassium permanganate, a strong oxidant which has been widely used in drinking water treatment over the past decades [2]. Thus, the oxidation kinetics and transformation route of seven NSAIDs, two  $\beta$ -blockers and one  $\beta$ -agonist upon reaction with potassium permanganate was investigated by liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-QTOF-MS). Only three of the investigated drugs significantly reacted with permanganate: indomethacine, diclofenac and salbutamol. Hence, degradation kinetics of these three drugs was investigated at different concentrations of permanganate, chloride, phosphates and sample pH by means of a full factorial experimental design. Moreover, the use of an accurate-mass high resolution LC-QTOF-MS system permitted the identification of several by-products. The transformation path of the drugs consisted mainly of hydroxylations, decarboxylations and oxidation of aromatic double bonds, with ring opening. Finally, the reaction was also tested with real water matrices, where several transformation products were detected. Finally, a software estimation of the putative toxicity of transformation products was also performed.

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## Natural and reconstituted arkosic sedimentary rocks as landfill barriers for major solutes transport retardation

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Landfills are often lined to minimize the migration of harmful contaminants into the surrounding soil and groundwater. The most important engineering specification for geomaterials, used as landfill liners, is a low hydraulic conductivity (less than  $10^{-9}$  m/s) but also is necessary to assess their chemical stability and performance during the operation of the landfill. Soils amended with bentonite (smectitic swelling clay) are commonly used as barrier materials. The addition of relatively small amounts of bentonite, approximately 5–10% of the dry weight of the sandy material (Kenney *et al.* (1992)), can improve the performance of a granular material providing both a low permeability and an enhanced solute retaining capacity and transport resistance by means of adsorptive mechanisms (Mitchel *et al.*, 2007).

Arkosic sedimentary rocks from the Madrid Basin (Spain), once kneaded and compacted, were studied as analogue materials to siliceous sand-bentonite mixtures by means of implementing transport tests through the compacted materials (Ruiz *et al.*, 2012). Based on this study, the same tests have been carried out comparing the behaviour a natural arkose and an artificial reconstituted arkose. For this experiment, different arkoses, from the SE of Sierra de Guadarrama (Central System), have been characterized in order to establish a reference natural mineral barrier. The averaged arkose reference contains 80% sand-size material (siliceous sand) and 20% silt and clay-size material (fines powder). An artificial arkose has been prepared with previously separated sand and fines powder, uniformly mixed and kneaded with distilled water, in the same proportion than the natural selected sample. The experiments were performed with both samples, natural and artificial arkose, compacted into permeability cells and a synthetic leachate, representative of a municipal solid waste landfill plant ( $\text{NH}_4\text{Cl}$  0.25 M, NaOAc 0.15M and  $\text{NaHCO}_3$  0.1M, pH 7.8).

This study probed that separated arkosic fines have smectitic composition and can be mixed with sand, kneaded and remoulded to have similar transport resistance than the natural materials. Ammonium is selectively retained in these materials.

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## Elimination kinetics of perfluorohexanoic acid in humans and comparison with mouse, rat and monkey

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In response to concerns associated with the bioaccumulation and slow bioelimination of long-chain perfluoroalkyl substances (PFAS) in biota, new products have been developed based on short-chains (e.g. fluorotelomer-based products with six fluorinated carbons). One of the key attributes of this new generation of short-chain perfluoroalkyl substances is rapid bioelimination which results in very low to non-detectable concentrations in biota including humans.

Perfluorocarboxylic acids (PFCAs) are generally recognized to be stable under normal environmental and biological conditions. The detection of low concentrations of PFCAs in human blood represents the net result of the simultaneous processes of uptake via various routes of exposure and bioelimination. Minor additional amounts of PFCAs are formed from uptake and metabolic conversion of polyfluorinated precursors. In contrast to the multi-year elimination half-lives determined for long-chain PFCAs such as perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA), short-chain PFCAs such as perfluorohexanoic acid (PFHxA) rapidly eliminate from biota, resulting in low to non-detectable plasma and tissue concentrations.

This poster summarizes current reported biomonitoring results for PFHxA (CAS 307-24-4) in human blood, plasma and serum and presents an evaluation of the rate of PFHxA bioelimination from mice, rats, monkeys and humans. Previously published biomonitoring data from professional ski wax technicians was used to provide an evaluation of the bioelimination half-life of PFHxA from humans. PFHxA is rapidly eliminated from all species with elimination half-life shown to be proportional to body weight. As a result, the elimination behavior of PFHxA is shown to be both rapid and predictable across a wide range of mammalian species.

## Calculation of elimination half-life with an ongoing source: The example of perfluorooctanoic acid

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Determination of the chemical bioelimination rate from human blood is a critical component of toxicokinetic exposure assessment. Analysis of longitudinal biomonitoring data without consideration of ongoing exposure results in apparent elimination half-life values that are longer than the intrinsic value. Confusion between intrinsic and apparent half-life values can lead to misinterpretation of biomonitoring results.

This poster demonstrates the difference between intrinsic and apparent elimination half-life values in longitudinal biomonitoring studies and provides appropriate equations to estimate the extent of potential bias in half-life calculations. In addition, an approach is proposed to estimate the extent of exposure reduction based on the observed rate of decline in biomonitoring data.

The extensive published human biomonitoring data for perfluorooctanoic acid (PFOA, CAS 335-67-1) is used to provide examples of low, medium and high bias in determination of the intrinsic elimination half-life of PFOA. Based on analysis of several large-scale biomonitoring studies, the best estimate of the intrinsic half-life of PFOA in the general population is 2.4 years. Some variation of this value can occur due to age (i.e. longer half-life is observed in older workers) as well as between genders (i.e. females have marginally shorter elimination half-life than males). Based on the rate at which the concentration of PFOA is declining in NHANES blood sampling of the general population, environmental exposure to this substance has been reduced by 20-30% over the period 1999-2008.

Accurate determination of the intrinsic elimination half-life of chemicals provides both a valuable means of understanding actual chemical behavior in biota as well as a tool for estimating the extent of exposure reduction. In subsequent toxicokinetic modeling, it is critically important to use intrinsic half-life values together with appropriate levels of ongoing exposure in order to accurately simulate long-term concentration trends in blood.

## Kinetics and transformation products of cocaine upon reaction with free chlorine

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In the last years, illicit drugs and their metabolites have been recognized as a new group of water contaminants. These substances enter wastewater after their excretion by consumers or as a consequence of direct disposals through the sewage system. Once there, their removal during wastewater treatments is usually incomplete, releasing them to surface waters and even permitting them reaching tap waters, if contaminated sources are used for drinking water production [1-2]. Although conventional drinking water processes have proved to eliminate most illicit drugs and metabolites [2], this apparent elimination may hide a concerning issue: the potential transformation of the parent compounds into different species (disinfection by-products, DBPs) of unknown toxicity and/or persistence. In this line, free chlorine, one of the most widely applied water disinfectants all over the world, is also a non-specific oxidant which has demonstrated to react with several classes of emerging contaminants to form different DBPs [3-5]. Therefore, the aim of this work was to evaluate the transformation of one of the most frequently abused drugs, cocaine, and its two main human metabolites, benzoylecgonine and ecgonine methyl ester, under chlorination experiments. Time courses of the parent compounds were followed by liquid chromatography-mass spectrometry (LC-MS) with a quadrupole-time-of-flight (QTOF) system. Factors potentially affecting the degradation of cocaine (the only drug showing a significant decrease) were evaluated by performing a Box-Behnken experimental design in which sample pH resulted to be the most important variable: both chlorination-mediated and non-chlorination reaction rates (ester hydrolysis) underwent an increase with an increase of the pH. From these reactions, four DBPs were detected, and subsequently identified, due to the high mass accuracy measurements acquired with the QTOF system: benzoylecgonine (BE), norcocaine (NCOC), norbenzoylecgonine (NBE) and *N*-formylnorcocaine (FNCOC). Their formation and cocaine degradation yields were evaluated by chlorinating two real river waters. In one of them, with a low anthropogenic impact, BE and NCOC were notably generated after only 1 hour of reaction, whereas at higher contact times also NBE and FNCOC were determined. In the second sample, highly affected by wastewater discharges, chlorine was rapidly consumed by the sample organic matter, so that only BE was produced.

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## Transformation of the fungicides triadimenol and fenhexamid under environmental conditions and UV exposure.

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Understanding the transformation routes of chemical compounds in the environment is one of the most challenging issues which face analytical chemists and environmentalists. In the particular case of pesticides, after application in agriculture fields, their dissipation kinetics are controlled by climate variables, such as temperature, humidity, rain events and solar irradiation. Furthermore, degradation rates, and even transformation by-products, generated from the same species, differ among water, air and solid matrices (soil surface, crops foliage and fruits). Identification of pesticides by-products in real samples (particularly in complex solid matrices) remains as an extremely difficult task, since by-products need to be first recovered from the matrix and then discriminated from other compounds contained in sample extracts. Moreover, their formation has to be correlated with precursor species depletion. Growth of fruits and vegetable leaves, as well as soil movements, inherent to agriculture practices, further increased the complexity of the above tasks. Thus, considerable attention has been paid to the use of model supports in order to investigate the transformation of chemical compounds under laboratory and environmental conditions. Supports provide preliminary data regarding the relative stabilities of investigated compounds, their possible byproducts and transformation routes. Obviously, the relevance of these findings has to be further confirmed in real-life samples (soil, fruit, leaves), under environmental conditions. Ideally, these supports should full-fill some basic requirements, such as (1) capability to incorporate a repeatable amount of precursor species, (2) stability under outdoors conditions, (3) suitability to retain generated by-products minimizing losses due to evaporation and rain washing, (4) inertness and (5) low cost.

The aim of this presentation is to investigate the suitability of a model support to follow the time-course of two fungicides (triadimenol and fenhexamid) under outdoors exposure conditions and in laboratory experiments. Depletion of precursor compounds and by-products identification was performed by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) after desorption of supports with a suitable organic solvent. Byproduct structures were elucidated from the information contained in their accurate ion product scan MS/MS spectra. Finally, identified by-products were compared with those reported in previous experiments performed with water samples and residues of both pesticides previously reported in agriculture soils, vegetables and surface waters.

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## ***Ips*o-hydroxylation initiates sulfonamide degradation by *Microbacterium* sp. BR1**

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Not much is known about the fate of sulfonamide antibiotics in the environment of which ~20,000 ton year<sup>-1</sup> are released into the environment. The abundance of antibiotics implies risks for humans like the formation of resistant pathogenic bacterial strains<sup>1</sup> etc. The most commonly used sulfonamide antibiotic in human medicine is sulfamethoxazole (SMX)<sup>2</sup>, which is known to be photo- and thermally stable<sup>3</sup> and therefore of special interest due to its persistence.

The previous isolation of the first bacteria which were proven to at least partly mineralize <sup>14</sup>C-SMX allowed the further investigation of the biodegradation of SMX by the isolate *Microbacterium* sp. BR1.

It could be shown that the initial attack of SMX is a *ipso*-hydroxylation which leads to the release of the parent compound into 3-amino-5-methylisoxazole (3A5MI), sulfite and benzoquinone-imine which will be reduced to 4-aminophenol. While the latter can be mineralized by *M. sp. BR1*, 3A5MI remains as a stable metabolite.

This pathway is of special interest, because it could be shown, that this mechanism is not only valid for SMX, but for all six other tested antibiotic sulfonamides with a heterocyclic moiety instead of 3A5MI and also the herbicide asulam, with a methylcarbamate moiety.

To complete the presentation of the first described sulfonamide degradation pathway which is initiated by the biologically rare *ipso*-hydroxylation, first characterization data of the responsible, purified protein will be shown.

Due to those results it is likely that many different sulfonamide antibiotics can be degraded with the same mechanism by *M. sp. BR1*. Furthermore the detection of the heterocyclic moiety as stable metabolites in other biotic sulfonamide degradation studies with isolates from different geographic locations<sup>4-6</sup> indicates, that the described mechanism here is a widespread phenomenon, and not necessarily a unique feature of the isolate *Microbacterium* sp. BR1.

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## Role of forest for atmospheric PAHs input into mid-mountain karst systems

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Last decade, it has been pointed out that mid-mountain forested areas behaved as a sink for atmospheric pollutants (1) such as persistent organic pollutants (POPs). This accumulation of pollutants, like polycyclic aromatic hydrocarbons (PAHs), is due to barrier effect of mountain ranges, atmospheric leaching by abundant precipitations and low ambient temperature.

This work deals with the role of forest in PAHs transport from the air to the karstic system. For this purpose, we intend to highlight fluxes and stocks of PAHs in different compartments and for various seasons. This study was carried out in prealps mountains (Bauges, Savoie, France). This mid-mountain region is characterized by a forest cover of spruce (*picea abies*) developed on cambisol which is over a limestone bedrock.

First results showed that maximum atmospheric concentrations of PAHs fluctuated between 7-12.5 ng/m<sup>3</sup> during winter, with more than 80% of PAHs in the vapour phase, due to PAHs emissions by household heating. Previously, researchers have demonstrated that needles acted as a passive sampler of tropospheric PAHs (2). In this sampling site, adsorbed PAHs reached 60 ng/g of dry needles in winter. In parallel, it has been measured that wet deposition rate of PAHs under forested cover accounted for 1800 ng/m<sup>2</sup>/j whereas rainfalls led to 400 ng/m<sup>2</sup>/j. The litter could contain about 165 ng PAHs/g of dry matter (DM) in winter, corresponding to an important possible source of PAHs input in karst system. Soil analysis reflected that more than 615 ng/g DM, mainly represented by high molecular weight (HMW) PAHs, could be stored in this compartment. PAHs fate in soil of mid-mountain forest could be explained by the high content of organic matter in soil which governs the adsorption process of POPs (3). PAHs emission from soil to atmosphere was estimated to be about 62-525 ng/m<sup>2</sup>/j in this season. In parallel, it could be observed that seepage water was almost loaded by most hydrophilic low molecular weight (LMW) PAHs, from 30 to 150 ng/L during snowmelt. This result could be linked to the high scavenging effect of LMW PAHs in gaseous phase by snow (4) or by the important dissolution potential of sorbed LMW PAHs by the snowmelt drain. Lastly, this study also emphasized the vulnerability of karst towards the seepage of PAHs in groundwater which one could be used for human drinking supply.

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## Photocatalytic degradation of Spironolactone by using Advanced Oxidation Processes (AOPs)

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AOPs are commonly designed to produce hydroxyl radicals (HO•) that react efficiently with most organic compounds present in the water. The use of photo-catalysis as advanced oxidation treatment has emerged as viable alternative for removing micro-pollutants and other organic contaminants from surface, ground and waste water. Photo-catalytic degradation is a process in which the organic contaminants are degraded by UV light in the presence of a catalyst. The catalyst used in this study was the semiconductor titanium dioxide (TiO<sub>2</sub>) chosen for its properties: low resistance to corrosion, low toxicity and low costs. Some reports about minimal concentrations of pharmaceuticals founded in the water cycle have raised concerns over potential human health risks from exposure to trace of these compounds in drinking-water. The aim of this work was the application of photo-catalysis for the degradation of spironolactone (SP) a steroidal compound. Spironolactone, chemically named as 7 $\alpha$ -acetylthio-3-oxo-17 $\alpha$ -pregn-4-ene-21,17 $\beta$ -carbolactone acid- $\gamma$ -lactone, acts as a competitive antagonist of the potent endogenous mineral-corticosteroid aldosterone. It is a drug included in a class called potassium-sparing diuretics (water pill). Such drug is widely used to treat high blood pressure, and fluid retention caused by various conditions, including heart disease. SP is indicated in the treatment of essential hypertension, edema associated with congestive heart failure, hepatic cirrhosis with ascites, nephritic syndrome, idiopathic edema, and in diagnosis of primary aldost.

Photochemical reactions were carried out by using a solar simulator and kinetic parameters were determined. Identification of the photoproducts was performed by liquid chromatography coupled with mass spectrometry (LC-MS ). The standard solution used as control in the darkness did not show any significant degradation during the experimental time. Photocatalytic reaction resulted of the first order (T<sub>0.5</sub> =19,08 h). Three photoproducts was identified. Results suggests that photocatalysis is an important process to destroy this kind of drugs on aquatic bodies.

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## Photodegradation and photocatalysis of Diazepam in liquid phase

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In recent years, the environmental occurrence, fate and effects of pharmaceuticals or pharmaceutically active compounds (PhACs) and their metabolites have received increased attention. PhACs have been detected in wastewater, river water, marine water and even sewage sludge and soil, and represent emergent pollutants. Although used in quantities similar to many agrochemicals and other organic micropollutants, PhACs are not required by law to undergo the same level of testing for possible environmental effects. Therefore, PhACs and their metabolites have been the subject of many years of unlimited issuing to the environment. The photolysis and the photo-catalysis as treatments of advanced oxidation are a viable alternative for the removal of organic pollutants and other contaminants from the surface-, ground- and waste-water. In the present study tests of photodegradation and photocatalysis were conducted taking as a model PhAC the Valium active substance called diazepam (7-chloro-1,3-dihydro-1-methyl-5-phenyl-1,4-benzodiazepin-2(3H)-one) an anti-anxiety drug. The experiments were performed using a Suntest CPS (solar simulator) furnished with Xenon lamp, which reproduces the spectral distribution of solar irradiation. The catalyst used was the semiconductor titanium dioxide (TiO<sub>2</sub>) chosen for its properties: low resistance to corrosion, low toxicity and low costs.

Kinetic parameters were determined. The identification of the photoproducts was performed by liquid chromatography coupled with mass spectrometry (LC-MS). The aqueous solution of the pure compound kept in the darkness as control for hypothetical hydrolysis did not show any significant degradation during the experimental time, while when was added with TiO<sub>2</sub> it showed a little decrease of the pharmaceutical content also in the absence of light irradiation. Photocatalysis was five times faster than photodegradation. Many photoproducts were detected and identified (7-chloro-1-methyl-5-p-methoxy phenyl-1H-benzo[e][1,4]diazepin-2(3H)-one C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>Cl with exact MW 315.08948; (5-chloro-2-(methyleamino)phenyl)(phenyl)methanone C<sub>14</sub>H<sub>10</sub>NOCl with exact MW 244.04454; 7-chloro-1-methyl-5-phenyl-2-hydroxy-3-hydro-1H-benzo[e][1,4]diazepine C<sub>16</sub>H<sub>16</sub>ON<sub>2</sub>Cl with exact MW 287.09457; ortho, para methoxy diazepam C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>Cl with exact MW 315.08963; 5-chloro-2-methylamino-benzophenone C<sub>14</sub>H<sub>13</sub>ONCl with exact MW 246.06802; 1-methyl-5-phenyl-2-hydroxy-3-hydro-1H-benzo[e][1,4]diazepine C<sub>16</sub>H<sub>15</sub>ON<sub>2</sub> with exact MW 251.11789; 5-(4-methoxyphenyl)-1-methyl-2,3-dihydro-1H-benzo[e][1,4]diazepin-2-ol C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub>Cl with exact MW 317.10513).

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## Photodegradation of Mefenamic Acid and Fenofibrate on Soil Surface under Simulated Sunlight

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Nowadays the emergences of pharmaceuticals in the aquatic and terrestrial environment have been a major concern. They have been detected in sewage-treatment plants, sediments, soils and drinking water. So far, there is limited information in the literature on the fate of these compounds when they are exposed to solar light at the surface of soil. The objective of the present study is to investigate the degradation process of mefenamic acid (MEF) and fenofibrate (FNF) at the surface soil when exposed to simulated solar light. We also concentrate our effort on the elucidation of the main intermediate products. Two types of soils were employed. The soil sample was collected in an agricultural field close to the treatment plant for waste water from Jerez de la Frontera (Spain). The irradiations of MEF and FNF on soil were accomplished by preparing thin samples in sterile petri dishes. The sterile petri dishes were used for the irradiation experiments in the Suntest system (from MTT Atlas) at 500 W/cm. In order to have a dark control, samples were left at room temperature in the dark for 24 h to ensure that a negligible thermal disappearance of MEF and FNF. The sampling was performed at a given irradiation time. Such extraction process ensures more than 70% recovery. Duplicate experiments were performed in parallel to check the results. The results show that MEF and FNF undergo fast degradation due to the presence of dissolved organic matter (DOM) on the non-sterile soil. The half life time under our experimental conditions was evaluated to 1 hour in non sterile soil and 4 hours at the surface of sterile soil. The elucidation of the major photogenerated products was performed using Ultra-performance liquid chromatography (UPLC) coupled to quadruple time-of-flight (QTOF) and the mechanism of their formation will be proposed. The formation of products was followed as a function of irradiation time.

**Keywords:** Photodegradation, Photoproduct, Mefenamic acid, Fenofibrate.

## Residues of Extraction and Refining of Crude Oil in Soils and Mobility of Oil Hydrocarbons in Snowpack

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Crude oil represents a complex mixture of variable organic compounds that were formed by geochemical transformations<sup>1</sup>. Crude oil and its products contain mainly hydrocarbons. Oil extraction, transportation, processing and utilization of its products leads to leakage of oil-derived hydrocarbons into the environment<sup>2</sup>. Oil spills result in contamination of the environment and the organisms in it<sup>3</sup>. Hydrocarbons, mainly aliphatic hydrocarbons, do not enter into the environment only from anthropogenic sources, but also from biogenic sources<sup>4</sup>. They have different distribution of *n*-alkanes, which is used to identify the origin of hydrocarbons<sup>5</sup>.

This study is divided into two parts. The first part is a study of the sources of contamination by petroleum hydrocarbons in soils from South Moravia, based on distribution of aliphatic hydrocarbons. Soil samples with anticipated oil pollution (active oil-well, petroleum stations, place with huge contamination, pipeline, road) as well as forest and agricultural land were analyzed. In all soils from different sites aliphatic hydrocarbons were found, predominantly of biogenic origin. Their biggest amount was found in forest soils in the upper soil layers, which are likely to be richer in organisms which produce these hydrocarbons. The most significant contribution of petroleum hydrocarbons have been found in place with huge contamination, less around the active oil-well, pipeline, road and agricultural soils. Distribution of *n*-alkanes showed distinctive pattern for age and extent of contamination. The second part of work deals with the study of mobility of oil components in ice and snowpack.

<sup>1</sup> Wang, Z.D. and M. Fingas, *Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography*. Journal of Chromatography A, 1997. 774(1-2): p. 51-78

<sup>2</sup> Wang, Z., et al., *Comparison of oil composition changes due to biodegradation and physical weathering in different oils*. Journal of Chromatography A, 1998. 809(1-2): p. 89-107

<sup>3</sup> Nicodem, D.E., et al., *Photochemical processes and the environmental impact of petroleum spills*. Biogeochemistry, 1997. 39(2): p. 121-138

<sup>4</sup> Wang, Z.D., M. Fingas, and D.S. Page, *Oil spill identification*. Journal of Chromatography A, 1999. 843(1-2): p. 369-411

<sup>5</sup> Nguyen Tu, T.T., et al., *Early degradation of plant alkanes in soils: A litterbag experiment using 13C-labelled leaves*. Soil Biology and Biochemistry, 2011. 43(11): p. 2222-2228

## Release of toxic organic compounds from contaminated building materials into air

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The objective of this study was to investigate the relationships between the concentrations of contaminants on surfaces of building materials and their concentrations in the surrounding air. This work was a part of the study to establish acceptable residual concentrations of chemicals following the decontamination of affected buildings and areas. The correlations between the surface and air concentrations were considered of a practical importance as they would link risks due to dermal contact and inhalation, respectively. Four commercial pesticides were tested: organochlorine lindane, carbamate carbofuran, and organophosphorus diazinon and malathion. Their release from six building construction and finishing materials, consisting of glass, acoustic ceiling tiles, polypropylene carpet, gypsum drywall, ceramic tiles, and vinyl flooring, was studied at 20°C and 40°C. Time and concentration profiles were determined. Concentrations in the vapour phase were compared to the time-weighted averages (TWAs) for the respective pesticides, thus helping assess associated health hazard and levels of decontamination required.

The highest concentrations measured in vapour phase were similar to the saturation concentration calculated for lindane, diazinon, and malathion. For carbofuran, the experimental results showed concentrations in vapour phase approximately 500 times greater than what was expected based on data in the literature. Vapour-phase concentrations exceeded the TWAs for lindane, carbofuran, and diazinon at 20°C and 40°C. Toxic byproducts were also detected. Some surfaces, such as ceramic tiles, appeared to catalyse by-product formation. Their resultant concentration depended primarily on the temperature and the type of surface materials. Based on these results and the release profiles, levels of decontamination required to maintain “safe” (as determined by TWAs) inhalation environments were estimated.

The experimental data were used to validate a contaminant release model for workspace environment. Under comparable conditions, vapour-phase concentrations obtained by the model and those measured in the experiment were of the same order of magnitude. The model yielded rough estimates of the time required to reach a complete release of the contaminant into air. Depending on the contaminant and test conditions, the time ranged from four days to ten years.

## Study of Stereoselective Degradation of Pharmaceuticals and Illicit Drugs in Wastewater and Receiving water bodies

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Pharmaceuticals and illicit drugs have been detected within wastewater and environmental matrices for several years now. However, to date, little emphasis has been placed upon the enantiomeric profile of those drugs. This may however lead to erroneous estimations of toxicity as the enantiomeric profile of chiral drugs plays an important role in both their pharmacodynamic and pharmacokinetic properties. Chiral analysis and enantioselective toxicology is well established within drug design, however ecotoxicology and analysis of chiral drugs in the environment is still usually assessed using whole parent drugs.

This talk will comprise two related topics, firstly the development of a novel method to analyse chiral drugs from both liquid and solid complex matrices and secondly the study of the mechanisms involved in the transformation of chiral drugs within the environment.

Enantiomeric profiling of chiral drugs within liquid environmental matrices has been demonstrated previously. However we have now also developed and validated a novel method which allows for the enantiomeric profiling of 25 chiral pharmaceuticals and illicit drugs from solid matrices (including illicit amphetamine-like drugs, beta blockers, anti-depressants, an anti-arrhythmic, an analgesic and a bronchodilator). This will allow for a more accurate measurement of environmental concentrations of drugs using chiral methodologies, particularly those which preferentially adsorb to solid material, as well as the study of enantiomeric profiles from solid matrices. Using this novel methodology in combination with established methods for liquid matrices we can present concentrations and enantiomeric fractions from a much wider variety of matrices than has been previously presented giving a more detailed picture of where and how chiral drugs transform within the environment. Results from wastewater and receiving waters will be presented. In brief, the methodology includes freeze drying, microwave assisted extraction followed by Solid Phase Extraction (SPE) and finally chiral Liquid Chromatography-Tandem Mass Spectrometry (chiral LC-MS/MS).

In order to study the mechanisms involved in the transformation and degradation of pharmaceuticals and illicit chiral drugs within receiving waters, microcosms (90% river water, 10% wastewater effluent) were set up to study biological (anoxic and aerobic, in the presence and absence of light) and abiotic factors (oxygenated, anoxic, light and dark processes). These were spiked with a mixture of 25 chiral drugs and samples taken every day for 2 weeks. The samples were then analysed in order to compare the rate of degradation as well as any change in the enantiomeric profile of the parent drug as a result of degradation under differing conditions.

## Sorption behaviour of trifluralin and alachlor on selected sorbents in aquatic matrices of different origin

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The sorption behavior of trifluralin and alachlor was assessed on Danube (D) and formulated sediment (F) from three water matrices (surface water (the river Danube), deep groundwater and distilled water containing 0.01 M CaCl<sub>2</sub>). The water sample DOC contents were 3.5, 7.2 and 0.5 mg/L DOC respectively. The sorbents had different organic carbon contents (1.2% and 2.0% for sediments D and F). Danube river sediment was mainly sand (just 1% clay), whereas formulated sediment was 5% sphagnum, 74% quartz, 20% kaolinite and 1% calcium carbonate. All sorption isotherms were performed in conventional batch experiments in duplicate in the concentration range 0.1-1 mg/l. The sorbent to water ratio was designed to have uptake of 20-80% (F sediment 0.5g/40 ml and D sediment 5g/40 ml). Characterization of the DOC in the ground and surface waters at the sampling sites was also performed, using XAD resins and LC-OCD analysis to gain insight into the distribution of DOC fractions in the different water types in the region. Results of the resin based fractionation of the surface and ground water show a slightly higher presence of hydrophobic fractions (57% and 54%, respectively). The LC-OCD method showed that the non-chromatographable portion (hydrophobic) accounts for 4% and 19% of DOC for the surface and groundwater, while the rest is hydrophilic, consisting of humic substances (65% and 48%, respectively), building blocks (13% and 16%) and LMW neutrals (14% and 16%). Molecular weights of surface and groundwater humic fractions are 751 g/mol and 707 g/mol, respectively. All sorption isotherms well fitted with the Freundlich model ( $R^2$  0.95 - 0.99). Distribution coefficients normalized on organic carbon content ( $\log K_{OC}$ ) were calculated at a selected equilibrium concentration (0.5 mg/l). Both alachlor and trifluralin sorbed more strongly to the F sediment (slightly higher content of organic carbon). Regardless of the fact that groundwater DOC is more hydrophobic, a decrease in sorption degree was observed in all samples for both compounds when water DOC content increases. The only exception was the case of trifluralin and formulated sediment, which showed slightly better sorption from the water matrix with higher DOC. Substances of different hydrophobicity showed different sorption behaviors on the sediment with higher kaolinite content, whereas their behaviour for natural sediment was similar. As well as the general higher organic content, one possible explanation might be additional NOM adsorption on kaolinite and subsequent interaction with the more hydrophobic trifluralin.

DOC (mg/l)	Alachlor		Trifluralin	
	$\log K_{OC}$ (0.5 mg/l)			
	Sediment			
	D	F	D	F
0.5	2.90	3.69	3.76	4.27
3.5	2.64	2.92	3.52	4.40
7.2	2.41	3.00	3.40	4.35

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## Surface to volume ratio effect on atrazine removal by polymer in water: cationic polymer mechanisms

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This study reports on the direct ability of cationic polymer in reducing atrazine concentration in water. Focus is given on the mechanism and mode of reaction of polymers with atrazine. The studies are carried in demineralised water as matrices to observe polymer ability and to exclude other interference found in wastewater. The adsorption is carried using multiple glass vessel followed by ultrafiltration with 1kD membrane. This is to exclude the polymer from the injection sample. Gas chromatography (GC) with liquid-liquid micro-extraction pre-treatment method is used for the atrazine concentration determination. The addition of polymers showed a capability in reducing the atrazine concentration up to a maximum of 40% that justified with the no-particle setup of this experiment. Theoretical L-type of isotherm of Giles classification is expected with increasing the dosage of polymer. However, in this study, the conventional type of isotherm is not achieved. A possible explanation was that cationic polyelectrolytes required free surface for attachment, and in this case it adsorbed to the glass wall of the bottle. Multiple layers of the polymer formed, and atrazine was adsorbed in between these layers and, in this way, removed from the solution. To prove the mechanisms involved between polymer and the glass surface, surface to volume ratio effect of glass vessel experiment is carried. The initial hypothesis of these experiments is to prove that polymer need surface in order to remove atrazine. The higher surface available the higher concentration of micropollutant will be removed. Surface to volume ratio effect on glass vessel is carried out using different vessel volume with the surface to volume ratio range from 0.4-1.8m<sup>-1</sup>. In this experiment higher removal of atrazine is achieved in a range of 40-80% from initial concentration of 5±0.2 µg/L. The results then used to explain and proved the multilayer formation and effect on atrazine reduction by cationic polymer. Atrazine is expected hydrophobically entrapped between the intertwined polymer chains.



