



### "16<sup>th</sup> European Meeting on Environmental Chemistry"

November 30<sup>th</sup> – December 3<sup>rd</sup> 2015

Torino, ITALY

## **BOOK OF ABSTRACTS**

Organized by

Maria Concetta Bruzzoniti and Davide Vione (Department of Chemistry, University of Torino)

Environment Park S.p.A.

On behalf of

ACE - Association of Chemistry and the Environment

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#### Foreword

The 16th European Meeting on Environmental Chemistry (EMEC16) is held at the Congress Center of the Environment Park in Turin, Italy, from 30 November to 3 December 2015. EMEC16 is organized by the Department of Chemistry (University of Torino) and Environment Park, on behalf of the European Association of Chemistry and the Environment (ACE).

Organized for the second time in Italy, EMEC16 is hosted by the city that on March 1861 assisted to the birth of unified Italy and that was proclaimed the first capital of Italy.

Over 160 scientists from 25 countries (Italy, France, Algeria, Serbia, Czech Republic, Spain, Switzerland, Russian Federation, Turkey, United Kingdom, Portugal, Romania, Slovenia, Tunisia, Greece, Germany, Morocco, Austria, Canada, Public Republic of China, Georgia, Hungary, Norway, Poland, USA) are attending EMEC16 with about 150 total contributions.

In line with EMEC tradition, both oral and poster sessions feature analytical methods for environmental analysis, characterization of natural and affected environments, the main compartments (atmosphere, water, soil and sediments), treatment and remediation techniques, as well as green chemistry, food and environmental photochemistry.

The opening of EMEC16 takes place under the auspices and the welcome of the vice-rector of the University of Turin (Professor Elisabetta Barberis). The meeting includes three invited plenary lectures: "Simple does not mean easy. A new generation of materials for solid-phase extraction" (B. Buszewski, University of Torun, Poland), "Atmospheric aqueous phase photochemistry: understanding the impact of oxidant species" (M. Brigante, Université Blaise Pascal de Clermont-Ferrand, France), "Chemical odor code of food: potentials and challenges for multidimensional gas chromatography platforms" (C. Cordero, University of Torino).

To stimulate the participation of young researchers, ten awards are also given by ACE and EMEC16 Organizing Committee, the winners being Maja Milanovic (Serbia), Dmitri Mazur (Russian Federation), Maria Chropenova (Czech Republic), Mirjana Cujic (Serbia), Natasa Djokovic (Serbia), Enrico Chiavazza (Italy), Lorenzo Ciofi (Italy), Jana Oborna(Czech Republic), Andrea Speltini (Italy) and Marta Stucchi (Italy).

Thanks are due to the members of the Scientific Committee (F. Ajmone Marsan, S. Arey, M.C. Bruzzoniti, B. Buszewski, J. Caslavsky, L. Celi, G. De Gennaro, M. Del Bubba, S. Gibb, A. Kettab, Lebedev, F. Passarini, P.Q. Tranchida, D. Vione) and Organizing Committee (F. Barsotti, D. Damosso, F. Gosetti, M. Minella, L. Rivoira) for their valuable contributions.

Professor J. Albaiges is also gratefully acknowledged for his availability to devote a special issue of the International Journal of Environmental Analytical Chemistry to scientific contributions presented at EMEC16.

We would like to thank our Sponsors (Sciex, Sigma-Aldrich, Agilent Technologies, Leco, Shimadzu, LabService Analytica, Horiba CEM, Carlo Erba) for the joint financial support and Waters Corporation for logistic support.

Special thanks are given to Drs. C. Massaza, C. Bianco and C. Tolani of the Environment Park for their assistance with the preparation of the location.

We hope that EMEC16 will stimulate fruitful discussions and the start of new scientific collaborations, thus providing an added value to the scientific endeavours of our esteemed participants.

Finally, we would like to encourage all of you to enjoy the general atmosphere of EMEC16, the social programme as well as the town, which you hopefully may have the opportunity to visit. On behalf the Organizing Committee of the 16th European Meeting on Environmental Chemistry, we welcome you in Torino and wish you a pleasant EMEC16!

Turin, Italy Maria Concetta Bruzzoniti and Davide Vione, EMEC16 Chairpersons

The EMEC16 Conference was organized under the patronage of:





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## **ORAL PRESENTATIONS**

**INVITED SPEAKERS** 

#### Plenary -1

## Simple does not mean easy – a new generation of materials for solidphase extraction

#### <sup>1</sup>Boguslaw Buszewski

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The development of modern analytical methods, based on physico-chemical phenomena and processes running in the environment and living organisms, has led to reduction of detection level and increase of measurement precision. The scope of the applicability of various analytical techniques is not only related to the characteristics and type of analytes but also connected with increase of the selectivity and reproducibility of the isolation and enrichment of analyte in the complex matrices (sample preparation). According to the literature just sample preparation is the most important stage in qualitative and quantitative assays. The contribution of this part in the comprehensive determination of analytes consume ca. 60 - 65% of the whole time necessary to perform the analysis.

Sample preparation methods, these based on surface phenomena (eg. adsorption/desorption, ion exange or/and extraction) are the dominant group of techniques used in routine trace analysis. This is due to by the possibility of directly coupling of them with other physico-chemical separation methods, eg. gas chromatography (GC), high performance liquid chromatography (HPLC/UHPLC) and electromigration techniques (CEC, ITP, CZE). Consequently, the high reproducible data, good measuring precision at relatively low unit cost of analysis have been obtained. An important factor is the simplicity of used techniques, not only from the operating process (equipment handling) or methodological (analytical procedures), but also compatibility. A technique that meets aforementioned requirements is, without any doubt, an extraction liquid – solid, known as solid phase extraction (SPE). This technique, was established more than 40 years ego and very offen is applied in various versions (the classic in small columns, disks, tips or fiber to the solid phase microextraction) in laboratory practice.

The evoltion is connected with introduction of a new packings and another exploatation materials (silica sorbents, polymer, fibers, nanotubes, nanoparticles, chips, ect) sucesfully used in SPE form and minatuiased variat like SPME and/or chip technology. The molecular imprinted material (MIP) appears to be of particular interest comprising a ferromagnetic centers or monoliths with various functional groups including nanoparticles or graphene structure. Generaly, during lecture will be presented a new generation materials named "dedicated" or "targed" materials (supramolecular chemistry). These issues, together with physicochemical characterization and molecular modeling, give the possibility to consider mechanisms for interpretation of processes going on at the cellular level (metabolomics, proteomics).

Acknowledgment: This work was supported by the project no. 2014/14/A/ST4/00641 (MAESTRO) from the National Science Center (Cracow), Poland

## Chemical odor code of food: potentials and challenges for multidimensional gas chromatography platforms

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Modern - omics disciplines dealing with food (foodomics, flavour metabolomics, sensomics, flavoromics[1,2]) investigate sample constituents considered collectively (primary and secondary metabolites, compounds generated by thermal treatments and/or enzymatic activity) and open interesting perspectives in the correlation between biological attributes and chemical composition.

Sensomics, in particular, focuses on revealing sensory-active compounds extending the investigation to all possible stimuli of the multimodal perception (aroma, taste, texture etc..) by comprehensively treating sample constituents and related properties (physicochemical properties, concentration in-the-matrix) together with their sensory activity (odor quality, odor threshold - OT, Odour Activity Value - OAV) [3].

Comprehensive two-dimensional gas chromatography coupled with Mass Spectrometry (GC×GC-MS), integrated with high concentration capacity (HCC) automated sampling approaches, represent a high-throughput/high-informative platform for food volatiles fingerprinting with interesting potentials in sensory characterization [4].

The lecture presents the principles and the investigation strategies of advanced sensomic investigation through illustrative case-studies. A sampling design inspired by the pathways aroma compounds follow to reach the regio olfactoria (i.e. orthonasal and retronasal) enables a comprehensive characterization of key-active compounds responsible of sample sensory quality contamporarily opening a window on technological indicators and botanical tracers. The advanced sensomic platforms provide straightforward results and represent a bridge between high-throughput screenings with a complete and almost comprehensive profiling of volatiles related to flavour perception. In such a context, the information potential of each analysis increases and an almost complete sensory profile can be objectively delineated.

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#### Plenary -3

# Atmospheric aqueous-phase photochemistry: Understanding the impact of oxidant species

#### <sup>1</sup>Marcello Brigante

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Atmospheric aqueous phase can be considered as a highly efficient photochemical reactor, where new reactions could start via absorption of sunlight. Anthropogenic and biogenic emissions may increase the concentration of organic and inorganic compounds in and on the surface of atmospheric water droplets. Such compounds can start photochemical and photosensitized reactions upon radiation absorption, modifying the oxidative capacity of this medium.

In the atmosphere, the hydroxyl radical (HO $\bullet$ ) is considered the most efficient environmental oxidant. Therefore, evaluating the production of this short-lived species (its lifetime is estimated to be less than 1 second) is a key step to determine the fate of many chemical compounds. Moreover, the HO $\bullet$ -mediated oxidation of organic compounds in the aqueous phase can lead to the formation of multifunctional organic species, thereby modifying the chemical composition of atmospheric particles.

In the atmospheric aqueous phase, inorganic and metal ions are considered as sources of HO• via photochemical or "dark" activation, while reactivity with dissolved organic compounds represents the main scavenging pathway.

Evaluation of this source/sink cycle is even more difficult because the organic and inorganic composition of cloud water is variable, complex and poorly characterized.

Relevant formation and reactivity pathways for the hydroxyl radical in the cloud aqueous phase will be presented in this talk, with particular attention to the photochemical reactivity investigated in mimic and real cloud waters solutions.

Moreover, the main spectroscopic and photochemical approaches (i.e. continuous irradiation and nanosecond transient spectroscopy) used to estimate the oxidative capacity and the impact on the cloud aqueous phase chemistry will be introduced.

#### Keynote- 1

## Biochemicals extraction from biomass: pretreatments optimization pathways

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Biochemicals extraction from biomass via pre-treatment, is one of the most promising processes to obtain compounds for the green chemistry like sugars, lipids, polyphenols, etc.

The recent development in the industrial process of extraction of biochemicals from biomasses, including second and third generation one, comes from a market demand but it is definitely a great opportunity to business improvement. Industrial sectors related to pharmaceuticals, cosmetics and nutraceuticals are in growing demand for active ingredients of natural extraction. One of the constraints that currently limits the dissemination of these processes is link to the fact that often the extraction yields of these compounds, related to traditional chemical industries methods, are low because of the inherent complexity of the biochemical structures of vegetable matrices.

However from the growing market demand for these types of substances, also associated to a greater awareness on environmental issues, comes the need for a rapid development of this sector; concurrently, most often this type of products have a high added value that justifies the inclusion of innovative technologies designed to improve the yields of the processes.

The physical, chemical and enzymatic pre-treatment of the biomass could provide valuable support in optimizing the yield of the chemical processes of extraction and fermentation.

The release of simple sugars from lignocellulosic biomass can rise up to 80% of theoretical value appropriately combining the process parameters of the pre-treatment; the reduction of the content of polyphenols in olive residues reaches 70%. The increase liberation of lipids, the enhance in extraction of organic compounds from bio-stimulants and antioxidants from the grape pomace, the optimization of the yield improvement of biomass energy are some of industrial applications that assume a value such as to justify the use of plants dedicated to the pre-treatment of biomass.

By taking advantage of the available pilot pre-treatment and fermentation plants, Environment Park, with the Green Chemistry sector, carries out tests devoted to process optimisation and pre-treatment of organic material to improve the extraction yield of substances useful to green chemistry, such as sugars, fats, antioxidants, solvents and biostimulants.

The pre-treatment plant is made up of three process lines and a mechanical shredding system: physico-chemical, based on the Steam Explosion (SE) process; chemical, based on acidic/basic hydrolysis, applied both directly to the biomass itself. Biological, based on enzymatic hydrolysis that could be applied on SE or chemical pre-treated biomass (on the separate fractions hemicellulose, cellulose and lignin) or directly on other types of biomass.

## METHODS FOR ENVIRONMENTAL ANALYSIS

## QuEChERS extraction followed by on-line clean-up and tandem mass spectrometric determination of selected drugs in wastewater and sewage sludge

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The determination of organic micropollutants of high environmental concern (e.g. carcinogenic and/or toxic and/or endocrine disrupting compounds) in effluent wastewater and sewage sludge is of great importance, above all when these wastewater treatment by-products are recycled for land applications. The assessment of micropollutant concentration levels in these matrices is also of paramount importance in order to investigate the wastewater treatment process, so as to differentiate actual degradation processes from simple matrix transfer phenomena.

Among the various organic micropollutants of high environmental concern, pharmaceuticals have a strong ability to interact with the endocrine systems of human beings and animals. Pharmaceutical compounds, after administration to humans and animals, are excreted as such and/or as metabolites, thus reaching wastewater treatment plants (WTPs) and, in the presence of an incomplete removal, surface waters too [1].

Within pharmaceutical compounds, nonsteroidal anti-inflammatory drugs (NSAIDs) are without doubts among the most utilised in Italy, as well as developed countries [2].

In this study, the determination of 7 common NSAIDs and 6 hydroxylated metabolites in wastewater and sewage sludge from GIDA (Prato, Italy) WTPs, was carried out by QuEChERS extraction [3] coupled with online SPE clean-up and liquid chromatographic-tandem mass spectrometric analysis.

After development and optimization of the method, which involved the selection of the stationary phase and gradient elution, followed by online SPE conditions and H2O/CH3CN ratio in the QuEChERS extraction, the analytical protocol was investigated for apparent recovery, source-dependent matrix effect, method detection and quantification limits.

The method was finally applied to the analysis of the 13 target analytes highlighting their presence in wastewater at ng/L levels and in sewage sludge in the concentration range from tens to hundreds  $\mu$ g/kg of dried sludge.

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# Potential of long chain ionic liquids for on-line concentration of bioactive compounds in capillary electrophoresis

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The unique properties of ionic liquids (ILs) made them useful in separation science. Previously we have established that ionic liquids based on imidazole provided a positively charged capillary wall coating forming the reproducible, pH independent and reversed electroosmotic flow in capillary electrophoresis (CE). At concentration above the critical micelle concentration, ILs form micellar phase. However, the possibility of using ionic liquids in the processes of on-line concentration to lower the limits of detection of bioactive analytes was still discussing, what is important for solving a number of medical and environmental problems. In this work the potential of long chain ionic liquids for on-line concentration techniques (field-amplified sample stacking (FASS), head-column FASS, sweeping) of ionogenic and neutral analytes in biological objects in different modes of CE: zone (CZE) and micellar (micellar electrokinetic chromatography, MEKC) modes was investigated. The compounds chosen were biologically and environmentally important biogenic amines and steroid hormones. Imidazolium-based ionic liquids with alkyl radicals  $C_{12}$  and  $C_{16}$  ( $C_{12}$ MImCl,  $C_{16}$ MImCl) were used both as modifiers of electrophoretic systems and as pseudostationary phase. The effect of type and concentration of two ILs, the pH and concentration of background solution (BGS) was studied. Obtained results were compared with traditionally used cationic surfactant - cetyltrimethylammonium bromide. It was observed, that sweeping with ionic liquid  $C_{16}$ MImCl micelles in BGS has provided 83-112fold sensitivity enhancement factors for catecholamines. The limits of detection were 0.1 µg/ml. We have obtained a synergistic effect of ionic liquid C<sub>16</sub>MImCl and sodium dodecyl sulfate in BGS on efficiency and separation selectivity of steroid hormones and catecholamines in MEKC. It was found out that using highly conductivity sample matrix in sweeping leads to a significant increase in efficiency of analytes up to 1.10<sup>6</sup> t.p. These reduced the LODs for catecholamines and steroid hormones to 50 ng/mL and 25-100 ng/ml, respectively. All this makes the method CE comparable to HPLC in sensitivity. We have applied this method, in conjunction with SPE, to the analysis of the corticosteroids in human serum and urine. Our results suggest that ILs can contribute significantly to CE-based separations.

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## Application of new highly fluorinated polymers in chromatography and capillary electrophoresis for the determination of biologically active compounds

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Highly fluorinated compounds are the promising materials for the separation methods due to combination of their high chemical and thermal stability, hydro- and oleophobicity and very weak intermolecular forces. But their low solubility in water-organic systems restricts their application as additives for the modification of mobile phase and running buffer solution. Thus, the goal of our study was synthesis of new highly fluorinated water soluble polymers and their application as new stationary phases in GC and as modifying additives to the mobile phase and running buffer solution in HPLC, HPTLC and capillary electrophoresis (CE) for the separation of biologically active compounds. The syntheses of new polyfluorinated copolymer of ethylene and different perfluoromonomers were carried out. By the 1H and 19F NMR data the structure of copolymers was proved and the molecular weight was established. Thus, five fluoropolymers with different terminal groups (carboxyl, sulfonate, amine, amide, sulfonamide) were prepared. By the constant of Mac-Reynolds and Kovats retention indices it was established that stationary phases for gas chromatography based on synthesized fluoropolymers are high polar stationary phases and have a high affinity to the fluoro-containig substances at the same time. The fluororinated copolymers with anionic and cationic terminal groups can be used both as pseudostationary phases for the MEC separation of steroid hormones with high resolution and as a dynamic modifier of the wall a quarts capillary. Using of copolymers with –SO2NH2 groups provide very high efficiency of determination of proteins: myoglobin, albumin and lysozyme (N = 200 000 t.p.). The additions of highly fluorinated polymers in the mobile phase (0.4 - 10 mg/ml)in HPTLC produced the increase of efficiency for hydrophilic analytes (water soluble vitamins and amino acids). While the additions of fluoropolymers with sulfonate terminal groups in the eluent in HPLC result in the decrease of total analysis time and increase of efficiency of hydrophobic analytes (steroid hormones and fat soluble vitamins). The combination of sodium dodecyl sulfate and fluoropolymers in the running buffer solution (pH 7) in MEC led to the best effeciency of hormones (N=1000000 t.p.).

## Application of a newly devised electro-activated GCE to on-line monitoring of emerging pollutants photo-degradation

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The presence of emerging contaminants in the environment, especially in surface water, is a problem of growing interest (R. Schwarzenbach et al., Science 2006: 313, 1072). These compounds are often toxic, they can disrupt the endocrine metabolism of aquatic wildlife (K. Kidd et al., Proc. Natl. Acad. Sci. USA 2007: 104, 8897) and promote mechanisms of fortification of the bacterial strains (K. Kummerer, Chemosphere 2009: 75, 435). However, micro pollutants can undergo chemical transformations due to abiotic processes such as photochemical reactions (A. Boreen et al., Aquat. Sci., 2003: 65, 320). The monitoring of the environmental contamination by e.g. pharmaceuticals is important for a reliable assessment of risks for the ecosystem and, through the food chain, for humans, as well as for the evaluation and maintenance of the water resource quality. The anti-inflammatory drug acetaminophen (AP) is one of the most widely sold over-the-counter drugs (R. Newson et al., Eur. Respir. J. 2000: 16, 817). AP is rather effectively degraded by biological processes, but appreciable concentrations can still be found at WWTP effluents or in surface waters (N. Stamatis J. Environ. Sci. Health. Part B 2013: 48, 800). For this reason, several studies have investigated the fate of AP in surface waters (E. De Laurentiis et al. Water Res. 2014: 53, 235), determining a complex net of photochemical reactions. The AP irradiated solutions were generally monitored by HPLC, using relatively high drug concentration to enable easy quantification without the need of pre-concentration steps that would introduce significant variability in the data. The degradation by-products were identified by highresolution mass spectrometry.