## The use of isotopic tracers to study the transformation rates, localization and biomolecular binding of Hg species at subcellular level in methylating and non-methylating sulphate-reducing bacteria

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Microbial Hg methylation is a key process in the Hg cycle controlling the MeHg concentrations in the aquatic environments (1). Despite our improved understanding of the microbiological mediated Hg methylation in the environment and the identification of the involved bacteria, we have only a vague idea of the underlying mechanisms and of the parameters that control the efficiency of that transformation. Because methylation extent can be controlled by both cellular uptake and reversible demethylation pathways, the use of multiple isotopically labelled Hg species may provide additional mechanistic insights of such processes.

In this work, pure sulfate reducing strains: *Desulfovibrio* sp. BerOc1 and *Desulfovibrio desulfuricans* G200 (which exhibit different Hg methylation potential) were incubated in the presence of isotopically labelled mercury species (<sup>199</sup>Hg(II) and <sup>201</sup>MeHg) under controlled anaerobic conditions. The quantification of the remaining and formed Hg species by GC-ICPMS in the different subcellular fractions (periplasm, cytoplasm, membranes) has allowed the determination of methylation and demethylation rates simultaneously, but also the comparison of the localization of the originally added and resulting species of such metabolic processes. A dissimilar Hg species distribution is observed. In general terms, MeHg added and formed show a similar pattern, being mainly present (90%) in the extracellular fraction. In contrast, IHg added to the culture is associated to the cells while after demethylation it is preferentially localized in the extracellular fraction. The analysis of the cytosol and the extracellular fraction by size exclusion chromatography-ICP-MS revealed divergences on the profile of biomolecules binding mercury corresponding to the control and the methylating strain. The results show that both specific metabolic pathways involving selective biomolecules binding Hg and cellular uptake/release seems to regulate net Hg methylation in anaerobic bacteria.

## ProbaBio (Probability of Biodegradation): a new concept in the evaluation of biodegradation

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For the registration of a chemical substance, the European REACH regulation requires, *inter alia*, the evaluation of its biodegradability. A large set of test methods is available since 1992. However, biodegradation results for molecules published in literature, show intra and inter laboratory incoherencies linked to the microbial community variability. Indeed, if biodegradation is achievable from the growth of specific microbial degraders with a substance as the sole source of carbon, the result of the test depends largely on the degraders' density at time zero. If this species are relatively rare in an environment that is normally used, the likelihood of inoculating a test with sufficient specific cells becomes a matter of probability.

With the alternative ProbaBio<sup>1</sup> approach developed in this study, persistence of a molecule is not only regarded as a simple intrinsic substance property, but also as the potential presence of specific degraders in various environmental samples (activated sludge, river water and sediment, soil and sea water) to degrade a chemical under realistic exposure (incubation temperature and temporal shifts due to potential seasonal influences) (Figure 1).

A miniaturized O<sub>2</sub> sensing platform has been developed for a high throughput screening to qualify the biodegradation event of readily to persistent molecules. Results show the probability, represented as environmental biodegradation fingerprints, of five molecules to be degraded according to the environment and its conditions.

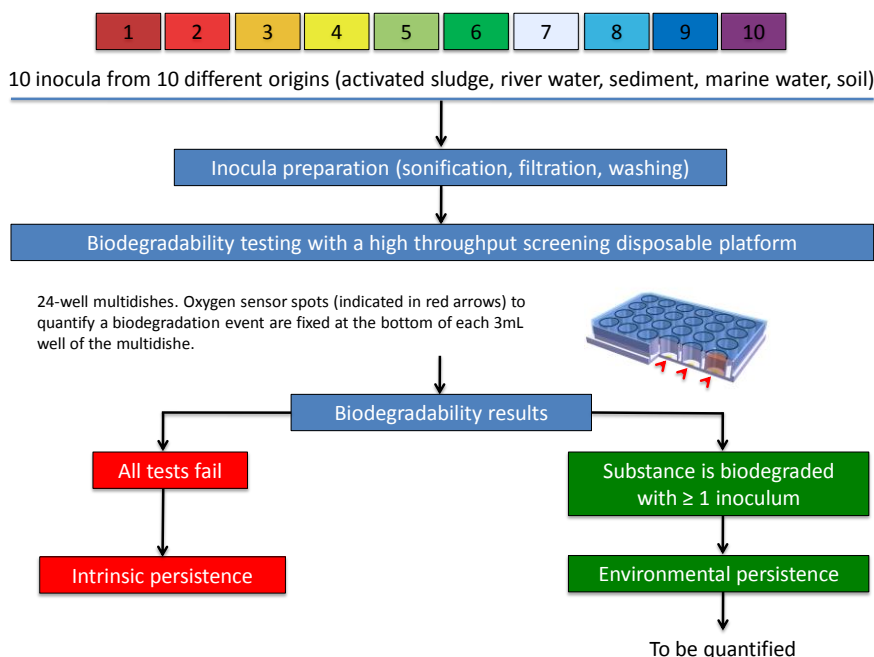


Figure 1. Overall scheme of the strategy used in the ProbaBio concept.

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## Fate of a pharmaceutical compound, pyrimethamine, in water under solar light irradiation

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The study of pharmaceutical compounds and particularly antibiotics is a hot topic in recent years. This interest is related to: (i) large amounts dispensed and released into urine or excreted after administration, (ii) their detection in water and wastewater treatment plants and in soils and (iii) the development of bacterial resistance. Thereby, many studies focused on the prediction of their environmental behavior to assess their fate and impacts on the environment. Nevertheless, data about the environmental behaviour of compounds that are often co-administered to antibiotics are missing. In fact, such compounds, like pyrimethamine (PYR), are frequently co-administered for amplified effects of many antibiotics because of antibacterial synergy. Thus, even if pyrimethamine was commonly used for malaria treatment, it is more recently found in various medicines for the prevention and treatment of dairy cattle for several infectious diseases like toxoplasmosis and to prevent prophylaxis of *Pneumocystis carinii* pneumonia for HIV infected patients and also combined with sulfadoxine for malaria treatment [1-3]. Only few studies related to pyrimethamine identification and quantification confirmed the presence of this compound in biological fluids of some animals [4]. Moreover, as some authors put in evidence agriculture soil, river sediment and sewage sludge contamination by pyrimethamine, this confirms the pollution of environmental compartments and reinforces the co-administered compound environmental fate concerns [5].

Considering these results, the main point of this work is to have a better insight into the photochemical behavior of PYR in aqueous solution. Kinetics of disappearance and quantum yields were determined as a function of various parameters such as pH, oxygen concentration and excitation wavelength (polychromatic irradiation using Suntest, 254 and 290 nm). The characterization of the main photoproducts was conducted by LC-ESI-MS-MS analysis and complementary analyses by ionic chromatography and laser flash photolysis allowed us to propose mechanistic pathways for PYR photodegradation. Such study leads us to the conclusion that whatever the conditions, the pyrimidine moiety is maintained.

The present work in aqueous solution is a preliminary approach to the study on the surface of soils and it is representative of transformations that could occur in environment and during germicidal process of wastewaters.

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## Atmospheric degradation of pesticides. Studies at EUPHORE Chambers.

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Pesticides are extensively used in agriculture, gardening and a variety of other household applications. They can be emitted into the atmosphere through dispersion during spraying, which is carried out mainly in spring and autumn, but also through volatilization from ground or leaf surfaces, especially in summer when the temperatures, particularly in Southern Europe, can reach 40 °C. Once in the atmosphere pesticides are distributed between the gas, particle and aqueous phases.

As for other organic compounds, the gas-phase degradation of pesticides in the atmosphere is controlled by photolysis and/or reaction with ozone, OH and NO<sub>3</sub> radicals.

However, studies of the gas-phase degradation of pesticides are problematic because of their low vapor pressures. One advantage of large outdoor simulation chambers, such as those at the European Photoreactor (EUPHORE), is that compounds with relatively low vapor pressures can be introduced into the chamber in the gas-phase. In addition, these facilities allow work under realistic atmospheric conditions, particularly as regards solar radiation intensity and wavelengths

In this work a general overview of the use of the EUPHORE chambers for studying the atmospheric fate of pesticides will be presented. Results obtained from the experiments on several type of pesticides (i.e organophosphorous type insecticides, chloroacetanilide and dinitroaniline type herbicides, fungicides) have been used to derive lifetimes, and provide information on particle and gas phase product formation. The results obtained show the usefulness of the EUPHORE facility as a sophisticated tool for studying the atmospheric fate of pesticides under controlled conditions. The data derived from such studies are of potential importance to assess the impact of these species on air quality and on human health.

## DEGRADATION OF ETHALFLURALIN UNDER ATMOPHERIC CONDITIONS

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The gas-phase degradation of the herbicide ethalfluralin, N-ethyl- $\alpha,\alpha,\alpha$ -trifluoro-N-(2-methylallyl)-2,6-dinitro-p-toluidine, has been investigated under atmospheric conditions at the large outdoor European simulation chamber (EUPHORE) in Valencia, Spain. The photolysis of ethalfluralin was investigated under solar radiation, and the mean photolysis rate coefficient determined,  $J(\text{ethalfluralin}) = (1.3 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$  ( $J_{\text{NO}_2} = 8 \times 10^{-3} \text{ s}^{-1}$ ). The rate coefficients for the reactions of hydroxyl radicals and ozone with ethalfluralin were also measured under atmospheric conditions using relative rate and absolute rate techniques respectively. Values of the rate coefficients for the reactions of  $k_{\text{OH}}(\text{ethalfluralin}) = (3.5 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $k_{\text{O}_3}(\text{ethalfluralin}) = (1.6 \pm 0.4) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , were determined at  $300 \pm 5 \text{ K}$  and atmospheric pressure. The results showed that removal of ethalfluralin from the atmosphere by reactions with OH radicals ( $\tau \sim 4$  hours) or ozone ( $\tau \sim 25$  hours) is slow compared to loss by photolysis. The available kinetic data suggest that the gas-phase tropospheric degradation of ethalfluralin will be mainly controlled by photolysis and provide an estimate for the tropospheric lifetime of around twelve minutes. The atmospheric implications of the use of ethalfluralin as a herbicide are discussed.

## Photocatalytic degradation of sulfamethoxypyridazine with TiO<sub>2</sub>, FeCl<sub>3</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub>: Biodegradability, toxicity assessment, and LC-UV-MS/MS identification of the photodegradation products in aqueous and sewage treatment plant effluent

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The antibiotic sulfamethoxypyridazine (SMP) undergoes phototransformation without complete mineralization. New phototransformation products (PTPs) are formed [1]. The photocatalytic degradation of SMP in ultrapure water (UP) and sewage treatment plant effluent (STP) was examined during the irradiation with a medium pressure Hg-lamp in the presence of TiO<sub>2</sub>, FeCl<sub>3</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub> catalysts at natural pH (without using buffer or pH adjustment) in UP and STP effluent samples and pH3 in STP effluent samples. The primary elimination of SMP was monitored and structures of PTPs were assessed by LC-UV-MS/MS and total organic carbon (TOC) analyzer. The biodegradation of SMP samples after photolysis and photocatalysis was performed using Closed Bottle Test (CBT; OECD 301 D). Additional data for an environmental risk assessment of SMP and its PTPs were collected using in silico QSAR models.

It was found that SMP underwent photocatalytic degradation and mineralization in the presence of TiO<sub>2</sub>, FeCl<sub>3</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub>. The total degradation time decreased from 128 min in direct photolysis in UP to 16, 4, and 4 min in photocatalysis with TiO<sub>2</sub>, FeCl<sub>3</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub>, respectively and complete mineralization took place in case of TiO<sub>2</sub> catalyst. In STP effluent, the degradation time decreased from about 64 min in direct photolysis to 32, 8, and 8 min in photocatalysis with TiO<sub>2</sub>, FeCl<sub>3</sub> (pH3) and TiO<sub>2</sub>/FeCl<sub>3</sub> (pH3), respectively. Based on the identified PTPs, a degradation pathway was proposed and a comparison between the three catalysts concerning the formed PTPs intensities was performed. On the one hand it was found that SMP and its PTPs were not readily biodegradable. On the other hand in HPLC-UV analysis, it was found that one of the PTPs showed full elimination at day 28 in CBT. QSAR results revealed that the formed PTPs might be more toxic than SMP to the environment with a higher risk of these PTPs on bacteria. Therefore, photocatalysis will be more preferable than photolysis as it offers complete mineralization. However the appropriate time period of irradiation has to be chosen.

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## Identification and initial toxicity assessment of Thalidomide and its photo transformation products

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Thalidomide (TD) became known as a sedative drug used for sleeping pills and morning sickness of pregnant women in the 1950s. In the 1960s, TD was withdrawn because of its teratogenicity. Recently, TD became a promising drug for the treatment of a number of cancers and inflammatory diseases. Consequently, a potential increased influx of TD into the aquatic environment has to be expected. Furthermore, incomplete degradation in surface water or effluent and drinking water treatment photolysis can occur. This makes it imperative to assess the fate and toxic effects of TD and its transformation products. In this study, the behavior of TD was monitored during irradiation with a medium-pressure Hg-lamp. The primary elimination of TD was monitored and structures of PTPs were assessed by LC-UV-FL-MS/MS. The estimation of the relevant properties of TD and its photoproducts (PTPs) and hydrolysis products (HTPs) was performed using *in silico* QSAR models. Mutagenicity of 47mg/L TD after 2, 4, 8, 16, 32, 64 and 128 min of irradiation was assessed in the Ames microplate format (MPF) aqua assay (Xenometrix, AG). In addition, toxicity towards environmental bacteria was investigated in a modified luminescent bacteria test using *Vibrio fischeri*.

New PTPs were formed during irradiation. They were more polar than TD. All the PTPs peaks increased with irradiation time until 32 min and then began to decrease. One PTPs peak was formed at 16 min then increased until 128 min. Two of the PTPs were isomers of TD with the same molecular mass. TD and its PTPs did not exhibit mutagenic activities in the *Salmonella typhimurium* strains TA 98, and TA 100 with and without metabolic activation. In contrast, QSAR analysis of PTPs and HTPs provided evidence for mutagenicity and carcinogenicity by investigating additional endpoints *in silico* compared with the experimental Ames tests. In the luminescent bacteria test, a steady increase of toxicity during the treatment procedure was observed. The acute toxicity started to increase significantly after 16 min of irradiation compared to the parent compound. After 128min of irradiation, a maximum of 96% acute luminescence inhibition of the reaction mixtures was measured [dilution 1:2 (v/v)]. The diluted reaction mixtures [dilution 1:50 (v/v)] showed no significant inhibition. The analysis of luminescence inhibition and growth inhibition showed a significant toxification starting from 32 min of irradiation. QSAR analysis with these endpoints provided evidence for positive alerts for acute toxicity on environmental bacteria in several identified PTPs and HTPs.

In conclusion, the UV irradiation eliminated TD itself but lead to the formation of several PTPs. Some of the PTPs are more toxic to the investigated bacteria than the parent compound but do not show mutagenic activity in the Ames test. Nevertheless the results show the toxic potential of the photo PTPs and deserve further attention.

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## Biodegradability of Corexit 9500 at 5 °C and 25 °C

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The reported persistence of the dioctyl sodium sulfosuccinate (DOSS), the surfactant present in Corexit 9500 (C9500), within the oil plumes formed during the Deepwater Horizon oil spill has contributed to concerns about the biodegradability of the dispersants used in the Gulf of Mexico (GOM). Hence, we studied the biodegradation of DOSS and South Louisiana crude oil (SLC) in laboratory microcosms. With this purpose, two cultures from the GOM were isolated, one from the surface (meso) and one from close to the area of the Macondo well (cryo), with each one enriched on SLC, the former at 25 °C and the latter at 5 °C.

DOSS biodegradation rates in the absence and presence of SLC at 25 °C were high and the removal extents topped 99% by days 8 and 14, respectively. For these treatments, we calculated the biodegradation first-order rate coefficients whose values were  $-0.46 \pm 0.03 \text{ d}^{-1}$  for C9500 + SLC and  $-0.30 \pm 0.02 \text{ d}^{-1}$  for C9500 alone. Hence, the presence of oil enhanced DOSS metabolism by a 1.5 factor: our culture, which had been enriched previously on SLC and thus pre-acclimated to hydrocarbons but not DOSS, likely grew to higher numbers faster and thus oxidized DOSS quicker by virtue of the greater population density. Data at 5 °C sharply contrasted with the 25 °C results since a 28-d lag period occurred before DOSS biodegradation ensued. In the absence of SLC, DOSS was depleted by 98% in 1 replicate on day 35 and 2 replicates on day 42 whereas, in its presence, the triplicates averaged 61% removal but with a slow, steady decline. These results suggest that the cryo culture needed an acclimation stage to synthesize the enzymes that facilitate DOSS breakdown. The findings from our study also showed that DOSS hydrolyzes in abiotic controls at 25 °C, but not within 42 days at 5 °C. At the end of the 25 °C experiment (28 d) only 10% of the initial DOSS concentration remained in the dispersed SLC controls, while 33% persisted in those for the C9500 alone treatment; the respective linear rates of surfactant loss in these controls were  $-185 \pm 14$  and  $-140 \pm 12 \mu\text{g} (\text{L d})^{-1}$ . The apparent 1st-order biodegradation rates reflect the overall process for DOSS disappearance in our live microcosms, regardless of chemical or biological contributions, with hydrolysis being negligible relative to the microbial uptake.

In conclusion, our study revealed that DOSS will not persist when applied to the water surface and the temperature is warm. However, if the temperature is near freezing, our data suggest that it is possible for DOSS to stay for a long period of time when used for spill response. This conclusion agrees with observations made in the GOM, where the primary explanation for lower DOSS concentrations downstream from the wellhead was dilution due to advection rather than biodegradation.



## Comparison of Hydrolysis and Oxidation Processes for Degradation of Bisphenol A (BPA) from Wastewater Sludge

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### Abstract

The growing urbanization has led to the release of toxic organic compounds into the environment, including Endocrine Disrupting Compounds (EDCs). The EDCs are defined as “exogenous substances or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations”. Moreover, these compounds and many of their metabolites end up in the environment as a result of emission from production sites and direct disposal from households- detected in wastewater (WW) and wastewater sludge (WWS) across Canada. The biggest problem associated with these compounds is their detection (ng or pg level) mainly in media with complex matrix. Bisphenol A (BPA) has been identified as EDC by the U.S Environmental Protection Agency (EPA) and World Wide Fund for Nature (WWF).

The effect of various pre-treatment methods, including alkaline hydrolysis (AH), thermal hydrolysis (TH), thermal alkaline hydrolysis (TAH), thermal oxidation (TO) and thermal alkaline oxidation (TAO), on solubilization and simultaneous degradation of bisphenol A (BPA), an endocrine disruptor, in wastewater sludge (WWS) were investigated. The results showed that among AH, TH and TAH pre-treatments, TAH significantly improved the solubilization of WWS (41.6% suspended solid (SS), 70.7% volatile suspended solid (VSS) and 48.5% chemical oxygen demand (COD)) with higher degradation of BPA (38.4%). SS, VSS and COD solubilization were observed to be lower in TO and TAO pre-treatment as compared to TAH pre-treatment. However, higher degradation of BPA (75.0% and 78.9%) was observed in TO and TAO pre-treatment due to the presence of oxidation process. The effects of rheology and zeta potential on degradation of BPA in raw sludge and different pre-treated sludges were also investigated. The results showed that decrease in viscosity and particle size and increase in zeta potential resulted in higher degradation of BPA. BPA degradation by laccases produced by *Sinorhizobium meliloti* in raw and pre-treated sludge was also determined. Higher activity of laccases (230.9 U L<sup>-1</sup>) was observed in TAH pre-treated sludge resulting in high degradation of BPA (21.9%) suggesting concomitant biological degradation of BPA.

**Keywords:** Bisphenol A, wastewater sludge, pre-treatment, rheology, zeta potential, laccase activity

# **Green and Sustainable Industrial Chemistry**

**Oral presentation: OG1-OG7**

**Poster presentation: PG1-PG25**

## Application of LCA methodology to a chemical process: the production of acrylonitrile by ammoxidation

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Acrylonitrile represents one of the most diffused organic chemicals produced on the world, about 6 million of tons in 2010, mainly due to the synthesis of polymers: ABS (acrylonitrile-butadiene-styrene) and SAN (styrene-acrylonitrile). Nowadays acrylonitrile is mainly produced by propene ammoxidation, that involves oxidation in the presence of ammonia and oxide-metal catalysts. However there is an increasing interest on finding alternative ways to produce acrylonitrile, more economic than propene (which represents 67% total production cost). Propane ammoxidation has been deeply investigated as alternative greener route, due to fewer stages in the production of alkane. So to evaluate which routes have better environmental performances, LCA (Life Cycle Assessment) methodology was applied to study the ammoxidation reaction for the production of acrylonitrile, by evaluating and comparing two alternatives from a life cycle perspective: the traditional process from propene (called SOHIO process), and those starting from propane, still undeveloped industrially. Six reference scenarios were created: two from propene (SOHIO Steam, in which propene is produced by Steam Cracking, and SOHIO FCC, using Fluid Catalytic Cracking as the starting process), and the remaining four from propane (ASAHI, MITSUBISHI, BP poor in propane and BP rich in propane). Despite the alkane has a lower global impact than the olefin, the comparison of these six scenarios shows global impacts greater for the alternative processes from propane. In fact, they show lower process yields than the SOHIO, causing a larger consumption of reagents fed to the reactor (ammonia and propane). A characterization analysis shows the results achieved by the scenarios for each impact categories: in particular, the alternative processes have increasing impacts for Fossil depletion, Climate Change and Particulate matter formation categories. Instead, as for Metal depletion category, a greater impact is reached by the processes that use propene, due to the greater percentage of metals used in the catalytic system with respect to the support. A contribution analysis was performed to evaluate which processes influence more the different categories. Results obtained show a greatest contribution for the Fossil depletion due to the reactants production (in particular propane and ammonia), and to the purification steps to obtain ammonium sulfate (produced by neutralization of unreacted ammonia). The same results are obtained for the Climate Change category, while for the category of Particulate matter formation major impacts are caused by the processes of production of ammonium sulfate, propane and sulfuric acid (necessary for ammonia abatement). The main contribution for the Metal depletion category is due to extraction of resources to produce catalyst. Lastly, to confirm the robustness of the model created, verifying results reproducibility, an uncertainty analysis has been performed through the Monte Carlo method, with a confidence interval of 95%.

## Synthesis of photoactive hydrophilic polymeric materials. Applications in synthetic chemistry and pollutant degradation

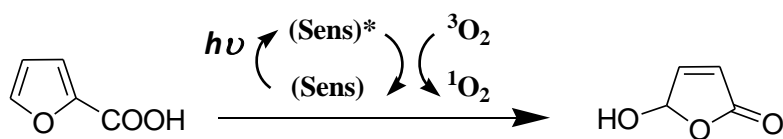
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Photocatalytic reactions are a specific kind of photochemical processes that occur only in the presence of a catalyst upon irradiation with light. Photocatalytic oxidations are gaining increasing acceptance provided they use light to trigger the reaction processes and hence allow the possibility to carry out oxidation in a more controllable manner than conventional thermal methods. [1] In this regard, the utilization of singlet oxygen ( $^1\text{O}_2$ ) is currently commonplace in many synthetic laboratories and it has been shown to be useful in diverse areas such as synthetic chemistry, biomedical and environmental sciences. [2]

Our research group has developed recently some polymeric structures where Rose Bengal is immobilized on microparticles derived from porous monolithic polymer matrices (PMP). These systems were tested to efficiently perform photocatalytic oxidations in non-aqueous medium and photodynamic action against melanoma cancer cells. [3] As a continuation of this research, we are interested in exploring the possibility of immobilize the photosensitizer RB on hydrophilic polymer matrices for the application of the photocatalytic oxidations in aqueous media. Moreover, the polymeric photocatalysts have been used for carrying out the synthesis of the product of interest, 5-hydroxy-5H-furan-2-one, from the photooxidation reaction of 2-furoic acid (figure 1). Additionally, the new materials have been studied as a new method for the degradation of the compound 2-amino-4-hydroxy-6-methylpyrimidine, which is considered as a basic structure for the synthesis of many *N*-heteroaromatics pesticides.



**Figure 1.** Photooxidation reaction for the synthesis of 5-hydroxy-5H-furan-2-one from 2-furoic acid.

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## Chemical engineering of intensified flow-chemistry guided by sustainability issues

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Process intensification is one encouraging concept to improve the sustainability of chemical processes. CoPIRIDE, an EU 7th Framework collaborative project, takes up this idea for a holistic, comprehensive, and integrated process and plant development. Chemical core processes, e.g. epoxidation, transesterification, and polymerization, are under redesign using intensified flow chemistry. In order to ensure a significant progress towards sustainability, the overall design process is supported by detailed life-cycle analyses starting at an early stage. Hot-spot up to holistic Life Cycle Management Analyses combined with an estimation of potential environmental risks are utilized in order to provide decision support for the most promising engineering alternative. The screening ends with a ranking of those alternatives according to their overall level of attractiveness applying multi-criteria decision making tools. The key criteria for process improvement determined by that are then taken into account within the next iterative step of process design. The evaluation is refined and narrowed down in parallel to the ongoing process development. At the end, the environmental impacts and costs of the newly designed chemical processes are compared with the established industrial production pathway.

The holistic design approach will be discussed by means of latest results from the CoPIRIDE project. One case example will be the comparative evaluation of different concepts utilizing, e.g., different feedstocks and catalysts, process conditions and heating devices for intensified biodiesel generation.[1] Following this approach, the key criteria for a future sustainable chemical production process could be defined in front of the transfer of the experimental flow chemistry results to pilot scale processing. Surprisingly, waste oil operation under harsh process conditions (referred to “Novel Process Windows” [2]) was found to be the best case option.

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## Sustainable Production of Hydrogen from Steam Reforming of Bioethanol Using a Recycled Catalytic Material

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The depletion of fossil fuel reserves, caused by the growing energetic consumption, and the environmental pollutant problems derived of the actual energy system, impose a continuous development of sustainable technologies for energy production. In this stage, hydrogen from renewable sources might be considered as the ultimate clean and climate neutral energy carrier system [1-3]. However, hydrogen is not a primary energy source; it must be produced from a primary one. At present the most favourable route to produce hydrogen comes from fossil fuels, mainly through steam reforming of natural gas [1-3], which is associated with the emission of large quantities of greenhouse gases, especially carbon dioxide (CO<sub>2</sub>). Consequently, a new eco-friendly hydrogen production route is needed for a clean and sustainable production of energy. Catalytic steam reforming of bioethanol (obtained from biomass fermentation) is being intensively studied as renewable hydrogen precursor [4-6]. However, the “green” nature of the catalysts used to produce hydrogen from steam reforming of bioethanol has not been still considered. In order to develop a global green process to produce hydrogen we have explored the possibility to use recyclable catalysts in the steam reforming of bioethanol. Specially, we have prepared a Co-based catalyst supported on recycled ZnO. The ZnO used as support in this study comes from the recycling of waste slag generated by certain toy industries. The special features of this recycled zinc oxide, prepared at the Technological Institute of Alicante Toy (AIJU), has allowed to develop an active material with interesting catalytic properties to produce hydrogen from bioethanol. The recyclable nature of the steam reforming catalyst together to the renewable nature of the hydrogen precursor (bioethanol) would contribute to make more sustainable the overall process of hydrogen production.

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## Polymers: out of REACH?

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In less than a century, man-made polymers have conquered the world, both in a positive and in a negative way. Many luxuries on which our modern mass consumption society is based would be unthinkable without the development of the versatile plastics that became available at low costs since the 1940s. Polymers gradually replaced more traditional materials such as wood, paper, glass, metal and leather. An huge number of types of plastics have been created since the first invention, and modern plastics have really revolutionized our lifestyle.

So far the good news. The other side of the medal is that plastics can be found almost literally everywhere around the globe nowadays. Because of their low degradability, polymers are likely to hang around for a long time, also on many places where they can be harmful for the environment. A famous example is the Great Pacific Garbage Patch (“plastic soup”), a huge ring of marine litter in the central North Pacific Ocean.

Recent research has shown that that microplastics, particles with sizes up to 1 mm, form a much greater threat to the environment than “macro-plastic”, the more visible, larger pieces of plastic. The microplastics can easily be ingested by many kinds of creatures, moreover they are more capable of absorbing toxic and pervasive pollutants, such as PCBs and pesticides, which make them more harmful inside the victims.

Microplastics can be formed by the physical degradation of macro-plastic debris in the environment. Nowadays, however, many microplastics are also produced deliberately, for example in consumer products like scrub materials and tooth pastes. These materials end up in the environment almost immediately after use and can not (or at least hardly) be removed in sewage treatment plants.

REACH is a European Union Regulation adapted in 2006, addressing the production and use of chemical substances and their potential impacts on both human health and the environment. All polymers, however, are exempt from registration and evaluation under REACH. This is understandable because of the gigantic amount of paperwork it would take to register and evaluate every kind of polymer ever produced. Instead, the manufacturers and importers of polymers are obliged to register only the monomers involved. In this way, the implementation of REACH has in fact made life easier for manufacturers, importers and users of polymers. Additional legislation is needed to repair this omission.

## Pre-treatment of paper pulp in the bleaching process with a biodegradable chelating agent

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Hydrogen peroxide is a common bleaching agent in the process of paper pulp bleaching. Its efficiency during the bleaching stage is affected by transition metals, such as Mn, Fe and Cu, present in the pulp, that catalyze peroxide degradation. [1] Chelating agents are commonly used to remove these metals in a treatment stage before the bleaching. However, the most used compounds, EDTA and DTPA, are not biodegradable and their discharge to water courses has negative consequences to the environment. [2]

The aim of this work was to study the application of a biodegradable chelating agent in the pre-treatment of paper pulp in the bleaching process.

Pyridine-2,6-dicarboxylic acid (PDA) was prepared from 2,6- dimethylpyridine by oxidation with potassium permanganate. [3] Biodegradability was tested according to the OECD guidelines for DOC-Die Away method and results indicated that PDA is ready biodegradable.

Oxygen delignified paper pulp (Eucalyptus Globulus) was obtained from a Portuguese pulp mill and characterized in terms of dry content, metal content and kappa number. Computer simulations were performed to evaluate the ability of PDA to complex with the metals in pulp and to optimize the pH and chelant concentration. The bleaching sequence (QP1PaaP2) was tested at a laboratory scale and the performance of PDA was evaluated and compared to EDTA. Metals removal was measured after chelation step (Q); peroxide consumption and kappa number were determined after both peroxide bleaching stages (P1 and P2). Results have shown a performance of PDA in the process comparable to the one obtained with EDTA. These facts suggest that PDA might be a promising biodegradable chelating agent for substituting the traditional non-biodegradable ones.

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## Effect of pickling process in chromium offer for bovine hide tannage

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### Abstract

Chromium tannage is one way to improve the thermal stability of bovine hide. Before the tannage step, pickling is necessary in order to adjust the hide pH to a value about 3,0. Pickling is done with salt (sodium chloride) and acids as formic and sulphuric.

This study had as objective the reduction of salt and chromium in the pickling and tanning process, in order to minimise the pollution load of the tanning bath.

The tests were performed in laboratory drums using limed bovine hide, split to a 3.5 mm thickness. Different amounts of salt (0%, 5% and 15%) and chromium salt (4%, 5% and 7%) were tested. The percentages were calculated based on the split limed hide weight.

It was possible demonstrate that pickling process for the tanning of leather can be improved in order to eliminate the salt and to reduce the chromium salt amount.

The results show that the best operating condition is a process without salt using only 5% of chromium salt compared to the traditional process (salt and 7% of chromium salt). At the same time, this process gives good results for the parameters of wastewater and for the chromium oxide content in the leather.

**Keywords:** Chromium, Tanning, Pickling, Salt, Leather.

**Acknowledgements:** The authors would like to acknowledge the Project NEWALK – Materiais, Componentes e Tecnologias para Calçado do Futuro.

## **New solid acid catalysts from waste biomass: synthesis, properties and application to the obtainment of biodiesel from algae and waste oil**

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The majority of the cheap sources of oil, such as waste cooking oils, or new generation oils, such as algal oils, are not suitable for synthesizing biodiesel under alkaline conditions because of their high water or free fatty acids (FFA) content. Acid catalysts, homogeneous (e.g. H<sub>2</sub>SO<sub>4</sub>) or heterogeneous (e.g. ion-exchange resins) could represent an alternative, but they suffer of some important drawbacks: ion exchange resins are expensive and do not resist to mechanical stress, H<sub>2</sub>SO<sub>4</sub> is highly corrosive and requires neutralization extra step.

Solid acid catalysts, prepared from cheap and easily available renewable sources can represent a more sustainable alternative. In the present study, new solid acid catalysts have been prepared from sulfonation of carbonaceous material resulting from the pyrolysis of sugar beet molasses, the cheap viscous by-product of the production of sugar, and waste products, like potato peels. Pyrolysis conditions for molasses and potatoes peel carbons preparation (temperature and time) were very important in determining the performances of the catalysts; the best combination came from pyrolysis at low temperature (420°C) for relatively long time (between 8 and 15 h), which ensured a better stability to the final material. The catalyst resulted to be highly active in the methanol esterification of fatty acids (100% yield after 3 h) as well as in the transesterification of acidic vegetable oils (55-96% yield after 8 h). Finally a "tandem process" using solid acid molasses catalyst followed by potassium hydroxide in methanol was developed to effectively convert algal oils containing high amounts of free fatty acids into biodiesel.

## THERMAL KINETIC STUDIES OF PVA-BENTONITE NANOCOMPOSITES

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Filled polymer systems are very popular in the composite industry, because of their low cost and story performance. In recent years, a number of studies have been devoted to obtain nanomaterials with better chemical–physical properties than the pure polymer. Polymer/clay nanocomposites, in which nanosized silicate plates of clay are uniformly dispersed in the polymer matrix, provide enhanced mechanical and thermal properties compared to conventional composites. Generally, the clays have poor compatibility with the polymer matrix. Therefore, the clay must be organically modified using organic modifiers to improve compatibility. Bentonite is an adsorbent aluminium phyllosilicate, essentially impure clay consisting mostly of montmorillonite. In this paper, we prepared a series of polymer/clay nanocomposite materials by effectively dispersing the inorganic nanolayers of bentonite samples in PVA matrix via solution dispersion technique. Bentonite was intercalated or exfoliated by dimethylsulfoxide (DMSO), methanol (MeOH) and 3-aminopropyltriethoxysilane (3-APT), and was calcinated at 150 and 650 °C. The synthesized polymer/clay nanocomposite materials were characterized by Fourier-transformation infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface areas of bentonite and modified bentonite samples were measured by NOVA 2200e BET surface area analyzer. The contact angles of PVA and its nanocomposites were determined for nanocomposites by sessile drop method. The thermal stabilities of PVA and its nanocomposite materials were also studied by DTA/TG and DSC under nitrogen atmosphere at different heating rates. The activation energies were calculated using different methods such as Kissinger, Ozawa-Wall-Flynn. The activation energies of the decomposition of PVA and PVA/bentonite nanocomposites were calculated using mentioned methods. The results show that activation energy values at both stages for PVA/bentonite nanocomposite were higher than those of pure PVA, indicating that addition of bentonite particles improves thermal stability of PVA.

**Key words:** PVA, bentonite, nanocomposite, thermal properties.

## Sampling of 5-ethylidene-2-norbornene in industrial flue gas

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UNI EN 14181:2005 defines a set of procedures for the quality control of a Continuous Monitoring System (Automated Measurement System - AMS) in order to meet the requirements of data uncertainty on the measured values by European legislation (EU Directive) and national or more generally by the competent authorities. 5-ethylidene-2-norbornene (ENB), is a reactive volatile organic compound used in industrial synthesis of terpolymers. Since there is no reference method for the determination of the mass concentration of gaseous ENB in industrial flue gases, a discontinuous method to be used as a reference for the calibration and the validation of the AMS installed on the plant has been developed. The plant selected for the sampling produces terpolymeric elastomers in a closed reactor. The plant is equipped with two abatement systems: two coal beds acting as a scrubber and a cyclonic scrubber. About 6 L of flue gas has been collected inserting a titanium probe (1 m length) in the stack at about 30-m height. The AMS installed on the plant is an online gas chromatography–flame ionization; it was calibrated and validated following the requirements of QAL2 (Quality Assurance Level 2) of the UNI EN 14181. The concentrations of ENB obtained with both the discontinuous and the online method were compared. In addition, several manual measurements were performed in parallel, and the resulting %RSD repeatability was <9 %. Furthermore, to ensure the calibration of the AMS for the widest possible range of concentrations, in agreement with the plant manager and the supervisory authorities, some measurements were carried out with abatement systems excluded, in order to evaluate the influence of humidity on the efficiency of the charcoal cartridges used for sampling. The measured concentrations were lower than those obtained by the online instrument.

ENB has a high volatility at ambient temperature (5.6 hPa at 20 °C); at the stack temperature (120 °C), the value is eight times higher. This characteristic leads to an error in sampling due to the potential polymerization of the molecule for its condensation passing from a higher to the environmental temperature. The method presented in this study involves the use of *para*-tert-butylcatechol (*p*-TBC) on activated coated charcoal cartridges to sample flue gas emissions.

After sampling, the coal was removed from the glass cartridges and desorbed with toluene. Decane and n-nonane were used as internal standards. Since ENB exists as *exo* and *endo* isomers, quantification has been done using the sum of the areas of both peaks. Beside the retention time, the ENB was identified by the ratio of peak areas (the ratio of *endo*/*exo* isomers was 76/24).

The developed method provides a discontinuous technique to measure reactive volatile organic compounds using easy-to-use instruments and assures a very good accuracy and precision even with high-humidity gas flows. The method could be extended to other reactive compounds of the same class.

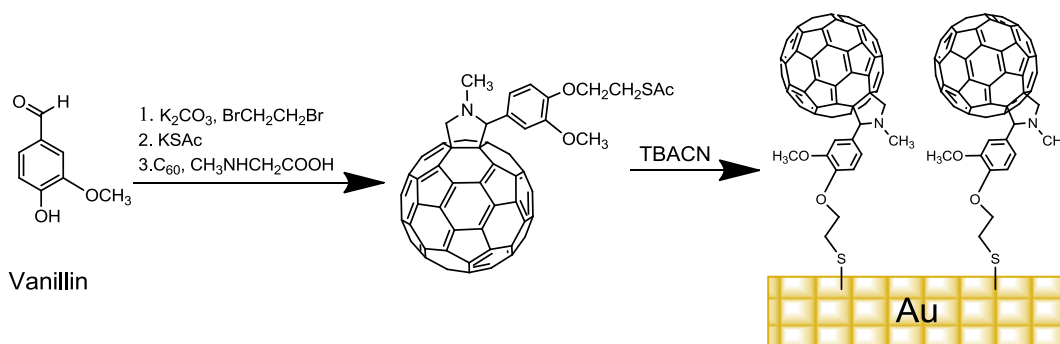
## Vanillin-derivatized C<sub>60</sub> fullerene SAMs on gold electrode surface as example of green engineering

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Green engineering is the design, commercialization and use of devices, which minimize generation of pollution at the source, risk to human health, and the environment when using renewable resources [1]. For this purpose, we produced fullerene based nanocomposites using vanillin, natural occurring compound extractable from the seed pods of *Vanilla planifolia*, which is widely used as a flavouring agent in the fragrance industry, foods, pharmaceuticals and as a chemoattractant for the isolation of diverse microorganisms. Of particular interest for our group is the field with potential applications of fullerene derivatives in the environmentally safe engineering. The unusual structure and electrical properties of C<sub>60</sub>, for example it can be reduced reversibly with up to six electrons [2], trigger numerous research projects aimed at developing new fullerene-based materials with useful applications. It is hoped that the combination of naturally sourced compounds with the advantageous properties of fullerene derivatives will contribute to the development of the green engineering [3].



In this work, we synthesized a series of vanillin-functionalized fullerenes from thioacetyl vanillin derivatives and C<sub>60</sub> fullerene according to the Prato method [4], thus, the desired green technology was applied from the start. Functionalization of fullerenes by attaching aromatic rings leads to electroactive and photoactive fullerene derivatives. Simultaneously, according to literature data [5], thioacetate derivatives can be efficiently deprotected *in-situ* and form well ordered and stable self assembled monolayers on gold surface. This gives a chance to produce nanocomposites by chemisorption of vanillin-functionalized fullerenes on Au (111) surface.

Our results show that thioacetyl-vanillin derivative functionalized fullerenes form highly ordered and stable self assembled monolayers on gold surface that may find practical application in various environmental friendly high-tech devices. The resulting products were analyzed by Mass Spectrometry (ESI-MS), Magnetic Resonance Spectroscopy <sup>1</sup>H NMR, Infra-Red Spectroscopy (IR), UV-Vis Spectroscopy, Scanning Tunneling Microscopy (STM) and electrochemical methods such as Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV).

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## Synthesis, Properties and Performance of Eco-friendly Curcumin-derived Plasticizers for Poly(vinyl chloride)

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Plasticizers are widely used for their effectiveness in reducing the hardness, density, melt viscosity, glass transition temperature, and volume resistivity of a polymer. They are employed in a wide range of industries such as the biomedical, construction, plastics, and others. Phthalate esters are the most widely used plasticizers for their suitable applications and availability, and account for 92% of the plasticizers produced worldwide. Its limitation lies in that phthalate esters have been reported to migrate out of the polymers, making them less flexible and less efficient. It is also associated with endocrine disruption, reproductive and developmental toxicity in humans, and with negative environmental impact on plants and animals. There is an urgent unmet need to develop eco-friendly alternatives to phthalates with reduced toxicity and improved overall characteristics.

Curcumin is the active ingredient in the curry spice turmeric, it is Generally Regarded as Safe by the FDA. The molecule is rigid in structure with two phenolic groups that can be modified covalently. We synthesized green eco-friendly plasticizers based on curcumin (curcumin diesters) via the mixed anhydride esterification method. The feasibility of the synthesis was established by using Stearic acid in the presence of minimum amount of acetic anhydride and 2% mole of Dimethylamino pyridine (DMAP). The Curcumin-distearate was isolated via column chromatography to produce the final product, yield 67%. The structure of curcumin-distearate was confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectroscopy (MS), and Infrared spectroscopy (IR). These plasticizers were blended to PVC in various percentages: 5%, 15%, 25%, and 35% to test their effectiveness in inducing depression of the glass transition temperature in the polymer/ plasticizer matrix. Leaching experiments in water and in hexane showed that the curcumin-derived plasticizer had improved resistant to migration under extreme conditions. The curcumin distearate has a reduced effect on the viability of Hela cells at concentrations higher than what would normally be found in the environment (0.125, 0.25 and 0.5 mg/mL). These results were compared to control samples: same polymer blended with Dibutyl Phthalate. The curcumin-derived plasticizer produced is better from both ecological and toxicological viewpoints.

## Gelatine recovering from wet-blue shavings

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Leather Industry is one of the oldest and most traditional, but also strongly problematic concerning the environmental aspect, mainly because of the high amount of solid waste and wastewater. Thus, in the promotion of increasingly demanding ecological values and environmental law compliance, intervention measures for the tannery wastes management have been studied, framed with the reality and with application viability. This work aims to contribute to solving this problem, as it is based on the study of new methodologies for recovering gelatine from wet-blue shavings.

In that way, gelatine extraction was carried out through an alkaline hydrolysis process with magnesium oxide. Different technical conditions were evaluated for their yield in gelatine production, such as amount of magnesium oxide, temperature and extraction time.

The results showed that, from all the tested conditions, the best extraction was carried out with a quantity of magnesium oxide of 12% (w/w), for 2 h of extraction time at 80°C, allowing for the recovery of about 60,3%. These conditions lead to a gelatine (organic phase), with a negligible concentration of chromium, and a chromium cake. For further use in several industries, as a raw material, gelatine must be concentrated and reduced its salinity.

**Keywords:** Wet-Blue shavings; Alkaline Hydrolysis; Gelatin

## Degradation study based in Ultraviolet light test of EVA encapsulant of photovoltaic modules

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The degradation study of photovoltaic modules is a subject of great interest for the industry sector. Although the degradation of PV cells has been previously studied [1, 2,3,4], these studies have been focused on the explanation of semiconductor material degradation. There are other causes such as glass breakage (front and back of the module), oxidation, junction box connections corrosion, delamination and bubbles formation in the encapsulant, back sheet polymer cracks, etc. The manufacturing process of photovoltaic modules is very standardized. Most are formed by a sandwich clear glass, low iron content, ethylene vinyl-polymer acetate (EVA), cells, EVA and backsheet (usually Tedlar-Polyester-Tedlar or only one film of polyester). The use of EVA as encapsulant polymer allows maintaining a good optical transmission in a prescribed spectral region providing high visible transparency, excellent mechanical properties, good electrical isolation, etc. However, EVA is one of the polymer materials developed for the encapsulation of crystalline Si-based PV modules. EVA film presents different degradations along the time: it can develop a slow degradation from light yellow to dark brown colour. However delamination and bubbles formation are the most concerning problems related to EVA. They are related not only to the bad quality of EVA but also to a bad process of lamination, where the cross-linking process has not been well performed. Due to ageing and temperature changes the EVA degradation can lead to a high power loss of the module or even its rejection.

The tests for this work were performed according to the recommendations of the UNE-EN 61646:2008 "thin-film photovoltaic modules for terrestrial use", with the necessary adjustments in order to apply to a single cell. The set of glass films and EVA were soaked to ultraviolet (UV) radiation at different exposure times. By optical analysis a correlation between degradation, time and EVA thickness has been observed. Defects like EVA delamination due to a lack of adherence and colour change were detected by visual inspection and they were found to be related to exposure time.

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## Biocompatible Gels from Amino Acids

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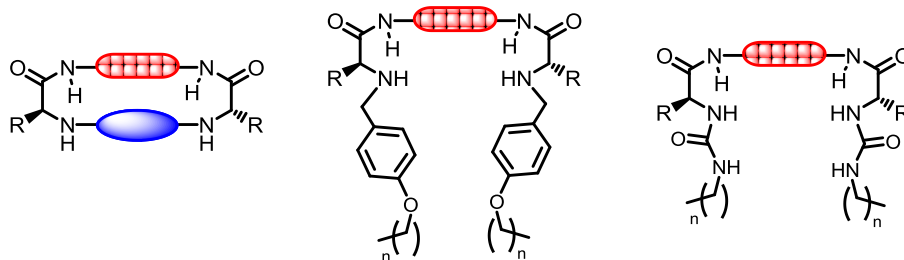
Gels have many applications, including alimentary industry, cosmetics, medicine... They are formed when a compound present in a solution forms a highly cross-linked fibrillar network in which the solvent molecules remain entrapped. The resulting material has intermediate character between solids and liquids. Usually, gels are classified according to the nature of the solvent involved. Thus, hydrogels refer to gels formed in the presence of water, while organogels are those in which organic solvents are involved.

Most of the commercial gels are based on polymeric gelators. Moreover polymeric materials of this class, even those considered non-toxic, are becoming a new class of emerging pollutants. Nevertheless, the use of low molecular weight gelators has an increasing interest because these materials are built by self-assembling on building blocks using non-covalent interactions that are reversible and highly controllable. This allows a more efficient design and fine-tuning of gelating agents. In general, good gelators can act in concentrations as low as 1–5% w/w, or even lower.

As a consequence, a large number of technological applications have recently been reported. For example, gels can be formed/destroyed by changes in temperature, pH, or a particular biomolecule. First of all, topical application in the form of gel increases the contact time, thus favoring the action of the active principles. In addition, it limits the application to the specific desired area, reducing the side effects on other areas, i.e., local irritation. Finally, the occlusion of the active principle in a complex matrix can control the release rate of the active principles, and the capacity of the gelator molecules to interact with other compounds via supramolecular interactions can be used to regulate this capacity.

Three main properties can be used to define the efficiency of a given gelator: the minimum concentration of the compound in a given solvent at which the gel is formed; the solvents for which the compounds are able to act as the gelator; and the stability of the gel in the presence of external stimuli such as pressure, temperature and pH changes.

In this context we will present our efforts towards the design and preparation of biocompatible organogelating based of pseudopeptidic structures similar to those depicted in the Scheme.<sup>1–3</sup> Some of those systems based on simple natural starting materials and easily biodegradable can reflect their intrinsic chirality in the self-assembly fibers provide in-situ gelation in water/alcohol systems<sup>2</sup> or give place to high-temperature stable gels in a large variety of solvents.<sup>3</sup>



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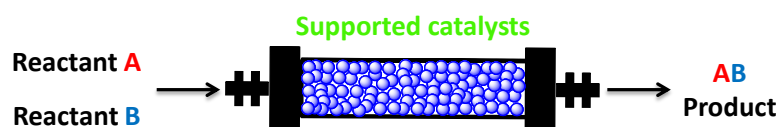
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## Sustainable Chemical transformations under continuous flow

Sergio Martín<sup>1</sup>, Raúl Porcar<sup>1</sup>, Eduardo García-Verdugo<sup>1</sup>, Belén Altava<sup>1</sup>, M. Isabel Burguete<sup>1</sup> and Santiago V. Luis<sup>1</sup>

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Many research efforts need to be driven to the development of practical processes for the preparation of Fine Chemicals and Pharmaceutical products. In this context, a large number of catalytic transformations have been described. One straightforward approach to implement the potential for practical use and their “Green character” is the catalyst immobilization on a solid support. This facilitates the work-up, particularly recycling and reuse, decreases the toxicity of catalytic materials and can significantly reduce the final amount of waste. In recent years, we have been exploring the use of functionalised polymers as heterogeneous reagents and catalysts.



**Fig. 1.** Sustainable Chemical transformations under continuous flow.

Functionalized resins of different nature (gel or macroporous type) and shapes (beads or monolithic polymer) are suitable to prepared fixed-bed catalytic microreactors that can be used efficiently even under flow conditions.

Here, we report the use of minireactors based on functional polymers with different catalytic sites. Such minireactors were assayed for different chemical transformations under continuous flow conditions. Interesting results were obtained in some cases including long-term stability, increasement of the activity and selectivity over the homogeneous analogues.

### Acknowledgements

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## Porous materials made from a paper mill by-product and the life cycle assessment of their environmental impacts

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Black liquor is a complex mixture of water, inorganic salts and organic matter. It comes from the pulp making process and results from the combination of lignin extracts and the chemicals used to produce the pulp. Until now most of the paper mills burn it to provide energy for their own purpose. However from a waste hierarchy point of view material recycling is preferred to energy recovery. Therefore we consider options to divert black liquor in other ways (biofuels, biopolymer...) particularly due to the presence of lignin.

We have developed a process allowing the preparation of porous monoliths directly from black liquor. This technique is based on an emulsion-templated polymerization and calls upon a one-pot strategy. Porosity is generated by using castor oil as porogenic agent and lignin is thermally crosslinked to form the solid polymeric network. The obtained material is a cylinder-shaped monolith showing a homogeneous macroporous structure (see Fig. 1&2).

A gate-to-gate life cycle assessment was performed to compare the environmental impacts of two different green chemistry approaches of the developed synthesis using laboratory data. Those two methods focus on the washing stages and the recycling of resulting by-products and solvents.



Figure 1: Cylinder-shaped monolith

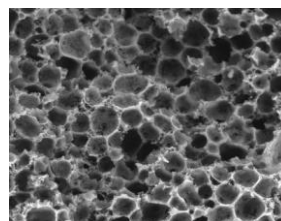


Figure 2: MEB image of the porous structure

## Simple Chiral Ionic Liquids (CILs) from amino acids for the development of chiral media

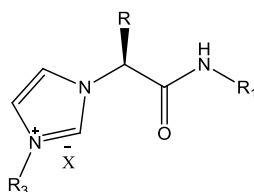
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Ionic liquids (ILs) are one of the most versatile green alternatives to traditional organic solvents and many applications have been reported for them, including their use as extraction liquids, electrolyte materials or as structured media for other technological applications such as enhancing the sensitivity of thermal lens measurements.<sup>4</sup>

On the other hand, the introduction of chirality adds new values to the ionic liquids, providing the access for the development of chiral media. In this context, our group has been involved in the last years in the preparation and study of different chiral ionic liquids (CILs).<sup>5</sup> Recently we have synthesized a new family of CILs using natural amino acids as the source of chirality and containing an amide group as an essential structural feature (1). We have described the synthesis of these chiral imidazolium salts as potential room temperature ionic liquids that leads to a large variety of configurationally and structurally diverse CILs (see Figure 1), and the studies of their supramolecular structure in the solid state (X-Ray) and in solution (<sup>1</sup>H NMR) of 1 (R = Ph, R<sub>1</sub> = Bn, R<sub>2</sub> = nBut).<sup>6</sup>

In this communication, we present an analysis of their efficiency as catalysts, co-catalysts and/or chiral media for the aldol condensation reaction. The results obtained confirm how this family of CILs provides new mechanisms for the transfer of chirality in the considered aldol reactions.



**Figure 1.** General structure for the room temperature CILs.

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## Calcined hydrocalumites as basic catalysts for the obtention of glycerol carbonate by transesterification of glycerol

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In the last years, the production of biodiesel has increased considerably as alternative to fossil fuels. In this reaction, glycerol is obtained as by-product in high amounts, being necessary its transformation to high-added value products to improve the economy of the whole process. Moreover, the use of microwaves for the preparation of materials decreases the synthesis time/temperature, saving energy. The aim of this work was the preparation of several hydrocalumites by coprecipitation of chloride (HC1) or nitrate salts (HC2) of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  ( $\text{Ca}/\text{Al}=2$ ) with NaOH. Samples were aged in autoclave at 180°C for 1 h with microwaves (AMw) or by conventional heating (AC) and later calcined at 450°C and 750°C (Table 1). Calcined hydrocalumites have been tested as catalysts for the transesterification of glycerol with dimethyl carbonate to obtain glycerol carbonate (GC), which is a product of industrial interest used as precursor of polymers, such as polycarbonates or polyurethanes.

**Table 1.** Characterization and catalytic activity results of calcined hydrocalumites.

Catalysts	Crystalline phases (XRD)	BET area ( $\text{m}^2\text{g}^{-1}$ )	Conversion (%)	Selectivity to GC (%)	Selectivity to Glyc (%)	Basicity Strength
HC1AC-450	Amorphous	10	56	70	30	6.8 <math>\text{H}^+> 8.2
HC1AMw-450	Amorphous	13	51	69	31	6.8 <math>\text{H}^+> 8.2
HC2AC-450	Amorphous	9	50	49	51	6.8 <math>\text{H}^+> 8.2
HC2AMw-450	Amorphous+ mayenite	15	76	61	39	6.8 <math>\text{H}^+> 8.2
HC1AC-750	Mayenite + CaO	5	99	87	13	13.4 <math>\text{H}^+> 15
HC1AMw-750	Mayenite + CaO	4	98	85	15	13.4 <math>\text{H}^+> 15
HC2AC-750	Mayenite + CaO	8	87	78	22	13.4 <math>\text{H}^+> 15
HC2AMw-750	Mayenite + CaO	11	95	86	14	13.4 <math>\text{H}^+> 15

GC: glycerol carbonate; Glyc: glycidol. Reaction conditions: 90°C, 3h, 0.15 g catalyst, inert atmosphere.

XRD patterns of the hydrocalumites calcined at 450°C were amorphous due to the formation of a mixture of the mixed oxides,  $\text{CaAlO}_x$ . Additionally, crystalline mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) was detected in low amounts for HC2AMw-450. After calcination at 750°C, a mixture of mayenite and CaO was obtained for all samples, resulting in higher basicity strength, as determined by Hammet indicators (Table 1) and  $\text{CO}_2$  TPD. Hydrocalumites calcined at 750°C showed higher conversion and higher selectivity to glycerol carbonate than those calcined at 450°C. This can be explained by the higher amount of stronger basic sites present in these samples. Catalysts obtained from chloride salts and calcined at 450°C were more selective to glycerol carbonate than those prepared from nitrate salts and later calcined at the same temperature. This has been correlated with the differences observed in the amount and surface density of basic sites for these catalysts.

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## Photocatalytic Hydrogen Production by Water Splitting Using ZnCdFeCuS Nanoparticles Under UV-vis Light Irradiation

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Photocatalytic water splitting with generation of hydrogen is a green process that concerns activity of a semiconductor material under sunlight irradiation and ambient pressure and temperature. This process has been regarded as a promising solution to resolve the global energy and environmental problems. In this research, photocatalytic hydrogen generation by water splitting ( $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2 (\text{g}) + 1/2 \text{O}_2 (\text{g})$ ) has been studied on photocatalysts based on ZnCdFeCu solid solutions, synthesized by coprecipitation of the metal precursors. Iron and copper nanoparticles were incorporated as cocatalysts to enhance the photocatalytic activity of the ZnCd solid solution. The effect of the different synthesis parameters (synthesis temperature, elemental atomic ratios, amount of Cu and Fe incorporated in the catalyst and calcination temperature) on the photocatalytic production of hydrogen has been studied in order to determine the best experimental synthesis conditions. The catalysts have been characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), and BET. The experiments of photocatalytic water splitting were performed in aqueous solution of the photocatalyst previously dispersed in a soft ultrasonic bath. The reaction mixtures were irradiated at different light wavelengths (from 220 to 700 nm) using a solar simulator and appropriate cutoff filters in a static air atmosphere. To facilitate the catalyst dispersion in the reactant solutions, a magnetic stirrer was used. The evolved gases were analyzed by gas chromatography with a thermal conductivity detector using  $\text{N}_2$  as carrying gas. The photocatalytic activity was found to be clearly dependent on the specific area of the photocatalyst.

## Synthesis, Characterization of Au@TiO<sub>2</sub> Nanowires and their Production of Hydrogen by Water Splitting Under UV-vis Light Irradiation

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The surface of the Earth's crust receives more than 95% sunlight in the range of visible light (mostly 400-600 nm) and for this reason visible light driven photocatalysts have been heralded as a crucial breakthrough in photocatalytic processes for water splitting. In fact, from a practical point of view, the most important factor for applying the sunlight absorption to water splitting for hydrogen production is the discovery of efficient and stable photocatalysts. These photocatalysts are semiconductor materials consisting of essentially an electron occupied valence band and an unoccupied conduction band. This process has been regarded as a promising solution to resolve the global energy and environmental problems.

In this research, photocatalysts based on Au@TiO<sub>2</sub> nanowires have been synthesized by hydrothermal approach. These catalysts were obtained as layers of ca. 100 nm-thick, that were grown on the surface of monocrystalline Si (100) wafers. The catalytic activity was measured by putting water (with Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagents) into contact with the Au@TiO<sub>2</sub>NWs catalyst supported on Si wafers, at room temperature and atmospheric pressure. The water splitting reaction was conducted in a quartz reactor equipped with a water-cooling jacket. The reaction mixtures were irradiated at different light wavelengths (from 220 to 700 nm) using a solar simulator and appropriate cutoff filters in a static air atmosphere. The evolved gases were analyzed by gas chromatography with a thermal conductivity detector using N<sub>2</sub> as carrying gas. The effect of the different synthesis parameters (synthesis temperature, Au-Ti atomic ratio, and calcination temperature) on the photocatalytic production of hydrogen has been studied in order to determine the best experimental conditions. The catalysts have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET.

## Carbon footprint analysis of rapeseed oil production in Romania

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A carbon footprint analysis to quantify the greenhouse gas (GHG) emissions of rapeseed oil production in Romania was conducted. Considering the LHV of diesel oil of 42,8 MJ·kg<sup>-1</sup>, 1,13 kg. of rapeseed oil was compared with 1 kg. of diesel. The results show that the use stage is the one with the highest impact for both fuels, in which rapeseed oil registers a total quantity of 2.808,521 kg CO<sub>2</sub> eq. and mineral diesel registers a total quantity of 3.156,499 kg CO<sub>2</sub> eq. The second most impacting activity for rapeseed oil is the extraction of the oil from the seeds, with a total contribution of 0,626 kg CO<sub>2</sub> eq. and the third activity with regard to greenhouse gas emissions is fertilizer application with an impact of 0,215 kg. CO<sub>2</sub> eq. Considering that rape plant absorbed during growth stage the same quantity of CO<sub>2</sub> as emitted into atmosphere during usage stage, when compared the two fuels, rapeseed oil obtains clear benefits against fossil diesel. Results show that by substituting diesel with rapeseed oil a total quantity of 5.964,300 kg. CO<sub>2</sub> eq. / 42,8 MJ can be saved. The results can still be improved by changing the type of fertilizer used with alternative ones from agriculture.



## **Emerging Pollutants**

**Oral presentation: OE1-OE16**

**Poster presentation: PE1-PE66**

## Contaminants of emerging concern in the agro-environment:

### Uptake by crops, fate and processes

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Due to water scarcity in the Middle East, reclaimed wastewater is essential water source to maintain productive agriculture. Irrigation with reclaimed wastewater accounts for 50% of total irrigation water in Israel. This unique situation of intensive irrigation with reclaimed wastewater and sludge application containing residues and active pharmaceutical and personal care products (PPCPs) provides an excellent opportunity to study the long-term exposure effects of these compounds in soils. The long-term introduction of PPCPs to arable land may affect the agro-ecosystem in various aspects which are not known to date.

PPCPs were detected in crops irrigated with treated effluents. Higher concentrations of PPCPs were detected in leaves versus roots and fruits. This is related to the mechanism of uptake and translocation. PPCPs concentrations in fruits and leaves were negatively correlated with the level of organic matter in the growing medium. Some PPCPs were detected in the soil's profile at the end of the growing season. Carbamazepine is highly persistent in soil ( $t_{1/2}$  of several years), whereas the other investigated PPCPs exhibited much lower persistency ( $t_{1/2}$  of days-weeks).