In this work we start developing an electrochemical set-up that could allow for the monitoring in real-time of the photo degradation of AP and the detection of its main photo-produced derivatives with a significant saving of time. This approach is based on a newly devised electro-activated glassy carbon electrode (E. Chiavazza et al. Electrochim. Acta submitted) that can detect AP at trace level ( $LoD=2\cdot10^{-9}$  M and  $LoQ=9\cdot10^{-9}$  M) and, therefore allows to carry out the experiments at concentrations closer to those of natural waters. The electrochemical measurements were carried out with a time train DPV/CV in order to achieve a quantitative and a qualitative result during the degradation process.

## Two birds with one stone: reliable GC/MS analysis of volatile and semivolatile water pollutants in a single injection

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Since introduction of GC/MS into the environmental analysis all the pollutants were divided into three groups: volatiles, semivolatiles, and those requiring derivatization. Sample preparation for these three groups is different. Liquid-liquid extraction is still the most popular approach for semivolatiles, although it is rather long and laborious, not "green" enough, and often results in the analyte losses. The most widespread methods for volatiles are headspace and purge-an-trap. The most well known Standard Methods for these groups of compounds are US EPA Methods 8270 and 8260 correspondingly. It was always desirable to combine analyses of the two mentioned groups. Certain success was achieved by application of SPE and SPME. Nevertheless the polymeric coating is quite selective, making the procedures not universal.

Last year we reported on AWASP method for the fast (5 min), cheap and reliable sample preparation for GC/MS analysis of semivolatile compounds. The method involves mixing 1 ml of a water sample, 1 ml of dichloromethane, and anhydrous sodium sulfate. After the mixture is shaken for several minutes, all the organic compounds appear in the organic phase with reasonable recoveries. One of the advantages of this approach is the absence of any concentration step. Hence there are no losses of analytes while the recoveries for more volatile pollutants are much better than in the standard EPA 8270 Method. Thus for aniline with 100% recovery by AWASP it is only 17% by Method 8270. Therefore the same approach was applied for the volatiles. The hypothesis was successfully proved on 47 priority pollutants. The detection limits for the majority of volatiles were better than in the standard EPA 8260 Method.

As the procedure of the sample preparation was the same for volatiles and semivolatiles a mixture of more than 100 compounds of these classes was analyzed. The results demonstrated complete success of the approach. It is worth mentioning that the analysis was done with high resolution instrument LECO-HRT GC/MS. Therefore the reliability of the results was additionally improved.

The proposed AWASP method for the GC-HRMS analysis of volatile and semivolatile pollutants in water samples is cheaper, faster, easier, and more reliable than the existing sample preparation methods. It is also universal, able to expand the range of analytes in one injection. Sample preparation may be carried out directly on site and may be automated.

## Solid-phase extraction and HPLC-FD analysis of fluoroquinolone antibiotics from waters on silica-pyrolytic carbon from water soluble Kraft lignin

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The potential use of silica modified with pyrolytic carbon from Kraft lignin as solid-phase extraction (SPE) sorbent for the pre-concentration of Fluoroquinolone (FQs) antibacterial agents followed by HPLC-FD analysis was explored. FQs are emerging contaminants of great environmental relevance whose determination requires accurate analytical methods [1].

Lignin, the most abundant aromatic natural polymer and the second richest source of organic raw material, is easily available in large amount and at low cost. Lignin, whose pyrolysis was recently investigated by our group [2], in this work was deposited at different percentages onto silica by vacuum pyrolysis, performed at different temperatures. This new material was first characterized by Raman spectroscopy, TGA, BET and SEM, then tested as sorbent phase for the SPE of FQs from water.

Recovery and precision were evaluated on tap water samples (50 mL, 1  $\mu$ g L-1, n=3) using alkaline aqueous-organic mixture as eluting solution to evaluate the best performing material (carbon content 2 wt%, 1200°C pyrolysis). Sample volumes up to 500 mL provided enrichment factors up to 100, achieving method detection limits in the ng L-1 level. Recoveries ranged from 70 to 91% (n=3). The reusability of the silica-pyrolytic carbon cartridge was also evaluated and verified. The proposed analytical procedure was applied to the determination of these emerging contaminants in actual water samples.

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## Target, suspected-target, and non-target LC-MS(/MS) screening: new strategies for emerging contaminants in water bodies

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Target screening, suspected-target screening and non-target screening as well as "Known Unknowns" and "Unknown Unknowns" are new keywords that are currently increasing in interest in water analysis. [1] The search for unknown or expected molecules in the matrix water brought about new instrumental technologies and analytical strategies. A great share is based on liquid chromatography separation (LC) with atmospheric pressure ionisation (API)-coupled mass spectrometric detection (MS) and is technologically very mature.

Trace organic compounds are widely detected in drinking waters, surface waters and wastewater effluents. The presence of these compounds (pharmaceuticals, personal care products, pesticides, herbicides, industrial chemicals (e.g. REACH), etc.) and their transformation products as well as metabolites leads to emerging concerns about possible adverse effects on the aquatic environment and human health.

The group of sartanes (aniotensin II receptor antagonists) and their degradation as well as transformation products will be presented as an example for the new strategies identifying emerging contaminants. [2]

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## Application of GC×GC for detection, quantification, and partitioning property estimation of overlooked bioaccumulative brominated pollutants

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Environmental measurements of persistent and bioaccumulative pollutants (PBPs) are challenging, due to the trace level concentrations of these chemicals, the presence of matrix effect, and the complexity of environmental samples. We developed a robust and highly sensitive analytical procedure for confident detection, quantification, and partitioning property estimation of PBPs in environmental samples. This method takes advantage of the separation power of comprehensive two-dimensional gas chromatography (GC×GC) coupled with the highly sensitive micro-electron capture detector (µECD) and electron capture negative chemical ionization with time-of-flight mass spectrometry (ENCI-TOFMS) detector. These two detectors are both selective for halogenated pollutants and have sensitivities that exceed TOFMS with conventional electron impact source by roughly two orders of magnitude. We applied this method to the analysis of two "overlooked" brominated PBPs, 1,3,5-tribromobenzene and 4bromobiphenyl. We were able to successfully detect and accurately quantify these pollutants in the water column of Lake Geneva with limits of quantification (LOQ) of 14 pg L-1 for 4BBP and 40 pg L-1 for TBB. LOQ values for analyzed sediments were 4 pg g-1. Additionally, our measured GC×GC retention times can be used to estimate the partitioning properties of these nonpolar analytes, for several relevant environmental compartments, based on a recently developed approach from our lab. These property estimates provide the basis to immediately classify the measured pollutants for their potential to bioaccumulate, undergo long-range transport, and contaminate Arctic regions. With these advances, GC×GC becomes a powerful analytical tool for separating, detecting, and quantifying trace level halogenated bioaccumulative pollutants in environmental samples, as well as providing a quantitative pre-assessment of their characteristic transport behaviors in the environment.

## Passive sampling of sulfonylurea herbicides in aquatic environment using polar organic chemical integrative samplers (POCIS)

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Sulfonylureas (SUs) are low dose herbicides, intensively used for the control of a wide range of weeds in different crops. However, due to their moderate to high mobility and increasing use, these weakly acid (pKa 3-5), highly polar (log Kow from -1.88 to 1.63), water soluble herbicides are significant potential water pollutants. This study aims to investigate the utility of passive sampling technique for the monitoring of sulfonylurea herbicides (amidosulfuron, iodosulfuronmethyl, metsulfuron-methyl, nicosulfuron, oxasulfuron, prosulfuron, rimsulfuron, thifensulfuron-methyl, tritosulfuron), present at trace levels in surface water. To obtain sampling rate (SR), a fundamental value for the determination of the pesticides concentration in water, the polar organic compound integrative sampler (POCIS) were calibrated for nine selected SUs in river-like flow conditions. POCIS were composed of a hydrophilic-lipophilic balance (HLB) adsorbent, sandwiched between two polyethersulfone membranes and locked with two stainless steel rings. The sorbent was previously spiked with  $1 \mu g/g$  of DIA-d5, as a performance reference compound (PRC). To determine Rs, calibration was performed using a channel system, filled with tap water (pH~8.4) and spiked with SU herbicides. Experiment was carried out at a constant temperature and flow velocity (8.3 cm/s). Ten POCIS were deployed in duplicate, for 2, 5, 8, 11 and 14 days. To determine the aqueous concentration of SUs in the channel system (by solid phase extraction, SPE), 100 ml of water were taken at the beginning of experiment and each time POCIS were removed. Additionally, a SPE procedure and method for determination of these analytes from water matrix and POCIS were developed. Analysis of nine SUs was performed by UPLC-ESI-MS/MS system. The method was validated in terms of recovery (98-109%, RSD=0.73-2.74%), precision (0.36-3.85%), linearity (r2>0.9995) and LOQ for all SUs, proving its successful usage for the intended application. The results obtained in this research showed that for most of the compounds, the uptake in POCIS follows a linear pattern throughout the 14 days exposure. The calculated SR values of the studied SUs ranged between 0.03-0.09 I/day. Finally, POCIS have been deployed in the real environment for the evaluation of the presence of SUs in the aquatic environment.

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### Screening and Quantitation of Pesticides in Difficult Food Matrices

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The screening and quantitation of pesticide residues in foods is one of the most demanding applications in food safety.

Most pesticides are analyzed with multi-residue method covering hundreds of compounds.

The use of accurate mass LC/MS is of growing interest since it allows the detection of large number of analytes without prior knowledge on fragmentation

conditions or retention times.

Moreover it allows the retrospective data mining for new entities without re-measuring the samples.

## Accurate Mass QTOF LC-MS/MS Workflows & Tools to Identify and Screen for Known and Unknown Contaminants – with ease

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Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS) is a powerful analytical tool for the analysis of polar, semi-volatile, and thermally labile compounds of a wide molecular weight range. Mass analyzers based on triple quadrupole technology operated in Multiple Reaction Monitoring (MRM) mode deliver highly selective and sensitive quantitative results and are therefore well established for multi-target screening and quantitation of environmental contaminants. However, the use of triple quadrupole based mass analyzers limits the number of compound to quantify and identify. In addition there is an increasing demand for retrospective non-target (unknown) data analysis to identify unexpected contaminants. High resolution and accurate mass instruments are capable of performing targeted and non-targeted screening in a single LC-MS/MS run.

Here, we present new information on the next generation high resolution accurate mass LC-MS/MS QTOF platform from SCIEX . Non-Target compounds were identified based on non-target peak finding and sample control comparison to separate chemicals of interest from matrix components. Accurate mass MS and MS/MS information was used to empirically calculate molecular formulae. Found molecular formulae war searched against ChemSpider to find matching structures. Structures were automatically compared against the MS/MS spectrum and theoretically fragmented to tentatively identify the detected compound. Qualitative data processing was performed in MasterView<sup>™</sup> software which allows quick processing and intuitive data review, whilst quantitative data was processed using MultiQuant.

### Synthetic musks in biota - a perspective

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Synthetic musks (SMs) are widely incorporated into personal care products in order to convey a pleasant fragrance. However, due to their lipophilicity, resistance to degradation and potential negative biological effects they may pose risk to ecosystems, including biota. Therefore, an assessment of the occurrence of SMs in biota is relevant to understand better the magnitude of the impact and potential effects on ecosystems.

Studies published between 1994 and 2015 were compiled, as well as two early studies from 1981 and 1983. Biota samples were ranked into three different categories: human (milk, blood and adipose tissue), aquatic species (sea and fresh water fish, aquatic mammals, shellfish) and terrestrial species (game, polar bear, fox and earthworm).

A shift of focus in the available studies was noticeable, mainly in those regarding humans. While until the early 2000s it was common to study all nitromusks, currently only the EU-restricted [1] musk xylene and musk ketone are included. Among the polycyclic musks, some studies also included galaxolide-lactone as a degradation product of galaxolide, one of the most widely used compounds of this class. Reports on the occurrence of alicyclic or macrocyclic musks are scarce, on the one side due to the novelty of these compounds and on the other due to the challenges in finding reliable methodologies for their analysis [2]. Galaxolide and tonalide were the SMs most often detected and usually the ones that occurred at higher levels, in the range of 101 to 102 ng/g.

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# Assessment of siloxanes release into the environment by personal care products

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Siloxanes are organic compounds that contain a backbone of alternating Si-O units linked in a cyclic or linear way, with methyl side chains attached to each silicon atom [1]. Due to their low surface tension, high thermal stability and smooth texture, they have been used in a wide variety of personal care products (PCPs), such as shampoos, hair conditioners, lotions, etc. Recent studies show that siloxanes may have toxic effects on aquatic organisms, but also on mammals. In fact, these compounds are suspected of causing impaired fertility, liver damage and oestrogen mimicry [2]. Due to their ubiquitous occurrence, bioaccumulation and toxic potential, siloxanes are compounds of concern for both environmental and human health. Therefore, it is essential to examine their concentrations in PCPs to enable a prediction of human and environmental exposure by measuring their inputs.

In this work, an analytical method based on quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction followed by GC–MS was used for the analysis of eight siloxanes in PCPs. These products were chosen according to the usage patterns of the Oporto population (Portugal). Low detection limits, high average recoveries (>80%) and precision (RSD <15%) were determined.

Siloxanes were detected in most analysed samples in a wide range of concentrations. In general, higher levels of siloxanes were detected in shampoos and hair conditioners. Cyclic siloxanes were determined more frequently in the analyzed products. The human daily exposure to siloxanes was estimated, as well as the release rates of these compounds into the environment. Wash-off products represent the greater emission source.

**Acknowledgments.** This work was financially supported by: Project UID/EQU/00511/2013-LEPABE, by the FCT/MEC with national funds and when applicable co-funded by FEDER in the scope of the P2020 Partnership Agreement; Project NORTE-07-0124-FEDER-000025 - RL2\_ Environment&Health, by FEDER funds through Programa Operacional Factores de Competitividade – COMPETE, by the Programa Operacional do Norte (ON2) and by national funds through FCT - Fundação para a Ciência e a Tecnologia (Scholarship SFRH/BPD/76974/2011).

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### Study of metal accumulation in needles of different pine species

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Vegetation is a useful indicator of environmental (heavy) metal contamination via root uptake as well as via precipitation on the outer surface. This fact can be used to monitor pollution across both spatial and temporal scales. Pine needles are considered to be good biomonitors of air pollutants due to their waxy surfaces, which accumulate not only gaseous pollutants, but also polluting particulates. The accumulation behaviour depends on the one hand on the present pollution situation and on the other hand on the species. Especially in areas with known high contamination of certain metals, the growth of special accumulators can reduce the impact on the surrounding environment. Thus the influence of hybridization of pines on the metal accumulation is of interest for environmental reasons. The present study focuses on the determination of Al, As, B, Ba, Ca, Cd, Co, Cu, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, and Zn in needles of Pinus nigra and Pinus thunbergiana as well as of their hybrids. The elemental concentrations were determined by ICP-AES and ICP-MS after acidic microwave assisted digestion. Regarding differences in accumulation of metals in the needles, the hybrids show higher amounts of Al, Cd, Mn, Ni, Mg, Mn, and Zn than parent pine species. For the majority of the metals investigated, the accumulation behaviour is dominantly influenced by the mother.

## Acetaminophen and Sulphatiazole Release from Biodegradable Copolymers

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This study is focused on release of acetaminophen and sulphatiazole from biodegradable copolymers. Acetaminophen is one of the most widely used analgesic and antipyretic. Acetaminophen it was chosen as a model drug for its good water solubility. The representative of sulfa antibiotics – sulphatiazole was chosen as another model drug. Sulphatiazole is used to treat burns and leg ulcers and it is practically insoluble in water [1].

Polymers allow creating the carrier for low-molecular medicament due to its structure and high molecular weight. Drug loaded to polymer structure will be circulating in organism longer. The medicament may circulate days, weeks to months depending on the polymer structure. It is possible to achieve a prolonged effect or controlled drug release [2]. Acetaminophen and sulphatiazole were released from copolymers based on poly(lactic-co-glycolic) acid and poly(ethylene glycol) PLGA-PEG-PLGA. This group of copolymers is considered the stimuli-responsive polymers. Copolymers based on PLGA-PEG-PLGA are sorted into groups of temperature-sensitive polymers. The sol copolymer becomes hydrogel copolymer with increasing temperature and vice versa [3]. Release of acetaminophen and sulphatiazole occurred at 37°C in MilliQ-water and phosphate buffer solution pH value 7.4. High performance liquid chromatography coupled with mass spectrometry was used for quantitative determination of acetaminophen and sulphatiazole.

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# Combining the highest performance GCxGC and TOF/MS with high resolution deconvolution (HRD)

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The Pegasus GC-HRT 4D provides the capability to obtain high-resolution mass spectral data using comprehensive two-dimensional gas chromatography (GCxGC). GCxGC provides high peak capacity by trapping compounds eluting from the first chromatographic column and then systematically injecting them into the second column to obtain the second separation. The separation on the second chromatographic phase is completed in seconds, resulting in very narrow chromatographic peaks (<200 milliseconds).

To obtain sufficient data to define a 2D chromatographic peak, acquisition rates of at least 100 spectra/second are required.

With the Pegasus GC-HRT 4D, data acquisition rates of up to 200 spectra/second can be utilized, giving sufficient data density to obtain spectral deconvolution (HRD) of the chromatographic peaks.

Combined, LECO's GCxGC chromatography and the Pegasus GC-HRT provide the ultimate solution in complex sample characterization.

**ATMOSPHERIC SCIENCES** 

#### ATMO - 1

### Tryptophan in cloud water: occurrence, photoreactivity and contribution to the carboxylic acid speciation under sun-simulated conditions

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Atmospheric aqueous phase can be considered as a complex photochemical system in which chemical cycles are affected by numerous photochemical induced transformations. Moreover the organic composition remains largely uncharacterized and up to now less than 10% of the total organic carbon as been characterized. In the present work the presence of tryptophan, tryptophan-like and HULIS in real cloud aqueous phases collected between October 2013 and November 2014 at the top of puy de Dôme station was determined by using Excitation-Emission-Matrix (EEM) technique. The presence of free and complexed tryptophan (TRP) up to  $10^{-7}$  M in cloud aqueous phase was quantified by HPLC-UV-fluo analysis and TRP photoreactivity under sun-simulated condition was investigated in synthetic and real cloud waters. TRP degradation due to direct photolysis is accelerated in the presence of naturally occurring hydroxyl radical photochemical sources. TRP polychromatic degradation quantum yield between 290 and 340 nm is estimated to be to be  $8.37 \times 10$ -4 corresponding to the degradation rate of  $1.29 \times 10^{-11}$  M s-1 under adopted irradiation conditions. The degradation was accelerated up to  $3.65 \times 10^{-10}$ and 8.26  $\times$  10<sup>-10</sup> M s-1 M s-1 in synthetic oceanic and continental cloud waters doped with 100µM of hydrogen peroxide respectively. Hydroxyl radical mediated transformation leads to the generation of hydroxylated products, formic and acetic acids as mayor degradation products.