Column-leaching experiments revealed that composted biosolids generally increase the retardation of PPCPs. However, treated effluents increased the mobility of weakly acidic PPCPs in the biosolids-amended soil columns. Experiments conducted with an environmentally relevant PPCPs concentration (1  $\mu\text{g/L}$ ) indicated a higher degree of irreversible sorption and low leachability as compared to higher PPCP concentrations.

This study emphasizes the potential uptake of active pharmaceutical compounds by crops in organic-matter-poor soils irrigated with reclaimed wastewater and highlights the potential risks associated with this agricultural practice.

## Occurrence of emerging organic micropollutants in urban wastewaters –

### Non-targeted analysis using GCxGC TOF MS and LC-HRMS

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Direct and indirect human consumption and use of chemical compounds (pharmaceuticals, personal care products, pesticides, plasticizers, etc...) induce a contamination of wastewater with a wide range of organic compounds. Identifying organic pollutants in environmental water is a huge concern to adapt water treatment process and provide the best water quality in a final objective of protecting environment and health. The BIOTTOPE project is designed to improve the quality of Waste Water Treatment Plants effluents, to reach a “good status” for coastal and inland waters. The project will implement, test and validate at two test sites, in France and in Belgium, a new prototype water treatment technology at the semi-industrial scale, based on activated carbon adsorption and on an accelerated settling step to remove micro-pollutants. Treatment efficiency is monitored with an on-line read-out system with small biological aquatic organisms - tadpoles or fish larvae – (to assess endocrine disruption effect) and also by targeted and untargeted chemical analysis. This presentation will focus on the results obtained on untargeted analysis.

First the strategie developed to highlight organic pollutants is explained. In order to analyse both apolar and polar compounds, samples are analysed with two screening techniques. Apolar and semi-polar molecules are extrated with the sensitive Stir Bar Sorptive Extraction (SBSE) and analyzed by in-line thermal desorption and Comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GCxGC TOF MS). Polar and mid-polar compounds are extracted with a large scale liquid/liquid extraction protocol and analysed on a LQT-Orbitrap high resolution mass spectrometer (LC-HRMS). Organic pollutants are identified thanks to homemade databases containing more than 1000 compounds for GCxGC TOF MS and 1500 compounds for LC-HRMS. The first results acquired on BIOTTOPE samples are discussed and compared to results obtained on a previous study, on 12 French sewage treatments plants. Recurrent organic micropollutants, mainly pharmaceuticals but also pesticides that are not targeted in our usual quantification methods were identified. 39 recurring organic compounds are detected with LC-HRMS in 100% of samples and 41 additional compounds in more than 80% of the samples. 30 molecules are identified as recurrent with GCxGC TOF MS. Some of these compounds are not included in French or European prioritisation lists. The toxicity evaluation of some recurrent compounds will be introduced. The talk will also present an attempt to explain the absence of recurrent substances from the existing prioritized lists.

All these results are useful in order to establish the list of relevant compounds that will be included in the future quantification methods and to improve the treatment process of wastewater.

## Toward a robust method for in situ separation, speciation analysis, and toxicity assessment of nanoparticles in natural water samples: Cloud point extraction of CuO nanoparticles

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To date, several detection and determination techniques of engineered nanoparticles (ENPs) suffer from environmental interferences. Hence, their application has been limited to synthetic, rather than real-world samples [1]. Previously, we found the optimum cloud point extraction (CPE) conditions using Triton X-114 (TX-114) for ZnO NPs by utilizing chemometrics [2]. This work reports the speciation analysis of some of the most toxic ENPs, CuO nanoparticles (CuO NPs) in aquatic environments, and in the presence of Cu(II) ions as well as environmental interferences (electrolytes, natural organic matters, particles). The efficiency was determined by inductively coupled plasma mass spectrometric determination of the TX-114-rich phase after microwave digestion. The best recovery of 89.3% was obtained for 1 mg.L<sup>-1</sup> CuO NPs with 0.3% w/v of TX-114, pH = 8.5, incubation time of 45 min, and incubation temperature of 40 °C. Enrichment factor was in the range of 81 (0.3%) to 151 (0.05%w/v of TX-114). The detection limit of 0.01 µg.L<sup>-1</sup> was achieved. The ionic copper species would likely adsorb onto the NP surface [3], co-extracted into the TX-114-rich phase, and co-measured. Hence, ethylenediaminetetraacetic acid (EDTA) as both the complexing ( $k_f = 5.0 \times 10^{18}$ ) and masking agent was used to separate CuO NPs from copper ions. The pH was set to 6.3 to avoid precipitation of Cu(OH)<sub>2</sub> ( $K_{sp} = 2 \times 10^{-19} \text{ mol}^3.\text{L}^{-3}$ ). The apparent efficiency did not increase significantly (<7%) in the presence of 3 mg.L<sup>-1</sup> Cu(II) and 10 mM EDTA.

The optimized conditions were successfully applied to spiked NPs in genuine samples (river and seawater, 0 – 100 µg.L<sup>-1</sup>). The results were compared with the direct measurement of CuO NPs in these samples. The recoveries of CPE and direct analysis were in the range of 78.5 – 84.4%, and 70.2 – 113.1%, respectively, exhibiting the interference of solution chemistry. The results show that the CPE technique enables speciation analysis of ENPs in their native states as well as facilitating their detection, thanks to the enrichment of the NPs in the surfactant-rich phase. The technique is robust for assessing exposure risks of ENPs to aquatic organisms as well as both cost-effective and environmentally friendly.

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## Agglomeration and sedimentation of Titanium dioxide nanoparticles (n-TiO<sub>2</sub>) in synthetic and real waters

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The recent detection of Titanium dioxide nanoparticles (n-TiO<sub>2</sub>) in wastewaters raised concerns about its fate in the aquatic environment, which is related to its mobility through water bodies. Laboratory experiments of n-TiO<sub>2</sub> (particle size distribution: 10-65 nm) dispersed into both synthetic and real aqueous solutions under environmentally realistic concentrations (0.01, 0.1, 1 and 10 mg/l) were conducted over a time of 50 h to mimic duration of ecotoxicological tests. Agglomeration and sedimentation behaviour were measured under controlled conditions of salinity (0-35 ‰), ionic composition and strength, pH and dissolved organic carbon (DOC). Physico-chemical parameters and particle agglomeration in the dispersions were investigated by Transmission electron microscopy (TEM), Brunauer, Emmett and Teller method (BET), and Dynamic Light Scattering (DLS). A fluorescence spectrophotometer operating in the nephelometric mode was employed to obtain the sedimentation rates of n-TiO<sub>2</sub>. The overall results showed that agglomeration and sedimentation of n-TiO<sub>2</sub> were affected mainly by the initial concentration. Sedimentation data fitted satisfactorily ( $R^2$  in the range of 0.74 to 0.98; average  $R^2$ : 0.90) with a first-order kinetic equation. The rate constant,  $k$ , and thus the settling rate, increased by approx. one order of magnitude moving from the lowest to the highest concentration, resulting very similar especially for dispersions at 1 ( $k = 8 \cdot 10^{-6} \text{ sec}^{-1}$ ) and 10 mg/l ( $k = 2 \cdot 10^{-5} \text{ s}^{-1}$ ) n-TiO<sub>2</sub>, regardless the ionic strength and composition of dispersions. The implications of these results on toxicological testing are discussed.

## Enhanced emerging contaminants removal during artificial recharge with a reactive barrier.

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Emerging contaminants such as pharmaceutical active compounds (PhACs), personal care products (PCPs) and pesticides are increasingly found in the environment. Several studies have demonstrated that many emerging contaminants exhibit a recalcitrant behaviour in conventional waste water treatments plants (WWTP) and in the aquatic environment. Therefore they reach surface and ground waters and in some cases even drinking water. Laboratory studies have shown that the behaviour of many emerging contaminants is affected by the dominant redox conditions. However, data from field experiments are scarce and often contradictory. Artificial recharge is an option both for facing water scarcity and for improving water quality. However, published results are also contradictory regarding its ability to remove these emerging contaminants.

We propose installing a reactive barrier at the bottom of an infiltration basin so as to enhance the removal of a broad range of contaminants. The reactive layer consists of vegetable compost, aquifer material, clay and iron oxide. The reactive barrier targets are 1) to add easily degradable organic matter to the recharge water to promote biodegradation and development of different redox zones, and 2) to increase sorption surfaces for neutral, cationic and anionic compounds. In this study, we present results of emerging contaminants removal using this concept at an experimental site.

The experimental site is located at Sant Vicenç dels Horts (Barcelona, Spain). Llobregat River water, which contains a high proportion of WWTP effluents, is used as recharge water. The infiltration system consists of a sedimentation basin and an infiltration basin. Infiltration tests have been performed before and after the installation of the reactive barrier. The system is equipped with a network of piezometers and suction cups. Infiltration, unsaturated zone and ground waters have been sampled and analyzed in order to elucidate the effect of the reactive barrier on contaminants removal. The results show the effectiveness of the reactive barrier in removing emerging contaminants from the infiltration water and thus improving the water quality.

## Chemodiversity of organic xenobiotics in the environment: a naming and scientific nightmare?

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Since the first discovery of organochlorine pesticides in the 60's, each following decade has shown new discoveries of organic environmental contaminants. Hydrocarbons (HCs, PAHs) in the 70s related to oil pollution, chlorinated compounds (PCBs revisited, PCDD, PCDF) in the 80s related to waste incineration and combustion sources, 2<sup>nd</sup> and 3<sup>rd</sup> generation pesticides (N-, S-, P-containing compounds) in the 90s linked to agriculture practices and finally nowadays the cloudy PPCPs used by everybody on the planet.

In parallel, the toxicity knowledge of organic compounds has strongly increased. In environmental monitoring studies, molecular markers of toxicity are now strongly associated with the detection level of contaminants.

As a consequence, a confusing puzzle of acronyms is associated with either chemical family names (PFOs, PBBs), physico-chemical properties (PBT), toxicity end-points (ED), or intended usage (PPCPs). These acronyms are used by many environmental stake holders (industry, research, regulatory agencies, NGOs) expanding the confusion.

This short presentation will focus on organic contaminants on research, toxicity and regulation aspects. It will attempt to clarify all these concepts and to show how some of them have been developed.

HC : Hydrocarbon ; PAH : Polycyclic Aromatic Hydrocarbon ; PCB, PCDD, PCDF : Polychloro-Biphenyl, - Dibenzodioxine, - Dibenzofurane ; PPCP : Pharmaceuticals and personal Care Products ; PFOS : Perfluorooctane sulfonate ; PBB : PolyBromoBiphenyl ; PBT : Persistent, Bioaccumulative, Toxic ; ED : Endocrine Disruptor

## Helping contaminants emerge: The role of high-resolution mass spectrometry in non-targeted analysis of organic micropollutants in aquatic systems

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The rate of identification of new and emerging contaminants in the aquatic environment has been limited heretofore by reliance on targeted analytical techniques, which depend on compound-by-compound verification using authentic standards. Recent advancements in high-resolution mass spectrometry (HRMS) and its application to the field of environmental chemistry has for the first time made possible identification of emerging contaminants in complex environmental mixtures without *a priori* knowledge of contaminant identity or occurrence. In this study, we present a strategy and analytical workflow based on LTQ-Orbitrap Velos HRMS and MS/MS in conjunction with new informatics tools (e.g. data processing, spectral library searching, and literature mining) for identification of emerging environmental contaminants in the aquatic environment *without* the aid of user-defined molecular databases. In this approach, high resolution ( $R > 100,000$ ) accurate mass (mass error  $< 2$  ppm) analyses of water & wastewater extracts are subjected to recursive peak assignment, adduct grouping, isotope pattern scoring, and molecular formula assignment. Chromatographic features and molecular formulas are then filtered using empirical indices (e.g., chromatographic peak shape, mass accuracy, isotopic pattern fit) and heuristic rules for the assignment of probable molecular formulas. Filtered chromatographic features are subjected to confirmation criteria for tentative identification. To this end, we demonstrate the capabilities of rule-based *in silico* fragmentation to aid in the structural elucidation of unknown contaminants without the benefit of reference standards. Utilizing a suite of environmentally relevant compounds, we have established a scoring scheme for assigning the certainty of identification and analytical figures of merit. Importantly, we demonstrate that the developed methodology exhibits low false-positive rates and acceptable false-negative rates for the intended applications.

We have applied this approach to identify organic microcontaminants in wastewater and wastewater-impacted surface waters in North Carolina, USA. Results illustrate our ability to identify a broad range of organic contaminants in water, including several compounds that have not been previously reported to occur in environmental systems. Beyond the structural characterization of organic microcontaminants in single compartments, we have determined differential contaminant occurrence profiles of *all detected compounds* by comparison of spatially distinct samples collected within engineered and environmental compartments. This approach surmounts previous challenges in the monitoring of transformation processes by highlighting contaminants possessing specific physicochemical characteristics (e.g., biodegradability, recalcitrance, etc.) without knowledge of chemical structure. These analyses have helped to illuminate environmental processes (e.g., biodegradation, photolysis) that may be important to the fate of micropollutants in aquatic systems.



## Development and application of a novel accurate mass based suspect screening methodology for the analysis of pharmaceutical residues in surface water by time-of-flight mass spectrometry

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The growing interest in analytical methods for multi-residue screening and target quantification of potential harmful micropollutants such as pharmaceuticals in the environment requests full-spectrum high-resolution mass spectrometry (HRMS). Instruments such as time-of-flight (TOF) MS have shown the potential to analyze and identify based on accurate mass a virtually unlimited number of analytes simultaneously and offer the ability for both suspect screening and target quantification [1-3]. In suspect screening using full-spectrum HRMS, there is no a priori need for standards because the acquired chromatograms are searched for the exact ion masses of a predefined list of suspect compounds within a certain mass tolerance. In a next stage, confirmation of the found suspects with analytical standards is possible, and a target quantification can be performed through validation of only the limited set of confirmed compounds. The challenge for such suspect screening and also the focus of the presented work is to define the optimum mass error tolerance and to develop a strategy that minimizes the false negative rate (5%) without detecting numerous false positives.

In a first step, different algorithms for the determination of the accurate mass were investigated. We showed that optimal mass accuracy was obtained after centroiding the spectra. Subsequently, a new suspect screening strategy was developed using large-volume injection ultra performance liquid chromatography coupled to TOF-MS aiming the detection of 69 pharmaceuticals in surface water. As a novel approach, the screening takes into account the signal intensity-dependent accurate mass error, which assured the detection of 95% of pharmaceuticals present in surface water. Application on five Belgian river water samples showed that 2/3 of the found peaks was finally confirmed by retention time of analytical standards.

The data obtained for the five Belgian river water samples revealed the occurrence of 30 pharmaceuticals belonging to different classes. Through full validation of the method, target quantification was performed and the applicability of the newly developed suspect screening method is discussed.

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## Environmental fate of nano-pesticides and implications for exposure assessment in the EU

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Pesticides are intensively used in agriculture and much effort is expended to manage and reduce possible deleterious effects on the environment. The development of new formulations for pesticides has long been a very active field of research. Nano-formulations are already used in the pharmaceutical or personal care products sector. In comparison, applications in the agrochemical sector are only just emerging and many predict a rapid growth in coming years. The anticipated new or enhanced activity of nano-pesticides will inevitably result in both new risks and new benefits to human and environmental health. It is unclear whether the current regulatory framework is adequate for the evaluation of these new products.

An extensive literature review was carried out to gain an overview of the current state of knowledge on nano-pesticides [1]. The objectives were (i) to explore potential applications of nano-technology within the pesticide formulation sector, (ii) to identify possible impacts on environmental fate, and (iii) to analyse the suitability of current exposure assessment procedures to account for their novel properties within the EU regulatory context. Nano-pesticides encompass a great variety of products and cannot be considered as a single category. Some nano-formulation are expected (i) to have significant impacts on the fate of active ingredient and/or (ii) to introduce new ingredients whose environmental fate is still poorly understood (e.g. nano-silver). Overall, the current level of knowledge does not appear to allow a fair assessment of the advantages and disadvantages that will result from the use of some nano-pesticides.

A more robust risk assessments framework for nano-pesticides is urgently needed. In this context, priority for research are to (i) identify the assumptions currently applied that are not valid in the case of nano-pesticides, (ii) evaluate the points or situations in which differences may impact significantly on the exposure assessment outcomes, and (iii) refine or adapt current assessment protocols as required. Preliminary experimental results for a series of nano-pesticides will be presented and discussed in this context.

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## Nano-Silver in drinking water and drinking water sources: stability and influences on disinfection by-products formation

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Nano-silver (nAg) is increasingly present in consumer products, from washing machines and refrigerators to products such as, “Magic Socks”. However, the nAg in these products may be released, ending up in surface water bodies used as drinking water sources. Little information is available about the stability of the nAg in sources of drinking water, its fate during drinking water disinfection processes and its interaction with disinfection agents and disinfection by-products (DBPs). This study aims to investigate the stability of nAg in drinking water sources and in the finished drinking water when chlorine and chloramines are used for disinfection, and to observe changes in the composition of DBPs formed when nAg is present in the source water.

A dispersion of Ag nano-particles (10 nm; PVP coated) was used to spike Ottawa River water, treated Ottawa River water, organic-free water and a commercial bottled water at concentrations of 1 mg/L and 0.1 mg/L. The diluted dispersions were kept at 4 C, for up to nine months and analysed weekly using UV absorption and atomic force microscopy imaging in order to assess the stability of the nAg particles. In a separate experiment, finished drinking water (i.e., treated Ottawa River water) containing the nAg dispersions was disinfected by adding sodium hypochlorite (chlorinating agent) in sufficient amounts to maintain a free chlorine residual of approx. 0.5 mg/L after 24 hours. The disinfected drinking water was then analysed for 34 neutral DBPs (trihalomethanes, haloacetonitriles, haloacetaldehydes, 1,1 dichloro-2-propanone, 1,1,1 trichloro-2-propanone, chloropicrin, cyanogen chloride) and the results were compared to the profile of DBPs obtained under the same conditions, in the absence of nAg and in the presence of an equivalent concentration of Ag<sup>+</sup> ions.

The stability of the nAg dispersions in untreated Ottawa River water (with a DOC concentration of 6 mg/L) was significantly higher than the stability of the nAg dispersions in distilled, organic-free water. Our data confirm previous observations that the natural dissolved organic matter stabilizes nAg particles. As expected, nAg was not stable in chlorinated Ottawa River water, but survived for many days in the Ottawa River water treated with chloramines.

The profile of DBPs formed in the presence of nAg was significantly different than the profile of DBPs formed in the absence of nAg but only for the 1 mg/L nAg concentration. The differences observed were mainly the reduced formation of some brominated DBPs and a small increase in the formation of cyanogen chloride. Some of the differences may be explained by the decrease in available bromide, due to the presence of Ag<sup>+</sup> ions. The concentration of 1 mg/L is significantly higher than nAg concentrations that would be expected in surface waters, but could be a significant issue for the disinfection of wastewaters.

## Persistent hydrophilic ethers (1,4-dioxane and glymes) in surface- and groundwaters

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In the present study six hydrophilic ethers were investigated: ethyl *tert*-butyl ether (ETBE), 1,4-dioxane, monoethylene glycol dimethyl ether (monoglyme), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) with respect to their distribution and behaviour in the surface- and groundwater at several locations in Germany and Poland. The selected ethers are highly miscible in water and have Henry's law constants ranging from  $1.04 \times 10^{-14}$  to  $1.64 \times 10^{-3}$  atm x m<sup>3</sup> x mol<sup>-1</sup> ensuring low volatility from aqueous solutions. Based on their octanol-water partition coefficient (log P<sub>ow</sub> = - 1.03 to 1.92) they exert negligible potential for bioaccumulation and are only weakly retarded by sorption to soil particles or suspended solids [1]. Therefore, the main target compartment of ETBE, 1,4-dioxane and glymes is presumed to be the hydrosphere. Moreover their physicochemical properties combined with their low biodegradability imply difficult removal from water and wastewater, which greatly increases the potential for surface-, groundwater and drinking water contamination.

The importance of investigating these compounds lies in their adverse toxicological effects. The International Agency for Research on Cancer listed 1,4-dioxane as a possible carcinogen to humans. Toxicological studies revealed that glymes pose risks to the reproductive and/or developmental systems causing infertility and harm to the unborn children [1]. Ethers chosen for this study have received increasing attention in the last years due to the large variety of their applications in industrial processes.

Solid phase extraction in combination with GC/MS-SIM was used to analyze numerous surface waters for the six hydrophilic ethers [2]. Initially, spot samplings of seven water bodies in Germany were done to determine the occurrence of the selected contaminants. Additional studies revealed an ubiquitous presence of 1,4-dioxane and glymes in the Rhine and the Oder River. 1,4-Dioxane concentrations in the Rhine and Oder River ranged from 0.184-1.541 µg/L and 0.364-1.923 µg/L, respectively. Tetraglyme was present in the Oder River from 0.041 to 2.133 µg/L. These results suggest a significant processing/use of these ethers in both Poland and Germany. In addition, presence of 1,4-dioxane was studied in 24-h composite samples for a period of two weeks. These results showed an inverse relationship of 1,4-dioxane concentration to the water discharge (m<sup>3</sup>/s), suggesting its continuous entrance with wastewater effluents.

Moreover, bank filtration and groundwater samples from the Oderbruch area have been analyzed. 1,4-Dioxane and tetraglyme were detected in the bank filtrate at concentrations 1.090 -1.467 and 0.693-1.403 µg/L, respectively. Also triglyme was present at significant concentrations (100- 149 µg/L). All three ethers were furthermore present in the groundwater up to 1150-2560 m from the Oder River with an estimated groundwater age between 5.9 and 41.9 years. These results show that 1,4-dioxane and glymes are not readily biodegradable and, therefore persist in the anoxic environment, demonstrating the need for further research.

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## THE PYRIDINE-ANALOGUE OF 2,3,7,8-TCDD IS FORMED IN THE THERMAL TREATMENT OF CHLORPYRIFOS AND 3,5,6-TRICHLORO-2-PYRIDINOL

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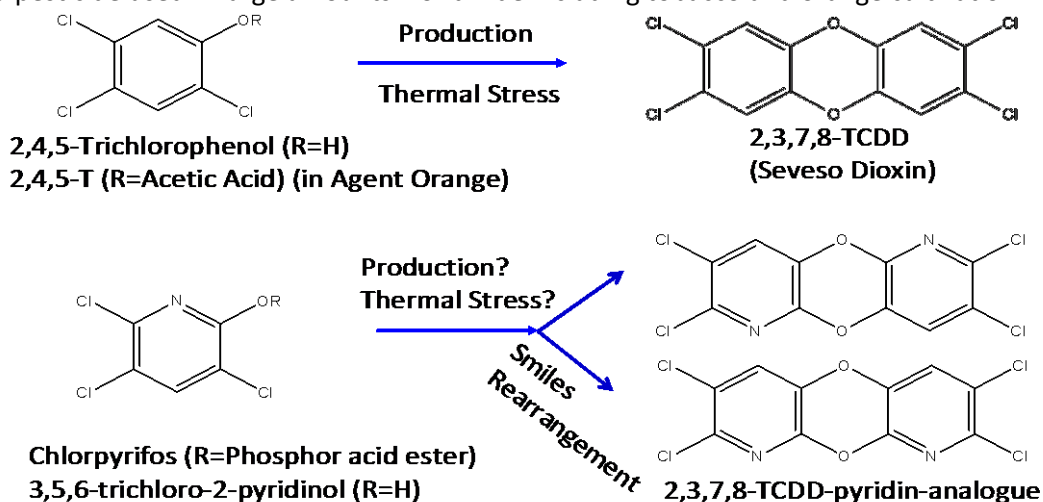
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Pesticides have contributed significantly to the global Dioxin contamination. From a historic perspective 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and 2,4,5-trichlorophenol – precursors of 2,3,7,8-TCDD (Figure) – resulted in large contaminated area during the Vietnam War, from agricultural application and from production/disposal. While today 2,4,5-T is not approved for use in the European Union, other high production volume pesticides used today – chlorpyrifos and chlorpyrifos-methyl – have as chlorinated aromatic moiety the pyridine-analogue of 2,4,5-trichlorophenol (3,5,6-trichloro-2-pyridinol) (Figure). Therefore, these pesticides are potential precursors of the pyridine-analogues of 2,3,7,8-TCDD (2,3,7,8-TCDD-Py; Figure).

In thermal treatment at 380°C (15 minutes) in ampoules both pesticides formed cis and trans 2,3,7,8-TCDD-Py. The formation levels from chlorpyrifos-methyl were six times higher than from chlorpyrifos. Levels were however approximately two orders of magnitude lower compared to the 2,3,7,8-TCDD-Py formation potential of 3,5,6-trichloro-2-pyridinol (TCPy). Dioxin-like toxicities were assessed with DR-CALUX<sup>TM</sup>. For chlorpyrifos (purchased as standard), no dioxin-like toxicity was detected in the crude sample (note that the detection limit was 20 ppm due to the small amount dissolved). Extremely high dioxin-like toxicity was detected from the treatment at 380°C of TCPy (143000 ng 2,3,7,8-TCDD bio-TEQ/g treated TCPy). Considering the detected dioxin-like activity, the formation of the 2,3,7,8-TCDD-Py from chlorpyrifos, chlorpyrifos-methyl and in particular their major degradation product TCPy highlights the necessity to investigate the formation of 2,3,7,8-TCDD-Py in real world scenarios like the combustion of post-harvest residues, cigarette smoking or fires in pesticide production or storage as well as in the original pesticides, in particular when considering that chlorpyrifos is a pesticide used in large amounts worldwide including tobacco and orange cultivation.



## Characterisation of perfluorooctane sulfonate in a contaminated terrestrial ecosystem in Belgium

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Studies on the distribution of perfluoroalkyl substances (PFASs) in terrestrial ecosystems are rare. In the current study, bioaccumulation of perfluorooctane sulfonate (PFOS) in a restricted terrestrial food chain was investigated with the omnivorous wood mouse (*Apodemus sylvaticus*) on top of this food chain. The detected levels are extremely high as a result of the presence of fluorochemical plant in the immediate vicinity of the study area. Soil, water, fruits of elderberry and blackberry, invertebrates (millipedes, isopods, worms and slugs), bank vole and wood mice were collected at two sites e.g. Blokkersdijk, adjacent to the manufacturing unit and Galgenweel, 2 kms further away. Mice were dissected and PFOS concentrations were determined in kidney, lung, spleen, pancreas and liver. In livers of the wood mice the concentrations ranged from 787 to 22 355 ng/g ww at Blokkersdijk and from 29 to 694 ng/g ww at the reference site. The PFOS levels in the livers were significantly correlated with those detected in the kidneys (<LOD-4 255 ng/g ww). The liver concentrations at Blokkersdijk increased with age. In the spleen, pancreas and lungs (pooled samples) concentrations up to 4 740 ng/g (pancreas) were found. Current results were compared to the findings of a previous study on wood mice, conducted at the same sampling sites. Over 4 years, the PFOS concentrations decreased significantly and this is most probably due to the phase out of PFOS and related products in 2002.

All the analysed samples in Blokkersdijk were significantly higher than those detected at Galgenweel. To the best of our knowledge, so far no studies reported PFOS levels in terrestrial invertebrates. At Blokkersdijk PFOS was detected in all invertebrate species (28 – 9 000 ng/g) and even at the control site, several samples contained measurable PFOS levels. Soil and water were also highly contaminated with levels of respectively 68 ng/g and 22 ng/L.

The bioconcentration factors were calculated with the average PFOS concentration in the organism, berries or liver versus soil and ranged from 0.1 to 85 for the livers of the wood mice. Previous studies have shown that this area in Belgium is highly contaminated and although the production of PFOS has phased out and the levels decrease, the contamination in the environment is still considerably high.

## Application of Visual Basic (VB) scripting and comprehensive GC/TOF for the identification of new halogenated contaminants in Norwegian ambient air samples

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The UNEP Stockholm Convention for the international regulation of Persistent Organic Pollutants (POPs), officially ratified in 2001 resulted in the international ban or restriction of a selected number of priority POPs identified as hazardous for humans and the environment. As a consequence of this international POP regulation, new and emerging POP-like chemicals can substitute the banned/ restricted chemicals until they are identified and officially regulated.

Comprehensive *in-silico* chemical modelling studies have identified many chemicals/ pharmaceuticals in commerce as potential POP like contaminants not yet identified in environmental samples. For POP analysis, today usually gas chromatographic methods in combination with selected ion monitoring (SIM) based mass spectrometry are used. However, for the above-described development, SIM based mass spectrometric detection methods are obviously not suitable for the “non-target” approach required for the identification of new POP-like pollutants in the environment. This is mainly due the fact that SIM based MS-methods largely overlook others than the selected ions (m/z) from the target analytes.

For the verification of the *in-silico* modelling results, new analytical methods have to be developed for the positive confirmation of potential pollutants. In order to achieve this, high volume ambient air samples from the Norwegian Arctic and southern Norway (Birkenes) were analysed for potential new contaminants by comprehensive gas chromatography and time-of-flight mass spectrometric detection (GCxGC/ToF-MS). The major focus of our study was the identification of new halogenated contaminants, e.g. chlorinated and/ or brominated, by using Visual Basic Scripts for the electronic post treatment of full spectra. These scripts flag peaks to their corresponding class by means of criteria given for masses (m/z), abundance of masses, and ratios of abundances between masses. This technique allows detecting of compounds without a commercially available library of known mass spectra. The library, however, was used either to identify the detected compounds or to determine if further investigation was needed to identify the detected compounds. Since sample pre-cleaning has various discriminating effects to the sample, we applied different pre-cleaning methods to several samples to evaluate the effects on the detected compounds. In addition, the samples were also scanned for potential new contaminants compiled by modelling approaches. By comparing the outcome of the models and the non-target screening, this can improve both the quality of the models and the “non-target” analytical methods and contribute to the identification of hitherto unknown environmental contaminants.

## Priority and emerging brominated flame retardants in gull eggs (*Larus michahellis*) from Atlantic and Mediterranean colonies: trends and impact

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The present study was aimed to evaluate the geographical distribution and temporal trends of priority and emerging brominated flame retardants (FR) in yellow-legged gull eggs (*Larus michahellis*) collected from 3 National Parks from Spain. Compounds studied were polybrominated diphenyl ethers (PBDEs) and emerging flame retardants which included hexabromobenzene (HBB), pentabromoethyl benzene (PBEB), pentabromotoluene (PBT), 2,3-dibromopropyl 2,4,6 tribromophenyl ether (DPTE), 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (EHTBB), bis(2-ethyl-1-hexyl)tetrabromo phthalate (BEHTBP), 1,2 bis (2,4,6 tribromophenoxy)ethane (BTBPE), hexachloro cyclopentadienyl dibromooctane (HCDBCO) and decabromodiphenyl ethane (DBDPE). In a first step, we developed an analytical method based in liquid-solid extraction, Florisil clean up using solid phase extraction cartridges (10 g, WATERS) and analysis by gas chromatography coupled to mass spectrometry in negative chemical ionization (GC-NCI-MS) to determine PBDEs (including BDE 209) and gas chromatography coupled to tandem mass spectrometry in electron ionization (GC-MS/MS) to determine emerging flame retardants. In a second step, fresh gull eggs were collected from 5 National or Natural Parks which represent the most important gull colonies of the Iberian Peninsula: Medes Islands, Ebro Delta, Cabrera and Chafarinas, representing Mediterranean colonies and Islas Atlánticas de Galicia representing the Atlantic colony. In each colony, 12 eggs were randomly collected and pooled from 3 areas of the colony during the period 2009-2012. PBDEs were detected from 100 to 21444 pg/g ww, being BDE 209 the most ubiquitous compound. Mediterranean colonies had higher levels of PBDE than Atlantic, due to the more industrial and mass urbanization in this area compared to the open Atlantic environments. In addition, very small time variations were observed, indicating the pervasive presence of these compounds in the studied areas. For emerging FR, only BTBPE was detected and at very low concentrations. The effect of FR in eggs was studied in terms of egg shell biometry, development of the egg and survival rate and it was found that the presence of PBDEs did not affect any of these factors.



## Determination of personal care products and pharmaceuticals in reservoirs water in Colombia by ultra-high performance liquid-chromatography-tandem mass spectrometry

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Colombia has built a large number of reservoirs to the generation of electric energy and to supply water to drinking water treatment plants. These reservoirs are supplied with water from rivers that have received domestic, industrial and agricultural wastewater discharges. For this reason, water quality monitoring in Colombia's reservoirs is an important health and environmental concern. Scientific and technological development, the increased use of chemicals and current consumption patterns can potentially put water quality under threat. The appearance of the denominated "emerging contaminants" in natural sources of water used to supply drinking water is perhaps one of the biggest concerns today, as their toxicological risk is not yet well known.

Pharmaceuticals and personal care products (PPCPs) encompass a wide range of chemicals compounds most of which are introduced into the environment by anthropogenic activities and excretion. In recent years there has been growing interest to understand the nature of these compounds, of how to enter and how they are in the environment and the potential adverse effects on human health and ecosystems.

This work describes the analysis of 9 pharmaceuticals and personal care products (benzophenone, benzophenone-3, carbamazepine, clofibric acid, methylparaben, ethylparaben, buthylparaben, diclofenac and ibuprofen) in samples collected in the water column from two reservoirs water that are used to provide drinking from Colombia. The analysis was carried out with a method for the simultaneous determination of these 9 compounds. The method was based on solid-phase extraction using Oasis HLB cartridges followed by ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). A detailed study of the extraction process efficiency and matrix effect was carried out in reservoirs water. The use of different isotope-labelled internal standards was investigated to compensate both SPE losses during the extraction procedure and signal suppression/enhancement. The method was successfully validated in two different reservoirs water samples. The recoveries of all the compounds were from 69 to 115% for three spiking levels (0.05, 0.25 and 0.45 µg/L). The limits of quantification (LOQ) of all the compounds were from 2.8 to 10.3 ng/L. The occurrence of benzophenone (9-107 ng/L), Methylparaben (5-425 ng/L) and ibuprofen (5-62 ng/L) was highly relevant in both reservoirs. On other hand, there were no evidences on the presence of diclofenac, clofibric acid, buthylparaben and carbamazepine in any reservoir. This study shows that Colombia is indeed affected by the presence of emerging contaminants and revealed the importance to continue monitoring these compounds as well as other emerging contaminants in Colombian water sources.

## Occurrence of Perfluoroalkyl Substances in Sewage Sludge and Point Source Characterization

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Conventional wastewater treatment has limited effectiveness in removing perfluoroalkyl and polyfluoroalkyl substances (PFASs) from aqueous waste streams, and therefore WWTPs act as most relevant point sources to the aquatic environment. Long-chain PFASs have a high affinity for organic carbon and proteins and, therefore, the sewage sludge produced in a WWTP may be an important sink of long-chain perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) entering WWTPs. Sewage sludge is the “archive” of a WWTP, integrating the mass-flow of sorbing pollutants entering a WWTP steadily or intermittently.

To better identify point sources of perfluorooctane sulfonic acid (PFOS) and other PFASs to the aquatic environment, a survey of anaerobically stabilized sewage sludges from 46 municipal WWTPs in Switzerland (n=2-3) was performed to evaluate the levels of PFASs. The targeted selection of the WWTPs was based on the occurrence of potential industrial and commercial emitters in the catchment of the WWTPs.

In 19 of 46 studied WWTPs (41%) PFOS concentrations were above 100 µg/kg. The application areas of metal plating and fire fighting foams (aqueous film-forming foam, AFFF) contributed the majority to the emissions of PFOS. PFOS is widely used in metal finishing processes as a foam suppressant and surfactant to reduce surface tension. Increased PFOS concentrations (up to 2'400 µg/kg) occurred in catchments of WWTPs where chromium electroplating industries are located. Individual WWTPs showed significant temporal variability of exposure because wastewaters are often released intermittently. However, the occurrence of metal plating industries in the catchment did not always correlate with higher PFOS concentrations. One reason could be that processes baths are not treated on-site.

The use of PFOS in AFFF in Switzerland is allowed until 30.11.2014 for fire-fighting in operational situations. PFOS emissions from AFFF (up to 1'600 µg/kg) exhibited a large temporal and spatial variability in sewage sludge depending on the use on training grounds of fire brigades and the occurrence of major fires.

Elevated levels of perfluorooctanoic acid (PFOA, 10–87 µg/kg) were measured in catchments with potential emitters of PFCAs like textile and carpet protection companies and AFFF. Higher levels of PFCAs compared to PFSAs can be attributed to emissions from textile finishing companies.

The high spatial and temporal variability of long-chain PFASs allowed to identify specific sources causing elevated sludge concentrations.

## Screening for Organic Micropollutants in the Prut River Basin at the Romanian-Moldavian border

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The 953 km long Prut River is the second largest tributary of the Danube River. It flows first in the Ukraine, then forms the border between Ukraine and Romania and then between Romania and Moldova (713 km). The objective of our investigation was to study the contribution of urban and agricultural sources of organic micropollutants in the Prut River at the Romanian-Moldavian border and in the Jijia Canal, a tributary with low dilution of wastewater from several villages (e.g. Iasi) at the Romanian site.

For two sampling campaigns in November 2011 and June 2012 a target screening was performed for approximately 380 pharmaceuticals, personal care products, pesticides, biocides, additives, corrosion inhibitors, musk fragrances, and industrial chemicals using liquid chromatography followed by electrospray ionization (ESI) coupled to high resolution Orbitrap mass spectrometry [Kern et al. (2009). *Environ. Sci. Technol.* **43**, 7039–7046].

In the Prut River 39 different pharmaceuticals and metabolites, 30 pesticides (including biocides) and transformation products as well as 7 household chemicals and 4 perfluoroalkyl acids totalling 80 target compounds, were determined above the LOQ. Relatively low concentrations levels were found. The highest concentrations occurred for the artificial sweetener acesulfame (750 ng/L), the pharmaceuticals metformin (240 ng/L) and 4-acetamidoantipyrine (a primary metabolite of the analgesic metamizole, 210 ng/L). Concentrations of the analgesic antipyrine (phenanzone), the anti-epileptic gabapentin, and the anti-diabetic metformin were above 50 ng/L. This also applies to the household chemicals cyclamate, saccharine and caffeine. Low levels of pesticides were found (< 10 ng/L). The herbicide bentazone was determined at slightly higher concentrations (11-27 ng/L). Maximum concentrations in samples from the Jijia tributary were higher than in the Prut. The highest levels in the Jijia were determined for acesulfame (2'000 ng/L), 4-acetamidoantipyrine (500 ng/L), metformin (440 ng/L). Concentrations above 50 ng/L occurred for sucralose, cyclamate, saccharine, benzotriazole, 4+5-Methyl-1H-benzotriazole, atenolol acid, carbamazepine, carbamazepine-10,11-dihydro-10,11-dihydroxy, diclofenac, gabapentin, metformin, sulfamethoxazole, and bentazone.

At Brinza, upstream of the confluence point of the Prut into the Danube, the average load of the determined compounds in the Prut River catchment amounted to 1840 kg/year. Of this total, pharmaceuticals and metabolites amounted to 685 kg/year, pesticides and transformation products to 252 kg/year and household chemicals to 903 kg/year.

The highly sensitive target analysis using HRMS provided a comprehensive picture of the overall contamination pattern with polar emerging contaminants.

## IDENTIFICATION OF ORGANIC COMPOUNDS MIGRATING FROM A POLYMERIC MATERIAL INTO DRINKING WATER

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Nowadays different kind of polymeric materials are used in pipelines for drinking water. In some cases old pipes are substituted by these polymeric pipes. The objectives of this study were to investigate and identify organic compounds migrating from a polymeric material used in a commercial pipe. Migration tests were carried out in accordance with UNE-EN 12876-1 using three different water matrices (30 samples), and organic compounds were analysed by several extraction methodologies: Closed loop stripping analysis (CLSA), Liquid-liquid extraction (LLE) and Stir Bar Solid Extraction (SBSE) and Solid phase extraction (SPE). Extracts were analysed using Gas Chromatography coupled to Mass Spectrometry (GC-MS), and Ultra Performance Liquid Chromatography (UPLC-MS/MS).

In addition, organoleptic properties of samples water from third migration were characterized according to EN 1622, which is based on a quantitative dilution method (Threshold Odor Number, TON), and results were compared with chromatogram obtained by Gas chromatography with an Odor detector ("sniffing") and Flame ionization detector (GC-ODP/FID).

Several organic compounds were identified in migration samples, and some of them were detected by three out of four techniques of analysis used in this study, such as 2,6-di-tert-butyl-p-Benzoquinone, 2,4-di-tert-butyl-Phenol and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene,2,8-dione. The presence of these compounds might be attributed to impurities or by-products of typical phenolic additives used as antioxidants in pipeline production. The samples tested organoleptically showed values of  $\geq 5$  TON, and in all of them were confirmed presence of these compounds.

## Particulate matter formation from photochemical degradation of pesticides

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The atmospheric particulate matter (PM) has a large impact on climate, atmospheric chemistry, biosphere, and human health, being considered an important air pollutant [1].

Actually, are emerging chemical pollutants precursors of particulate matter such as pesticides. Today's agriculture involves heavy use of synthetic pesticides, including herbicides, fungicides, acaricides, insecticides and avicides. Because the adsorption of these pesticides on the surface is not fully implemented, they and their products are detected in food, water, soil and atmosphere. Their entry into the atmosphere occurs during application or subsequent processes such as volatilization and re-suspension [2]. Furthermore, once they are emitted may be present in the gas phase and in the particulate phase since they are semi-volatile compounds. The number of patented pesticides is very high and many families belong authorized, prohibited or recently banned under Directive 91/414/EEC. These include organochlorines, chloroacetanilines, anilines, chloroanilines, dinitroanilines, triazoles and organofosforated pesticides used in Mediterranean agriculture in a broad range of applications.

However, there is a relative lack in the scientific knowledge about the behaviour of pesticides in the atmosphere. The major routes of degradation of pesticides in the troposphere involve photolysis, ozonolysis and reactions with hydroxyl and nitrate radicals. The result is a reduction of their concentration but especially PM is formed and has a toxicity, residence time and atmospheric chemical stability different than the original molecule. The relevant information was obtained in a high volume atmospheric simulation chambers with an extensive instrumentation for monitoring the particulate matter formed. They are closed systems where they reproduce experimental atmospheric reactions without factors such as dispersion, transport and meteorology. Thus, several experiments were performed in these facilities for pesticides such as propachlor, chlorpyrifos-methyl, hymexazol, diazinon and trifluralin.

The mass concentration yields obtained (Y) were 5 – 44 % in the photo-oxidation reactions in the presence and the absence of NO<sub>x</sub>, photochemical degradation pathway leading daytime. These results confirm the importance of study pesticides as significant precursors of atmospheric particulate matter due to the serious risks they can generate.

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## Determination of musks in vegetables and amended soil samples by stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry

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Agricultural application of sewage sludge has become the most widespread method for disposal since it is the most economical outlet for sludge and offers the opportunity to recycle plant nutrients and organic matter to soil for crop production. Nowadays, around 40 % of the sewage sludge produced in Europe is used as fertilizer in agriculture. However, in the last years concern has increased due to the confirmed presence of heavy metals, organic contaminants and pathogenic bacteria in sewage sludge. One way to study the possible introduction of organic contaminants to humans via the food chain is to study the uptake of such pollutants by different crop plants. Among concerning contaminants in sewage sludge application with agricultural purposes musk compounds are found. Currently, large quantities of synthetic musks are manufactured and used in a wide variety of personal care products, such as perfumes, skin creams, deodorants, and soaps, which are used in a broad group of everyday products. Musk fragrances, as all analytes classified as emerging organic compounds (e.g., X-ray contrast agents, pharmaceutical products, UV filters, and among others), have been investigated in recent years to detect their presence in environmental matrices [1-2].

The analysis of organic compounds in solid matrices such as amended soil or vegetables requires of an extraction step. Most of the applications in the literature are based on traditional extraction techniques (Soxhlet extraction, ultrasonic bathing or stirring) [3, 4] or pressurized solvent extraction (PLE) [5]. However, due to their low selectivity, extracts from complex samples such as vegetables have to be subjected to clean-up steps, usually by solid-phase extraction (SPE), to the detriment of analysis times and increasing solvent consumption. The aim of this study was to develop a sensitive and environment-friendly method based on stir-bar sorptive extraction (SBSE) followed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) to determine 8 synthetic musks (musk ambrette, musk ketone, celestolide, tonalide, galaxolide, phantolide, traseolide and cashmeran) in vegetables (lettuce, carrot and pepper) and amended soil samples. In a first step sorptive extraction was studied both in the headspace and in the immersed mode. The best results were obtained in the immersed mode which was further studied. The influence of the main factors (methanol and NaCl addition, extraction temperature and time and stirring rate) on the efficiency of SBSE was evaluated by means of experimental designs. In the case of TD, desorption time, desorption temperature, cryo-focusing temperature, vent flow and vent pressure were studied using both a factorial fractionated design and a central composite design (CCD). Finally, the method was applied to the determination of musks in vegetable samples that had been exposed to known concentrations of the target compounds.

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## Simultaneous extraction of several polar organic pollutants in vegetables and seafood using focused ultrasonic solid-liquid extraction and different clean-up approaches

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Emerging contaminants have drawn the attention of the scientific community because of their wide occurrence in the environment that is not commonly monitored due to the lack of regulation. These products are widely used and often pass through water treatment plants unaltered before being discharged into the environment. Moreover, the strong adsorption of these contaminants to solid matrices and their occurrence in highly complex mixtures, formed in some cases by many homologues, oligomers and isomers, pose additional difficulties to their analysis [1]. In this sense, the determination of these substances involves a sample preparation step that includes extraction, clean-up and occasionally derivatisation to enhance the analytical response of these compounds [2].

In the present work, focused ultrasonic solid-liquid extraction (FUSLE) was optimised for the simultaneous analysis of perfluorooctanoic acid (PFOA), perfluorooctanoic sulfonamide (PFOSA), perfluorooctane sulfonate (PFOS), triclosan (TCS) and triclocarban (TCC) in vegetable and seafood. Optimisation was performed using carrot and seafood freeze-dried samples that had been exposed to known concentrations (1 ng/ $\mu$ L) of the target analytes. The variables studied during the optimisation process were: percentage of maximum power (10-56 %), extraction time (0.5-5 min), sonication time (0.2-0.8), composition of the extraction solvent (acetonitrile: water, 9:1; acetone; methanol; methanol; acetic acid, 9:1; acetic acid and KOH: methanol, 10 mM). The volume of the extractant was also evaluated (4-10 mL) and the extraction was performed at 0 °C in an ice-bath during the optimisation process. All these variables were studied using an experimental design approach by means of The Unscrambler software. Under the optimised extraction conditions consecutive 2.5 min periods were tested in the case of both matrices: carrot and seafood samples. Different clean-up strategies by means of solid phase extraction (SPE) using both Oasis HLB and Oasis SAX cartridges and polyethersulfone (PES) sorptive extraction were optimised and evaluated for FUSLE extracts before the chromatographic analysis. In all the cases the analysis were performed by liquid-chromatography- triple quadrupole mass spectrometry (LC-MS/MS). The optimised method was applied to vegetables (carrot and lettuce) and seafood (hake and prawns) samples.

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## Estrogens in suspended particulate matter: a quick, simple and reliable method

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Due to aquatic suspended particulate matter (SPM) disturbs the surface water analysis it is often ignored that organic hydrophobic contaminants, like estrogens, can sorb substantially on water SPM. Furthermore, SPM analysis are crucial to understanding distribution and bioavailability mechanisms of contaminants in water due its ability to deposition-resuspension and transport. In this work we evaluated a method performance for estrogens (E1, E2, E3 and EE2) analysis on SPM, investigating general validation parameters (precision, accuracy, linearity, robustness and matrix effect). The estrogens analysis was carried out using HPLC-FLD. The method involves: 1) SPM obtainment from 0,5L superficial water; 2) SPM extraction with MeOH:MeCN (1:1, v/v) using a Vortex mixer and centrifugation; 3) dryness of extract under gentle N<sub>2</sub> stream and re-suspension in MeCN for analysis. Average recoveries for spiked SPM samples (50; 250; 500 µg g<sup>-1</sup> for E1 and 500; 2500; 5000 ng g<sup>-1</sup> for E2, E3 and EE2) ranged from 72 to 101% with relative standard deviations (RSD) below 13%. After the statistical outliers elimination, the analytical curves were constructed ranging from 2.0 to 10.0 ng mL<sup>-1</sup>, all correlation coefficients were higher than 0.99. Matrix effect was evaluated by comparison of analytical curves constructed on solvent and SPM extract and the observed effect was no-significant for all estrogens. This method have been applied to an estrogen occurrence study in developing at a Southeast Brazilian hydrographic basin, showing that SPM is too a matrix enriched with these compounds with concentration ranged from 34 to 876 µg g<sup>-1</sup> for E1, 196 to 503 ng g<sup>-1</sup> for E2, 123 to 639 ng g<sup>-1</sup> for E3 and 207 to 757 ng g<sup>-1</sup> for EE2.



## DETERMINATION OF EMERGING AND COMMON FLAME RETARDANTS IN NORWEGIAN SERUM SAMPLES

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Halogenated flame retardants (HFRs) are chemicals used to prevent or reduce the spread of fire in many consumer goods and household products, such as electric and electronic equipment, furniture foams, and textiles. Their content reaches percentage amounts by weight and in many cases these HFRs are not chemically bonded to the products allowing them to leach out and pollute the indoor environment. Several HFRs have been banned as they are toxic, highly persistent and accumulate in food chains, thus being a risk for human health.

To assess human exposure in general populations, blood serum is a suitable matrix. However, determination of lipophilic pollutants in blood samples at trace levels is challenging because of the low lipid content and often limited amount of sample available.

We developed and optimized an off-line solid phase extraction GC-LRMS(ECNI) method for determination of 7 emerging HFRs in serum, i.e. hexabromobenzene (HBB), Dechlorane Plus<sup>®</sup> (DPs, *syn* and *anti* isomers), decabromodiphenylethane (DBDPE), 1,2-bis[2,4,6-tribromophenoxy]ethane (BTBPE), hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO), dechlorane 602 (Dec602) and dechlorane 603 (Dec603). The method also comprises 15 tri- to decabromodiphenyl ethers (PBDEs) allowing simultaneous determination of emerging HFRs and PBDEs in a single run. The method has been thoroughly validated according to international guidelines using spiked horse serum. Absolute recoveries of the analytes ranged from 67 – 142 % (mean 100 %), 36 – 105 % (mean 90 %), 34 – 93 % (mean 80 %) at 30, 300, and 3000 pg spike levels, respectively with overall RSDs between 1 – 27 % (mean 7 %). Intermediate precision after 3 months ranged from 2 to 44 % (mean 9 %). The overall method was linear in the range of 0.1 to 1000 pg/μL and its limits of detection ranged from 0.3 to 20 pg/g serum.

We have applied the method to human serum samples from 46 Norwegian women residing in the greater Oslo area. In summary, 5 of the emerging HFRs, as well as the common 7 PBDEs, were detected in 2 g of serum. This is the first time these emerging HFRs have been identified in serum from the Norwegian population.

## Fate of selected emerging contaminants in River waters

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Pharmaceuticals have become an important issue in the last few years as they are ubiquitous environmental pollutants that contaminates the environment through a number of point sources. They are at present a major source of bioactive molecules in the water. Their low volatility forces their spreading by transport in water and their polar nature prevents the removal from aqueous system by facilitating the dispersion through the food chain. Improper disposal of unused or expired medicines, industrial and hospital waste, facilities for aquaculture, the run-off from farms and livestock contribute significantly to the detection of such compounds in natural waters and other environmental media. However, the main source for pollution, responsible for 70-80% of the contamination, is excretion by pharmacological treated patients. Some of these compounds show long environmental persistence, being only partially or slowly biodegradable. Other compounds have a rather less persistence but, due to their continuous release into the environment or the formation of transformation products arising from their degradation, may impact on the aquatic ecosystem and human health.

With this in mind, this study was aimed to enlighten the fate of two antibiotics, lincomycin and clarithromycin, an antiepileptic drug, carbamazepine, and two anticancer drugs, cyclofosfamide and methotrexate, in Po river water (North Italy), focusing on the drugs degradation and identification of their transformation products and trying to recognize the main transformation routes followed by these drugs when discharged in the environment.

The goal was attained in two steps. Firstly, laboratory experiments in the dark and under illumination were performed on river water spiked with drugs to simulate all possible transformation processes occurring in the aquatic system. Under illumination, these pharmaceuticals were degraded and transformed into numerous organic intermediate compounds. Analyses were performed by liquid chromatography-LTQ-FT-Orbitrap mass spectrometry and unknown compound were characterized by analyzing MS and MS<sup>n</sup> spectra.

Secondly, all the possible main and secondary transformation products (TPs) were searched for in several samples collected from the Po River sampled in an urban area. The selected pharmaceuticals and several TPs were detected in all samples. This approach has permitted not only to assess the selected drugs presence in natural waters, but also to identify which of the transformation routes recognized in simulation experiments, also occurred in the aquatic environment. Several TPs were identified. Some of them seems to be formed through a biotic or abiotic process. Specifically for the case of carbamazepine, it was possible to find some key TPs that could be considered as markers for its photochemical environmental transformation in the aquatic environment.

## ORGANOCHLORINE PESTICIDES IN AKKAR PLAIN GROUND WATERS IN NORTH LEBANON

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Pesticides are commonly used in agriculture not only to protect crops from being harmed but also to increase crop production. The quality of the water in Lebanon has been threatened by agricultural activities due to pesticide discharges affecting the groundwater. Indeed, these compounds can easily be transported by water and can reach rivers, soils and sediments to finally reach groundwater. Their impact is directly related to their concentration and their toxicity. Hence, the control of reliable analytical methods is a necessity. Due to the uncensored use of pesticides in the agricultural regions of Lebanon, the contamination risks of drinking water by organic residues increase periodically in planting seasons. In this context, the aim of that study was to evaluate the contamination of groundwater by Organochlorine pesticides in the Akkar district (northern Lebanon). Solid-phase extraction (SPE) followed by gas chromatography coupled with mass spectrometry (GC/MS) was used to quantify pesticide concentration. The levels of Organochlorine pesticides recorded in groundwater samples of Akkar district exceeded the limits set by the Stockholm Convention on persistent organic pollutants with total amounts that can reach 14.22 ppb (at Massoudieh). Contamination was also found to be more important inland with the frequent presence of banned pesticides such as HCH isomers, 4,4'-DDT, aldrin and endrin.

*Keywords:* Lebanon, Groundwater, Organochlorine pesticides, Solid-phase extraction, GC-MS

## Atmospheric deposition of polybrominated diphenyl ethers to remote European regions: geographical trends, congener patterns, and sources.

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Polybrominated diphenyl ethers (PBDEs) were analyzed in bulk atmospheric deposition samples taken in four European remote mountain areas over a period of two years (2004-2006): Pyrenees (Spain), Tyrolean Alps (Austria), Grampian Mountains (Scotland), and Tatra Mountains (Slovakia). PBDE composition was dominated by BDE 209 in all sites, with levels ranging between 71 ng m<sup>-2</sup> mo<sup>-1</sup> (Alps) and 162 ng m<sup>-2</sup> mo<sup>-1</sup> (Tatra Mts), four to six-folds higher than other PBDE congeners. BDE 47 and BDE 99 were the dominant low-brominated congeners, followed by BDE 100, and BDE 183. Mean deposition fluxes of these four compounds varied between 24.2 ng m<sup>-2</sup> mo<sup>-1</sup> in Tatra Mountains and 40.0 ng m<sup>-2</sup> mo<sup>-1</sup> in Scotland. A slight decrease in PBDE deposition to these remote sites has been detected from 2004 to 2006, although only statistically significant in Scotland, which could be related to decreasing emissions of these compounds in Europe after PBDE use restrictions promoted by UE.

PBDE composition was similar between sites and consistent with PBDE technical mixtures used in Europe. Main differences in composition are related to the BDE 47/BDE 99 and BDE 99/BDE 100 ratios, that can be explained by differences in volatility and reactivity between individual PBDE compounds in the Alps and Pyrenees, while in Scotland and Tatra Mts, they could be attributed to direct impact of nearby sources.

The investigation of the influence of meteorological and environmental factors on PBDEs levels showed different results depending on sampling site; nevertheless, on-going emissions from source areas, particle content, and air mass origin seem to be the most relevant factors determining PBDE levels and composition in atmospheric deposition to remote background regions of Europe.

## Hazard Assessment of Emerging Pollutants: QSAR/QSPR models developed in the FP7 European Project CADASTER

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Four classes of emerging pollutants (brominated flame retardants, fragrances, perfluorinated compounds and (benzo)triazoles) were studied within the FP7 European project CADASTER (Case studies on the Development and Application of in-Silico Techniques for Environmental hazard and Risk assessment). The EU-REACH regulation encourages the use of alternative *in vitro* and *in silico* methods in order to minimize animal testing, costs and time. Among these methods, quantitative structure-activity relationships (QSARs) represent a useful tool to predict unknown activities/properties for existing or even not yet synthesized chemicals. The development and validation of QSAR models was the central part of this project. The final goal was to exemplify the integration of information, models and strategies for carrying out hazard and risk assessments for large numbers of substances, organized in the four representative chemical classes.

The aim of this poster is to summarize the Insubria modelling activities within the CADASTER project, and the QSAR/QSPR models developed for the four classes of compounds under investigation.

For each class, *ad hoc* QSARs (both regression and classification models) were developed for the available experimental data (i.e. physico-chemical properties, environmental and mammalian toxicity, biodegradability) in order to characterize environmental behavior and activity profile of the chemicals. In agreement with the OECD principles for the validation of QSARs for regulatory purposes, all the proposed models were checked for their robustness, external predictivity and applicability domain to new chemicals.

QSAR predictions, together with structural analysis (e.g. similarity analysis and multivariate ranking methods), were used for the identification of priority compounds (also present in the ECHA pre-registration list), in order to focus necessary experimental testing.

## A new membrane-based device for the monitoring of sulfamethoxazole in aquatic system

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Sulfamethoxazole (SMX) is an antibiotic widely found in reclaimed water and other environmental samples due to its broad use. For this reason, it is of interest to develop reliable analytical methods for the routine monitoring of this antibiotic in aquatic system.

Passive sampling is an inexpensive analytical technique involving the deployment of samplers for extended periods of time (from days to weeks) at multiple locations within the aquatic system of interest. These passive samplers yield time-weighted average concentrations of the target chemical species. In most cases the sampling process is based on diffusion across a hydrophilic or hydrophobic barrier, which is usually a porous membrane, into a receiving phase [1]. Passive sampling of organic species is often conducted by polar organic chemical integrative samplers (POCIS), which consist of a sorbent as the receiving phase which is contained between two microporous membranes. After sampling, the organic species accumulated in the sorbent are extracted into a suitable organic solvent and the extract is often analyzed by an appropriate chromatographic technique [2]. The complex and time-consuming extraction procedure can be eliminated if semi-permeable membrane devices (SPMDs) incorporating a polymer inclusion membrane (PIM) as the semi-permeable barrier and a suitable solution as the receiving phase are used instead. Then, the preconcentrated receiving solution can be analysed directly at the end of the passive sampling period.

Thus, in the present work, we have evaluated a PIM composed by cellulose triacetate as a polymer, Aliquat 336 as a carrier and nitrophenyl octylether as a plasticizer incorporated in special home-made devices to be used as passive samplers for the monitoring of SMX in different water environments. A 0.5M NaCl solution was used as a receiving phase. Results obtained using devices incorporating 1.5 cm<sup>2</sup> membrane and 1.2 mL receiving solution, immersed in 120 mL of well waters or wastewaters spiked with SMX in the range 0.5-80 µg L<sup>-1</sup>, showed good relationship between the initial concentration of the antibiotic and the one found in the stripping solution for the different types of water tested. Therefore, these results demonstrate the potential of the PIM-based passive sampler for the monitoring of SMX in aquatic systems .

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## Environmental occurrence, fate and transformation of benzodiazepines in water treatment

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Benzodiazepine derivatives are prescribed in large quantities globally and are potentially new emerging environmental contaminants. Unfortunately, a dearth of data exists concerning occurrence, persistence and fate in the environment. This paper redresses this by reviewing existing literature, assessing the occurrence of selected benzodiazepine anxiolytics (diazepam, oxazepam and bromazepam) in wastewater influent and effluent and surface water from Slovenia, evaluating their removal during water treatment and identifying the transformation products formed during water treatment. Their occurrence was monitored in hospital effluent, river water and in wastewater treatment plant influent and effluent. The study reveals the presence of benzodiazepine derivatives in all samples with the highest amounts in hospital effluents: 111 ng L<sup>-1</sup>, 158 ng L<sup>-1</sup> and 72 ng L<sup>-1</sup> for diazepam, bromazepam and oxazepam, respectively. Removal efficiencies with respect to biological treatment of diazepam were 16–18% (oxic), 18–32% (anoxic → oxic), 53–76% (oxic → anoxic) and 83% (oxic → anoxic → oxic → anoxic cascade bioreactors), while the removal oxazepam was 20–24% under anoxic conditions. Coupled biological and photochemical treatment followed by the adsorption to activated carbon resulted in a removal efficiency of 99.99%. Results reveal the recalcitrant nature of benzodiazepine derivatives and suggest that only combinational treatment is sufficient to remove them. In addition, eight novel diazepam and four novel oxazepam transformation products are reported.

## Occurrence of benzotriazole, benzothiazole and benzenesulfonamide derivatives in sewage and river water

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Industrial and households discharges are the main intrusion source of several chemical products into the environment. An example of polar high production volume chemicals with a high broad application are benzotriazole (BTR), benzothiazole (BT) and benzenesulfonamide (BSA) derivatives. They are mainly used as corrosion inhibitors in dishwasher detergents, aircraft de-icing fluids or industrial cooling systems, among others. Some of them are also used as vulcanisation accelerators or plasticizers and biocides or disinfectants. BTR and BT derivatives are considered as ubiquitous water contaminants, but BSA derivatives have been less studied. Because of their extended use and the fact of these chemicals have been classified as being toxic to aquatic organism and bacteria, these contaminants have been classified as emerging contaminants.