#### ATMO - 2

## Evaluation of hydroxyl radical photochemical sources in a cloud chemistry model : experimental vs. modeled formation rates

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It has been known since a long time that the aqueous phase photochemical reactions of constituents present in atmospheric water such as  $H_2O_2$ ,  $NO_3^-$ ,  $NO_2^-$  and Fe(III) aquacomplexes or organic complexes can form hydroxyl radical (HO•) within the water drop. This radical leads to the oxidation of many chemical species, particularly the organic compounds. However, the literature lacks of precise data concerning the rate of HO• formation and the relative contribution of the photochemical sources; also the organic speciation of iron in the cloud aqueous phase is still unknown. Cloud chemistry models such as the Multiphase Model for Cloud Chemistry (M2C2) are able to simulate the photoreactivity of chemicals that produce HO• in cloud aqueous phase. However, these models have never been evaluated towards experimental data. Here, we propose to simulate with the M2C2 model the hydroxyl radical formation rates that have also been measured directly in the cloud aqueous phase during three field campaigns from 2013 to 2014 at the top of the puy de Dôme station in France. Forty-one cloud samples were collected, and the corresponding air masses were classified as highly marine, marine and continental. Hydroxyl radical formation rates were evaluated coupling a photochemical setup (Xenon lamp that can reproduce the solar spectrum) with a chemical probe in order to trap all generated radicals. The total hydroxyl radical formation rates were measured as ranging from approximately 2x10<sup>-11</sup> to 4x10<sup>-10</sup> M s-1. These experimental values were then compared with modeled formation rates calculated by the model M2C2, considering only the chemical sources of the hydroxyl radicals. The comparison between the experimental and the modeled results suggests that the photoreactivity of the iron species as a source of HO• is overestimated by the model, and H<sub>2</sub>O<sub>2</sub> photolysis represents the most important source of this radical (between 70 and 99%) for the cloud water sampled at the puy de Dôme station.
# Chemical composition of atmospheric aerosol at Ny Alesund (Svalbard Islands): a focus on Elemental and Organic Carbon and organic acids

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The Arctic is experiencing substantial climatic changes since the past decades and the atmospheric aerosol plays a key role in the current climatic changes, influencing the energy budget of the surface and lowermost atmosphere. In particular, during polar sunrise, the Arctic troposphere is a unique chemical reactor, due to emissions both from human activity in the mid/high latitude areas and from natural sources in the Arctic Ocean; moreover, light-induced chemical reactions cause changes in atmospheric composition. The coupled effect of meteorological patterns and extreme variations in solar irradiance starting in spring makes difficult to unravel the factors of the production and removal of many environmentally relevant chemical compounds. Hence, daily PM10 and size-segregated (by 4-stage impactor) aerosol samples were continuously collected at Gruvebadet station (Ny Ålesund, Svalbard Islands, 78.9°N, 11.9°E) during the spring-summer period (March-September) along five consecutive years (2010-2014) and were analysed for ion, metal and EC/OC (Elemental/Organic carbon) content. Here we focus on the EC and OC fraction of the aerosol and on selected organic anions (oxalate, acetate, propionate, formate, glycolate and pyruvate), because of their importance in the absorption of solar radiation (EC) and their sensitivity to oxidation processes and to the dynamic atmospheric production/consumption triggered and/or mediated by solar radiation (organic compounds). Most of the determined organic anions show very low concentration in all the years, with the exception of oxalate, which is always dominant among the organic anions. The temporal trends of the measured compounds is studied in comparison both with the broad band UV solar irradiance data in order to evaluate the effect of the photochemistry on the studied compounds. Moreover, correlations among different chemical markers are studied, together with backtrajectory analysis, so to spot the long-range transport events delivering these compounds together with pollutants from the anthropized areas of the Northern hemisphere. For instance, in particular periods, significant correlation between nitrate and organic acids are found, whose nature is still to be ascertained and which could be related to common photochemical production processes. Besides, the similarity in the spring pattern of sulphate and oxalate hints at a common anthropogenic source of the latter in this period and requires further investigation

# Influence of non-steady state condition and of pellet quality class to residential pellet stove emissions

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In last years, the use of pellet devices as heating system in Europe-28 has strongly increased [1]. Besides advantages of renewability and greenhouse gas emission mitigation, emission from residential wood combustion has been considered as a major contributor to ambient air pollution [2]. Emission factors for residential pellet heating systems are obtained from measurements during stationary operation, quite far from a realistic utilization, since non-steady conditions, i.e. start-up, shut-down and changes in power, are very recurring in an operation day.

Pellet certification is based on qualitative standard on raw material and on pellet production and working processes. Combustion emissions are not taken into consideration at all. The aim of this study is to evaluate if non-steady phase contribution to the total emissions of a pellet stove in real domestic operations is significant compared to steady state one. Moreover, emission factors were measured for pellets with different ash content, to assess how they differ from a pellet class to another.

The emission factors were measured for the different stove phases (ignition, partial load, power increase and full load) and for pellets with different ash content, based on certification classes (A1, A2 and B). The flue gases composition was on-line analysed, while particulate emissions were collected in a dilution tunnel, to take into account the condensable fraction. The PM characterization includes: As, Ni, Cd and Pb, inorganic ions, PAHs, WSOC and TC. Results show that the emission factors are higher during ignition phase for several determined contaminants. Particularly, this phase contribution to PAH total emission in real domestic operations is prevalent. On the other hand, power increase emissions not appreciably differ from full load, since this phase starts in hot combustion chamber. However, differences were highlighted for PAH emission factors, they are higher than steady state ones. Moreover, non-steady state phases emit more toxic PAHs. Emission factors are generally inversely proportional to pellet quality class, thus better combustion conditions were reached when stove is fueled with A1 pellet. On the other hand, the emissions of the most dangerous TSP components at nominal load, such as WSOC and PAHs, are lower for A2 and B pellets.

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# Adsorbents and Carbon Technology for Air Sampling and Thermal Desorption

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In this presentation, an overview of the different adsorbents for air sampling and thermal desorption will be given. Characteristics of the different carbon media will be discussed, along with hints and tips and a tool for choosing the best adsorbent for a particular application e.g. for Fenceline Monitoring (FLM) etc.

# Study of the emission dynamic from residential wood combustion of pollutants of interest: PM, BC, OM, VOCs and levoglucosan

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During this last decade in Europe, the use of wood burning for residential heating has significantly increased because it is a renewable source of energy. The determination of wood combustion pollutant emission factors (EFs) is usually performed by measurements directly carried out at the emission source. In these conditions, the results obtained are not representative of the PM chemical composition and concentrations observed in ambient air due to post-emission physicochemical processes: dilution, condensation and photo-oxidation of semi-volatile species. The main objective of the Champrobois project was to study the physicochemical evolution of the aerosol emitted by two different residential log wood stoves (RWS, old and modern = 4\* and 5\*) from emission until its introduction in ambient air, in controlled "real" conditions. Measurements were performed directly at the emission source, at about 1 m from the exhaust stack (very close field, dilution factor about 10-20) and at about 50 m from the emission exhaust (close field, dilution factor about 500). Using dedicated on-line instrumentation (TEOM, TEOM-FDMS, Aethalometer, ACSM, PTR-MS and PILS-IC/PAD) in the close field, one specific objective was to study the emission dynamic of PM, specific VOCs and biomass burning tracers [Black Carbon (BC) and levoglucosan] for different wood combustion conditions.Results obtained showed that the pollutant emission dynamic and concentrations were closely linked to the combustion conditions (wood load, output) and phases (lighting, pre-load). As an example, BC accounted for the main part of the solid fraction of PM2.5 during all the combustion process in nominal output conditions while, at the beginning and at the end of the combustion cycle, the emission of other species (i.e organic compounds) was major in reduced output conditions. We also showed that the emission of the widely used biomass burning molecular tracer, namely levoglucosan, seemed only emitted under specific combustion conditions (cold start, pre-load, reduced output, large wood load inducing a decrease of the RWS temperature). This result is of primary interest in terms of PM source apportionment and evaluation of the contribution of the biomass burning source on ambient air PM concentration levels. This work was supported by ADEME (French Environment and Energy Management Agency) and the French Ministry of Ecology, Sustainable Development and Energy (MEDDE).

# Organic ecotoxicants in atmosphere of Moscow in winter period. An ESI-FT-ICR study of snow samples

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Human health is being influenced by several factors regarding the environment. One of the main factors is the air quality people breathe. Air and what's more important various aerosols and dust particles in the air could have either positive or negative effect on human health. Therefore it is very important to control quality of air, especially in highly populated areas.

Previously we have demonstrated effectiveness of snow samples analysis for estimation of priority pollutants in Moscow air in winter period by gas chromatography coupled with mass spectrometry method (GC-MS) with electron ionization (EI) [1]. However, to deal with polar and nonvolatile substances in snow samples (as in any others) it is better to use other ionization methods, for instance electrospray (ESI) rather than EI. Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry coupled to ESI ion source can provide ultrahigh resolution and mass accuracy making it a unique analytical tool for the analysis of complex mixtures with several thousands of components. Accurate mass measurement allows estimating formula of each substance in the spectrum. 8 samples of snow were collected in winter 2012-2013 along the Moscow belt road. Each sample contained over 2000 of organic compounds, in m/z range from 130 up to 700 Da. Statistical data processing performed with principal component analysis highlighted 3 groups of samples (A,B,C). Each group contains a number of specific compounds present only in definite area. So, it was found that in group A due to high emissions of SO2, dominate CHOS type of compounds with various double bond equivalent (DBE) values. Group B contains a large amount of oxidized hydrocarbons of different nature. These hydrocarbons appear due to emissions from traffic, neighboring oil refinery, and power plants. Another family of compounds specific for this region was CHNO formed during oxidation processes including NOx and NO<sub>3</sub>-radical as emissions of NOx in this part of the city are evidently higher. Group C is rich in CHO type of compounds with high H/C and low O/C ratios, which is characteristic of aliphatic acids, aldehydes and ketones. CHNO type of compounds in group C are probably nitro derivatives of PAH. The revealed distribution of pollutants gives a chance to develop new strategies in air quality control and further studies of Moscow environment.

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# Do high mountain ski areas have contamination caused by perfluorinated compounds?

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A typical representative tree species of high mountains is Swiss mountain pine (Pinus mugo Turra). Pinus mugo needles meet all basic criteria for selection as a type of passive sampler for ambient air pollution. Research is significantly lacking on determination of organic compounds in Pinus mugo needles; therefore a new laboratory method was established [1] and used to evaluate the burden of perfluorinated compounds (PFCs) in ski resorts of the Western Carpathians (Slovakia). PFCs like perfluorocarboxylic acids (PFCAs) and sulfonates are primary adsorbed on airborne particles, while more volatile compounds such as fluorotelomer alcohols (FTOHs) are in gaseous form [2]. Compounds bound to airborne particles may deposit on the wax surface layer of needles. This process occurs on all trees because of wet and dry deposition and does not explain the possible higher occurrence of these substances in needles. This study identified differences in concentrations of PFCs between an urban reference site and typical background high mountain site. Results showed more than seven times higher concentration at the high mountain site (38.708 ng/g dw of pine needles) compared to the urban site (5.032 ng/g dw) which was normally polluted by POPs. Several studies have identified a higher level of PFCs in the blood of professional ski waxing technicians, in snow and soil samples with positive correlations between concentrations and distance from the start of ski trails [3,4]. Therefore, high concentrations of PFCs can be attributed to the use of ski waxes and special outdoor clothes of skiers and tourists containing fluorinated membranes. This interpretation was supported by analysis of samples from other selected ski resorts and final results confirm our hypothesis.

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# New sample preparation strategy of bio-indicators for air quality monitoring

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Total reflection X-ray fluorescence spectroscopy (TXRF) is a well-established technique for elemental analysis of environmental samples [1,2]. The possibility to detect simultaneously many environmentally relevant elements, also in trace, present in samples makes TXRF a suitable technique for screening [3] Moreover, it is particular suitable for the chemical analysis of surfaces. In this work, leaves are used as bio-indicators for the determination of potentially toxic elements in atmospheric aerosols. Leaves were collected in different geographical park areas of Brescia city (Italy). This study proposed a new approach of sample preparation procedure developed by Smart Store for elemental chemical analysis of bio-indicators by means of TXRF. The method consists in sandwiching the sample in two polymeric foils, allowing to protect it from external contamination, to avoid any material loss and to store it for further investigations. After preparation, the samples can be directly analyzed. Indeed, it is already demonstrated a successful application of this new strategy for direct TXRF analysis of air particulate matter (PM) collected on teflon filters [4]. Furthermore, in this work the total solubilization of the samples by microwave acid digestion was performed. Quantitative analysis by means of internal standard addition was performed in digested samples. Good agreement of results reported by both sample preparation procedures was achieved. Linear discriminant analysis together with the elemental concentrations allowed the differentiation of washed and unwashed samples. It was observed that Fe and Pb have the main contribution to the differentiating component. The advantages and drawbacks of this procedure and future possibilities in sample preparation prior to TXRF analysis are outlined.

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# Characterization of biosurfactants from cloud microorganisms

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The formation of cloud droplets from aerosol particles in the atmosphere is still not well understood and a main source of uncertainties in the climate budget today. According to Köhler theory, three parameters drive these processes, the Raoult's term, the surface tension and the size of the initial atmospheric particle. The presence of trace compounds refered to as surfactants decrease the surface tension of droplets in the cloud and thus might directly impact on climate by increasing the number of activated cloud condensation nuclei (CCN). CCN may increase the amount of solar radiation reflected by clouds (Twomey effect) and may increase cloud lifetime (Albrecht effect).

Within a project devoted to bring information on atmospheric surfactants and their effects on cloud droplet formation, we dealt with production and characterization of biosurfactants (microbial origin) present in atmospheric waters. From our unique cloud microbial bank isolated from cloud water collected at the puy-de-Dôme (France), we undertook screening production, extraction and purification of atmospheric biosurfactants. After extraction of the supernatants of the pure cultures, surface tension of crude extracts was determined by the hanging drop technique. Results showed that a wide variety of microorganisms (47% of the strains) are able to produce biosurfactants. The best producers (16% of the strains) exhibit strong biosurfactants or high yields of biosurfactants as the resulting tension surface decreases to values less than 45 mN m-1, and until 25 mN m-1.

Purification was achieved by adsorption chromatography on a polystyrene resin. The adsorption of the active compounds on the resin was monitored by measuring the surface tension of the column outlet. Biosurfactants were separated by ultra-performance flash purification column. The molecular structure of the biosurfactants is investigated by means of Liquid Chromatography/Mass Spectrometry (LC/MS) and Nuclear magnetic resonance (NMR) techniques. Preliminary analytical characterization of biosurfactants, harvested after isolation from overproducing cultures of Pseudomonas and Sphingomonas, allowed us to identify them as belonging to three main classes, namely glycolipids, lipopeptides and glycopeptides.

# Production of siderophores by cloud microorganisms: occurrence and potential impact on cloud chemistry

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Iron plays a key role in cloud aqueous phase chemistry as it is a major source hydroxyl radical  $(HO \cdot)$  due to Fenton and Photo-Fenton reactions. In cloud waters it has been shown that, although the environment is highly oxidant, both Fe (II) and Fe(III) are present. This result suggests that most of iron is under the form of organic complexes. These complexes would stabilize iron in its reduced form Fe(II) preventing it to be re-oxidized. In atmospheric chemistry models, the iron-oxalate complex is used to as a model of organic complexes. However iron could be chelated by other organic ligands from biological origin in cloud waters such as HULIS, EPSs or siderophores as observed in sea waters and more recently in rainwaters.

As it has been shown that living microorganisms are present in cloud waters, they potentially need to acquire iron from this environment by synthetizing siderophores.

In order to test this hypothesis we have isolated 458 strains (bacteria and yeast) from clouds collected at the puy de Dôme station (1465 m, France). These strains have been identified and screened for their in-lab production of siderophores. For this purpose the CAS (Chrome Azurol S) method has been adapted for 96 wells microplates in order to get a high-throughput detection method. This test allowed a quantitative evaluation of the siderophore production and a qualitative determination of the chelating functional groups (catechol, hydroxamate, carboxylate). 42% of the tested microbial isolates were able to produce siderophores.

Our results as discussed in terms of the implication of the presence of siderophores in clouds for atmospheric chemistry.

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# Leaching behavior from MSWI bottom ash – a multi analytical approach

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MSWI bottom ash is as a complex inorganic material elevated amounts of inorganic pollutants. These amounts are currently the main restrictive factor for reuse as secondary raw material in construction. Moreover, bottom ash can be chemically and mineralogically altered over environmental conditions. Alteration products are considered to be the foremost solubilitycontrolling minerals playing a key role in major and trace elements leaching. Several methods are commonly used to describe the underlying leaching behavior of potential pollutants. Furthermore, geochemical simulations based on pH variation, mineral dissolution/precipitation, adsorption or complexation with organic materials are also required to have a better understanding of solubility-controlling behavior. Both experimental research and geochemical modeling using PHREEQC software were performed to study the correlation between leaching behavior of major (Al, Ca, Fe, Si), mineral trace elements (MTE: Cr, Pb, Zn, Ni, Sb) and anions (Cl-,  $SO_4^{2-}$ ) with pH variation in a fresh MSWI bottom ash. Particularly, MTE leaching often exceeds the French environmental threshold limits. The experimental pH-dependent influence on elements leaching was evaluated by means of acid neutralizing capacity (ANC) test. Modeling predictions based on precipitation/dissolution, surface complexation and adsorption reactions were applied to explain the experimental results as well as the main physico-chemical parameters governing mobility. It was found that Ca, Al and Fe modeled curves described quite satisfactory the experimental data. pH leachate was the main factor influencing MTE leachability. Depending on the element, leached concentrations over a wide pH range have showed to closely approach 'equilibrium' model curves. These results demonstrated that pH dependent experiments combined with mineralogical and modeling approach constitute a crucial set of tools for MSWI bottom ash leaching behavior characterization processes.

# CHARACTERIZATION OF NATURAL AND AFFECTED ENVIRONMENTS

#### CHAR\_ENV - 1

# Distribution, sources and ecotoxicological risks of PAH pollution in surface sediments from the Greek coastal zone

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Polycyclic aromatic hydrocarbons (PAH) are hazardous environmental chemicals, included in the European priority pollutant lists. The aim of this work was to study the pollution from PAH in the coastal marine environment of Greece. For this reason, the distribution, composition and sources of PAH mixtures (43 compounds) were assessed in surface sediments (152 samples) collected from almost all the Greek coastal zone, by using a molecular marker approach and several diagnostic criteria and indices. In addition, ecotoxicological risks were estimated by evaluating the PAH values against effect-based Sediment Quality Guidelines. PAH concentrations were determined by GC-MS, after Soxhlet extraction and fractionation by silica column chromatography and the mean quotient Effect- Range Median (m-ERM) was used to evaluate the probability of observing toxicity. The highest contamination (PAH values well above 3000 ng/g) was recorded in marine areas directly influenced from the operation of industrial units in the coastal zone. Several "hot spots" were also indentified in other marine areas and correlated with local pollution sources. Regarding the main Greek estuarine systems, Evros river in Northern Greece was found to be the major PAH supplier into the marine environment, followed by Strymon river located also in Northern Greece. Based on the characteristics of both the parent compound and the alkyl homologue distributions, the potential sources of PAHs were identified, whereas special isomeric compound ratios were calculated to evaluate the relative importance of different origins. At almost all the stations, the pyrolytic PAHs coming from anthropogenic combustion processes were predominant, while the petrogenic inputs were less important. High quantities of terrestrial - biogenic compounds were also found in some cases indicating the transportation of land derived organic material into the sea. With respect to the ecotoxicological effects, a high probability of toxicity (76%) with m-ERM values higher than 1.5, was found only in 3% of the samples examined, while 82% of the samples had m-ERM values below 0.1 indicating a very low probability of toxicity.

## CHAR\_ENV - 2

# Geochronological studies on aquatic sediments as archives for building up pollution histories - potentials and pitfalls

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Increasing emissions of anthropogenic contaminants (e.g. persistent organic pollutants, pharmaceuticals, technical additives, personal care products, heavy metals, nutrients etc.) has been recorded for the last 200 years as a result of the dawn of industrialization and a correlated growth of population. A huge proportion of the contamination has been discharged in particular to river ecosystems, which has caused a huge impact on water quality. Since environmental issues raised interest not till the beginning 1960'ies, the knowledge about former or even historical contamination is often very limited.

To get historical information about quality and dimension of river pollution retrospective approaches need to be used. In this regard, especially the usage of archives may give access to this 'buried' information. Consequently, aquatic sediment archives have been intensively used to assess the extent and effect of historical human pollution on river systems. Briefly, geochronological investigations of anthropogenic pollutants in aquatic sediment archives are a useful tool to follow variances in the contaminant inventory over a broad time interval and to provide insights into the historical development of pollution in aquatic systems.

This contribution will present studies applied on different aquatic sediment archives in order to demonstrate how:

•Identification and usage of indicative marker compounds can work to unravel the complex emission situation in river systems, recently and in the past

•the non-extractable fraction for identifying specific marker compounds can be included

•pollution histories for different parts of the river systems can be build up and how pollution sources with major environmental relevance can be monitored over time

The presented investigations cover different river and marine systems from Europe and US, as well different spectra of organic compounds detected and analyzed with respect to the above mentioned aims. The results will be discussed with respect to the overall potential of geochronological studies but also pointing to restrictions and pitfalls.

## CHAR\_ENV-3

# Summer evolution of metal fractions in the sea water of Terra Nova Bay (Ross Sea, Antarctica)

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The aim of this work was to study the distribution of Cd, Pb and Cu fractions (total, dissolved, inorganic particulate and phytoplankton) in the seawater of Terra Nova Bay (Ross Sea, Antarctica). During the 2013-2014 Antarctic summer four seawater samplings were carried out along the water column from mid-November 2013 to mid-February 2014, in the Gerlache Inlet area, near the "Mario Zucchelli" Italian Station. CTD profiles were also carried out. Seawater samples were divided in aliquots subjected to different treatments for the determination of the total concentration and dissolved, inorganic particulate and phytoplankton fractions. The algal fraction was separated from the inorganic particulate by a procedure previously set-up [1-2]. All the samples were subjected to microwave digestion before Cd, Pb and Cu determination by Square Wave Anodic Stripping Voltammetry (SWASV).

For Cd, total (Cdtot) and dissolved (Cddis) concentrations were similar (~60/80 ng/L), within the experimental errors, with some exceptions. Both fractions decreased in the surface layer reaching extremely low values in February (~20 ng/L). Pbot decreased during the summer varying from ~200 ng/L to ~50 ng/L. Pbdis didn't vary substantially during the summer, remaining stable (values around 40 ng/L) with the exception of one sampling. Concerning Cu, both total and dissolved fractions tend to decrease during the summer especially in the first 100 metres: Cutot from 350 ng/l to 150 ng/l, Cudis from 200 ng/L to 100 ng/L. Cudis represented a variable percentage of the total (40-100%). Preliminary results shows the influence of the phytoplankton on the distribution of Cd, Pb and Cu in Antarctic seawater.

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# Hydrophobic organic pollutant concentrations exhibit strong spatial variability in the deep water column of Lake Geneva

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It is frequently assumed that hydrophobic pollutants have uniform spatial distributions in surface water bodies such as lakes, due to the logistical challenges of sampling and measuring for these compounds. Using both conventional passive samplers and a newly developed accelerated sampling device, we conducted vertical and horizontal measurement transects of 11 quantifiable hydrophobic organic pollutants (HOPs) in the water column of Lake Geneva. We successfully detected and quantified these 11 HOPs in 16 distinct water column sampling locations, using comprehensive two dimensional gas chromatography coupled to an electron capture detector (GC×GC- $\mu$ ECD). We further confirmed the identity of these target analytes in a selected subset of samples, employing GC×GC coupled to electron capture negative chemical ionization time-of-flight mass spectroscopy (ENCI-TOFMS).

In a vertical profile from 70 to 166.5 m (bottom) depth, systematic concentration variations were found for several pollutants, with observed concentration differences of up to a factor of 3 over the measured depth range. Additionally, based on sampling at 5 statistically grouped geographical locations in deep waters near the lake bottom (80 to 305 m depth), we observed horizontal concentration differences of up to a factor of 60. We also analyzed 4 sediment samples collected from 4 different locations in the lake, in which we successfully detected and quantified 9 out of the 11 target analytes. The sediment concentration distribution of these pollutants was consistent with the observed trends in water column concentrations at adjacent locations, which implied that local sediment-water exchange processes were faster than mixing between these different water masses of the lake. These spatial concentration distribution data also suggested potential source areas for some pollutants.

Our results demonstrate that assessments of inventories, exposures, and inter-compartment transport may be significantly in error if they are based on water column measurements at only a single location in a water body. Thus, for many pollutants, reliable assessments and fate modeling would require measurement datasets based on several sampling locations in the water column of this lake, as well as physical modeling of water mass movement, which is non-trivial for a 4-dimensional system such as Lake Geneva.

## CHAR\_ENV-5

# Profile of some pharmaceuticals in the Romanian Tisza River Water System

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Pharmaceuticals are compounds intensively used to treat human and animal diseases that end into the surface waters coming from the industrial production, hospitals or households. Because of their toxicity and relative persistence in the water bodies, pharmaceuticals are considered as main micropollutants thereof. Some unexpected health effects have been observed during the last time that are explained by an increased resistance of human and animal bodies to pharmaceuticals caused by their uncontrolled input in surface waters. As a result, the European Union started to pay a special attention to this subject, the European Parliament amending the Water Framework Directive (2000/60/EC) being preoccupied to introduce some emerging pollutants, namely diclofenac (anti-inflammatory) and 17beta-estradiol (hormone), in the list of priority substances and to establish their maximum allowable concentration in surface waters.

In this work, the authors present the profile of some pharmaceuticals in the Romanian Tisza River Water System. These compounds include nonsteroidal anti-inflammatories, hormones and antibiotics that are widely used in the human and veterinary treatments. Different water and sediment samples collected from the Tisza River and its Romanian tributaries were analyzed.

The isolation of the investigated pharmaceuticals from water samples was performed by solidphase extraction (SPE) on Strata C18-U and Strata X cartridges and from sediments by ultrasound assisted extraction (UAE). The determination of pharmaceuticals was achieved by high performance liquid chromatography coupled with diode array detector and/or mass spectrometer. The SPE/UAE-HPLC-DAD/MS developed procedures were validated and applied to real river water and sediment samples.

In the investigated samples were found diclofenac and ibuprofen as anti-inflammatories, estrone and 17beta-estradiol as hormones and tetracycline, doxycycline and ceftazidime as antibiotics. The obtained results show the importance of the study of pharmaceuticals in surface waters and sediments for a better risk assessment.

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## CHAR\_ENV-6

# Distribution and sources of polycyclic aromatic hydrocarbons in the Tisza River and its Romanian Tributaries

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Polycyclic aromatic hydrocarbons (PAHs) are an important class of environmental contaminants derived from both natural and anthropogenic sources. Due to their toxic, mutagenic, carcinogenic and bioaccumulation potential there is a continuous concern over the PAHs content in the aquatic media. Moreover, some of these compounds have been classified as priority substances in the frame of Water Framework Directive being established the Environmental Quality Standards limits. According to the formation mechanism, PAHs can be classified as pyrogenic (hydrocarbon compounds associated with the combustion of petroleum, wood, coal, creosote, coal tar) and petrogenic (hydrocarbon compounds associated with the origin of the PAHs in the aquatic media and can help the public authority responsible for the water management to establish actions to reduce the pollution.

The aim of this work was to evaluate the distribution of polycyclic aromatic hydrocarbons in the Romanian Tisza River Watershed, to assess their occurrence and to establish the origin (pyrogenic/petrogenic) of pollution sources.

Fifteen PAHs were investigated in surface water and sediment samples collected from Tisza River and its main Romanian Tributaries (Iza River and Viseu River). The target compounds were isolated by solid phase extraction from water samples and by ultrasound assisted extraction from the sediment samples. The quantification of the target compounds were performed by high performance liquid chromatography coupled with fluorescence detector (HPLC-FL). For a better identification of these compounds, gas chromatography coupled with mass spectrometer (GC-MS) was also performed. PAH diagnostic ratios have been used as a tool for the identification and the assessment of the pollution emission sources.

The results of our study showed that in the investigated area mixed sources, pyrogenic and petrogenic, occur and their contribution to the pollution depends on the sampling point and the intensity of human activities. Thus, the pyrogenic contribution occurs in the Iza and Tisza Rivers (sampling points situated down stream of Sighetu Marmatiei city) while a diffuse petrogenic signature is evidenced in Viseu River, an area with a low density of population.

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FOOD AND AGRICULTURE

# HPLC and capillary electrophoresis of bioactive compounds in plant tissues and food matrices of plant origin: fundamental and practical aspects

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This communication discusses the results of our recent studies carried out to investigate a variety of factors that influence both electrophoretic and chromatographic behaviour of bioactive compounds extracted from plant tissues and food matrices of plant origin. Most of these compounds are secondary metabolites produced within the plants besides the primary biosynthetic and metabolic routes. They hold various types of important functions in plant tissues, required for the plant survival in the environment, such as to confer effectiveness against microbial attack, resist environmental stress or function as signalling molecules in interplant communication. Moreover, most secondary metabolites, present as "non-nutritive" compounds in plant food, have found to play an important role in disease prevention and health-promoting effects.

The presentation evaluates the influence of the composition of either the electrolyte solution (BGE) or the mobile phase on the selective separation of the above compounds in capillary zone electrophoresis (CZE) and in reversed phase high performance liquid chromatography (RP-HPLC), respectively. Appropriate selection of the chemical composition of either the BGE in CZE or the mobile phase in RP-HPLC involves the evaluation of the equilibrium in solution that might take place between the analytes and the components of such solutions. In addition, the chemical composition of the liquid phase affect the physical-chemical properties of the separation medium, such as pH, ionic strength and surface tension, which, in both techniques, might influence the separation performance to different extents. The incorporation of organic solvents into either the BGE or the mobile phase also has a strong impact on both electrophoretic and chromatographic behaviour of the bioactive compounds found in plants tissues and derived plant food and feed, which, in most cases, are complex molecules bearing a variety of functional groups.

In conclusion, the potentiality of CZE and RP-HPLC in separating bioactive compounds in plant tissues and food matrices of plant origin is illustrated and the possibility of tailoring selectivity and efficiency of the considered separation systems by incorporating suitable buffering agents, organic solvents, and/or additives into the BGE or the mobile phase, respectively, is discussed.

# Determination of diazinon in feeding bee syrup sugar

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Organophosphates (OP) are a group of insecticides, used worldwide for controlling insects. The interference of OPs with AChE signaling pathways of pests is desired, but on the other hand this may have serious impact on beneficial insects, such as bumble bees and honey bees. The latter are important pollinators and have economic significance for a man. Disturbances in the cholinergic transmission system of the honey bees impair their orientation, olfactory learning and navigation abilities. Honey bees can be exposed to OPs via dermal, inhalation or oral route. The objective of the present study was to determine trace amounts of diazinon in honey bee food by HPLC-DAD after the extraction applying modified SPE extraction protocol since the matrix was very complex.

For the purpose of analysis of diazinon in the honey bee food, diazinon standard (1-5 mg/L) was prepared in 3 different media: absolute ethanol, 1.5 M sucrose solution and double deionized water and incubated in syringes (PP+PE, open or closed) or glass vials under similar environmental conditions as honeybee experiment and sampled at different time intervals (0, 2 h, 24 h and 48 h). After incubation time, samples were subjected to 2 extraction methods. In first method, all diazinon samples were transferred directly into mobile phase (70: 30 acetonitrile : double deionized water) and instantly measured with HPLC-DAD ( $\lambda$  = 250 nm). In second one, samples of the diazinon in 1.5 M sucrose solution (5 mg/L) were extracted applying modified SPE extraction protocol. The samples were previously diluted in different rations to facilitate SPE. Three different solvents were tested for the elution, acetonitrile, methanol, and absolute ethanol, and the latter proved to be the most effective.

Results have shown no change in concentrations with time when using glass vials, while in the case of PP+PE syringes the concentration varied. The additional experiments, testing possible adsorption of diazinon on plastics, have been performed but they did not confirm the adsorption of diazinon on plastic, applied in the experiment.

# The response of lettuce to environmental stresses is cultivar specific: role of phenolic acids and flavonoids

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There is an increasing interest for the inclusion of fresh fruits and vegetables in the human diet, mainly due to the health benefits associated with their consumption. Several epidemiological studies have revealed that diets rich in fruits and vegetables are associated with a reduced risk of cardiovascular diseases and various types of cancer. These beneficial effects are believed to be due to phytochemicals such as phenolic compounds, which can protect the key biological constituents of the cell. Having defense functions, their concentrations can increase when plants are subjected to environmental stresses. This practice represents a great potential for enhancing the health promoting properties of food products. The aim of this work was to study the changes in the composition of phenolic acids and flavonoids in two differently pigmented lettuce cvs when submitted to high light (700 PAR) or elevated  $CO_2$  (700 ppm) or to a combination of both. The two cvs were very different for the contents and composition in phenolic acids and flavonoids, with the red one showing the higher values. In response to both high light and elevated CO<sub>2</sub>, total flavonoids and phenolic acids increased mainly due to increases in guercetin, quercetin-3-O-glucuronide, chicoric acid and chlorogenic acid, these changes being cv. specific. Cyanidin also reached a higher value in the red cv. following stress. When high light was applied together with elevated CO<sub>2</sub>, flavonoids of the green cv. were subjected to a much higher increase than when high light or elevated  $CO_2$  were applied separately. The red cv. showed a different trend with elevated  $CO_2$  not having a positive effect on the amounts of phenolic acids. These results suggest that the application of high light or elevated  $CO_2$ , alone or in combination, can induce the production of some phenolics increasing the health benefits of plant products such as lettuce. As each treatment alters in a distinct way the composition of phenolics and each phenolic compound has different nutraceutical properties, the choice of the treatment can be done on the base of the desirable compound to be enhanced.

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# In depth study of the effects of the fungicide BEAM<sup>™</sup> on the thylakoid membranes of rice plants

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Fungicides are very important for agriculture, since they prevent and cure plants diseases, which can have severe adverse effects on crop yields and quality. While many researches are focused on the study of the formation of degradation products from fungicides promoted by sunlight irradiation and hydrolysis [1], particular attention should be devoted to their effects on the photosynthetic process in plants.

In photosynthesis, the light-dependent reactions take place in the thylakoid membranes of the leaf, where Photosystem II is one of the key protein complexes, carrying out the conversion of solar energy into electrochemical potential energy. The aim of the present study is to enhance the understanding of the effects of the fungicide BEAM<sup>™</sup> on the thylakoid membranes of rice plants.Rice (Oryza sativa L., cv Vialone nano) grains were grown for three weeks under controlled conditions, simulating the natural environment. Half of the plants were treated with an aqueous solution of BEAM<sup>™</sup> at 500 mg/L, a concentration usually used by farmers, while the other non-treated plants were used as control. About 1 g of leaves from each sample was collected after the treatment at fixed times. Thylakoids were isolated from plants according to the method described by Pagliano et. al [2]. The proteomic analysis of the thylakoid membranes, extracted from treated and untreated plants, was conducted in SWATH-MS (Sequential Window Acquisition of All Theoretical MS) acquisition mode. SWATH-MS is a new strategy for high throughput label-free protein quantitation. The method combines the traditional shotgun proteomics with the quantitative accuracy and reproducibility of selected reaction monitoring (SRM). The modulated expression of proteins in the thylakoid membranes of treated plants was further correlated with in vivo chlorophyll fluorescence measurements (i.e., Fv/Fm), which can monitor stressful effects of the fungicide on Photosystem II. These results, taken together, highlight that the fungicide BEAM™ influences the mechanisms of utilization of sunlight by rice plants.

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# Bio-geochemical evaluation of the "irrigation water – soil – hay groundwater" system in Crau area (South France)

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The construction of a spatio-temporal dynamic view of the "irrigation-meadow-soilgroundwater" system evolution in the Crau has been based on modeling of the chemical composition acquisition of the water during its transfer through the soil from initial state (irrigation water) to the final state (groundwater). In Crau, surface irrigation is used for grassland production via channels network that is fed from the Durance River since the 16th century. Over the years, an agricultural system has been created thanks to alluvium brought on irrigated area, which is rich in minerals and trace elements. Over this soil meadows grow producing high quality hay that is exploited in three cuts per year. First cut (cut1) in May, second cut (cut2) in July and third cut (cut3) between August and September. This irrigation is also involved in more than 75% of aquifer recharge, but it is threatened by global changes (urban sprawl and climate change), which ultimately risks to compromise the sustainability of the irrigated grassland system. Regular analyses are performed on the water every 15 days during the irrigation period (April -September), by measuring in situ the pH, electrical conductivity (c  $\mu$ S/cm 25°C) and temperature and, in the laboratory, the alkalinity (meq / L), major anions and major cations. For hay, there is, on one hand, records of chemical analysis of hay minerals content acquired for 3 cuts since 1960 and, on the other hand, recording of the floristic and chemical compositions of the hay made on sampling at maturity stage for three cuts in 2015. Moreover, soils of grassland and coussouls of the three types of Crau depending on the age of their formation, and fertilizers are also analysed by X-ray diffraction. Initial results showed that the processes that take in consideration through water transport in the system are: evaporation, the reaction with the partial pressure of  $CO_2$  in the soil, the mineral intakes in the hay, the effect of the rhizosphere and the effect of mineralsolution interactions in the surficial formations up to the aquifer. Statistical analysis of the chemical analyses of hay showed that the total content of hay minerals followed the sequence: cut 3 > cut 2 > cut 1. It was also observed that the calcium content variation was correlated in the hay, depending on the cut considered, with the irrigation water supply and the distribution between grasses and legumes in the hay as function of the time.