To achieve the lower quantification limits required to determine these contaminants at trace levels, an analytical method based on tandem solid-phase extraction (SPE) and liquid chromatography-tandem mass spectrometry has been developed (LC-MS/MS). Limits of detection (LOD) and quantification (LOQ) were from 1 to 20 ng/L and 2 to 100 ng/L depending on the compound and matrix. Recoveries were close to 90%, repeatability was less than 15% (%RSD, n=3) and matrix effect was less than 20%. The occurrence of five BTR, four BT and five BSA derivatives were studied in river water, influent and secondary and tertiary effluent sewage samples from different STPs located in Catalonia.

The results demonstrate that the occurrence of these contaminants is very relevant in sewage samples. The total average concentration in influent sewage samples was 4,790 ng/L for BTR, 845 ng/L for BT and 382 ng/L for BSA derivatives. In secondary effluents these compounds were found at 2,928 ng/L for BTR, 232 ng/L for BT and 377 ng/L for BSA derivatives. The most representative compounds found for each family in sewage were 1-H-benzotriazole, 2-hydroxybenzothiazole and *para*-toluenesulfonamide. Because secondary treatments are not fully effective to remove organic contaminants, some STPs include tertiary treatments based on UV irradiation followed by chlorination disinfection and sand filtration or advanced membrane-based treatments. In this study, samples of both tertiary treatments were analysed and the total average concentration found was 2,353 and 124 ng/L for BTR, 168 and 157 ng/L for BT and 393.3 and 7.3 ng/L for BSA derivatives, respectively. Concentrations found in tertiary sewage samples seem to indicate that membrane-based treatments are most effective to remove BTR, BT and BSA derivatives than other tertiary treatments.

Due to the incomplete removal of these contaminants during sewage treatments, discharges of sewage can transfer these contaminants into river water as observed with the results obtained for the samples analysed. The total average concentration found was 239 ng/L for BTR, 32 for BT and 71 for BSA derivatives in river water samples.



## **Analysis of engineered nanoparticles in complex samples: concepts, common pitfalls, and recent solutions**

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The analysis of engineered nanoparticles (ENPs) in complex samples as for example consumer products, food and the environment is a highly challenging task. Due to the lack of reliable techniques for the detection and quantification of ENPs at relevant concentrations and in complex samples advancement in our understanding of fate, transport, and (eco-) toxicological effects of ENPs is slow.

The analysis of ENPs differs from traditional chemical analysis because both, the chemical and physical forms must be considered. The challenge is to construct a method which allows selectively accessing the particle size distribution of the ENPs, their chemical composition, proving their identity as being engineered substances and finally report quantitative particle concentrations. In complex samples the analysis has to be conducted in the presence of potentially interfering substances which are often micro- and nanoparticles themselves. The matrix compounds can support nanoparticle stability what can cause aggregation after removal of the matrix compounds or they can support attachment of the nanoparticles to them, what makes a separation for subsequent sizing difficult.

The basic approach of most currently developed methods is (i) to separate and purify the target particles from the matrix, (ii) if direct analysis is not feasible, provision of an analytical separation of sample compounds, ideally together with a particle size analysis, (iii) detection and quantification of the particles after analytical separation, quantitative at least for the target particles, (iv) if possible provision of evidence for the manufactured origin of the determined particles or differentiation of the target particles from background.

Additional to merely quantifying the particles concentration in a given environmental matrix, the distinction of the manufactured or engineered nanoparticles from the background of natural nanoparticles is great challenge. For this task identifiers need to be established which clearly distinguish the man-made ENPs from the natural ones. As long as artificial labels appear to be too costly to implement, typical characteristics may be employed.

One example for this approach is CeO<sub>2</sub> nanoparticles. Bulk samples of soil and sediments showed a clear correlation of Ce with La and Nd concentrations regardless of the cerium anomaly. We could show with FFF-ICP/MS for natural colloids and nanoparticles that this correlation is still valid in the nano range. Additionally high resolution TEM analyses showed that in natural CeO<sub>2</sub> containing nanoparticles Ce and Nd are co-located. Therefore we hypothesize that the Ce/La and the Ce/Nd ratio can be utilized to

The presentation will give an overview about the current state of the art, latest developments and future perspectives of nanoparticle analysis in complex samples.

## Sorption behavior of carbon nanotubes: effects of dispersion and surface chemistry

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Over the past decade, carbon nanotubes (CNTs) have gained increasing attention due to their unique properties. The production of CNTs is expected to increase rapidly in the future and their release to the environment is thus inevitable. CNTs have strong affinity toward organic contaminants and have been proposed as superior sorbents for remediation applications. Understanding the interactions between organic contaminants and CNTs is therefore essential for evaluating the materials' potential environmental impact as well as the potential efficiency as superior sorbent. Even though a great deal of work was carried out, data are still limited due to limitations associated with the generally-applied sorption set ups.

We applied a passive sampling method to gain a better understanding of the interactions between polycyclic aromatic hydrocarbons (PAHs) and CNTs over a wide range of conditions. Sorption data and extensive characterization of the CNTs systems were combined in order to support mechanistic interpretations of the results. The main results are summarized below:

- (i) Conversely to previous studies carried out in the high concentration range, sorption isotherms in the low concentration range (pg–ng/L) indicate that sorption can be described using single sorption coefficients [1]
- (ii) Sorption coefficients for 13 PAHs showed that no competition occurred in the low concentration range and sorption affinity was directly related to the solubility of the subcooled liquid of the compounds [1]
- (iii) Conversely to previous observations restricted to large aggregates, our study highlights the importance of considering both the size and structure of sorbent aggregates [2]
- (iv) The impact of surface functionalization on sorption behavior greatly depends on the CNT dispersion status. The suppression of sorption by natural dispersants is affected by the CNTs surface chemistry.

Overall, this study demonstrates that aggregation/dispersion significantly affects the sorption behavior of CNTs. Both the nature (e.g., sonication, presence of dispersants or functionalization) and the chronological sequence of the dispersion events are essential in determining the extent and irreversibility of the effects on sorption behavior of CNTs.

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## Perfluorinated Compounds (PFCs) in Modern Textile Materials

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Perfluorinated compounds (PFCs) is a diverse and large group of chemicals which are added to a wide range of commercial and industrial products in order to change their physico-chemical properties<sup>1</sup>. The addition of PFCs to the products makes them resistant to water, stain, oil, and fire. They have been produced and applied in large volumes on the global scale during the last five decades with the largest producers being 3M, DuPont, Atofina, Clariant, Daikan and Asahi Glass.

The most common applications (depending on respective compounds) include; textiles (e.g. carpets, furniture materials, clothing etc.) and leather products, paper and packaging, coating additives, cleaning products, pesticides, firefighting foams, the photographic industry, photolithography and semiconductors<sup>2</sup>. PFCs are mostly just use as a surface layers additives and as non-bound compounds can be released from final products to the environment during their lifecycle.

In 2009, PFOS and related compounds were listed under Annex B of the Stockholm Convention on Persistent Organic Pollutants, which restricts manufacturing and use to a few specific applications<sup>3</sup>. Within European Union including the Czech Republic is the use of PFOS regulated by European Commission Regulation. For textiles or other coated materials, the amount of PFOS has to be lower than  $1 \mu\text{g}\cdot\text{m}^{-2}$ <sup>4</sup>. On the other hand, regulated group of PFCs targets PFOS and its salts as well as several other identified precursors and intermediates<sup>5</sup> are in the production process replaced with other perfluorinated compounds with same properties but other length of fluorinated chain. The impact of these “new PFCs” is unknown.

PFCs are present in various consumer products used every day in homes, schools or workplaces. Information about contamination of these products and materials are limited and international research is ongoing to learn more about potential PFCs contamination PFCs in different consumer products<sup>6-7</sup>.

To have a picture about distribution and amounts of PFCs more than 50 individual samples of various upholstery, textile and food packaging materials were collected. All collected materials were analyzed to determine the content of PFCs such as perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), perfluoroalkylcarboxylic acid (PFCAs) and perfluoroalkylsulfonates (PFASs).

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## Occurrence and behaviour of illicit drugs and therapeutic opiates in municipal wastewater treatment

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An integrated procedure for multiresidue analysis of the dissolved and particulate residues of selected urinary biomarkers of illicit drugs and therapeutic opiates in untreated and biologically treated wastewater using liquid chromatography-tandem mass spectrometry (LC/MS/MS) was developed and applied to study their behaviour during the wastewater treatment. The enrichment of illicit drugs from suspended solids and aqueous samples were performed employing pressurised liquid extraction (PLE) and fractionated solid-phase extraction (SPE) based on mixed cation-exchange (Oasis MCX) cartridges, respectively. The performance of different SPE cartridges was investigated in order to optimise the overall recovery and to reduce the matrix effects. The method was applied for the analysis of raw wastewater (RW), activated sludge (AS) and secondary effluent (SE) samples, collected in 4 different wastewater treatment plants (WWTPs). The average contributions of the particulate drugs in the RW was 1-28 %, which suggested that the total mass loads of some drugs might be underestimated by neglecting the particulate fraction. Moreover, relatively high distribution coefficients, determined for 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP; RW: 1211 L/kg) and 11-hydroxy- $\Delta^9$ -tetrahydrocannabinol (THC-OH; RW: 1786 L/kg) in activated sludge, implied that the adsorption might play a significant role in their removal during biological wastewater treatment. The overall elimination efficiency of the investigated compounds was variable. Rather high removal efficiencies were obtained for THC-COOH (99 $\pm$ 2%) and THC-OH (98 $\pm$ 4%), morphine (89 $\pm$ 9%) and amphetamine (85 $\pm$ 14%), while lower removal rates were determined for cocaine (67 $\pm$ 15%), benzoylecgonine (60 $\pm$ 15%), codeine (57 $\pm$ 22%), MDMA (48 $\pm$ 21%), methadone (30 $\pm$ 14%) and EDDP (9 $\pm$ 6%).

## Presence of halogenated flame retardants in marine biota and sediment samples from the UK

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Several studies have shown the widespread distribution, persistence and bioaccumulation capacity of brominated flame retardants (BFRs) in the marine environment [1]. These results have led to increasing regulation and restrictions on the production and use of these compounds, and also to their substitution with other non-PBDE BFRs. The number of such chemicals is so large, that an effort has been made to unify their abbreviations to avoid confusion [2]. Some of the most commonly found of those chemicals are the 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB or EHTBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH or BEH-TEBP), hexachlorocyclopentadienyl dibromocyclooctane (HCDBCO or DBHCTD), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) and Dechlorane Plus (DPs or DDC-CO). Although there is little information on the fate of these FRs, recent papers have shown the presence of some of these compounds in the environment [3, 4] and also their bioaccumulation capacity [5, 6].

In order to investigate the occurrence of FRs in the UK marine environment, >20 halogenated flame retardants plus 16 PBDEs have been analyzed in marine mammals and sediments. The method used employs pressurized liquid extraction, followed by double clean-up with gel permeation chromatography (GPC) and solid phase extraction (SPE) using Florisil, with subsequent analysis by GC-MS/MS and GC-NCI-MS. 21 blubber samples of harbour porpoises collected in 2008 as part of the UK Cetacean Strandings Investigation Programme (CSIP) were investigated. Additionally, 40 marine and estuarine sediment samples collected in the UK over the period 2010-2012 were analysed. Preliminary results show that some FRs such as DBHCTD (HCDBCO), PBEB, PBT, 2,2',4,4',5,5'-hexabromobiphenyl (BB153) and DDC-CO (DPs) are present in UK samples, currently at much lower concentrations than PBDEs. Over half of the non-BDE halogenated flame retardants analysed for were not detected in any samples.

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## Combined nanofiltration and photo-Fenton for treating water containing pollutants at $\mu\text{g L}^{-1}$ initial concentration in natural water

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The growing demand of water and the continuous discovery of new potentially harmful contaminants make clear the need for further research in all areas that can contribute to protecting human health and the environment, achieve sustainable water use and mitigate the effects of the drought and climate change. However, this problem is further compounded because these new contaminants (detergents, pharmaceuticals, personal care products, flame retardants, antiseptics, industrial additives, steroids, hormones, etc) are not eliminated with conventional treatments, because they are designed for resisting against organisms. Physical treatment, such as membrane nanofiltration (NF) and reverse osmosis (RO) are shown to be the most promising treatment to remove these micropollutants. However, these techniques are not destructive so that all micropollutants are encountered in the concentrate that must be treated, although they are normally discharged into the aquatic environment untreated. The combination of membrane physical treatments with AOPs at the outlet of a Municipal Wastewater Treatment Plant (MWWTP) secondary stage has been studied in the last years. Pérez-González et al. 2012 reported the state of the art and review of the concentrate treatment by AOPs. The main technologies applied on NF/RO concentrates are: ozonation ( $\text{O}_3$ ), Fenton process, photocatalysis and photooxidation, sonolysis and electrochemical oxidation, but as they are mainly based on removing DOC, the study of the micropollutants elimination is very limited. The purpose of this study was to compare the efficiency of the solar photo-Fenton process in mild conditions for the treatment of water containing micropollutants with the application of the same process to the concentrate produced by nanofiltration (NF) (less volume, higher concentration of micropollutants, higher salt content). The concentration factors studied were 1, 4 and 10, comparing hydrogen peroxide consumption and treatment time in all cases. The main objective was to determine if, after micropollutants pre-concentration, hydrogen peroxide was more efficiently used and the reaction rate was higher than direct application of photo-Fenton. Effect of other water components pre-concentration (inorganics) was also evaluated. Five different pharmaceuticals (carbamazepine, flumequine, ibuprofen, ofloxacin and sulfamethoxazole) dissolved ( $15 \mu\text{g L}^{-1}$  each one) in natural water were used. The NF system consists of two membranes operating simultaneously with a total surface area of  $5.2 \text{ m}^2$ . The photo-Fenton experiments were carried out in a  $3\text{-m}^2$  CPC solar pilot plant with a 35-L total volume. The efficiency of the combined process NF/Photo-Fenton in terms of hydrogen peroxide consumption and illumination time (and accumulated energy) was clearly higher than photo-Fenton alone.

## Multivariate optimization on UV filters extraction from natural water

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Ultraviolet filters, has many applications, the main one being as component of Personal Care Products (PCPs). Their effectiveness in reducing the effects of solar radiation, especially skin cancer, these compounds started to be added not only in sunscreen products, but also became a part of the formulations of many products for daily use, such as cosmetics, skin creams, body lotions, sprays and hair dyes, shampoo and several other. Due to diversity of applications, the amount of UV filters reaching the environment is specked high. An aggravating factor are recent research has reported on the ability of these substances interact with estrogen receptors and thus interfere with the normal functioning of the endocrine system of living beings. Sample preparation is a crucial step in the analytical process and may involve a large number of variables. The study of these variables one by one, may take a long time, many costs and can lead to erroneous conclusions. The aim of this work was the study multivariate of factors that influence the procedure of solid phase extraction (SPE) of the UV filters (figure 1): Benzophenone-3 (BP-3), Ethylhexyl methoxycinnamate (EHMC), Ethylhexyl salicylate (ES) and Octocrylene (OC) from aqueous samples. The analysis was performed using a GC-MS/MS (Varian, Saturn 2000) with a ZB-5MSi (Phenomenex) fused -silica capillary column (30 m x 0.25 mm I.D. x 0.25  $\mu$ m film thickness). For SPE (Strata X, Phenomenex) optimization was used a fractional factorial design ( $2^{5-1}$ ). The variables studied were: pH (2 and 6), breakthrough volume (200 and 500 mL), eluent volume (3 x 2 mL and 3 x 6 mL), type of eluent (ethyl acetate and ethyl acetate:hexane 75:25) and solvent washing composition(water and methanol 10% in water). The experimental design and the analysis of the data were performed using the STATISTICA<sup>®</sup> software package (version 8.0 StatSoft, Tulsa, USA). Using the Pareto chart for the normalized recoveries, from spiking river water samples, only the variable pH was statistically significant. The use of experimental design in the optimization of the SPE procedure allowed to reach the development of the extraction method quickly, simply and efficiently, with recoveries from 51 to 105% for all studied UV filters.

## Legacy and emerging brominated flame retardants in shellfish from the French coasts: levels and temporal variations

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Selected Brominated Flame Retardants (BFRs) were investigated in filter-feeding molluscs collected at 20 sampling sites along the main coasts of France in 2010, 2011 and 2012. The study contaminants were HBCD (hexabromocyclododecane), PBDEs (polybrominated diphenyl ethers) and their replacement compounds BTBPE (1,2-bis(2,4,6-tribromophenoxy)ethane) and DBDPE (decabromodiphenyl ethane). These emerging substances are frequently referred to as novel BFRs. Other non-PBDE BFRs were also investigated, namely, hexabromobenzene (HBB) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153).

Extensive identification of PBDE congener pattern was performed using HRGC-HRMS (High Resolution Gas Chromatography-High Resolution Mass Spectrometry). PBDE congener patterns were dominated by the tetra- and penta- brominated congeners BDE-47 > BDE-99 > BDE-100 > BDE-49, their sum representing 72% relative to the sum of the 32 analysed congeners. BDE-209 was also found at significant levels in the samples (12% of the sum of congeners, on average).

The predominant PBDE congener, BDE-47, and alpha-HBCD (predominant HBCD isomer) concentrations were found at similar concentration levels. In samples from 2011, these compounds were between 0.02 ng g<sup>-1</sup> wet weight (ww) (Arcachon Bay, Atlantic coast) and 0.24 ng g<sup>-1</sup> ww (Nivelle estuary, Atlantic coast), and between 0.01 ng g<sup>-1</sup> ww (Arcachon Bay) and 0.24 ng g<sup>-1</sup> ww (Nivelle estuary), respectively. Novel BFRs (BTBPE and DBDPE) exhibited concentrations that were 20 times lower than those of BDE-47. Historical BFR (HBB and BB-153) concentrations were 10 times lower than those of the novel BFRs. The temporal variations of the concentrations were compared with regards to regulation and usage of the compounds.

The results showed that samples from the Mediterranean coast were more contaminated (median values) by all compounds except by BTBPE (higher median value in samples from the English Channel). High concentrations were determined in samples from the Seine estuary (English Channel) for all compounds. Geographical distribution of BDE-47 and alpha-HBCD concentrations showed a high correlation, suggesting similar sources (urban and industrial), and revealing widespread contamination of the coastal environment by these BFRs.

The presented results constitute a reference for the future monitoring of French coastal contamination by emerging contaminants.



## Screening of emerging environmental contaminants with time-of-flight mass spectrometry

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It is very important to assess chemical pollution by new compounds to get an early warning of their presence in the environment and stop using chemicals before they cause harmful effects. One approach to find new compounds in environmental samples is to conduct non-target analysis. This means identification of sample's components without any preselection of the analytes. Time-of-flight mass spectrometer (TOF-MS) can be used for such analysis as its mass resolution and sensitivity are high. Post-target analysis is also possible with TOF-MS even in a retrospective way since all data is saved during acquisition.

We developed non-target and post-target multiresidue methods for different water sample types using TOF-MS techniques. Non-target analysis with UPLC-TOF-MS was not very practical as there were usually only a few peaks in the spectrum. Furthermore, there were many candidate compounds suggested by the software when the molecular mass accuracy cut-off value was 20 mDa. This combined with the problems in the library search software often led to many false positive identifications.

An UPLC-TOF-MS post-target analysis method was validated by spiking a wastewater sample with model compounds (pesticides and pharmaceuticals). 81 of the 88 model compounds were correctly identified when retention time information was available and mass error cut-off value of  $\pm 30$  mDa was used. Without retention time information the post-target method was more challenging. Mass error cut-off value was set to  $\pm 5$  mDa for candidate compounds to qualify. Then we used information about the lipophilicity ( $\log K_{ow}$ ) of the compounds in relation to retention time in UPLC to decrease the number of candidate compounds. In addition, the isotopic pattern of the spectra was examined to conclude whether there are chlorine or bromine atoms in the molecules. In this way 46% of the compounds were correctly identified in positive ion mode and 90% in the negative ion mode.

A six-stage identification procedure was developed during the validation of a GC-TOF-MS non-target multiresidue method. A complex landfill leachate sample was spiked with 11 different organic compounds and eight of these could be correctly identified while three compounds were not detected at all. When the method was applied to the non-spiked leachate sample, 44 compounds could be tentatively identified.

When the GC-TOF-MS method was applied to the analysis of surface water samples, 36 compounds could be tentatively identified in the non-target analysis and further 18 compounds in the post-target analysis. The identification of ten of these compounds could later be verified by using authentic model compounds.

## OCCURRENCE OF ARTIFICIAL SWEETENERS IN FINNISH RIVERS AND LAKES

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Artificial sweeteners are used as food additives as well as in some personal care products to enhance taste. In the present study, the concentrations of four non-caloric sweeteners - saccharin (SAC), acesulfame potassium (ACS), cyclamate (CYC) and sucralose (SCL) - were analysed in surface water samples. The four sweeteners are synthetic molecules, which are excreted from the human body largely unaltered. The breakdown of ACS and SCL at wastewater treatment plants (WWTPs) is limited: only up to 40% of ACS and less than 20% of SCL are removed. Over 90% of SAC and CYC are eliminated in the wastewater treatment processes. However, levels as great as several ppb have been found in WWTP effluents. Thus the four sweeteners can end up in the receiving rivers and lakes. ACS and SCL are very soluble in water, and have been shown to be persistent in environmental water, which makes them ideal tracers of domestic wastewater. The stability and high water solubility of sucralose and acesulfame can lead to increasing environmental concentrations, which can affect aquatic ecosystems.

Water samples were collected from lakes and rivers, which are influenced by wastewater. The river water samples were collected in major rivers in southern part of Finland. Lake water samples were sampled from southern and central Finland. Filtered and pH adjusted water samples were extracted with weak anion exchange solid phase extraction. The instrumental analysis was performed by UPLC-MS/MS. An LC gradient consisting of methanol and water, and a C18 column (1.8  $\mu\text{m}$ , 2.1 x 50 mm) were applied. Electrospray in negative polarity was used as an ionization technique. Mass analysis was done in multiple reaction monitoring mode with two specific transitions for each analyte. The method limits of detection (LoD) were 1.0 ng/L, 2.0 ng/L, 3.5 ng/L and 20 ng/L for CYC, ACS, SAC and SCL, respectively. The quantitation limits (LoQ) were 13 ng/L for CYC, 25 ng/L for ACS and SAC, and 200 ng/L for SCL.

All four sweeteners were found in surface water. The most abundant sweetener in all samples was ACS, which is in accordance with previous European and North American studies. ACS was quantified in all samples at concentrations ranging from 0.056  $\mu\text{g/L}$  to 9.5  $\mu\text{g/L}$ . SAC, CYC and SCL were detected in 94%, 78% and 41% of the samples, respectively. The highest individual concentrations were obtained in river water, where 9.5  $\mu\text{g/L}$  of ACS, 0.15  $\mu\text{g/L}$  of SAC, 0.12  $\mu\text{g/L}$  of CYC and 1.0  $\mu\text{g/L}$  of SCL were measured.

## Adverse effects of fullerenes (nC<sub>60</sub>) spiked to sediments on a benthic *Oligochaeta*, *Lumbriculus variegatus*

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Carbon nanoparticles, such as fullerenes (nC<sub>60</sub>), are a very promising group of engineered nanoparticles. Their unique properties make them usable i.e. in electronics, optics, and cosmetics. Increasing manufacturing and use of fullerene-containing products raise a risk that fullerenes can enter to the environment. In addition, some of the uses of fullerenes suggest that they will be directly released to wastewaters.

Fullerenes have often tendency to settle to the bottom in natural waters. Thus, they can become available for benthic species. In the current study, a black worm *Lumbriculus variegatus* (*Oligochaeta*) were investigated to assess possible effects of nC<sub>60</sub> on a benthic species. Survival, growth, reproduction, and feeding activity of the black worms were determined. Also histological studies were performed to investigate possible effects of nC<sub>60</sub> on the main organs of exposure route, epithelium and a gut track.

Natural sediments were collected from a clean area and they were then spiked with fullerenes to mimic situation where fullerenes have released to aquatic environment. Control sediments without spiking fullerenes were included. Black worms were exposed to 0, 10 and 50 mg fullerenes/kg sediment dry mass for 28 days. Tested concentrations did not impact survival of the black worms or their reproduction compared to control. Instead, the feeding activity slightly decreased in both test concentrations indicating disruptive effect on feeding. This may affect health and welfare of black worms in a long run. In addition, depuration efficiency decreased in the high exposure concentration. Histological observations revealed that 16% of the epidermal cuticle fibers of the worms were absent in the high concentration, which may make black worms susceptible to other contaminants or environmental stressors. Black worms also relocated fullerenes to the sediment surface via egestion where they can be available for other species.

## Modelling the fate of ciprofloxacin in activated sludge systems – The relevance of the sorption process

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The sorption process can impact the removal of specific pharmaceuticals in municipal wastewater treatment plants (WWTPs). Ionic interactions (e.g., pH-driven equilibria and complexation), rather than hydrophobic interactions, are known to affect the sorption of zwitterionic pharmaceuticals. In a previous study [1], a daily systematic reduction of ciprofloxacin removal in a full-scale WWTP (Bekkelaget, Norway) was associated to deteriorated sorption. Therefore, in this study we further investigated the sorption of ciprofloxacin onto activated sludge at laboratory- and full-scale. Targeted batch experiments were performed to estimate sorption model parameters using Freundlich isotherms under specific pH and iron salt dosing (used for chemical phosphorus removal) conditions. We used the previously tested activated sludge framework model for xenobiotic trace chemicals (ASM-X) to assess the fate of ciprofloxacin in a full-scale activated sludge system. Sorption was described by linear kinetics and, in an extended version of ASM-X, using a Freundlich-based submodel. In the latter case, Freundlich parameter values estimated from the batch experiments were used for model calibration. The prediction accuracy was statistically evaluated in the two cases by comparing the model output with measured data.

Batch experiments showed that maximum sorption capacity occurred at pH=7.4, corresponding to the isoelectric point of ciprofloxacin. A pH increase resulted in a significant reduction of sorption capacity as compared to the effect of the pH decrease applied in the experiment. Additionally, iron salt dosing was found to enhance sorption under both aerobic and anoxic conditions. Using the extended ASM-X model, results obtained in scenario simulations – based on the batch experimental Freundlich parameters – suggest that pH conditions, rather than reduced salt dosing, can be responsible for the decrease of ciprofloxacin sorption in the full-scale WWTP. The most accurate predictions were obtained for Freundlich parameter values of  $K=0.01$  ( $\mu\text{g}^{(1-1/n)} \text{L}^{1/n} \text{mg}^{-1}$ ) and  $1/n=1.33$ . A pH increase was therefore estimated to cause reduced sorption in the anoxic and the aerobic reactors, possibly being a consequence of the lower sorption extent exhibited by the anionic ciprofloxacin species. Comparable prediction accuracy was obtained using linear sorption. A 20-fold decrease of the anoxic and aerobic  $K_D$  values (1.1 and  $0.42 \text{ L gX}_{SS}^{-1}$  under normal conditions, respectively) was estimated in the time interval when deteriorated sorption was hypothesized.

[1] Plósz, B.G.; Leknes, H.; Thomas, K.V. (2010a). *Impacts of competitive inhibition, parent compound formation and partitioning behaviour on antibiotic micro-pollutants removal in activated sludge*. Environmental Science & Technology, 44 (2), 734–742.

## A novel analytical method for the determination of amphetamines and ecstasy related stimulants from water and urine by solid-phase microextraction combined to gas chromatography-mass spectrometry

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The potential of estimating drug consumption from wastewater analysis has fostered the development of new analytical methods in the last years [1]. Moreover, drugs of abuse may become a environmental serious risk due to their high illicit consumption and the ineffective removal in wastewater treatment plants.

In this work we show that solid-phase microextraction (SPME) combined to gas chromatography-mass spectrometry (GC-MS) may be a good and less expensive alternative to conventional solid-phase extraction (SPE) procedures for the determination of amphetamine, methamphetamine and three ecstasy derivatives (MDA, MDEA, MDMA). In-sample derivatization of these drugs was performed using a water-stable reagent, *iso*-butyl chloroformate (iBCF), and a basic catalyser, a phosphate buffer. All parameters affecting extraction and derivatization were carefully evaluated and under optimized conditions, 100 mL of sample with 2 g of dipotassium monohydrogen phosphate trihydrate and 100  $\mu$ L of iBCF (1:1 in acetonitrile) were mixed during 1 hour at 60  $^{\circ}$ C with a polydimethylsiloxane-divinylbenzene (PDMS-DVB) SPME fibre directly exposed to the sample. Subsequently, the fibre was desorbed during 3 minutes at 250  $^{\circ}$ C into the injection port of the GC-MS. This method led to limits of detection (LOD) between 0.4 and 2.0  $\text{ng L}^{-1}$ , excellent precision in surface and wastewater samples (0.7-14.2 %RSD) and relative recoveries rounded 100% in all samples. Finally, methamphetamine, MDA and MDMA were detected in all environmental water samples at concentrations lower than 30  $\text{ng L}^{-1}$ .

The method was also successfully applied to urine samples. In that case, 1 mL of urine was diluted 10-fold with ultrapure water and the rest of method downscaled. LODs obtained for urine were between ten to one hundred times lower than most published methods dealing with urine, SPME and amphetamine related stimulants.

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## Determination of Tributyltin in whole water samples

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The widespread use of organotin compounds (OTC), for example as pesticides, antifouling coatings and PVC stabilizers, results in an extensive release into the environment. OTCs show toxic effects already in trace levels. The public concern is focused on the toxic and endocrine disruptive tributyltin (TBT) and its metabolites. Other substances like the phenyltins also exhibit strong biocide effects on aquatic organisms like fish, algae and shells.

In 2000 the European Waterframework Directive (WFD 2000/06/EC) was remitted to standardise the monitoring of aquatic ecosystems and ground waters within the EU. Furthermore, the improvement of water quality and the sustainable usage of water are main objectives of the WFD. Within the scope of the project "Traceable measurements for monitoring critical pollutants under the European Water Framework Directive" of the European Metrology Research Programme (EMRP) quantitative methods for priority hazardous substances, like TBT, will be developed. For TBT a limit of quantification of 0.06 ng L<sup>-1</sup> is specified for the whole water body by the Directive 2009/90/EC (Quality Assurance/Quality Control Directive). A sensitive analytical method is required to achieve this detection limit.

GC-ICP-MS offers the possibility to detect emerging pollutants at trace levels. This method evolved to the method of choice for the element specific analysis of water samples within the last years. Optimization of gaschromatographic and ICP-MS-parameters are essential for an effective analysis and good sensitivity of detection. Therefore, different instrumental settings were investigated and improved and will be presented. The GC-ICP-MS method was optimized for different water samples spiked with butyl- and phenyltin compounds. The feasibility to quantify TBT in real water samples at the WFD concentration level will be shown. Further results on stability and transformation of OTCs and the influence of environmental factors like humic acid and suspended particulate matter on OTC analysis will be presented.

## Matrix solid-phase dispersion followed by gas chromatography quadrupole time-of-flight mass spectrometry (GC-QTOF-MS) for benzotriazole UV absorbers determination in sludge

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Organic UV light absorbers are high volume production chemicals incorporated in a variety of commodities, such as sun screens and other personal care products, paints, surface coatings and building materials, with the aim of retarding light induced degradation reactions. Benzotriazole UV stabilizers (BUVSs), also referred as Tinuvin, constitute the most important family of UV absorbers employed in paints, varnishes and coatings. Recently, residues of these additives have been found in biota samples [1-2], dust from indoor atmospheres [3] and raw sewage water (low ng L<sup>-1</sup> levels) [4]. Given that BUVSs display moderate to high lipophilic properties, it is deemed that they might be accumulated in sludge at sewage treatment plants (STPs). This fact has been recently demonstrated in the first monitoring campaign carried out in STPs from 30 Chinese cities [5]. The aims of this study are to develop a simple procedure for the selective determination of BUVSs residues in sludge from sewage treatment plants (STPs) and to obtain additional information regarding their levels in this matrix. Matrix-solid phase dispersion (MSPD) was chosen as sample preparation technique since (1) the use of mild extraction conditions leads to less complex extracts than those provided by Soxhlet and Pressurized Liquid Extraction (PLE) and (2) MSPD permits integrating extraction and clean-up in the same step. After extraction, the suitability of gas chromatography followed by quadrupole time-of-flight mass spectrometry (GC-QTOF-MS) for their selective determination in freeze-dried sludge extracts is discussed. Availability of accurate ion product scan (MS/MS) spectra allowed the unambiguous identification of BUVSs in sludge. UV-326, UV-328 and UV-234 were the most abundant congeners, with individual concentrations above 100 ng g<sup>-1</sup> in some of the processed samples. Also, the presence of BUVSs was noticed in two reference materials of sludge proceeding from different geographic areas.

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## New Method and Procedures of Determination of Alkylphenols in Indoor and Ambient Air

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Alkylphenols are massively produced for manufacturing of alkylphenol ethoxylates used as surfactants in common consumer products such as detergents, disinfectants, surface cleaners and as plasticizers. Bisphenol A is mainly used as monomer in the fabrication of epoxide resins and polycarbonate plastics. Both alkylphenols and bisphenol A are considered important indoor air contaminants.

They have been identified as xenoestrogenic in vitro and in vivo. Due the similarity with 17 $\beta$ -estradiol they are able to bind with the estrogen receptor and initiate transcription of estrogen-responsive genes. A recent study has also reported that these chemicals can act by additional endocrine mechanisms<sup>1</sup>.

Due to extensive use of these chemicals for the last 50 years, they have become widespread in the environment. The indoor concentrations of alkylphenols are often highest than outdoors, degradation processes indoors are limited. Existing studies show indoor concentrations of alkylphenols are generally around 100 ng·m<sup>-3</sup>, while outdoor concentrations are about 10 times lower. Levels of alkylphenols in the particulate phase of air samples are substantially lower than in the gas phase<sup>1</sup>.

A new method has been developed to assess the occurrence of the alkylphenols (4-tert-octylphenol, 4-octylphenol, the isomers of nonylphenol) and bisphenol A in gas phase and aerosol samples. For sampling gas and particulate phase XAD-2 resin and quartz fiber filters were used, respectively. If necessary (samples were not clean enough), accelerated solvent extraction (XAD-2) and Soxhlet extraction (quartz filters) was followed by column chromatography clean-up. Before final HPLC-ESI-MS/MS analysis, analytes were derivatized with dansyl chloride. This step distinctly enhances sensitivity of the method and decreases limit of detection by a factor of 1000.

The widespread use of the analytes in plastic resins resulted in sample contamination. For this reason a careful choice of sampling material was necessary and laboratory procedures were modified to reduce the contamination risk. In order to meet quality control standards recovery efficiency of the method was evaluated. Laboratory and material blanks were routinely analyzed. The absolute limits of detection and determination were in the range of pg per compound, which is a prerequisite for the quantification of the analytes in relatively unpolluted air.

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## Preliminary assessment of emission of fluorotelomer alcohols from waterproofing impregnation sprays using thermal desorption-gas chromatography-mass spectrometry

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Fluorotelomer alcohols ( $C_nF_{2n+1}CH_2CH_2OH$ ; n:2 FTOHs, where usually n=4, 6, 8, 10) are a group of volatile polyfluoralkyl substances. They are key raw materials in the synthesis of fluorotelomer acrylates and metacrylates, which are used to manufacture fluorotelomer-based polymers. These polymers provide water, oil, and stain repellency to many industrial and consumer products, i.e., clothing fabrics, leather, upholstery, carpets, and coatings for paper. They have also found applications in other commercial products such as household cleaning and impregnation agents. In recent years, FTOHs have been detected ubiquitously in the environment; especially high concentrations were found in indoor air samples collected in private homes and occupational settings. The wide spread presence of FTOHs in indoor environments is explained by evaporation of FTOH from commercial goods. FTOHs have recently raised much concern because they are precursors of the persistent and partly toxic family of perfluorocarboxylic acids.

The aim of this study was to assess the emission of 4:2, 6:2, 8:2, and 10:2 FTOH from commercially used waterproofing impregnation sprays available on the consumer market. The FTOH content of the sprays were assessed by direct measurement of the spray liquids. Treated textiles were placed in a test chamber, from which air samples were collected by active sampling with a constant flow air sampling pump at room temperature. Sampling time varied depending on the characteristics of each spray. The analysis was performed by thermal desorption (TD) of the analytes retained on the sorbent tubes coupled with gas chromatography (GC)/ mass spectrometry (MS).

## On-line coupling of solid-phase extraction to gas chromatography-mass spectrometry to determine musk fragrances in wastewater

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An on-line solid-phase extraction coupled to gas chromatography mass spectrometry through an on-column interface procedure has been developed for the first time to preconcentrate trace amounts of a group of musk fragrances extensively used in personal care products from wastewater. A 10 mm x 2 mm I.D. precolumn packed with Oasis HLB (60µm) or C18 (60µm) was tested for the optimization of the solid-phase extraction process. Both the solid-phase extraction variables (e.g. elution solvent, sample volume ,...) and the parameters affecting the transfer of the analytes from the precolumn to the GC system (e.g. flow-rate, temperature and solvent vapor exit time) were optimized. Methanol as organic modifier was added to the sample before the extraction process to avoid adsorption problems.

The use of the MS detector under selected ion monitoring acquisition enabled the analytes to be quantified at sub ng L<sup>-1</sup> levels preconcentrating only 10 mL of sample, and the limits of detection were between 1 ng L<sup>-1</sup> and 6.6 ng L<sup>-1</sup> depending on the target analytes. The method also provided good levels of repeatability with relative standard deviations varying between 2% and 8% (n=3, 1,000 ng L<sup>-1</sup>).

The applicability of the method was tested with different water samples from wastewater treatment plants. The analysis of influent wastewater revealed the presence of most of the compounds analysed with concentrations ranging between <MQL of celestolide to 42.9 mg L<sup>-1</sup> of tonalide. While in effluent wastewater a decrease on the concentrations was showed. Only HHCB-Lactone maintains its concentration because it is the degradation product of galaxolide and then it can be generated during the wastewater treatment process.

## Enrichment free LC-HRAM/MS screening method of anthropogenic sewage pollutants in waste water, receiving, ground and drinking water samples

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In last decade, there has been growing public concern of potential contamination of water and environment with anthropogenic compounds and their degradation products and possible negative influence to the nature and public health. As a response to this fact, there is an increased interest in more efficient screening techniques of larger number of possible pollutants compared to that traditionally carried out by triple quadrupole mass spectrometers. The high resolution and accurate mass does not require optimization of compound specific parameters and has the ability to properly separate matrix from compounds of interest.

Fast and highly selective methods are necessary to screen, confirm and quantify different classes of contaminants in complex matrix and at low concentrations. High resolution mass spectrometry – using full scan analysis mode – has been described as the preferred screening tool due to the possibility to look for a large number of compounds and also because it enables retrospective analysis [1]. Furthermore, the use of a resolving power of 50,000 FWHM is reported as being more selective than 2 SRM transitions when using triple quadrupole instruments [2,3].

In this work, the large volume direct injection has been applied to the screening of anthropogenic sewage pollutants in different matrices using a quadrupole-Orbitrap analyser – Q Exactive™. The experiment consisted on combining full scan mode at a resolving power of 70,000 FWHM with data dependent MS/MS spectra acquired at a resolving power of 17,500 FWHM. The MS/MS spectra were generated by using a high energy collision induced dissociation cell (HCD). This experiment was tested and evaluated in terms of quantification and confirmatory capabilities for the analyses of anthropogenic sewage pollutants. Different sample types were tested, including waste water, ground water and drinking water representing different steps within the water cycle of densely populated and intensively agriculturally used areas.

*Keywords: HRMS, screening, pesticides, drugs, waste water, enrichment free*

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Rapid Communications in Mass Spectrometry, 2011, 20, 3161-3166

## Removal of quinolone antibiotics from wastewaters by sorption and biological degradation in laboratory-scale membrane bioreactors

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The increasing public concern about the hazards associated with pharmacologically active compounds (PACs) in the environment has triggered activities by scientific, industrial, and regulatory bodies to assess the exposure and effects of these chemicals in different environmental compartments [1]. WWTPs act as point sources of the aquatic environment and play an important role in the life cycle of PACs. Therefore, it is not surprising that these compounds are routinely present at detectable concentrations in surface and ground water, treated wastewater, biosolids, soils or sediments [2].

In this work, laboratory-scale batch experiments were developed in order to investigate the main removal routes for 6 commonly found quinolones (ciprofloxacin, moxifloxacin, norfloxacin, ofloxacin, piperimidic acid, and piromidic acid) in wastewaters, at  $\mu\text{g L}^{-1}$  levels in an aerobic sludge system from a membrane bioreactor (MBR) pilot plant. It was demonstrated that biotransformation and sorption were the main removal routes for the target antibiotics over other possible pathways, as volatilization or hydrolysis, under the experimental conditions. Mass balances indicated that sorption on sludge played a dominant role in the elimination of antibiotics from waters. The sorption coefficient  $K_d$  depended strongly on temperature and on the quinolone type and were higher at lower temperatures and for piperazinylic quinolones.  $K_d$  values were between 516 and 3746  $\text{L kg}^{-1}$  in the temperature range of 9–38°C. Higher mixed liquor suspended solids (MLSS) increased quinolone removal efficiency mainly by sorption. Quinolone biodegradation constituted a secondary pathway, and could be described by first-order kinetics with degradation-rate constants ranging from  $8.0 \times 10^{-4} \text{ h}^{-1}$  to  $1.4 \times 10^{-2} \text{ h}^{-1}$  within the same temperature range and MLSS from 7,000 to 15,000  $\text{mg L}^{-1}$ . Biodegradation depended on the MLSS and temperature, but also on the initial chemical oxygen demand (COD). Higher biodegradation rates were observed at higher MLSS and temperature, as well as at low initial COD. Ciprofloxacin and moxifloxacin registered the highest biodegradation percentages (52.8% and 47.2%, respectively, at 38°C and 15,000  $\text{mg L}^{-1}$  MLSS), which is evidence that, despite the known persistence of this group of antibiotics and removal from waters mainly by sorption, it was possible to improve their removal by biodegradation, with an appropriate selection of conditions and control of process variables, as a preliminary step towards the elimination of these antibiotics from the environment. Further research is needed on the possibilities of removing sorbed antibiotics from sludge.

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## UPLC-MS/MS method for the determination of parabens in compost from sewage sludge. Comparison of the efficiency of two extraction techniques

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Parabens, the alkyl esters of 4-hydroxybenzoic acid, are a family of compounds with anti-fungal and anti-bacterial properties that are often used in a variety of foods, drugs, cosmetics and personal care products. Parabens have been used as preservatives in cosmetics since the 1920s by almost all cosmetic manufacturers as the rates of skin problems are reported as being amongst the lowest in dermatological patients. Recently, it has been demonstrated that parabens exhibit activity as endocrine disruptors, because they interfere with the function of endogenous hormones [1, 2]. Therefore, there is a growing need to determine the fate of these compounds in the environment. Since it has been reported that many compounds with estrogenic activity have a great tendency to associate with particulate matter, it is of high importance to study the presence of these compounds in solid matrices. In that context, it is necessary to develop analytical procedures that permit a fast but accurate identification and quantification of these compounds.

In this work, we compare two extraction techniques—ultrasound-assisted extraction (USE) and pressurized liquid extraction (PLE)— and evaluate their efficiency in the determination of parabens in compost samples. The extraction parameters for each technique were accurately optimized to achieve the highest recoveries. The selected compounds were detected and quantified using ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS), operating in negative electrospray ionization (ESI) and in selected reaction monitoring (SRM) mode. The analytes were separated in less than 5 min. Ethylparaben (ring-<sup>13</sup>C<sub>6</sub> labelled) was used as internal standard. Two selective, sensitive, robust and accurate analytical methodologies were developed. The limits of detection (LOD) of the methods ranged from 3 to 7 ng g<sup>-1</sup> and the limits of quantification (LOQ) from 10 to 23 ng g<sup>-1</sup>, while inter- and intra-day variability was under 6% in all cases. Given the absence of certified materials, the methods were validated separately by using matrix-matched calibration and recovery assays with spiked samples. Recovery rates ranged from 94.0% to 105.0%. Compost samples were taken from a composting plant, located in the province of Granada (Spain). Although the statistical comparison demonstrated no statistically significant differences between the two extraction techniques for the determination of parabens in compost samples, the method based on PLE was more sensitive than the USE-based method.

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## Biological Tools to Optimize Treatment Technologies to Remove Micropollutants and Endocrine Disrupters (BIOTTOPE).

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The ecological and human health impact of endocrine disrupting compounds (EDCs) and other emerging micropollutants detected in the aquatic environment has come to the attention of scientists, environmental regulators, water suppliers as well as the general population. Many of these compounds may be found at low concentrations in treated wastewater and environmental water. Chemical and biological analysis became essential to assess their presence in environmental matrices as well as for the determination of the effectiveness of treatment systems. However it is not possible to determine molecule by molecule the risks to the environment, global approaches are thus required. In this framework, the aims of the BIOTTOPE project are as a first step to develop an automated tool for the analysis of the endocrine disruption potential of wastewater directly on site. This tool, based on small biological aquatic models genetically modified in order to be fluorescent when they are in contact with specific EDCs, will be able to follow over time the endocrine disruption potential of the wastewater and evaluate adapted treatments in order to reduce the pollution and the impact of the wastewater treatment plant (WWTP) effluents on aquatic ecosystems. In a second step the performance of a new wastewater treatment technology, based on activated carbon adsorption and on an accelerated settling step, is monitored using untargeted chemical analysis approach. The strategy to analyze both non polar and polar compounds requires two high technological instrumentation: comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GCxGC TOF MS) and liquid chromatography coupled to high resolution mass spectrometer (LC-HRMS). Organic pollutants are identified thanks to homemade databases containing more than 1000 compounds for GCxGC TOF MS and 1500 compounds for LC-HRMS.

Results show that the WWTP effluents can have or not endocrine disrupting effects. This effect may depend on fluctuations in human activities and/or in the operation of the WWTP. Tertiary treatment technologies as adsorption on activated carbon can remove micropollutants that impact the endocrine system in living organism. Some of chemical compounds identified in raw wastewater are not included in French or European prioritisation lists. The next step will consist in the toxicity evaluation of some recurrent compounds to evaluate their relevance.

**This poster is related to conference:** "Occurrence of emerging organic micropollutants in urban wastewaters – Non-targeted analysis using GCxGC TOF MS and LC-HRMS"

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## UHPLC-MS/MS for the quantification of plasticizers in water samples and beverages

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Phthalates and alkylphenols are a group of substances added to plastics to modify their physical properties such as flexibility or durability. These compounds have been used for a long period of time in the plastic industry, in particular, in the fabrication of food packages. They are considered as emerging pollutants as a result of their extensive use, potential risk to humans by uptake through food and beverages and due to their endocrine disrupting properties.

The aim of this work was to develop a method for the analysis of 22 plasticizers in water and beverages. Compounds studied were dimethyl phthalate, diethyl phthalate, benzophenone, benzyl butyl phthalate, dibutyl phthalate, acetyl tributyl citrate, bis(2-ethylhexyl)adipate, bis(2-ethylhexyl) phthalate, bisphenol A, 7 butylphenol isomers, 4-tert-amylphenol, 4-cumylphenol, 4-heptylphenol, 4-octylphenol, 4-nonylphenol, 4-dodecylphenol, which were analyzed by ultra high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) operating in multiple reaction monitoring mode. The column used for the chromatographic separation was an Acquity UPLC BEH C18, 100 mm x 2.1 mm, 1.7 µm particle size (Waters, USA). The mobile phase was composed by MeOH/H<sub>2</sub>O. The extraction method was optimized by solid phase extraction using six cartridges of different characteristics. Finally, the OASIS HLB cartridges were selected for its better performance in terms of extraction capacity, repeatability and reproducibility.

The method was applied to the analysis of bottled water, distribution water and beverages and different compounds were detected at the low µg/L concentrations. Total Daily Intake was estimated according to the consumption of each type of drink.

### Acknowledgements

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## Assessment of pesticide exposure in general population from Catalonia

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Pesticides are widely used in agriculture to prevent or reduce losses by pests and to improve the yields and quality of the products. However, the extensive use of these compounds involves some unwanted effects such as the chronic exposure of the general population to low amounts of pesticides which are incorporated from food, air and drinking water.

Diseases such as cancer, allergies, neurological and reproductive disorders have been related to pesticide exposure. Concern on pesticide use and its impact on human health and environmental quality have increased significantly. Measurement of these contaminants and their metabolites in body tissues and fluids provide useful assessment on the exposure risk of the population.

Gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) affords the necessary sensitivity and selectivity for the analysis of these compounds in human tissues. Accordingly, a multi-residue method for the quantification of a large number of pesticides such as pyrethroids, organochlorine compounds, organophosphorous compounds and polychlorobiphenyls in human serum samples has been developed and validated. The analytes were isolated by solid-phase extraction using C18 and silica gel cartridges for clean-up and subsequent analysis by GC-MS/MS.

The method was used to investigate the pesticide content in serum samples from volunteers living in Barcelona (Catalonia). The analysis showed the presence of several persistent organochlorine compounds and non persistent compounds like organophosphate compounds (methyl bromophos, Chlorpyrifos, Diazinon, Disulfoton, Malathion, Mevinphos) and pyrethroids (Permethrin) at concentrations above the detection limit in the majority of samples.

The results of non-persistent pesticides in serum were compared with those from the NHANES reports, which determined pesticide metabolites in urine. In our study, quantifiable results of the following pesticides were found: chlorpyrifos (0.088 µg /L), diazinon (0.028 µg /L), malathion (0.0976 µg /L) and permethrin (0.054 µg /L). In the NHANES reports, only the urinary metabolite for chlorpyrifos, 3,5,6-trichloro-2-pyridinol (1.56 g / L) was found above the detection limit.



## Migration of plasticizers from Tritan™ and polycarbonate bottles and toxicological evaluation

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Plastic is a processable material based on polymers and is widely used around the world for primary packaging. In the water bottling sector, polycarbonate (PC) is used for repeated use bottles and it is manufactured with the monomer 4,4'-dioxo-diphenyl-2,2-propane (bisphenol A, BPA). Due to the worldwide concern about the human exposure to BPA from food and water and its potential endocrine disrupting effects the packaging industry is searching new plastics. Tritan™ copolyester, a BPA free plastic, is a potential substitute of PC. Tritan™ copolyester was introduced in 2007 as a polymer produced from dimethyl terephthalate (DMTP), 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol.

The present study is aimed to perform migration assays with reusable PC and Tritan™ bottles according to legislated conditions described in the Commission Regulation (EU) No 10/2011, Directive 82/711/CE and Directive 85/752/CEE. Bottles were tested with milli-Q water in 3 consecutive incubation periods as described in legislation and they showed the migration of BPA up to 2.416 µg/L in PC and the migration of dimethyl isophthalate (DMIP) up to 0.902 µg/L in Tritan™.

After migration assays, water samples were used to analyze their endocrine disruptor activity. In addition, BPA and DMIP were tested to make a comparison between sample and individual compounds. The *in vitro* tests Yeast Estrogenic Screen (YES), Yeast Antiestrogenic Screen (YAES), Yeast Androgenic Screen (YAS), Yeast Antiandrogenic Screen (YAAS), Retinoic acid receptor (RAR) and Vitamin D receptor (VDR) activity using yeast-based recombinant receptor-reporter gene bioassays were used to test the samples and the specific compounds. In PC samples, an increase in absorbance was observed along the migration assay obtaining the highest absorbance in the 3<sup>rd</sup> incubation period (2.416 µg/L BPA). In Tritan™ samples, a decrease in absorbance was observed along the migration assay obtaining the highest absorbance in the 1<sup>st</sup> incubation period (0.902 µg/L DMIP). However, no significant differences were observed in these samples in comparison with control test because activity was too low in the water samples.

*In vivo* tests were performed with *Potamopyrgus antipodarum*, considered as a sentinel for estrogen-like compounds, for BPA and DMIP. Exposure to 30 µg/L BPA resulted in a statistically significant increase of reproduction. DMIP effects were less pronounced. In snails exposed to 30 µg/L DMIP resulted in a slight but not significant increased embryo production. This fact is in accordance with *in vitro* data where DMIP was less estrogenic than BPA.

## Liquid chromatography coupled to tandem mass spectrometry and Orbitrap mass spectrometry as analytical tools to characterize multi-class cytostatic compounds

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Cytostatic compounds used in the treatment of cancer have emerged as a new generation of water contaminants due to the continuous amounts administered to patients and to the fact that a variable proportion is excreted unchanged. In this study, we have evaluated the performance of liquid-chromatography-tandem mass spectrometry (LC-MS/MS) and high resolution mass spectrometry (HRMS) (LC-Orbitrap-MS) for the multiresidue determination of multi-class cytostatic compounds. In a first step, ionization conditions were tested in positive electrospray mode and optimum fragmentation patterns were determined. For LC-MS/MS, two selected reaction monitoring (SRM) transitions were optimized and for LC-Orbitrap-MS, the molecular ion with 5 ppm error and two product ions were defined. Following, the chromatographic conditions were optimized considering that compounds analyzed have a very different chemical structure and chromatographic behavior. The best performance was obtained with a Luna C18 column, which permitted the separation of the 26 compounds in 15 min. Finally, the performance of LC-MS/MS and LC-Orbitrap-MS was compared in terms of linearity, sensitivity, intra and inter-day precision and overall robustness. While LC-MS/MS provided good identification capabilities due to selective SRM transitions, LC-Orbitrap proved to be 100 times more sensitive. This study provides a comprehensive overview on the MS conditions to determine the outmost used cytostatic compounds and provides a spectral library to be used for the identification of these compounds in water or biological matrices.

### Acknowledgements

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## Improved analytical tool for epidemiological studies and biomonitoring - simultaneous determination of PFAS and POPs from a low volume human serum samples

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Environmental pollutants have been associated with various health outcomes. In large epidemiological studies perfluorinated alkyl substances (PFAS) have most consistently been associated with increased total and LDL cholesterol, and persistent organic pollutants (POPs) with type 2 diabetes and cardiovascular disease.

Epidemiological studies on the health effects of the environmental pollutants often employ biobank samples where only a limited volume of stored serum can be allocated for the analysis. Therefore we have developed an improved analytical tool for the simultaneous determination of multiple PFASs and POPs from a low volume human serum sample (50 – 200 microliter). The serum sample was pre-treated by the solid phase extraction and cleanup steps. The PFOS, PFOA and 11 other sulfonates/carboxylates were separated and detected with LC-MS/MS, whereas the selected POPs (HCB, beta-HCH, oxychlorane, trans-nonachlor, DDT, DDE, BDE-47 and PCB-118, PCB-138, PCB-153, PCB-156, PCB-170 and PCB-180) were analyzed with GC-MS/MS system. For both the PFASs and POPs the linearity and LOQ were tested with calibration and low concentration serum samples, respectively. Several AMAP interlaboratory comparison samples, which provide consensus values for the measured PFAS POPs, were used to test the method accuracy and repeatability.

The correlation coefficients for the linearity were  $\geq 0.9970$  for all the PFAS and  $\geq 0.9987$  for all the POPs. LOQs for PFASs were 0.1 ng/ml, except for PFOA (0.2 ng/ml). LOQs for POPs varied from 4.2 pg/ml to 44 pg/ml. The accuracy for PFASs and POPs from assigned values of AMAP samples were 92 – 106 % and 82 – 117 %, respectively. The coefficient of variation for PFAS was 2.4 – 7.3 % and for POPs 2.0 - 15 %.

In conclusion the method shows an excellent linearity and accuracy, is applicable for sample volumes from 50 to 200 microliters, and is sufficiently sensitive for samples from general populations. The throughput time for 110 serum samples is one week.

## Probing the environmental fate of artificial sweeteners: occurrence and toxicity study

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Artificial sweeteners are widely used in the production of beverages, food and even in drugs and sanitary products to substitute natural sugar. Due to its chemical stability, these compounds are cumulative in the environment and persistently affecting aquatic life. Being frequently detected in various natural water bodies worldwide, artificial sweeteners are regarded as emerging contaminants which attracted much attention from environmental scientists recently.<sup>1</sup> To date, data on the state of contamination in Hong Kong is unavailable. Despite their well-known chemical stabilities, knowledge on the environmental impact due to photodegradation of these sweeteners remains largely unknown.

In our work, the regional and seasonal occurrence profile of four commonly used artificial sweeteners (acesulfame, sucralose, saccharin, and cyclamate) in the marine environments of Hong Kong was firstly reported. Using solid-phase extraction (SPE) clean up followed by ultra performance liquid chromatography-triple quadrupole mass spectrometry (UPLC-MS/MS), occurrence profiles of the target analytes were established. Among all sweeteners, acesulfame was found in all 13 sampling spots with the highest average concentration. The distribution and concentration profiles were closely related to demographic features.

With the objective to provide a better understanding on the environmental fate of artificial sweeteners, this study further proposed the ecotoxicity of the photodegradation products of two most persistent artificial sweeteners (acesulfame and sucralose) using Microtox acute toxicity tests. From our findings, the degradation products give several ten to hundred times of increment in toxicity compared with the mother compound. A laboratory simulated removal system with elimination efficiency higher than 99% was developed for completed removal of these artificial sweeteners. The occurrence and toxicity findings not only provide useful data for a comprehensive risk assessment,<sup>2</sup> but also present valuable insight guiding prospective research on improved wastewater treatment for a complete removal of this group of emerging contaminants.

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## Assessment of air-soil exchange of chlorinated organophosphate flame retardants (OFR)

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The impact of atmospheric deposition on soil concentrations as well as air-soil exchange of chlorinated organophosphate flame retardants (OFR) were studied by collecting soil samples in Osnabrueck, Germany, in 2010/11 during a period of snow falling to snow melting, a period of rainfall and a dry period. Snow and rainwater samples were also collected at the soil sampling site, close to the university campus of Osnabrueck (52°16'56.85" N, 8°1'12.51" E) located about 3 km from the city centre. Soil samples were freeze dried, extracted for 12 h with 150 mL of toluene in a Twisselmann extractor, extracts were evaporated to dryness, redissolved in a mixture of 13 mL of tap water and 1 mL of methanol for 60 min using an ultrasonic bath and filtered through a cellulose acetate membrane filter with pore size of 0.2 µm. A volume of 7 mL was then analysed using solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS). Rainwater concentrations of chlorinated OFR such as Tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl)phosphate (TDCP) were used to assess air concentrations from the scavenging ratios at equilibrium conditions.

Values of scavenging ratios, calculated from Henry's law constants, were  $3.8 \cdot 10^6$  for TCPP,  $1.7 \cdot 10^7$  for TDCP and  $5.5 \cdot 10^7$  for TCEP. From median rainwater concentrations 46 (range: 41-48) ng/L, 187 (range: 78-234) ng/L and 372 (range: 371-385) ng/L, values of air concentrations were calculated to be 0.0034 ng/m<sup>3</sup>, 0.042 ng/m<sup>3</sup> and 0.99 ng/m<sup>3</sup> for TCEP, TDCP and TCPP, respectively. These concentrations were comparable with chlorinated OFR concentrations measured in outdoor air in other studies.

Concentrations of chlorinated OFR, TCEP and TCPP in soil samples were measured between 5.07 and 23.48 ng/g dry weight (dwt), while TDCP concentrations were below the limit of detection. Enhanced soil concentrations for both compounds, TCEP and TCPP, were observed during snow melting period, indicating snow as efficient source of chlorinated OFR in soil. However, no significant correlation between precipitation amounts and soil concentrations was observed.

Soil and air fugacity values calculated from chlorinated OFR concentrations measured in soil and rainwater were used for the air-soil exchange assessment. Fugacity fractions were lower than 0.5 (range: 0.011 - 0.103, median 0.027) for TCPP, indicating net deposition as dominant process in air soil exchange. The same behavior is assessed for TCEP, since air-soil fugacity fractions were calculated in range from 0.005 to 0.073 with median value of 0.023. These observations suggest that precipitation could be the dominant deposition process of chlorinated OFR from air to soil. Influence of precipitation, especially of snow melting process was found to be more efficient for TCEP than for TCPP. Snow was more efficient scavenger and transporter of chlorinated OFR into soil compared to rainwater, since concentrations of TCPP and TCEP in soil were almost two and four times higher after snow event than after rainfall. The detection of chlorinated OFR: TCEP and TCPP in soil samples in the absence of any point source of OFR e.g. irrigation with river water or spreading of sewage sludge, indicates that pollution of soils from diffuse atmospheric sources has to be considered in risk assessments.

## Seasonal distribution of pharmaceuticals in surface waters and sediments from Mediterranean coastal lagoon (Mar Menor, Spain).

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The occurrence of pharmaceutical products in surface waters, sediments and wastewater treatment plants effluents has been confirmed in the last years, especially in different rivers basins. Even less information is available in relation to their presence in coastal areas, which could be relevant in semi-confined systems. This is the case of coastal lagoons, such as the Mar Menor one, an hypersaline and shallow lagoon (mean depth 3-4 m) located at the south-east of Spain. This lagoon is surrounded by one of the more intensive agriculture areas in Europe (Campo de Cartagena), and also by several touristic urban areas, where the population is subject to significant seasonal variations (till ten-fold in some places). The lagoon is fed by groundwaters, surface runoffs and discharges from wastewater treatment plants (WWTPs). The seasonal distribution of pharmaceuticals in surface water (four seasons analyzed and 31 sampling points) and sediments (two seasons analyzed and 18 sampling points) from the Mar Menor lagoon has been characterized.

42 compounds, out of the 71 pharmaceutical products considered in this study were detected in the Mar Menor lagoon, where 13 of them reached up to 50 % of total annual detection frequency. Summer was the season with the highest number of analytes quantified. The most distributed pharmaceuticals around the lagoon were antibiotics (sulfamethoxazol, trimethoprim, azithromycin, erythromycin and clarithromycin), a calcium channel blocker (diltiazem) and an anti-inflammatory (salicylic acid). The most ubiquitous analyte was trimethoprim with a 100% of detection frequency in all samples analyzed. Antibiotics reached the highest spot concentrations in all seasons where the hot spot sampling points around the lagoon were associated to the Albuñón's wadi mouth, in the central part of the lagoon next to the urban area of Los Alcázares and in the north of the lagoon where a marina and fish farms are close.