# GREEN CHEMISTRY AND SUSTAINABLE USE OF RESOURCES

# Environmentally sustainable strategies for the recovery of a critical raw material from electronic waste

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In the last twenty years, a significant growth of electrical and electronic equipment production was observed. The continuous development of technology, combined with a low lifetime of these devices, caused an increase of waste to dispose of. Generally, they end up either in a landfilling site or in an incinerator, with the consequent loss of several precious materials inside. The example of liquid crystal displays (LCDs) is significant: indeed these devices are replacing the old cathode ray tube systems for their best performance, showing a lifetime between 3 and 8 years. The precious metal contained in LCDs is indium, used with tin to produce a transparent conductive layer. The importance of indium was defined by the European Union that classified this metal as a critical raw material on the basis of economic importance and supply risk. Today, almost half of the primary indium is mined in China, therefore, the recovery of this metal from end-of-life LCDs is a hot topic for Europe. For this reason, we developed a process, within the FP7 project HydroWEEE, that allows a complete indium recovery from LCD scrap. The first step of the treatment consists of an acidic leaching, using sulfuric acid. Considering the indium concentration in the waste, around 150 ppm, a cross-leaching configuration is used in order to ease the further indium recovery and improve the resource efficiency. A cementation by zinc powder follows the leaching step with a final complete indium recovery. An environmental perspective of the process for indium recovery was also provided by means of life cycle assessment. The impacts of process were compared with conventional end-of-life LCD panels management routes, i.e. incineration and disposal in landfilling site. As a whole, these results support the advantage to the environment associated with indium recovery from end-of-life LCDs, despite the quite low indium concentration in the panel. Considering the high efficiency obtained, this process is promising in a perspective of the development of urban mining strategies in Europe.

# Comparison of catalytic and photocatalytic water oxidation materials through the reaction kinetics in a three-phases bubbling reactor

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There is an ever-increasing necessity in society for energy resources which are cost effective and sustainable. Researchers all over the world are investigating photochemical water splitting (WS) to  $H_2$  and  $O_2$ , as a promising way to store solar energy. A widely studied approach to the make light-driven WS reaction consists in separating the functions of light harvesting and conversion from fuel-forming catalysis. Recently, we developed a reactor system and a mathematical model to investigate the kinetics of O2 evolution, with a high precision. The reactor has been designed and implemented to measure  $O_2$  evolution, into which Ar flows at a constant rate and bubbles into the continuously stirred liquid phase. The oxygen concentration in the outgoing gas mixture is measured through a micro gas chromatograph. Thus, the actual oxygen flow and cumulative  $O_2$  production are determined. Coupled with the information on the  $O_2$  dissolved in the liquid phase (measured with a Clark-type electrode), we have developed a comprehensive mathematical model (based on O<sub>2</sub> formation at the catalyst surface, then diffusion at the dispersed gas bubble interface, and finally mixing with the stagnant gas in the pocket on the top of the liquid surface), able to retrieve the actual  $O_2$  evolution reaction rate (RO<sub>2</sub>) from the recorded data, in order to study the chemical kinetics of different photocatalytic system. This methodology has been employed in our laboratories to study several catalysts and photocatalysts (e.g. Co- and Mn- oxides, as well as BiVO4 and WO3) in order to retrieve their intrinsic activity for the WO reaction under visible light irradiation.

# Catalytic wet air oxidation of lignin over perovskite-type oxides as catalysts

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The development of an efficient model of integrated biorefinery based on renewable lignocellulosic biomasses seems to be fundamental to ensure a sustainable production of fuels and chemicals. Generally cellulose and hemicellulose are hydrolyzed into the corresponding sugars constituting their structures and then transformed mainly into ethanol, while the lignin fraction is considered as a waste and it is mostly burned to produce energy or steam. Despite years of efforts, the development of a commercial plant for biomass-to-biofuel conversion is still economically tricky. Coupling the production of fuels with high-added value chemicals may be fundamental to achieve the economic sustainability of these processes.

The aim of our work has been to take a residue, steam exploded lignin derived from wheat straw, and to transform it firstly into substituted phenols and secondly into carboxylic acids through an oxidative process with air as first oxidant agent. Perovskite-type oxides have shown high oxidative activity in similar processes [1], therefore several perovskites have been prepared through the solution combustion synthesis (SCS) and tested in the oxidation of lignin. The experiments have been carried out in a pressurized batch reactor loaded with water or aqueous solutions as solvent. The process takes 1-4 hours with temperatures ranging from 150 to 250°C and air pressure between 20 and 50 bar, showing lignin dissolution up to 80%. A  $\mu$ GC analyzer has been adopted to monitor the undesired production of CO<sub>2</sub>, while the reaction mixture is analyzed by means of GC-MS and ionic chromatography. Catalysts such as LaMnO3, CeFeO<sub>3</sub> and LaFeO<sub>3</sub> have been characterized through XRD, XPS, TPR and FE-SEM analysis.

Best catalytic performances have been achieved with a basic environment and a solubilization pre-treatment of the raw lignin before the CWAO reaction, giving a 8% mass yield in aromatics and showing phenol, vanillin and p-hydroxybenzaldehyde as main compounds. Moreover, the obtained yield in organic acids is up to 12%, main products are lactic acid, glycolic acid and succinic acid. Even though the yields are limited, the novelty of the process is the generation of saturated C4, C5 and C6 dicarboxylic acids not observed before in similar processes [2].

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# Pd-based catalysts for hydrodechlorination of Aroclor 1260

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PCBs are known recalcitrant and toxic pollutants and significant amount of contamination could be found in water. It is known that PCBs can be hydrodechlorinated using Pd-based catalysts, but due to technical challenges catalytic hydrogenation has only been limitedly applied at the field-scale [1,2]. Therefore the research to identify more efficient catalysts, preferably heterogeneous catalysts, able to work in an aqueous phase, less sensible to deactivation and easily removable at the end of the treatment, remains a considerable interesting goal. Different Pd-based catalysts, many of which prepared by us with innovative methodologies, were tested in the hydrodechlorination reaction of the Aroclor 1260 PCBs mixture with hydrogen under hydroalcoholic conditions ( $H_2O/$  EtOH 2/1). The degree of PCBs dechlorination was found to be dependent by the nature of Pd-based catalyst and of base used to neutralize the produced HCl. Working with a substrate/catalyst 8/1 molar ratio, at 3 MPa H<sub>2</sub> and 60°C in 20 h a significant removal of highly chlorinated PCBs ( n° Cl atoms  $\geq$  6) was obtained. Some results, obtained by GC-MS analysis, are reported in the Table and seem promising for remediation of groundwater contaminated with PCBs.

	STD aroclor 1260	Run 1	Run 2
n° Cl	%	%	%
0	0.02	3.37	1.97
1	0.05	2.04	1.07
2	0.24	8.41	4.41
3	0.50	15.40	8.83
4	0.59	14.42	11.40
5	10.65	20.18	21.61
6	46.69	21.22	29.29
7	33.57	12.24	17.65
8	6.86	2.48	3.42
9	0.78	0.23	0.34
10	0.05	0.01	0.01
	Table		

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# Life cycle analysis of alternative industrial routes to maleic anhydride

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Sustainability in the chemical industry represents a recent issue which reached importance during the last decades, in particular after the release of the Green Chemistry and Green Engineering principles. However, in order to address sustainability along the entire production process, a Life Cycle Assessment (LCA) approach with its holistic perspective seems very useful to support the further established green metrics, such as E-factor and Process Mass Intensity. Moreover, LCA is a standardized methodology (ISO 14040 and 14044) internationally well recognized and established. Therefore, in order to assess the LCA potentiality applied to chemical industrial sector the synthesis of maleic anhydride (MA) was selected as a case study. MA is commonly obtained by direct oxidation of benzene or n-butane as feedstock. In this study, three different routes were modeled in order to compare the obsolete synthesis from benzene with the alternatives pathways which use n-butane using both a fixed-bed reactor and a fluidized-bed technology (ALMA process). A cradle to gate perspective was considered, from raw materials extraction up to the MA production, including all the intermediate stages and utilities. Direct industrially available data were used in order to fill the life cycle inventories. The ReCiPe and Cumulative Energy Demand (CED) were selected as analysis methods to carried out the impact assessment stage. Scores achieved for the climate change category revealed a lower sustainability associated with the benzene based process, while the butane oxidation using fixed-bed reached higher impacts in terms of fossil fuel depletion. The mainly reason is the lower energy efficiency of the fixed-bed reactor, confirmed also by the CED method. On the other hand, although the ALMA process reaches a slightly lower yield, the fluid-bed technology seems more efficient reaching the lower global impact classifying it as the more environmental friendly route.

# Effects of synthetic parameters on the catalytic performances of Au/CeO2 catalysts for furfural oxidative esterification

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Recently, the production of fuel and chemicals from biomass, involving the transformation of selected platform molecules, received much attention due to the possibility to replace the products coming from petrochemistry. The potential for biomass valorization in the framework of biorefineries is enormous. However, successfully replacing petroleum based fuels and chemicals with biomass-based products will require high-yield, low-cost and energetically efficient targeted upgrading processes. The application of heterogeneous catalysis and molecular  $O_2$  to oxidation reactions offers a green alternative to traditional, toxic chemical oxidants. Dehydratation of C5 biomass sugars leads to furfural formation and by its oxidative esterification it is possible to obtain methyl-furoate, which is used as flavor and fragrance component and is a higher added value product. However, the process was initially carried out in the presence of a base, which negatively affects the sustainability of the reaction [1]. Au based catalysts on different supports for a base free reaction were investigated [2-3]. Cerium oxide is a very interesting support for oxidation reactions due to its ability to store and release oxygen. Therefore, the study of an efficient  $Au/CeO_2$  catalyst able to operate without the presence of a base is here reported. The goal is to investigate the effect of different calcination temperatures of the support and of the final catalysts on Au size and ceria support and to check the role of such features on conversion and selectivity. TG/DTA analysis, N<sub>2</sub> adsorption/desorption, XRD, HRTEM, CO pulse chemisorption, DRUV–Vis and FTIR spectroscopies were employed. Unexpectedly, the larger is the Au size, the higher is the activity, whilst no influence on the selectivity to methylfuroate was observed. Lower amounts of carbonate species at the surface of the most active catalyst calcined at 500°C can explain the enhanced activity. A clean surface is directly related to the ceria capability to provide activated oxygen. It has been proposed that reverse oxygen spillover can occur at the perimeter of the Au nanoparticles and that these Au sites could be involved in methanol activation.

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# PHOTOCHEMISTRY AND PHOTOCATALYSIS

# Antioxidant effect of dissolved organic matter on excited triplet- and radical-induced oxidation of aquatic contaminants

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Dissolved organic matter (DOM), a heterogeneous, complex mixture of organic molecules derived from the metabolism and degradation of living organisms, can both enhance and diminish the oxidation of organic contaminants in sunlit natural waters. While in aquatic photochemistry DOM is mostly known for its photosensitizing properties, it can also decrease oxidation rates of organic contaminants, either by light screening, scavenging of the reactive oxidants or interfering in the oxidation pathway of the contaminants. The latter aspect, which was recently investigated in our research group, is presented and discussed in detail in this contribution. The oxidation of target organic contaminants, in particular anilines and, as a subgroup of these, sulfonamide antibiotics, was carried out under stationary irradiation using photo-active precursors of oxidizing species. In the main part of these studies, aromatic ketones were used as precursors of their oxidizing excited triplet states. The triplet-induced oxidation of the aforementioned contaminants was significantly inhibited in the presence of DOM. Several phenolic compounds, known for their antioxidant character, were employed as DOM surrogates, showing a similar inhibition effect as DOM. The results obtained so far indicate that the strength of the inhibition effect of DOM on oxidation is correlated with the phenolic content of DOM and its electron donating capacity. The consequences of this inhibition effect for indirect photochemical transformations of contaminants in natural waters will be discussed. In additional studies, hydrogen peroxide and the persulfate ion were employed as precursors for the hydroxyl and sulfate radical, respectively, acting as the oxidizing species. For the sulfate radical, inhibition of oxidation (measured as the reduction in second-order rate constant in the presence of DOM) was shown to occur for several anilines and sulfonamides, while for the hydroxyl radical no inhibition was detected. Hence, such inhibition effects could be important when planning the treatment of contaminated waters by advanced oxidation technologies.

# Model photosensitizers for the photochemical production of hydroxyl radical from dissolved organic matter

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Understanding of dissolved organic matter (DOM) photochemistry has implications in both natural and engineered systems. DOM attenuates light in this system, causing decreasing direct photochemical degradation of organic contaminants, while for some compound classes, degradation is enhanced by DOM through photosensitized processes. The latter is due to production of reactive intermediates from DOM photolysis, such as singlet oxygen (10<sup>2</sup>), hydroxyl radical (•OH), and triplet excited states (3DOM\*). Mechanisms for the formation of 102 and 3DOM\* are well known, while the formation pathways of •OH are largely unknown. Understanding of DOM photochemistry has implications for water treatment. For example, DOM is believed to form both •OH radical as well as hydroxylating species with a lower oxidation potential. Degradation of organic contaminants is known to occur quickly in the presence of •OH radicals. Therefore, understanding the mechanism and extent to which free •OH radical is formed in these systems would aid in evaluating water treatment design and efficacy. In this work, we measured production of •OH from model sensitizers under a variety of conditions in order to assess the production of free •OH. Furthermore, the temperature dependence of •OH formation from these sensitizers will be presented, which allows comparison of the energetics of activation that will be compared to identical parameters from DOM.

# Experimental approaches and paradigms for shape controlled synthesys of TiO<sub>2</sub> nanoparticles

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Titanium dioxide is one of the most studied metal oxides due to its interesting chemical, surface, electronic and (photo)catalytic properties. These properties provide this material of multisectorial applications, ranging from healthcare, photocatalysis, smart materials with self cleaning and self sterilizing properties and solar energy harvesting (photovoltaics and water photosplitting). However it is difficult to correlate the functional properties of  $TiO_2$ nanomaterials to the properties at single nanoparticle level due to the high polydispersity in shape, size and surface properties of the currently available  $TiO_2$  nanoparticles (NPs) Although intensive experimental and theoretical studies have been conducted on the reactivity of different surfaces of metal oxides such as TiO<sub>2</sub> [1,2] much less attention is paid on the dependence of functional properties, like photocatalytic activity, dye adsorption, open circuit potential and fill factor in dye sensitized solar cells, on crystal facets in different orientations [3]. One of the goal of SETNanoMetro is the development of design rules to tune crystal facets of TiO<sub>2</sub> NPs in order to optimize and control functional properties. By tuning the ratio of different facets, the functional properties would be correspondingly changed. In the present work we have developed a series of design rules in order to obtain sets of anatase TiO<sub>2</sub> NPs with low polydispersity and to tune their shape and their size though hydrothermal processing of Ti(IV)-Triethanolamine complex in presence of different shape controllers (OH-, triethanolamine, fluoride). Through a careful experimental design the influence of many process parameters (pH, temperature, shape controller type and concentration) on the synthesis outcome (size, shape and polydispersity), a predictive soft model was developed. The model is able to predict reasonably well the synthesis outcome allowing to tune the shape factor from 5 (prisms) to 1.5 (bipyramids) to 0.2 (platelets). This allows to control the main crystal facets exposed ranging from (100) to (001).

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# Photodegradation of pharmaceuticals drugs in water by micro-size TiO2 catalysts both in powder form and as coating material

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Nowadays, the scientific community has focused research on "emerging pollutants". The term "emerging pollutants" stands for the substances that are released in the aquatic environment for which currently no regulations are established for their monitoring, furthermore, conventional wastewater treatments are not suitable [1].

In the present study, we focused on the photodegradation of two common analgesic and antipyretic drugs, acetylsalicylic acid and paracetamol, in aqueous medium, by means of titanium dioxide micro-sized catalysts, both dispersed as powders and deposited as coating on porcelain grés tiles. The micro-size form of  $TiO_2$  is an interesting choice in respect to nano-size one, considering its no- potential human health risks [2], and its easily reclaiming at the end of the wastewater treatments. The nano-sized catalyst powder Evonik P25 was taken as reference for comparing the photocatalytic activity of the micro-sized catalysts (Kronos 1077 and Hombitam AN). The experimental setup consists of two different batch reactors and a recirculating reactor, where the polluted solution flows on the surface of the catalytic tile.

The oxidation test of the single pollutants and the mixture of them was monitored by HPLC and TOC analyses; while XPS and FTIR analyses were carry out to study the changing of the catalyst surface. The identification of the intermediates of reaction allows to determine the influence of the substituents and their relative position on the aromatic ring (orto or para substitution) on the oxidation kinetic.

The acetylsalicylic acid degradation path shows that the break-up of aromatic ring leads to a sixmembered aliphatic chain, the muconic acid. Instead, the paracetamol degradation path shows a progressive accumulation of the aromatic specie, hydroquinone. The co-presence of the two pollutant molecules influences their adsorption-desorption step on the catalyst surface and reverses their degradation rates. The conversion results reached by the photocatalytic tiles were encouraging, about 50% for paracetamol and 90% for acetylsalicilyc acid; however, the remarkable by-product accumulation affects the final mineralization degree.

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# Photoactive nanostructured anatase films templated on silicon substrates using organophilic interfaces

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We have reported in various studies the use of the organophilic interface of organoclays in combination with the sol-gel approach as a way to generate in a controlled manner silica and diverse metal oxide nanoparticles that remain attached to the silicate surface.[1] Moreover, the nature of the organic surfactants at the organophilic interface seems to play a relevant role in the growing of such nanoparticles revealing a possible template effect of the organic species.[2] In the present study an alike approach using organophilic interfaces was applied for the controlled growing of mesoporous nanostructured materials on silicon wafer surfaces previously modified with organic surfactant species. Thus, mesoporous TiO<sub>2</sub> has been prepared using an advanced dip-coater apparatus for the deposition onto silicon wafers of a surfactant coating that creates the organophilic interface upon which is deposited a gel that contains preformed oxoclusters of titanium dioxide.[3] The employed equipment allows the preparation as well as the in situ characterization of the  $TiO_2$  coating (thickness and porosity), which can be analysed by means of UV-vis variable angle spectroscopy ellipsometry. Textural properties of the films can be also analysed from water adsorption-desorption isotherms at 25 °C in situ measured working at different humidity values. The study shows that in contrast to the common EISA method [4], in this new two-steps method the process is influenced by the dynamics of reactants at the organophilic interface of the system, affecting the hydrolysis and polycondensation of precursors, which determines the final porosity distribution of the coating which has a significant influence in the photocatalytic behaviour of the formed coatings. This new approach has been successfully applied to the formation of TiO2 coatings on other siliconbased materials, which is relevant as the resulting materials can be of potential interest in applications related to air depollution and stream restoration.