25 pharmaceuticals out of 33 considered were detected in the surface sediments. No analyte was detected in all sampling points. The most detected and distributed analytes were an anti-inflammatory (salicylic acid), and an anthelmintic (thiabendazol). The highest concentrations found were associated close to the Albuñón's wadi mouth and in the south of the lagoon, where salicylic acid reached the highest spot concentrations in both seasons.

## Seasonal occurrence and distribution of pharmaceuticals in surface waters from littoral watercourses

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Emerging contaminants include a wide range of compounds, such as pharmaceuticals and personal care products, which have been present in our life for decades. However, their occurrence in the environment, and particularly in the aquatic environment, has been only confirmed in the last years. Even less information is available in relation to their input from surface water into coastal areas. El Albuñón watercourse is the main collector of the drainage basin of Campo de Cartagena area and flows continuously to the Mar Menor lagoon (SE Spain). This watercourse is fed by groundwaters, surface runoffs and discharges from wastewater treatment plants (WWTPs) of several touristic urban areas, where the population is subjected to significant seasonal variations. The seasonal input of pharmaceuticals into the Mar Menor lagoon through El Albuñón watercourse was characterized and their daily variation determined. With this purpose 2-3 samples were taken daily for a week in Spring, Summer, Autumn and Winter. In addition water samples were taken along the watercourse and its tributary (at six different sampling points) with the aim of identifying the sources of these pollutants in surface water.

55 compounds, out of the 71 pharmaceutical products considered in this study were detected in the watercourse, where antibiotics reached the highest concentrations. Significant daily variations were observed in all cases, showing a high detection frequency in many of them. It is also relevant that similar distribution and temporal variations for each family of pharmaceuticals were observed. In Spring and Winter the highest inputs correspond to lipid regulators and cholesterol lowering statin drugs, antibiotics,  $\beta$ -blocking agents and calcium channel blockers, although in Winter, much lower levels of all the drugs were found. In Summer the highest loads were found for psychiatric drugs, diuretics and antihypertensives. Finally Autumn was the season with the lowest number and amount of pharmaceutical loads. Regarding spatial variation along the watercourse, a clear increase in the concentration for the majority of pharmaceuticals was detected downstream the WWTP in the four seasons.

## Occurrence and toxicity of haloacetaldehydes in drinking waters: first evidence of iodo-acetaldehyde as a water disinfection byproduct.

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The present work aims to investigate the occurrence of iodo-acetaldehyde as a water disinfection byproduct (DBP) and compare its levels with those measured for chloro- and bromo-acetaldehydes, and to evaluate the in vitro genotoxicity and cytotoxicity of the complete class of haloacetaldehydes (HALs) in mammalian Chinese hamster ovary (CHO) cells.

Two analytical methodologies were developed and validated to investigate the occurrence of target HALs in water. Mono- and di-HALs were derivatized with pentafluorobenzylhydroxylamine (PBFHA) and subsequently liquid-liquid extracted. Trihaloacetaldehydes were extracted by means of solid phase extraction. Analyte detection was performed with gas chromatography coupled to electron ionization mass spectrometry. These methodologies were applied to the analysis of source and water samples collected from 6 different water treatment plants in the USA which run different treatment scenarios, i.e. chlorination, chloramination, chloramination with pre ozonation. Analysis of real drinking water samples revealed that: (1) all target HALs, but bromo-acetaldehyde, were formed during all drinking water treatments at ppb levels; (2) iodo-acetaldehyde formation was observed under chloramination scenarios at levels below 2 ppb; and (3) source waters were free of HALs, except in one case where tribromo-acetaldehyde was also detected.

Toxicity results showed that: 1) the cytotoxicity and genotoxicity of these compounds were not statistically correlated; 2) tribromo-, dibromo-, bromo-chloro, dibromo-chloro, and iodo-acetaldehyde presented higher cytotoxicity than all regulated trihalomethanes (THMs) and haloacetic acids (HAAs); 3) dibromo, dibromo-chloro, and chloro-acetaldehyde presented higher genotoxicity than most regulated HAAs; and 4) no toxicity trends were observed in terms of the type of halogen or the number of halogens attached.

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## Determination of pharmaceuticals in waterbodies of North-Western Russia

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Potential risks from the environmental presence of pharmaceuticals and personal care products (PPCP) reveal in abnormal physiological processes and reproductive impairment, increasing number of cancer incidences and the development of antibiotic resistant bacteria.

PPCP in the environment have not been monitored in Russian Federation yet and little data is available on their presence in freshwaters. Moreover there are no official guideline values for their presence or release in environment. For our investigation we selected some priority pharmaceuticals, components of most used medical drugs in the Russian Federation: Caffeine, Ranitidine, Ketoprofen, Diclofenac, Ciprofloxacin, Ampicillin, EthinylEstradiol and Triclosan.

Solid phase extraction (Oasis HLB, pH 3) was used during cleanup procedure of water samples. Liquid extraction from sediment samples was carried out by ultrasonication. Recoveries and detection limits were evaluated for each compound using a model system. The analytes were quantified using isotope-labeled internal (recovery) and analytical standard.

Analyses were carried out by the method of liquid chromatography high-resolution mass-spectrometry, using LTQ Orbitrap (Thermo Finnigan). Mass spectra were recorded in several modes: full scan, SIM and MRM using positive and negative ionization. Resolution was 30000. Identification was realized by registration of defined mass of protonated (ESI+) or deprotonated (ESI-) molecular ion or other characteristic ions (MS-MS) with accuracy better than 4 ppm. The applied analytical procedures were characterized by good selectivity and low limits of detection (from 0,32 to 4,0 ng/L) allowing their application to analyses of environmental samples.

The method was successfully applied for the PPCP determination in water and sediment samples of the water bodies of Saint-Petersburg, Leningrad Region and the Republic of Karelia, including recreation zones. Water and sediment samples were collected from different points in summer period of 2010-2012. Caffeine, as an anthropogenic marker of surface waters, was determined in most samples. The range of determined caffeine concentrations was 10 to 450ng/L. Diclofenac were detected in several samples (in the range of 3,9-270,0 ng/L). The maximum concentrations of Ketoprofen (260 ng/L, the Neva river) and Ciprofloxacin (271 ng/L, the Karpovka river) were determined in summer period of 2012. Triclosan was mostly detected in sediment samples (0,3-23,6 mkg/kg dry weight). Several samples also contained other studied substances detected in low concentration (about tens ng/L). Ethinylestradiol, Ranitidine, Ampicilline were not detected.

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## Determination of persistent and emerging organic contaminants and their metabolites in fish bile

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The huge amount of anthropogenic organic pollutants spilled continuously into water bodies is one of the main environmental concerns worldwide. The capacity of certain persistent and emerging organic pollutants to be bioaccumulated and to induce lethal toxicity on species results in biodiversity loss and threat to human health. Besides, many of these compounds are metabolised or transformed by the species before being excreted. In this sense, methodologies for the simultaneous determination of both persistent and emerging contaminants in fish bile samples are compulsory.

In this work, the solid phase extraction (SPE) and the clean-up steps were fully optimised for the determination of a large variety of priority and emerging contaminants in fish bile by means of gas chromatography-mass spectrometry (GC-MS). Regarding SPE (Plexa cartridges) optimization, the effectiveness of different solvents (ethyl acetate, ethyl acetate: acetone (50:50, v/v) and ethyl acetate: *n*-hexane (50:50, v/v)) and volumes (2, 4, 6 and 8 mL) were studied. Recoveries closed to 100 % for all the target analytes except for musks 90 % were obtained using 4 mL of ethyl acetate so this solvent and volume were used for further steps. Afterwards, the clean-up step was optimised using Florisil® cartridges. Different load solvents (ethyl acetate, isooctane and *n*-hexane), elution solvents (different amounts of *n*-hexane: ethyl acetate, *n*-hexane: toluene and *n*-hexane: ethyl acetate) and elution volumes (1-4 mL) were evaluated. Slightly higher recoveries were obtained loading the sample with 1 mL of ethyl acetate and eluting the non-polar analytes with 3 mL of *n*-hexane: ethyl acetate (90:10, v/v) mixture and polar analytes with 3 mL of ethyl acetate: methanol (75:25, v/v) mixture. One of the pesticide metabolite (3, 5, 6-trichloro-2-pyridinol, Chlorpyrifos metabolite) was eluted with non-polar compound so this fraction had to be fractionated and added to the polar elution fraction. Finally, the optimised procedure was applied to non-contaminated fish bile spiked at known concentrations of both analytes and their metabolites. Good recoveries were obtained for all the analytes (60-133 %) except for *n*-butyl benzyl phthalate (147 %), nonylphenol mixture (18 %) and mono-*n*-octyl ester (171 %). Good repeatability (< 17 %) and limit of detection (ng/mL level) were obtained for all the analytes. Besides, matrix effect was also evaluated. This method is being currently applied in the biomonitoring study of mullets by means of exposure experiments to effluent water of two wastewater treatments plants (WWTPs).

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## Assessment of commercially available low-cost polymeric materials for sorptive extraction of priority and emerging non-polar organic pollutants in environmental water samples

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The occurrence of certain persistent and emerging organic pollutants in the environment has been a subject of concern for the last decades due to their proven persistency in water and soil. This worry has pushed more robust and sensitive analytical methods that reveal the broad range of environmental organic contaminants that may be found in natural waters. In the framework of the analysis of organic contaminants in water samples, sorptive extraction devices have proven to be adequate for monitoring organic pollutants and thus, the suitability of different sorptive materials is a matter of further research.

In this sense, the aim of this work was focused on the study of the capabilities of six commercially available and low cost polymeric materials (i.e., polypropylene, polyethylene, a mixture of polypropylene and polyethylene (raffia), polyamide and polyethersulfone (PES)) for the extraction of organic compounds (i.e., HCH isomers, organophosphorous compounds, octylphenols, pesticides, phthalates and musks) in environmental water samples. Previous to their use, the homogeneity of the sorbent materials was confirmed by means of Raman spectroscopy. Thereafter, the parameters affecting the extraction procedure (i.e., the effect of methanol addition and ionic strength, agitation conditions and extraction time) as well as the liquid desorption step (i.e., desorption solvent, type and mechanism) were thoroughly studied. Preliminary results showed that the higher extraction efficiencies were obtained for PES and raffia. Therefore, a sorptive microextraction method followed by large volume injection – programmable temperature vaporizer – gas chromatography – mass spectrometry (LVI-PTV-GC-MS) was proposed using those sorbents for the simultaneous determination of 17 organic pollutants in water samples. The final optimised protocol consisted of overnight extraction of 150 mL of sample solutions containing 10% NaCl at room temperature and at 1200 rpm, followed by a 30 min rotation-assisted desorption with 300  $\mu$ L of ethyl acetate. The performance of the analytical method was validated attending to linearity ( $r^2 > 0.99$  for both polymers), precision ( $< 20\%$  and  $< 15\%$  for raffia and PES respectively) and detection limits (between 15 - 35  $\text{ng}\cdot\text{L}^{-1}$ ). The effect of organic matter was also studied and the use of isotopically labelled compounds as surrogate standards was evaluated. The optimized method was applied to determine the concentration of the target compounds in effluent and influent wastewater treatment plants.

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## Matrix solid-phase dispersion extraction of halogenated flame retardants from mollusk samples

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The objective of this work was the development and validation of an analytical method capable of determining the simultaneous presence of fifteen halogenated flame retardants (HRFs), including brominated diphenylethers (BDEs) and six novel HFRs, in different mollusk samples. Matrix solid-phase extraction (MSPD) was selected in order to achieve the extraction of analytes from the sample based on its advantages, such as simplicity of the analytical procedure, low volume of solvent and quantity of sample required, low global price or integration of extraction and clean-up into a single step. Gas chromatography coupled to negative chemical ionization-mass spectrometry (GC-NCI-MS) was used for the determination.

During method optimization, different parameters were studied: beginning with the solid support (dispersing agent), followed by a detailed co-study of the clean-up sorbent and solvent. Under optimal conditions, 0.5 g of sample was dispersed with 0.5 g of PSA and transferred to a polypropylene syringe. The cartridge was previously filled with 0.5 g of silica gel, followed by 3.5 g of co-sorbent materials: 1.75 g of acidified silica gel (10% (w/w) H<sub>2</sub>SO<sub>4</sub>) and 1.75 g of florisil (deactivated with 5% Milli-Q). Subsequently, analytes were eluted with 10 mL of dichloromethane and this eluate was concentrated to dryness under a nitrogen stream and reconstituted to a final volume of 200 µL in isooctane. Internal standards were added as surrogates, and a standard addition over the extracts was necessary to avoid the injection overestimation caused by the matrix.

In the above mentioned conditions, excellent detection limits, from 0.0006 to 0.014 ng g<sup>-1</sup>, except for decabromodiphenylethane (DBDPE; 0.12 ng g<sup>-1</sup>), were achieved. The accuracy of the method was evaluated with three different types of spiked mollusk species and recoveries were in the 70-120 % range. Moreover, the method was further validated with standard reference materials of salmon and mussel tissues for BDEs. Finally, the method was applied to the determination of HFRs in different kind of mollusks: mussel, cockle and clam. Levels up to 0.8 ng g<sup>-1</sup> wet weight have been detected in raft cultured mussels.

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## Low and high resolution liquid chromatography-mass spectrometry determination of ethyl sulfate in wastewater for alcohol consumption tracing

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### Abstract

Health problems created by excessive ethanol consumption have been rapidly growing in many countries. Estimate of the average alcohol can be derived from alcohol sales statistics and from interview and questionnaire-based information from population. On the other hand, a new method based on sewage epidemiology, i.e. tracing a marker of alcohol ingestion in wastewater has been recently proposed [1]. Ethyl sulfate (EtS) is excreted in urine (0.010-0.016 %, on molar basis) following the intake of alcohol, and as such it is a convenient biomarker for alcohol tracing through the sewage epidemiology approach. Thus, a new method for the direct (after filtration and internal standard and ion-pairing agent addition) determination of ethyl sulfate in wastewater by liquid chromatography-(tandem) mass spectrometry (LC-MS(/MS)) has been developed. Different LC columns, pHs and detection systems have been tested. Thus, a triple-quadrupole (QqQ) instrument and a quadrupole time-of-flight (Q-TOF) system were compared. The QqQ provided a better limit of detection (LOD=0.02  $\mu\text{g L}^{-1}$ ), however the Q-TOF system LOD (0.1  $\mu\text{g L}^{-1}$ ) was still good enough for wastewater concentrations, while avoiding problems with transition ratios on the QqQ. The repeatability of both systems and linearity was also comparable, with RSD values between 4-5% for QqQ and 4-14% for Q-TOF. The stability of EtS was also tested and it has proven to be stable in wastewater for at least one week at room temperature and more than one month at -20°C. The application of the method to samples collected during a week in a Galician (NW Spain) city showed concentrations of EtS in the 3-26  $\mu\text{g L}^{-1}$  range, which translates into alcohol consumption levels between 192 and 873 g/day 1000 inhabitants, with a noticeable increase during the weekend compared to weekdays.

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## DESIGN OF EXPERIMENT APPROACH (DoE) FOR THE OPTIMIZATION OF POLYBROMINATED DIPHENYL ETHERS (PBDES) DETERMINATION IN FINE AIRBORNE PARTICULATE MATTER (PM 2.5) BY MICROWAVE-ASSISTED EXTRACTION AND GC-MS/MS

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A design of experiment approach (DoE) [1] was used for the optimization of large volume injection (LVI) [2] and microwave-assisted extraction (MAE) [3] parameters for the analysis of PBDEs (BDE-28, BDE-49, BDE-47, BDE-66, BDE-100, BDE-119, BDE-99, BDE-155, BDE-154, BDE-153, BDE-139 and BDE-183) in fine airborne particulate matter (PM 2.5) using GC-MS/MS. A central composite design (CCD) was used to build the response surface for each PBDE compound, and find the factor settings that maximize the injection and extraction efficiency for all analytes using the MINITAB software. For the optimization of the LV injection, the most important parameters were: injection temperature ( $T_{inlet}$ ), vaporization temperature ( $T_{vap}$ ), vaporization time ( $t_{vap}$ ) and evaporation flow (Flow). Results showed that the optimal conditions were  $T_{inlet} = 50$  °C,  $T_{vap} = 80$  °C,  $t_{vap} = 2$  min, and flow = 10 mL/min. For the optimization of MAE parameters, the three main factors were solvent volume, exposure time and temperature and their optimal values were: 50 mL, 2 min., 75 °C, respectively. In addition to both optimizations by DoE approach, other conditions of the method were studied: GC-MS/MS parameters, extraction solvent and matrix effect.

The final method consisted on the extraction using MAE with n-hexane:acetone (1:1, v/v), followed by GPC clean-up and GC-MS/MS determination. Separation was carried out on a HP-5MS capillary column, 30 m × 0.25 mm i.d., 0.25 μm film. The oven temperature program was as follows: initial 80 °C (2 min); 25 °C min<sup>-1</sup> to 230 °C; 5 °C min<sup>-1</sup> to 320 °C (5 min). The mass spectrometer operated in the electron impact mode (EI) using a voltage of 70 eV and a filament current of 50 μA. The ion source temperature and the transfer line temperature were set at 250 °C and 300 °C, respectively.

Validation of the method was achieved by the study of linearity, accuracy, precision and limit of quantification (LOQ). Linearity was accomplished with matrix-matched calibration and internal standards (BDE-28 <sup>13</sup>C12, BDE-47 <sup>13</sup>C12, BDE-99 <sup>13</sup>C12 and BDE-153 <sup>13</sup>C12), in the range of 0.3 – 10 ng/mL in vial. Accuracy and precision were studied in terms of recovery and relative standard deviation (RSD) by analyzing spiked field blank samples at two different concentrations: the LOQ level (0.063 pg m<sup>-3</sup> – 0,210 pg m<sup>-3</sup>) and the higher level of the calibration curve (2.104 pg m<sup>-3</sup>). Mean relative recoveries at LOQ level ranged from 80% (BDE-66) to 106% (BDE-28) with relative standard deviation below 20%. The validated method was tested with eight real samples and results showed levels of BDE-47 in a range of 0.063-0.112 pg m<sup>-3</sup>, and BDE-99 in a range of 0.107-0.212 pg m<sup>-3</sup>.

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## Biomonitoring of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Fishes of Lake Constance, Germany

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Lake Constance is an important drinking water reservoir and habitat for fish and other aquatic organisms. Organic micropollutants can enter the lake via tributary streams, especially if they have a heightened wastewater load. There is a risk that these substances deposit in sediments and accumulate in fish and mussels. Typical representatives of strongly particle-bounded micropollutants are polybrominated diphenyl ethers (PBDE) and polychlorinated biphenyls (PCB). Due to the physico-chemical properties of these persistent substances they are able to accumulate in aquatic organisms.

In the present study a biomonitoring of 105 fish samples corresponding to a total of 547 individuals (bream) was performed. At seven sampling points 547 individuals were collected and combined to 105 filet samples divided into six groups of length. The determination of the organic micropollutants was performed via high resolution gas chromatography directly coupled with a mass selective spectrometer (HRGC agilent 6890, LRMS agilent 5975). The quantification was done using <sup>13</sup>C<sub>12</sub>-labelled congeners (PCB-28, PCB-52, PCB-101, PCB-153, PCB-138, PCB-180, PCB-194; BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183).

PCB<sub>6</sub> (sum of the PCB-congeners 28, 52, 101, 138, 153 and 180) could be detected in a median concentration of 22.2 µg/kg fresh weight (maximum value 298 µg/kg fresh weight). Regional deviations were not observed and the congener pattern of the PCB<sub>6</sub> was homogeneous with the dominating congener PCB-153 followed by PCB-138 > PCB-180 > PCB-101 > PCB-28/PCB-52. The median concentration of PBDE<sub>7</sub> (sum of the BDE-congeners 28, 47, 99, 100, 153, 154 and 183) was 2.0 µg/kg fresh weight with dominating BDE-47 (75 % of PBDE<sub>7</sub>) followed by BDE-100 > BDE-154. The hepta-brominated BDE-183 could not be detected in the samples. The PBDE-pattern found differs from the technical penta-BDE-mixture which mainly consists of BDE-99 > BDE-47 > BDE-100. This fact indicates either congener specific bioaccumulation or specific biodegradation of the substances. Pattern shifts of the PCBs could not be observed considering the formerly common used technical PCB-mixtures. The correlation between PCBs and PBDEs for the congeners PCB-153 and BDE-47 indicates - despite of some regional effects - the comparable environmental behavior of the investigated substance classes.

## Measurements of selected pesticides in ambient air in the Valencia Region.

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Atmospheric samples for the detection of pesticides in gas and particle phase, have been collected from 2008 to 2009 at three agricultural sites and one remote site, in the Comunidad Valenciana (Spain). Samples were analyzed for 30 pesticides using GCMS and LCMS techniques, 23 different pesticides were detected in a wide range of concentrations: from 0.013 ng/m<sup>3</sup> for pyriproxifen to 24.5 ng/m<sup>3</sup> for abamectin. The majority of the pesticides analyzed are currently used, although some of them are recently forbidden or were considered as persistent compounds.

The results are discussed in terms of the meteorological conditions during the specific sampling periods and the general information available related with the application periods for each pesticide measured. The majority of the pesticides detected showed a seasonal behaviour, with most of the detections with the highest concentrations during spring and early summer.

At the remote site some pesticides with relatively short timelife (< 2 hours) have been detected in the gas-phase although they were not applied in the surroundings. A study of reverse dispersion in backward mode was carried out, taken into consideration their life time in air.



## DETECTION, IDENTIFICATION AND STRUCTURAL ELUCIDATION OF UNKNOWN CONTAMINANTS DURING A ROUTINE NON TARGETED SCREENING OF RIVER WATER SAMPLES USING A NEW SCIENTIFIC INFORMATION SYSTEM.

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Analysis of environmental waters for pesticides is common practise. However, other contaminants such as personal care products or veterinary drugs and their metabolites may also be present at similar trace levels. All could be equally as harmful to the aquatic ecosystem, or to downstream consumers.

The use of Time-of-Flight (ToF) screening has steadily increased in environmental monitoring laboratories over the last few years. Generally, the technique has become known as non targeted screening due to the fact that data is collected in a non targeted way when compared to the traditional targeted screen of specific compounds on a tandem quadrupole instrument. The advantage of a non targeted acquisition is the ability to re-interrogate historical data for unexpected compounds discovered at a later date and to screen for a much larger suite of compounds..

With the correct sample list format, non targeted ToF screening data generated can be used:

- To screen for a specified list of compounds from a database or scientific library.
- To isolate “unknown” samples of interest using PCA or other statistical analysis methods.
- To isolate “unknown” compounds of interest using a binary compare of an analyte and control sample.

This work describes how a new integrated scientific information system was used to acquire and process non targeted screening data from local river water samples. Initially the data generated was screened against a target list. Within the same analysis a binary compare of an analyte and control sample was able to detect and isolate “unknown” compounds of interest. Using the structural elucidation tools within the scientific information system the unknown compounds of interest were identified. Confirmation of identification was made with an MSMS comparison of samples and purchased standards.

## From basic to advanced characterization of engineered nanoparticles (NPs): the Nanotest project

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Despite of the remarkable increase of industrial and commercial applications of engineered nanoparticles (NPs) and of studies reporting their potential toxicological effects obtained by both *in vitro* and *in vivo* tests, general conclusions about their hazard are often contradictory because of limited physico-chemical characterization. Here we report on the FP7 NanoTEST project methodological approach, performing both the primary/basic physico-chemical characterization of NPs (TiO<sub>2</sub>, nanosized polylactic-glycol, nanomagnetite and fluorescent silica in aqueous dispersions) and the advanced characterization focusing on the behavior of NPs in biological media in order to evaluate toxicological effects. Primary characterization, carried out on the NPs provided by the suppliers (i.e. before toxicological testing), included measurements of average and crystallite size, shape, chemical composition and specific surface area, by conventional techniques, as well as the determination of toxicological impurities, and photocatalytic and redox properties. The advanced characterization focused mainly on TiO<sub>2</sub> and SiO<sub>2</sub> NPs, which were firstly dispersed in tailored stock dispersions and then in several biological media for *in vitro* toxicological applications, by employing Dynamic Light Scattering (DSL) technique.

The overall results showed that the methodological approach for the proposed NPs characterization provided useful information for better understanding and forecasting the NPs toxicological behavior. The merging of data acquired from suitable experimental design and results from structure-activity relationships is highly recommended.

## Incidence of chemotherapy drugs in the aquatic environment and their elimination by non conventional wastewater treatment by *Trametes Versicolor*.

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### Abstract

Chemotherapy drugs have become a group of micropollutants that could be playing an important role in the aquatic environment due to the increment of their consumption in last years and also because they are not removed from the wastewater by conventional treatments. Many of the anticancer drugs have shown to be recalcitrant and therefore, there is a high likelihood to find them in the aquatic environment. In order to undertake a proper environmental risk assessment of these compounds, it is necessary to evaluate the discharge and presence of anticancer drugs onto the urban wastewater system, as well as their potential removal by non conventional treatments, which is nowadays scarcely documented

In the present work, some selected anticancer drugs such Azathioprine, Cyclophosphamide, Ciprofloxacin, Docetaxel, Etoposide, Ifosfamide, Methotrexate, Paclitaxel, Tamoxifen and Vincristine, were measured from a sampling campaign performed in the municipal area of Girona (Spain), which included an hospital effluent, the influent and effluent of a urban wastewater treatment plant (WWTP) as well as the river receiving the sewage effluents. Ciprofloxacin, Docetaxel, Tamoxifen, Cyclophosphamide, Methotrexate and Azathioprine were found both, in hospital and also in urban wastewaters, whereas only Ciprofloxacin, Cyclophosphamide and Tamoxifen were still found in effluents of the WWTP as well as in surface water.

In the light of the results obtained from the monitoring, where several anticancer drugs were not completely eliminated in the WWTP, the potential removal of these drugs by white rot fungi was evaluated in a fluidized bed reactor as an alternative to the conventional wastewater treatments. In addition, the generation of the transformation products along the treatment was explored using the high resolution mass spectrometry, in particular an Orbitrap spectrometer. A novel non-targeted approach was used in order to highlight significative differences between the samples.

## Economic valuation of polishing WWTP effluents using ozonation to enhance PPCPs removal: environmental benefits

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Continuous release of pharmaceutical and personal care products (PPCPs) present in effluents from wastewater treatment plants (WWTPs) is nowadays leading to the adoption of specific measures within the framework of the Directive 2000/60/EC (Water Framework Directive). The ozonation process has proven its potential to eliminate PPCPs from secondary effluents. However, there is a significant drawback related with the economics associated with its implementation. Hence, this work presents an economic valuation of the environmental benefits derived from the ozonation of treated effluents to eliminate 5 PPCPs (ethynilestradiol, sulfamethoxazole, diclofenac, tonalide and galaxolide) from wastewater.

The elimination rates depended on the functional groups and molecular structures of the compounds. Thereby the two musk fragrances studied, galaxolide and tonalide, presented slower rates than the pharmaceuticals. Shadow prices, which represent a proxy to the economic value of the environmental benefits arisen from undischarged pollutants, were calculated for each PPCP and expressed as €/kg: ethynilestradiol (73.73); sulfamethoxazole (34.95); diclofenac (42.20); tonalide (10.98); galaxolide (8.87). Their value illustrates that the removal of pharmaceutical compounds involves higher environmental benefits than the elimination of musk fragrances. This result is consistent with the current policy and management measures aimed to protect European water bodies. However, to estimate the total environmental benefit not only the shadow prices have to be considered but also the quantity of each pollutant removed from wastewater. In this sense, it has been verified that the DFC is the PPCP whose elimination contributes more to the total environmental benefit. Following an exemplary case-study, the total benefit associated with the elimination of the studied PPCPs would be of 1833.3 €/year. However, to avoid an underestimation of the total environmental benefits associated to the ozonation post-treatment, the shadow price of the rest of micropollutants removed, not only 5, should be considered. In a rough estimation, the average environmental benefit might be around 20 times higher than our calculations.

This paper contributes to value the environmental benefits of implementing post-treatment processes aimed to achieve the quality standards required by the Priority Substances Directive.

## Modern analytical methodology based on UHPLC-MS/MS for the sensitive determination of illicit drugs in urban wastewaters with emphasis in amphetamine and derivatives

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Updated analytical methodology based on ultra high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) has been developed for the determination of nine widely consumed drugs of abuse and some major metabolites in urban wastewaters. From a previous method developed<sup>1</sup>, we moved from the use of Oasis MCX cartridges towards the most universal polymeric Oasis HLB in the solid-phase extraction (SPE) step. The scope of the method has been also increased, including amphetamines, MDMA, cocaine, cannabis, opioids and ketamine. The generic sample treatment based on Oasis HLB SPE did not lead to satisfactory results for amphetamine and amphetamine-type stimulants, which were highly problematic due to matrix interferences. Therefore, an aliquot of the “HLB” extract was subjected to a clean-up with Oasis MCX and primary secondary amine (PSA) for the analysis of these compounds. The extract obtained after the first step (HLB) was used to analyse cocaine, cannabis, opioids, ketamine and their metabolites. Moreover, this extract was also to be used for qualitative screening for many more drugs (around 100 compounds)<sup>2</sup> using a QTOF MS. The present method allows the simultaneous identification/quantification of analytes with a chromatographic run of only 6 min. The reliable identification was assured by acquisition of three SRM transitions per compound, which was feasible using a UHPLC-MS/MS instrument with fast-acquisition triple quadrupole mass analyzer. Correction for possible SPE losses or degradation during storage was made thanks to the use of isotope-labelled internal standards (ILIS), available for all compounds, which were added to the samples as surrogates. The effect of sample volume loaded on the SPE cartridge was tested in influent wastewater as a simple way to minimize matrix effects and to improve the robustness of the method. The method was validated in effluent and influent wastewater at two concentration levels (25 and 200 ng/L in effluent; 100 and 800 ng/L in influent). The developed method was applied to the analysis of 14 influents and 14 effluents wastewater samples collected over two weeks in Castellón (Spain) within a wide European collaborative study.

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**Routine 'Trace level screening' for a broad range of volatile and semi-volatile organic pollutants in a range of Environmental waters using 'full scan' GC-MS with a 950 compound target screening database and deconvolution software**

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To address the 'chemical monitoring challenge' of the Water Framework Directive, the National Laboratory Service (NLS) has developed 'trace level' routine screening method for a broad range of volatile and semi-volatile pollutants. This comprehensive 'one run' method covers virtually all GC-amenable pesticides as well as hundreds of other organic pollutants which can be identified from a single sample with minimum preparation at ppt levels.

Extracted samples are analysed using full scan GC-MS with mass spectral deconvolution and automated quality checking against libraries and retention time locked screening databases to ensure the highest data integrity and quality.

This method forms the basis of the UK Environment Agency's screening protocol for all water types and sample matrices analysed include fresh water, ground water, saline, sewage effluents, trade effluents, leachates and solids/sediments.