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# Unraveling the fluorescence properties of humic-like substances (HuLiS): the role of phenol oligomers. A computational approach

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Compounds with fluorescence in the humic-like substances (HULIS) region are known to be formed under conditions where the oligomerization of phenolic compounds is operational, because of the formation of phenoxy radicals [1]. However, there was no evidence to date that such fluorescence emission was really due to phenol oligomers. In this work, the fluorescence of phenol and some of its oligomers was studied by computational methods (TD-DFT [2] [3] with the PCM approximation [4]) and it was compared with experimental data, when allowed by the availability of commercial standards. The oligomer fluorescence depends on the contribution of different stable conformers, which differ from one another for the dihedral angles between the aromatic rings. These differences are also observed between the ground states and the corresponding excited singlet states. The predicted wavelengths of fluorescence emission increase with increasing the number of aromatic rings, up to a plateau at around 450 nm. In this work it has been showed which phenol oligomers formed by two, three and four rings are characterized by the presence of different conformers, which gives its own contribution to the absorption and fluorescence spectra of the investigated compounds. In particular, 4PP and 4PPP have three stable conformers each, while 4PPPP has six conformers. The predicted wavelengths of fluorescence emission, which correspond to S1 $\rightarrow$ S0 transitions, increase up to a plateau with increasing the number of aromatic rings. Considering that the transitions producing fluorescence involve at most three aromatic rings, important changes in the emission wavelength are not expected when further increasing the molecular size. The predicted emission wavelength (~450 nm) is in the fluorescence range of HULIS, so the oligomeric compounds might thus account for the HULIS-type fluorescence, which has been observed under conditions where phenol oligomerization was operational due to the formation of phenoxy radicals, which has been observed could form some phenol oligomers [1]. Interestingly, the plateau in the emission wavelengths predicts that a mixture of phenol oligomers could not show fluorescence in a different spectral interval than that experimentally observed: the increasing molecular size would initially shift fluorescence from the phenolic region to the HULIS one, but further increases of the ring number are not expected to produce important modifications in the wavelengths of the emission signal, because the transitions causing fluorescence involve only three consecutive rings [5].

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#### РНОТО - 7

### Photocatalytic hydrogen production on Pt-loaded TiO2 inverse opals

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TiO2 inverse opals present increased photocatalytic production of H2. TiO2 inverse opals with different pore size and TiO2 macroporous structures with disordered arrangement of the pores have been tested in the photocatalytic production of hydrogen in aqueous solution with a formate buffer as hole scavenger. TiO2 inverse opals belong to the family of metamaterials and exhibit unique catalytic properties arising from their peculiar interaction with light. To discriminate the effects of slow photons the hydrogen photoproduction experiments were carried out at two different wavelengths, at 365 nm where the effect of slow photons is maximized, and at 254 nm where it is negligible. The resulting hydrogen production rates suggest a strong effect of the slow light and of the polymer template used in the synthesis of the TiO2 powders. The chemical properties of the polymeric sacrificial template determine the crystalline phase of the sample and as a consequence affect the catalytic performances of the resulting TiO2 structures.

### РНОТО - 8 Formaldehyde abatement by photocatalysis: fast detection by PTR-MS.

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Formaldehyde is the simplest aldehyde and belongs to the family of VOCs (Volatile Organic Compounds), which consistently contribute to the increase of the atmospheric pollution, both outdoor and indoor; formaldehyde in particular is easily found in the indoor environments, being a molecule present in a lot of substances of common use. Recently, the regulations about its dangerousness have been modified:

it has been added to the mutagenicity hazard class and passed from category 2 (suspected carcinogen) to category 1B (carcinogen); therefore, all the obligations about health and safety are now much more stringent [1]. Several analytical techniques have been developed to detect atmospheric formaldehyde despite the potential difficulties of, is following a photocatalytic reaction in a short time interim, the time requested for the analysis, the very low stability of the molecule and the by-products formation as well. Proton transfer reaction mass spectrometry (PTR-MS) is an online technique that allows measurement of VOCs at the sub-ppbv level with good time resolution; recently, it was used to measure concentration of HCHO [2,3] with a lot of advantages including high time resolution and the ability to simultaneously detect a large number of VOCs [4]. The photocatalytic abatement by three TiO<sup>2</sup> commercial samples and some photoactive industrial tiles prepared using a micrometer titania, were tested by means of a PTR-MS instrument. All the formaldehyde photodegradation kinetics have been followed successfully. The results are consistent with the typical features of the different samples of titania, in particular related to their particles dimensions. Formaldehyde, methanol, and formic acid were simultaneously and constinually monitored, as well as the humidity and the temperature inside the reactor. The possibility to use the PTR-MS instrument for studying a photocatalytic process is shown, introducing several new possibilities related to its high sensitivity, the high time resolution and the possibility to monitor several compound simultaneously.

#### РНОТО - 9

## Efficient mineralization of greywater pollutants by photocatalytic ozonation: catalyst and reactor design

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Greywater is less polluted fraction of wastewaters released from households [1]. Even if this wastewater contains surfactants, textile dyes and other contaminants, represents a source of water, which could be reused after appropriate treatment [2]. Photocatalytic properties of titania (TiO<sub>2</sub>) in anatase form can be used for various purposes, including photocatalytic purification and disinfection of wastewater. To avoid post-filtration step, catalyst immobilized on a proper support represents a better choice. A good adhesion of a catalyst on various supports was successfully achieved by immobilization of commercial TiO<sub>2</sub> powders (P25, P90, PC500) with a sol-gel silica-titania binder [3,4].

For the purpose of simulated greywater treatment, special compact reactor was designed and developed, utilizing Al<sub>2</sub>O<sub>3</sub> porous reticulated monolith foams as TiO<sub>2</sub> carriers and UVA-lamps inside the reactor. To increase process efficiency, TiO<sub>2</sub> photocatalysis was coupled with ozonation. The result of the two processes is combined synergistic process, known as photocatalytic ozonation process (PH-OZ), which normally occurs in neutral and acidic pH [5,6]. With degradation of LAS+PBIS and Reactive blue 19 (RB 19) as representatives of surfactants and textile dyes respectively, commonly found in household greywater, and phenol as trace contaminant, an evaluation of PH-OZ and photocatalytic processes in two reactors has been performed. Synergistic effect of PH-OZ was generally much more expressed in mineralization reactions of the three types of pollutants, showing TOC half lives of less than one hour for the mixture of pollutants in compact reactor. PH-OZ process employing efficient photocatalysts is due to its superior cleaning capacity suitable for treating wastewaters also with higher loading of organic pollutants.

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### SOIL, SEDIMENTS AND REMEDIATION

## Distribution and availability of heavy metals in particle size fractions of urban road-deposited sediments and roadside soils

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Road-deposited sediments (RDS) are recognized as one of the main sink of pollutants in urban environments. Their position at the interface between environmental compartments increase their importance, since fine particles can be carried to rivers and roadside soils after runoff and re-suspension or affect human health.

Many studies on RDS and roadside soils have concentrated on total concentrations, but few studies have assessed concentrations and bioavailability of heavy metals in grain size fractions. Therefore, we have assessed the metal availability and bioaccessibility in the fine fractions (in particular, particles less than 10  $\mu$ m), considered to be the most important in relation to human health.

Sediment and soil samples were collected from the outskirts to the city centre, in main and secondary roads. In selected roads we sampled near a roundabout or a traffic light and on the straight. We determined the pseudo-total content of Pb, Zn, Ni, Cu, Cr, Cd, Sb, Mn and Fe in the bulk samples as well as the mass loadings in the selected grain size fractions (10-2.5 and <2.5  $\mu$ m). The enrichment with respect to the local background was then calculated and metal availability and accessibility to the human body was determined with different extractions (Acetic acid, DTPA) and estimated with the Simple Bioaccessibility Extraction Test (SBET).

The results show that some elements concentrate in the finest fractions and may represent a relevant threat to human health and the environment.

### Soil environmental quality in urban areas

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The urban ecosystems have usually a large footprint, importing large quantities of energy and matter and producing large amount of waste. The use of ecological resources is extreme in urban environments. While air and water are regularly monitored, less attention is paid to the soil despite it being the major sink for contaminants. Various studies worldwide show that, with very few exceptions, urban soils are contaminated to the point that they generate a pedogenetic paradox by which urban soils are more similar in different cities than they are with their neighbour soils. The proximity to other environmental compartments, and to humans in particular, exacerbates the contamination concerns. As an example, it is particularly felt in a city that pollutants are transported by soil particles in the air.

Nevertheless the problems with environmental quality of soils in urban area the contrasting interests of the stakeholders has prevented so far a definite approach to the issue. In fact, current phenomena such as soil sealing and urban agriculture seem to have overlooked the role of soil quality.

The European Commission has not been able, so far, to reconcile the issues risen by the various stakeholders so its legislative effort has been minimal. In some countries, however, soil protection has been enforced.

The options for the future include a multi-disciplinary and multi-stakeholder research effort in view of a holistic solution.

## Interaction of biochar with soil organic contaminants: reduction of phytotoxicity

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Among the most dangerous pollutants released by human activities into the environment every year, polycyclic aromatic hydrocarbons and chlorophenols are also listed because they can cause serious effects, such as disease, birth defects and death in humans and animals.

New remediation systems and technologies, always more efficient and less expensive, are used to recover polluted soil. Recently, among various materials, biochar rises particular interest due tohigh porosity and remarkable capacity toadsorb pollutants.

The purpose of this study was to evaluate the ability of biochar, produced from poplar and conifers, in the absorption of a polycyclic aromatic hydrocarbon, phenanthrene (Phe), and a chlorophenol, pentachlorophenol (PCP). The effect onextractable contaminants and phytotoxicitywas evaluated after different remediation times. The coexistence of biochar and organic matter in form of compost was also tested in order to individuate an enhancement of the remediation process.

The remediation process was influenced by contaminant and biochar nature. In fact hydrophobicity influenced the interaction between contaminants and biochar: biochar from conifers, due to higher specific surfaceand porosity, was much more efficient in the adsorption of the contaminants than that from poplar. In addition the amount of biochar added in remediation test affected the treatment efficiency, especially for PCP.

Organic matter, in terms of compost addition, led to reduce the contaminant extractable fraction because of sequestration process in organic and organo-mineral aggregates.

All these factors as well as remediation time was an important factor in favouring the immobilization of contaminants on carbonaceous matrices thus limiting their bioavailability. Even if further investigations need to be carried out to confirm these interesting results, the use of biochar can be considered a valid in situ remediation technique.

# Abandoned boats as a source of metal contamination in coastal sediments

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Abandoned boats are a common site on the foreshores of estuaries and pose hazards to navigation, human health and the local sediment. In this study, fragments of boat paint have been sampled from derelict boats on the intertidal mudflats of two estuaries in eastern England. Samples were analysed for Cu, Pb and Zn by field portable X-ray fluorescence (XRF) spectroscopy. Lead was detected in all cases (430 analyses of 155 fragments) and median concentrations on each boat ranged from about 350 to 35,000 ug g-1, with individual concentrations exceeding 20% in several cases. Zinc was detected in most samples with median concentrations ranging from about 50 to 10,000 ug g-1 and a maximum individual concentration of 24%. Copper was detected in fewest (277) cases and mainly on samples taken from the outer hulls, with median concentrations on each boat ranging from about 50 to 1900 ug g-1 and an individual maximum concentration of 17%. The relatively high abundance and persistence of Pb in the paints resulted in greatest contamination of local sediment by this metal, with concentrations exceeding quality guidelines (of 112 ug g-1) in several instances. Among the metals considered, therefore, Pb is of greatest concern from both environmental and human health perspectives. Contamination arising from peeling paint on abandoned craft is likely to be a general, albeit localised problem, whose significance depends on the size, age, condition and nature of the boat. Recommendations include clear legislation preventing the abandonment of boats and the creation of facilities designed to assist boat owners with the disposal of end-oflife vessels.

### Radioactivity Levels in Surface Sediments of the Tema Harbour (Ghana) and their Radiological Significance

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We assessed activity concentrations of <sup>238</sup>U, <sup>210</sup>Pb, <sup>226</sup>Ra, <sup>232</sup>Th, <sup>228</sup>Ra, <sup>222</sup>Th, <sup>40</sup>K and <sup>137</sup>Cs in Tema Harbour surface sediments and modelled the potential radioactivity concentrations in reference organisms and associated dose rates using the ERICA Assessment Tool. Sediments exhibited a higher potential to accumulate radionuclides than biota except phytoplankton in the case of <sup>210</sup>Pb. Phytoplankton exhibited the greatest potential for bioaccumulation of radionuclides among the reference organisms and therefore could be a bioindicator of radionuclide contamination in the harbour. The measured radioactivity concentrations in the harbour sediments are unlikely to result in significant biological effects in humans and the reference organisms, except phytoplankton.

**Keywords:** Tema Harbour sediments, <sup>238</sup>U series radionuclides; <sup>232</sup>Th series radionuclides, ERICA Assessment Tool, Dose rates.

# Sustainable removal of heavy metals from water channel sediments by cation exchange with calcium ion and related water stability

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Water channel sediments, resulting from dredging activities, behave like a sink for organic and inorganic pollutants coming from neighbouring fields and wastewater treatment plants (WWTPs). Although they are usually characterized by a medium-low level of heavy metal pollution, they cannot be employed for agricultural or construction purposes. To overcome this type of pollution and to avoid transport/disposal costs, many solutions (from harsh acidic/alkaline extraction to mild phytoremediation) have been proposed [1]. In this study, the efficacy of the exchange with calcium ion on the removal of heavy metals from dredged sediments with a medium content of heavy metals was assessed and the water stability of the treated material evaluated for bank shaping.

Water channel sediments collected in the Emilia-Romagna region (Northern Italy) were sampled at different distances from the output of a municipal WWTP built to supply 7000 population equivalent. They were characterized for organic/inorganic pollutants and for the distribution of heavy metals among five granulometric fractions (see figure). The sediment samples were then subjected to cation exchange with 1 N CaCl<sub>2</sub>. The metal speciation, as well as the total and bioavailable metal content, of treated samples were finally assessed and compared to the control.

Preliminary results show that sediments were mainly polluted by Cu and Zn. The exchange with calcium allowed the removal of Cu and Zn up to 30 and 10% of total amount, respectively. These findings were also compared to those obtained on the same sediments treated with 1 N HCl, which can be considered a harsher condition with respect to Ca exchange. Finally, with the aim at employing the treated sediments for bank shaping, their aggregate stability and resistance against water abrasion were assessed by wet sieving and compared to the control.

The obtained results can be considered a first step for the systematic assessment of the sustainability of known technologies for quick and in situ decontamination of sediments in the light of their recycle for agricultural purposes.

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## Adsorption of dissolved organic matter on iron oxide-vermiculite systems

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The reactions at the solid-solution interface affect organic matter (OM) turnover, stabilization and loss on one hand, and the identity, crystal growth rate, and surface properties of mineral phases on the other. Sorption processes are primarily controlled by variable surface charge minerals, mainly Fe and Al (hydr)oxides, which can in turn precipitate onto phyllosilicates. This results in complex systems with different reactivities for OM, which depend on the type and degree of (hydr)oxide-phyllosilicate association. These interactions are particularly dynamic in soils subjected to alternating redox conditions, and may thus play an important but still not well understood role in soil OM turnover. Our aim was to understand mineral surface modifications brought about by different Fe (hydr)oxides-phyllosilicate associations and the implications on OM sorption. Paddy soil-derived OM was used in sorption isotherms on mixed mineral phases obtained by precipitating different amounts of Fe (hydr)oxides on vermiculite. Results evidenced that the surface properties of vermiculite strongly drive Fe (hydr)oxide precipitation and consequently OM adsorption mechanisms on these mixed phases. The change in surface charge with increasing Fe content resulted in a higher retention of OM. Adsorption isotherms of N containing compounds and FT-IR carboxyl vibrational shifts revealed the occurrence of two adsorption mechanisms, one driven by electrostatic attraction of N containing compounds by the negatively charged vermiculite surface, and another involving ligand exchange with the positively charged oxides precipitated in localized nucleation sites. Moreover, selective adsorption of aromatic compounds was an important process for all (hydr)oxide-covered substrates, particularly at high C loadings, as a consequence of OM conformational rearrangements.

## Environmental assessment of the reuse of marine sediments as fine aggregates in cemented mortars

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The management of harbors requires regular dredging, which generates millions of tons of marine sediments, contaminated to varying degrees with trace metals. Despite increasingly regulations and determinations to encourage sustainable management of these wastes, dumping at sea and landfill disposal are still extensively practiced.

Through an experimental approach, based on multidisciplinary investigations [1, 2] and dynamic leaching tests [3], this study was interested to the environmental assessment of a reuse of marine sediments as fine aggregates in cemented mortars.

Results firstly showed sulfides present in studied marine sediments associated to highly concentrated trace metals such as copper, lead and zinc (Couvidat et al. 2015c). Nevertheless a substitution of sand by these treated sediments with 80µm granulometric cutoff greatly improved mechanical behavior [4]. Finally due to the low release of trace metals observed during leaching experiments, the mortars formulated with these contaminated marine sediments can be considered as environmentally safe and this reuse appeared as an interesting approach to couple valorization and contaminated waste management [4].

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## Geochemical characterization of phosphogypsum to evaluate management options

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Phosphogypsum (PG) is the byproduct of the production of phosphoric acid and phosphate fertilizers from phosphoric rocks by acid digestion with sulfuric acid at high temperature. The most widely used process, the dehydrate, generates among 5 tons of PG for every ton of phosphoric acid produced. Even though reclaim of this waste has been widely studied, most of the PG produced worldwide is still stockpiled. As a substitute of natural gypsum, PG has been recycled in building materials in the composition of cement and concrete, to produce plaster and plasterboards or as a road base material. Or it has been used in agriculture as fertilizer, thanks to its high content of S, Ca and P. Nevertheless, the presence of phosphate, fluorine, metals and radioactive elements imposes some limits to its reuse. Knowledge of geochemical characterization and investigation of his evolution in time could contribute to the choice of management strategy and evaluation of reclaim suitability of a stacked PG. This study focused on the geochemical characterization of a gypstack including mineralogical characterization, leaching test and geochemical modeling of four core samples. Mineralogical characterization and total content showed a homogeneous waste, and gypsum was the only phase that could be identified. Beside this mineralogical similarity, residual acidity varies considerably, clearly showing an evolution of the PG with depth. The existence of a trend with depth was confirmed by leaching tests. Leachates of deeper samples showed a higher concentration in major anions (F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and in most of the analyzed cations (Fe, Cr, Cu, Na, Si, Zn). Results pointed out that the solubility did not strictly depend on total content. The pH, and the dissolution/precipitation of minor phases are the causes of the solubility differences with depth. Investigations on elements solubility as a function of pH provided evidences on the effect of neutralization on metals, fluorine and phosphates availability and allowed determining base consumption for the three samples. Results of influence of the pH on the leaching behavior tests, associated with mineralogical characterization and total content analysis were used to formulate hypothesis on phases defining PG leaching behavior. Modeling batch leaching tests corroborated the identification of minor phases controlling solubilization. In conclusion, this approach is a valuable base to evaluate management options.

### WATER TREATMENT AND ITS IMPLICATIONS

## Nutrient Dynamics in marine waters influenced by municipal sewage effluents (Aegean Sea-East Mediterranean Sea)

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Saronikos gulf receives effluents from Athens Metropolitan area (population over 5 million). Until 1994, domestic and industrial sewage of Athens was discharged untreated into the surface water layer of Keratsini and Elefis bay, whereas, after 1994, the sewage of the Athens Metropolitan area were primarily treated in Psittalia Sewage Treatment Plant and discharged in the inner Saronikos Gulf at 63 m depth. The secondary stage of the Psittalia Sewage Plant operated at the end of 2004. In this work we study nitrogen (N) and phosphorus (P) dynamics in the inner Saronikos gulf, as they have changed over the last almost thirty years, in relation to the sewage discharges from the Sewage Treatment Plant of Athens in Psittalia Island. The sewage plume is characterized by relatively high nutrient concentrations (ammonium, phosphate and nitrite). During the warm period (June-October) the sewage plume is trapped bellow the pycnocline at 50-60 m. Significant changes in nutrient dynamics were observed after the operation of the primary sewage treatment plant with higher nutrient concentrations to be recorded in the inner Saronikos gulf. The high amount of the primarily treated effluents that discharged in the inner Saronikos gulf lead to the significant increase of nutrient concentrations in the water of the inner Saronikos gulf. After 2005, when the secondary sewage treatment operated, a general decrease in nutrient concentrations in the inner Saronikos gulf was observed. Moreover, a significant increase of the nitrogen to phosphorus (N:P) ratio was observed after 2005. It is also noteworthy, that high nutrient concentrations and low Dissolved Oxygen values (< 3.00 mL/L) were detected near the bottom of the inner Saronikos Gulf. This was more prominent near the bottom of the stations located southwest and also in a distance from the Psittalia Sewage Plant (~6-14 Km), indicating that the organic matter which is carried by the waste water plume, follows the prevailing circulation and finally decomposes in a distance from the sewage pipe, resulting to the DO decrease. According to our study, it seems that there is a systematic variation pattern of the DO values throughout a year, with a significant increase during February –March, due to the homogenization of the water column and the oxygenation of the deep layers.

## Bio-based substances isolated from green compost: application in wastewater treatment

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The development of processes to valorize the organic fraction of urban waste is a challenge that is increasingly attracting research groups from all over the world. At this purpose, in recent years is becoming of predominant importance the development of the so-called biorefinery. Here different processes for organic waste treatment are integrated in order to obtain, beside energy and bio-fuels, also added-value chemicals to be released on the market for specific applications or to be used as building blocks in further synthetic processes. In such context, from the compost obtained by aerobic treatment of the green fraction of urban wastes, soluble bio-based products (SBO) have been isolated. In previous studies SBO have shown promising performances in the formulation of detergents and textile dyeing baths, as emulsifiers, auxiliaries for soil/water remediation, flocculants, dispersants and binding agents for ceramics manufacture, in the synthesis of nanostructured materials for catalysis and for application in agriculture and animal husbandry. Investigation of the chemical nature of SBO has shown that they bear chemical similarities with humic substances (HS) naturally present in waters and soil. Particularly interesting at this regard is the fact that HS contain light-absorbing species capable of promoting photochemical transformation of organics of anthropogenic origin present in waters. Based on this similarity, in the present research SBO from green compost have been studied as photosensitizers for the degradation under simulated solar light of phenols, azodyes and aromatic sulphonic acids. Experiments have been designed in order to: i) gain further insight into the main reactive species involved in the SBO assisted photodegradation process; ii) optimize the photodegradation process at laboratory scale under simulated solar light; iii) verify the system detoxification. The abatement of all the studied target molecules was achieved and the photoproduction of singlet oxygen and OH radicals was hypothesized. Additional experiments were performed to verify the photostability of SBO themselves. A progressive decrease of both absorbance and fluorescence of SBO was observed upon irradiation; the obtained data suggested an increased SBO hydrophilicity and solubility. The development of SBO for water detoxification can therefore be attempted as a green process, taking organic urban waste as source of material for environmental application.

### Environmental application of ecofriendly photosensitizers: degradation of pollutants by hybrid waste-derived substances

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Over the last few years, urban wastes have become a major source of contamination of soil, water and air, especially when they are not properly disposed of. Recycling and reusing of wastes have therefore become mandatory for the sustainable development of our society. In this context, several papers reported that the recalcitrant lignin-like fraction of fermented urban biowastes is a cost effective source of soluble bio-based substances (SBO). These ones bear chemical similarities with humic substances, showing surfactant behavior behaviour and photosensitizing properties. For example, it has been demonstrated that SBO are quite effective in enhancing photodegradation of water pollutants. Most of the published papers deal with CVT230, a SBO isolated from urban public park trimming and home gardening residues aged, under aerobic conditions, for 230 days [1]. This product has been tested with promising results as homogenous photosensitizer for the degradation of phenolic compounds. [1] In this work, soluble CVT230 was turned into an insoluble form by immobilizing it within a silica support, [2] obtaining organic-inorganic hybrid materials. The aim of this research is to exploit the photoactivity of these new compounds toward wastewaters cleaning, as well as to take advantage of the CVT230 heterogenization in order to recycle the material and perform repeated photodegradation cycles. This ecofriendly perspective offers considerable advantages for the engineering of remediation systems operating in a real environment. The CVT230-Silica hybrid materials were deeply characterized by several techniques and the photosensitizing activity was evaluated using, for example, 4-methylphenol as probe under simulated solar light irradiation with satisfactory results in terms of pollutant degradation, stability and reusability.

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### First principles computational chemistry predictions of equilibrium and kinetic constants for electrophilic reactions in water

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Aqueous electrophilic reactions are broadly important in environmental chemistry, but the thermodynamic equilibrium constants, rate constants, and mechanisms describing these reactions are often difficult to determine by experiment. Here we report on our efforts to establish thermodynamic and kinetic constants of aqueous electrophilic reactions by way of ab initio computational chemistry. To accomplish this, we employ a modular suite of specialized computational techniques. We first estimate reaction free energies (for equilibrium constants) or activation free energies (for rate constants) in the gas phase, employing a combination of high-quality Coupled Cluster computations and Density Functional Theory methods. To account for the influence of aqueous solvent, we conduct additional simulations with implicit solvation models and/or microsolvated clusters of solute and water molecules, with careful attention to the handling of standard states. The resulting model predictions are relatively independent of experimental parameterization and can be applied to a very broad range of reactions, in principle.

We report on comparisons of our computational results with available experimental data for several electrophilic reactions in water. These include: the equilibrium constants describing the reaction of NH<sub>3</sub> with HOCl and HOBr to form NH<sub>2</sub>Cl and NH<sub>2</sub>Br, respectively; the equilibrium constant for the dehydration of HOCl to form Cl<sub>2</sub>O; the kinetic constant of O<sub>3</sub> reaction with bromide to form HOBr; and the kinetic constants for the reaction of HOBr with NH<sub>3</sub> and the reaction of HOBr with dimethylamine.

These preliminary results suggest that the tested prediction approaches have order-ofmagnitude uncertainty for equilibrium constants involving neutral solutes, and 2-3 orders-ofmagnitude uncertainty for rate constants. As we illustrate with selected case studies, this level of accuracy is sufficient to provide useful estimates of thermodynamic and kinetic properties in cases where they have not been successfully elucidated by experiment. For example, our recent computational estimates of thermodynamic properties enabled us to ascertain the relative stabilities of bromamines, chloramines, and bromochloramines during disinfection of drinking and swimming pool water.

## Personal care products removal during chlorination of aqueous solutions; impact of bromide and ammonia

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Personal care products (PCP) are nowadays considered as emerging contaminants in the environment and particularly in water resources. These compounds can be found in a large number of products of daily use such as shampoos, cosmetics etc...and can enter the aquatic environment directly via wash off or indirectly via waste water treatment plants. Recent concerns have been focusing on the toxic effect of PCP on human health and several studies have confirmed their endocrine disrupting ability. An important exposure route of PCP for humans is the aquatic environment as well as swimming pool waters.

Chlorine, a widely used disinfectant in water treatment and swimming pools is found to be very reactive with organic compounds. However when applied in the presence of inorganic moieties, particularly bromide and ammonia, chlorine reacts to form two main oxidants: bromine and chloramines. The aim of this work was to evaluate the impact of bromide and ammonia on the chlorination of two of the most commonly used PCP: benzophenone-3 (BP3) and methylparaben (MP).

At first, the rate constants of chlorine, bromine and monochloramine with BP3 and MP were determined at various pH values. BP3 and MP were found to react rapidly with chlorine and bromine, whereas low reactivity of monochloramine was observed. Moreover, in order to evaluate the impact of the inorganic content of the water on the degradation of BP3 and MP, chlorination experiments with different added concentrations of bromide and/or ammonia were conducted. BP3 and MP degradation is enhanced in the presence of bromide due to the formation of bromine whereas it is inhibited in the presence of ammonia due to chlorine transformation into chloramines. However, in the presence of equal high concentration of bromide and ammonia, the global effect on the elimination is pH dependent. The promoting effect of bromide seems to be more relevant at pH 7 and the inhibitory effect of ammonia is predominant at pH 8.5. A kinetic model was also established in order to predict the elimination profile of BP3 and MP during chlorination in aqueous solutions in the presence of bromide and/or ammonia. Finally, transformation products of BP3 and MP during chlorination of pure and bromide containing waters were identified. During chlorination in the presence of bromide, BP3 and MP removal by bromine is favored. Brominated transformation products known for being more toxic than chlorinated by-products would be formed.

# Advanced oxidation of organic pollutants in water by air non-thermal plasma

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The application of air non-thermal plasma above the water surface is becoming a promising alternative to the more established advanced oxidation processes for water remediation [1]. In these systems a humidified air flow above the water is subjected to an electrical discharge generating air plasma which contains reactive oxygen species, such as ozone and OH radical, capable of oxidizing organic pollutants to CO<sub>2</sub> and H<sub>2</sub>O. In the dielectric barrier discharge reactor developed at the Department of Chemical Sciences of the University of Padova [2,3] complete mineralization of phenol and hydrochlorothiazide, used as model pollutants, has been obtained [4]. The efficiency of the process is highly dependent on the ratio between the concentration of the pollutant and of the reactive species. Indeed, in the case of phenol, the carbon mass balance of the treated solution, performed by HPLC and total carbon analysis of the liquid phase and FT-IR analysis of the gaseous phase, showed that, under given sets of discharge parameters, which determine the concentration of the reactive species, the mineralization yield increases as the pollutant initial concentration decreases [5]. At the same time the fraction of unidentified carbon, attributed to large molecular species formed by radical recombination side reactions, decreases. The mechanism of oxidation of the organic pollutants in our system was investigated by the use of chemical probes, as for example t-butanol, which reacts with OH radical but not with ozone, and by comparison with ozonation, using the same concentration of ozone as formed in the plasma. Moreover, experiments with mixtures of two different pollutants allowed to point out competition of the pollutants for the different reactive species. An overview of the results will be given, focussing on the process efficiency, intermediates, products and byproducts and on the mechanisms occurring in these complex systems.

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### Monitoring priority micropollutants in wastewater and surface water of Prato area (Tuscan, Italy): the 20 year experience of GIDA

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GIDA is a no-profit company that manages the wastewater from the industrial textile district and the city of Prato, as well as the domestic and industrial wastewater from the civil and textile areas of Bisenzio valley (Tuscany, Italy). The wastewater is treated in five wastewater treatment plants (WTPs), namely "Baciacavallo", "Calice", "Vernio", "Vaiano" and "Cantagallo", characterized by different levels of technologies, depending on the quality and quantity of sewages to be treated. Constructed wetland stages have been also implemented at pilot scale for investigating their applicability as polishing treatments.

Starting from 1996, GIDA has paid great attention to the evaluation of the fate of organic micropollutants inside WTPs and to the estimation of the point-source pollution for receiving water bodies, due to WTP effluents. Accordingly, many studies have been coordinated by GIDA, in collaboration with the Department of Chemistry of the University of Florence, and a number of organic micropollutant classes, such as pharmaceuticals, phthalates (PHTs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols ethoxylates (APEOs) and their carboxylic and phenolic metabolites, have been monitored. Inorganic priority pollutants, such as hexavalent chromium, have been also investigated for their removal.

Among the various researches carried out by GIDA, the mass balance of various organic pollutant classes (i.e. PAHs, APEOs and PHT) in the "Baciacavallo" WTP, evidenced the high rate of actual degradation, as well as the great removal efficiency of the ozonation stage for PAHs, PHTs and APEOs. Moreover, the study of the temporal evolution of APEOs evidenced their great reduction since 1996 to date, probably due to the adoption in Italy of Directive 2003/53/EC, that restricted the commercialization and use of these compounds in Europe. However, these analytes are still present at tens to several hundreds ng/L concentration levels in influent wastewater.

### An alternative to the neutralization of alkaline tunnelling waste water using CO<sub>2</sub>(g): characterization of the process and assessment of toxic potential

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Underground structures play a key role in different countries. Such structures are constructed in many civil activities such as development of road and railways, subways, water, gas and sewage lines, underground subways, nuclear wastes land filling, fuel storage and military installations [1]. In many tunnelling processes, the wastewater produced is highly alkaline and can be very toxic to aquatic organisms. A neutralization step is then required to ensure safe discharge into potential sensitive environments. The neutralization step has been traditionally performed with mineral acids such as hydrochloric or sulphuric. These strong acids are potentially dangerous to handle for the operators and pose a risk of accidental over acidification, which may cause massive death of aquatic organisms downstream of the discharge [2]. These drawbacks have made of  $CO_2$  a very attractive alternative as acidification reagent.

In this work we describe a scheme to perform the neutralization step of alkaline water from synthetic solutions (simulating tunnelling produced water) and we assess the effect of temperature on the kinetics of the neutralization process. The know-how gained with these solutions is then transferred to the treatment of water from a real drilling scenario -the Gran tunnel, located in the National road 4 in Norway-. The effect of the huge content of suspended solids of this water in the neutralization process is discussed. In addition to the neutralization kinetics, the accumulation of  $CO_2$  (g) in the solution was also monitored in real-time employing a selective sensor.

The results demonstrate that pH decreased rapidly to 8.0 when  $CO_2$  (g) was added to the drilling alkaline solutions. The rate of pH decrease was significantly slower below pH 7.0. The  $CO_2$  concentration was low (<40 mg/L) at pH values higher than 8.0, but increased rapidly as pH dropped below 8.0. Initially, the pH dropped faster and the  $CO_2$  concentration increased faster at 4 °C than at 15 °C, but there were no clear differences when the experiments ended. According to previous studies and available bibliography, the aqueous  $CO_2$  concentration in tunnelling waste water at pH 8.0 is probably not acutely toxic to fish.

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# Fate of phosphorus in the surface sludge deposit of a vertical flow constructed wetland

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Phosphorus is a critical environmental issue due to the risks of eutrophication associated to its release into surface water and the depletion of natural resources. For domestic wastewater treatment Vertical-flow constructed wetlands (VFCW) have proven their good performances in nitrification and organic matter removal from domestic wastewaters of small communities. However, total nitrogen (TN) removal and phosphorus (P) retention are still a matter of research and development.

A particularity of these VFCW is the formation of a surface deposit usually called sludge by accumulation of the suspended solids at the surface of the 1st stage. The layer's thickness grows at a rate of about 2 cm/year. The sludge thus accumulated is planned to be removed by dredging every 10 to 15 years. Its implication in the performance of the system was poorly known and has to be studied. In addition, phosphorus speciation in this sludge is also a key factor in the availability of phosphorus to crops in the perspective of using the sludge as a soil conditioner in agriculture.

This study concerns the AZOE<sup>®</sup> process patented by SCIRPE company in which the treatment line combines (i) a biological aerobic trickling filter, (ii) ferric chloride (FeCl3) addition for dissolved phosphate removal and (iii) two stages of partially flooded VFCWs. Through an experimental approach conducted at different scales this study was interested to (i) the characterization of the sludge composition using several complementary, with regard on the effect of aging on the evolution of phosphorus speciation in the sludge, (ii) the influence of extreme pH and redox condition on the release of elements from sludge.

Results showed a mineralization of the surface sludge deposit [1]. Phosphorus appears to be mainly retained with mineral part of the sludge with an effect of aging on the speciation [2]. Moreover, this sludge has a relatively high buffering capacity when submitted to extreme conditions of pH and redox [3].

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## Evaluating biosorption for radio-nuclide removal from aqueous wastes

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Decontamination of wastewater from the nuclear industry to meet regulatory requirements presents unique challenges. A specific concern in reactor decommissioning is addressing effluents containing radioactive Strontium (Sr-90), due to its long half-life (29 years) and biotoxicity. Conventional treatments such as chemical precipitation may be ineffective, whilst zeolite composites and selective ion-exchange resins can be expensive or compromised in highly saline effluents [1]. Recently, it has been shown that naturally abundant and waste biomass materials may offer potential to remove radio-nuclides from aqueous waste through 'biosorption' [2]. 'Biosorption' is defined as the passive (or non-metabolic) uptake of substances from solution by non-living biological materials.

In this work, four biosorbents, seaweed (Fucus vesiculosus), waste coffee grinds, crab carapace and spent distillery grain were evaluated for their ability to remove Sr (II) from single metal solutions and simulated nuclear wastewater. Their performance was compared with four commercial adsorbents Clinoptilolite (White and Green<sup>™</sup>) and ion-exchange resins IONSIVE-911<sup>™</sup> and SrTREAT<sup>®</sup>. Batch adsorption and flow through column studies were used to assess the effects of agitation rate, contact time, concentration and pre-treatments on Sr(II) removal efficiency.

Results showed all materials were capable of Sr(II) removal at concentrations of 1-200 mg/L range and also from simulated low-level waste effluents containing 1.5 mg Sr(II)/L. Strontium removal proceeds via a rapid initial uptake to surface sorption sites followed by a slow approach to equilibrium. The order of removal efficiency for biosorbents was seaweed > coffee > spent grain > crab carapace and for commercial materials SrTREAT<sup>®</sup> > IONSIV-911<sup>TM</sup> > Clinoptilolite-Green<sup>TM</sup> > Clinoptilolite-White<sup>TM</sup>. The experimental sorption data correlated well with the Lagergren Pseudo 2nd order knetic and Langmuir adsorption isotherm predictive models. Fucus vesiculosus was deemed unsuitable for column trials due to its swelling properties.

All of biosorbents showed potential; however, in practice the calcium carbonate rich crab carapace was considered most suitable being stable enough for integration into the current treatment processes and for long term storage.

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### **POSTER PRESENTATIONS**

### METHODS FOR ENVIRONMENTAL ANALYSIS

### QuadraSil TA – selective sorbent for the determination of Palladium, the optimization and application in environmental analysis

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QuadraSil TA (registered trademark of Johnson Matthey Finland Oy) is in terms of chemical composition solid sorbent based on modified silicic acid, which is highly selective for the sorption of selected metal ions. There are several modifications QuadraSil sorbent according bonded functional groups. Triethanolamine (TA) is a functional group selectively sorbing ions of metals Au, Cd, Co, Cu, Fe, Pd, Pt, Rh, Ru, V, Zn and Pb. For this reason, the sorbent was selected for determination of palladium in environmental samples. Environmental palladium largely enters due to its catalytic properties when is used in automotive catalysts. Because of the high temperatures of the exhaust flue gases, mechanical abrasion catalytic surface, riding style and the cold start catalytic layer is undermined. Due to the massive and compulsory use of automotive catalysts its level is constantly growing. Palladium and its compounds are becoming part of the exhaust gases and come into airborne dust, road and tunnel dust, deposited along roads in soils and vegetation. In terms of selectivity this sorbent was chosen for solid phase extraction for preconcentration of palladium from environmental samples. As these samples were analyzed lichens placed at the traffic frequented locations in the city of Brno in the Czech Republic. For sampling "dry bag" monitoring technique on lichen Hypogymnia physodes was used. Lichen samples were collected from traffic free areas and placed in traffic-frequented locations for five months. The samples were then leached by agua regia on the wet way, applied optimized preconcentration and separation technique using SPE sorbent QuadraSil TA and palladium subsequently analyzed on ET-AAS spectrometer with Zeeman background correction at line 247.6 nm. During the optimization process the amount of QuadraSil sorbent was tested, which was filled into empty plastic boxes with a volume of 3 ml. After sorption Pd in the presence of 0.1 mol/l HCl, was retained Pd eluted with 0.05 mol/l thiourea. The eluate was collected in a 10 ml volumetric flask and then calculated sorption efficiency after measure of the content of Pd by ET-AAS. It was observed 95% palladium sorption efficiency under these conditions. In samples distributed over the Brno were found average content of Pd in the range of 2-20 ng/g.

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### Surfactants and methods of their determination

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Surfactants have amphiphilic structures consisting of a hydrophilic and a hydrophobic part. This structure causes their characteristic surface-active properties. Surfactants may be classified according to the nature of the hydrophilic part as anionic, nonionic, cationic and amphoteric. Surfactants are produced predominantly synthetically and they are used in industrial and domestics detergents.

Surfactants can be determined by several analytical methods. Spectrophotometry is the method recommended for determination of anion surfactants in form of methylene blue active substances by EPA Method 425.1. The influence of eventual interferents was studied in this work because wide-spread utilization of this method.

Capillary electrophoresis (CE) may be applied for the separation and determination of individual surfactants. This method was used for determination of selected anionic surfactants, namely Sodium Dodecylbenzene Sulphonate, Sodium Octylsulphate and Sodium Dodecylsulphate.

Chromatographic methods are powerful analytical techniques with high separation efficiency and sensitivity. HPLC is used more commonly than GC because of low volatility of surfactants. Method of HPLC with UV detection was optimized for determination of three cationic surfactants (Benzyldimethyldodecylammonium Bromide, Benzyldimethyltetradecylammonium Chloride and Benzyldimethylhexadecylammonium Chloride) and Triton X-100 as a representative of nonionic surfactants. Anionic surfactants with non-aromatic structure – Sodium Alkylsulphates were separated and determined by optimized LC/MS methods.

This paper deals with the results of application of the above mentioned methods for determination of the various surfactants in running water samples.

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# Elemental urine excretion profile during the monitoring of a chelating therapy by ICP-MS: a case study

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In this study we determined the elemental profile in urine during the monitoring of a chelating therapy; the study was focused on a single case of chronic metals intoxication: a patient who presented symptoms apparently not related to each other (pollen and food allergies, weight loss and inability to gain weight, myalgia and arthralgia, thyroid cancer, osteoporosis, basal and stress lactic acid above cut-off values). After having excluded other pathologies, a metals intoxication was suspected and a chelating therapy was attempted [1]. Chelating therapy by CaNa<sub>2</sub>EDTA was administered every two weeks and urine samples were regularly collected along the therapy for 17 months [2]. The samples, after being mineralized with HNO<sub>3</sub> 69%, were analyzed by ICP-MS and the data collected were treated by multivariate statistical methods.

The analysis of the collected urine samples allowed to follow the excretion of metals following the infusion of CaNa2EDTA and thus to assess the dynamics of a prolonged chelation therapy.

Before undergoing the chelating therapy, the patient performed blood tests in search of lead, that excluded acute lead poisoning. The results obtained show that large amounts of different metals are expelled for the whole period of administration of the therapy within the first 12-24h after the infusion, while excretion reaches the basal level 24-36h after the treatment: therefore, it can be demonstrated the importance of the therapy for the elimination of the metal ions deposited in the body, whilst they are not present in the blood.

The overall picture resulting from this researches shows that the chelating therapy is very effective in mobilizing and eliminating the heavy metals present in the body, but raises some issues on the need to further optimize and possibly personalize the administration protocol, given the possibility that a continuous infusion of a lower concentration of the chelating agent could perform better than a single spot high concentration infusion.

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### New extraction approach to determine organic compounds in beachrock samples from temperate latitudes

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Beachrocks are consolidated coastal sedimentary formations resulting mainly from the relative rapid cementation of beach sediments by different calcium carbonate polymorphs. Biomarkers are strongly useful as they can provide information about the organic matter in the source rock, environmental conditions during its deposition and diagenesis as well as the degree of biodegradation and some aspects related to the age. Among different organic biomarkers, polycyclic aromatic hydrocarbons (PAH) and hopanes must be highlighted due to their presence within the cements could confirm the influence of biologically mediated processes in the first stages of cementation.

In order to find these compounds in beachrock units, the present work describes a fast, ecofriendly and very sensitive method (FUSLE-LVI-PTV-GC-MS) that allows the detection of this type of compounds at low concentration levels (ng/g). This method was applied to two grain size fractions of beachrock samples collected in different beaches located close to the estuary of Bilbao (Basque Country, North of Spain). Concretely, the accumulation of biomarkers is mainly expected in the finest fraction (< 75  $\mu$ m) that corresponds to the cements.

The analyses revealed the presence of the 16 EPA priority PAHs that could have a pyrolitic origin according to the calculated isomeric ratios. In addition some other organic biomarkers were also detected, such as 17a(H),21b(H) hopane which is related to hypersaline environments as well as 17a(H),21b(H),28,30-bisnorhopane, 17a(H),21b(H)-norhopane, 22S-17a(H),21b(H)-homohopane, 22S-17a(H),21b(H)-bishomohopane and 22R-17a(H),21b(H)-bishomohopane. These last six compounds are known to be related to microbial activity. The collected data render some important clues to reinforce the importance of the biological processes involved in the formation of beachrocks located at non-expected temperate latitudes.

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### Non-target analysis of e-waste samples from China

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The processing of electronic waste (e-waste) in developing countries has become an environmental problem because of a lack of regulation and the increasing amount of e-waste generated as countries like China and India have increased demand for electronics. Most electronics contain environmental contaminants such as brominated flame retardants, which are a vector for environmental contamination. Though, potentially the most damaging environmental contaminants are produced by the improper processing of these components to form toxicants such as polybrominated dibenzo-p-dioxins and dibenzofurans. This study aimed to chemically characterize new and emerging organic contaminants in environmental matrices surrounding an e-waste site using comprehensive two-dimensional gas chromatography high resolution time-of-flight mass spectrometry (GC×GC-HRT). Chemical extracts were prepared from dust samples and particulate from an e-waste shredder. A 60 m x 0.25  $\mu$ m x 0.25 mm (Rtx-Dioxin2) was used as the primary column, and a 1.3 m x 0.25  $\mu$ m x 0.25 mm (Rxi-17SilMS) was used as the secondary column. The primary oven program was 80 °C (1.5 min hold), 3.5 °C/min to 320 °C (15 min hold) for a total run time of 85 min, with a He gas flow of 2.0 mL/min. The secondary oven was run with a +5 °C offset from the primary oven, and the modulator was run +15 °C relative to the secondary oven with a 3 sec modulation period. Comprehensive twodimensional gas chromatography combined with high resolution time-of-flight mass spectrometry provides unsurpassed analyte resolving power by leveraging four degrees of orthogonality. Peaks were separated in two orthogonal chromatographic dimensions and then deconvolved mass spectrometrically, with accurate mass as the fourth dimension. Peak True (Deconvoluted) Spectra were searched against commercially available library databases such as NIST 14 and Wiley 10 for tentative identification. Hits with a similarly greater then 800 (out of 1000) and a mass accuracy less than 1.5 ppm were considered to be correct in the absence of an authentic standard. Accurate mass was used to determine chemical formula for peaks with a library hit less than 800, and the mass spectrum was used to elucidate a structure where possible. Many legacy contaminants such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons and chlorinated pesticides were identified, in addition to several other classes of chemical contaminants. This presentation will focus on the identification of new and emerging contaminants in e-waste related samples.

## Exploring the complexity of yeast metabolome using enhanced chromatographic and mass spectral resolution

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Unprecedented methodology combining GCxGC for enhanced chromatographic resolution with high resolution time-of-flight mass spectrometry for rapid and conclusive compound characterization.

Yeast has been used since ancient times for the production of bread and wine. In modern times, yeast is used as a "cellular factory" to manufacture bioethanol and organic acids. Yeast metabolism must be clearly understood to facilitate its bioengineering and improve yields of these valuable products. Gas chromatography - time of flight mass spectrometry, a "Gold Standard" for metabolomic studies, has been successfully implemented for the study of blood, plasma, urine, and plant materials. The next generation instrument for metabolomic exploration combines the power of GCxGC with high resolution time-of-flight mass spectrometry (GCxGC-HRT). The GCxGC-HRT greatly exceeds LC-based chromatographic capabilities and was successfully utilized for identification of acids, diacids, amino acids, sugars, nucleosides, nucleotides phosphorylated metabolites and in veast. Yeast powder was spiked with twenty three D and 13C labeled standards. It was extracted with 1:1 methanol/chloroform and filtered into 2mL vials. Sample components were derivatized using a two-step procedure: 1) Treatment with methoxylamine hydrochloride and 2) MSTFA. They were analyzed using a combination of EI and CI, GCxGC-HRT. Compounds were separated using an Rxi-5MS column in the first dimension and Rxi-17MS in the 2nd dimension and detected with the HRT operating at a resolution of 25,000 (m/z =219). System performance was monitored using internal standards (e.g., octafluoronaphthalene and fatty acid methyl esters). Confident characterization of metabolites was facilitated through spectral deconvolution, database searches combined with accurate mass formula generation. The study resulted in the confident identification of hundreds of compounds in yeast. Compound characterization was facilitated through effective peak deconvolution of data which was critical for identification of coeluting labeled and native components. This was clearly evident from the ability of software to separate and provide deconvoluted spectra for coeluting D5, 13C11 and native tryptophan (3TMS). Native compounds were matched to spectra in large, well-established databases (NIST, Wiley, etc.) and accurate mass molecular, adduct and fragment ions were leveraged to confirm the identity of metabolites through formula determination. For example, the average mass accuracy and spectral similarity values for a representative set of derivatized amino acids (Glycine, serine, methionine, 5-oxo-proline, aspartic acid, ornithine, phenylalanine, glutamic acid, asparagine, lysine, tyrosine and tryptophan) were 0.72 ppm and 916/1000 respectively. This enhanced chromatographic and mass spectral resolution was particularly useful for the identification of unknowns where characterization via retention indices and database searches were inconclusive.

**ATMOSPHERIC SCIENCES** 

#### P-ATMO - 1

### Compositional characterization of brake pads by ICP-AES analysis: initial components and particulate matter emitted into the atmosphere.

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The study of the chemical composition of particulate matter (PM) is essential because of its known correlation with the onset of respiratory and cardiovascular diseases in humans. In particular, the influence of the vehicular traffic on the metal content present in the PM is known. In the last decades several laws have been enacted in order to decrease the contribution of the emissions from the exhaust fumes of motor vehicles to the content of heavy metals in the PM. However, non-exhaust emissions, originated from brake, tyre and road wear, are unaffected by such measures in Europe and may become the dominant PM source in the near future. In this context, representatives of U.S. environmental agencies (EPA and ECOS) and motor vehicle industry associations recently signed a Memorandum of Understanding (MOU) with the purpose to reduce copper, asbestiform fibers, cadmium, chromium (VI), lead, mercury and their compounds in motor vehicle brake pad friction materials. Since the ingredients of the brake pad formulations may contain different heavy metals (major components or trace levels), they potentially can contribute significantly to the toxicity of PM. It is necessary to take into account the fact that the motor vehicle brake parts are not homogeneous in chemical composition, but strongly depend on the different applications and different industries that produce them. This high variability results in a not simple identification of appropriate chemical markers useful for investigate the PM. In addition, the friction materials used for the production of brake pads are constituted by various types of substances (abrasives, friction modifiers, fillers, reinforcements and binder materials). The compositional characterization of brake pads is a goal not so simple to achieve. In particular, the determination of the metal content in the raw materials and mixes in question may be made by ICP-AES analysis. This technique provides the use of liquid samples, and the biggest obstacle is to extract the analytes of interest by this type of materials. For this purpose, procedures of microwave acid digestion are applied, which must be optimized for both the individual raw materials and the final mixes. In this study the dependence of the result of the acid digestion by parameters such as temperatures, times and acid mixtures for the mineralization is evaluated, using technical data sheet of raw materials and formulations of brake pads friction material.

#### P-ATMO - 2

## Assessment of source contribution of PAHs in ambient air in the city of Novi Sad, Serbia, using multivariate statistical methods

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City of Novi Sad is one of the most important economic centers in Serbia with developed oil, food and chemical industries. In addition, production of cement occurs at a distance of about 20 km from the city center. Within the city territory, there are also seven heating plants, all using natural gas, as a fuel. In order to assess the source contribution of particle-bound polycyclic aromatic hydrocarbons (PAHs) in Novi Sad, data on PAHs in ambient air have been analysed using multivariate statistical methods. While PAHs are emitted both from natural and anthropogenic sources, within urban and industrial localities, they are almost entirely anthropogenic in origin. Two sampling campaigns, during non-heating and heating seasons, have been carried-out at three sampling sites in Novi Sad. The first site was located near an industrial area, with a refinery, power plant and heavy-traffic road in the vicinity. The second site was nearby the heavy traffic area, especially busy during the rush hour. The third site was situated in a residential district. Non-heating sampling campaign lasted from June 26th to July 9th 2008, while sampling of ambient air during the heating season was conducted from January 22nd to February 4th 2009. Air samples were collected using a high volume air sampler TCR Tecora H0649010/ECHO HiVol with quartz fiber filters. 16 US EPA polycyclic aromatic hydrocarbons were determined in all samples using a gas chromatographer Shimadzu GC-2014 with a flame ionization detector. The total average concentrations of PAHs detected in the heating season was one order of magnitude higher in comparison with non-heating period. Two multivariate statistical methods, Positive Matrix Factorization (PMF) and cluster analysis, have been used to assess dominant emission sources of atmospheric PAHs. Results obtained by the PMF method have showed that traffic (exhaust gases of vehicles powered with diesel and gasoline) is the dominant source of PAH emissions during both periods examined in the present study. In addition to traffic, at a lower percentage, stationary sources, primarily industrial processes, have been detected as sources of PAHs. Results of cluster analysis have confirmed the assumption that traffic is the dominant source of emission of particulate fractions of PAHs during the summer and winter periods. Besides traffic, PAHs emission from domestic furnaces which use coal and wood as an energy source during the heating season, was also observed.
#### P-ATMO - 3

### Chemical fractionation of Cd, Pb and Cu in antartic aerosol

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A three-step sequential extraction and analysis by Square Wave Anodic Stripping Voltammetry (SWASV) was applied to determine the water-soluble (soluble), dilute-HCl-extractable (extractable) and inert fractions of Cd, Pb and Cu in Antarctic aerosol (PM10) collected during summer in the vicinity of the "M. Zucchelli" Italian Station (Victoria Land) [1,2]. The aerosol mass determinations were carried out gravimetrically, by differential weighing of filters using an analytical microbalance in a climatic room at controlled temperature and humidity [3,4]. Metal mass fractions varied as follows (min-max, in µg/g): Cd 1.4-38, Pb 26-83, Cu 149-840. In terms of atmospheric concentrations, the values were (pg/m<sup>3</sup>): Cd 0.93-39, Pb 17-60, Cu 88-482. The extractable fraction predominates in the first part of the season for Cd and Pb, with maxima at mid-December (Cd 8.8 μg/g, 5.2 pg/m<sup>3</sup>, 96%; Pb 81 μg/g, 48 pg/m<sup>3</sup>, 98%), and at mid-summer for Cu (peak at mid-January of 421  $\mu$ g/g, 218 pg/m<sup>3</sup>, 56%). The soluble fraction tends to predominate late in the season, with maxima at mid-end of January for Cd (3.3  $\mu$ g/g, 1.7 pg/m<sup>3</sup>, 59%) and Pb (16.8  $\mu$ g/g, 9.2 pg/m<sup>3</sup>, 55%), and in February for Cu (280  $\mu$ g/g, 184 pg/m<sup>3</sup>, 43%). The inert fraction fluctuates considerably during the summer, with similar behavior for Pb and Cu, showing maxima at the beginning of December (Pb 37  $\mu$ g/g, 21 pg/m<sup>3</sup>, 61%; Cu 267  $\mu$ g/g, 154 pg/m<sup>3</sup>, 32%) and in February (Pb 23 μg/g, 15 pg/m<sup>3</sup>, 64%; Cu 216 μg/g, 142 pg/m<sup>3</sup>, 33%), while Cd content shows a different trend, it peaks in the middle of the season, with a maximum of 32  $\mu$ g/g, 32 pg/m<sup>3</sup>, (84%) at the end of December. Insights in interpretation of chemical fractionation in terms of major sources was obtained by Principal Component Analysis (PCA). PC1 expresses the contrast between anthropic and marine contributions; PC2 interprets the crustal contribution; the temporal evolution is well shown in the plane of PC3 vs. PC1.

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#### P-ATMO - 4

## Role of bacteria in atmospheric chemistry: biodegradation rates of compounds present in cloud water

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Clouds are multiphasic system in which dissolved organic matter is subjected to multiple chemical transformations. Until recently, degradation of major organic compounds present in cloud water such as formate, acetate or succinate, was supposed to be only-performed by photochemical processes and especially by the activity of •OH radical. It has been recently shown that metabolically active microorganisms are present within cloud water and are able to use these carbon sources. Microorganisms also interact with reactive oxygenated species within cloud water, and especially with hydrogen peroxide.

The aim of this project was to determine biodegradation rates to implement an atmospheric chemistry model (M2C2) developed in the "Physics Meteorology Laboratory" located in Clermont-Ferrand.

In order to study the contribution of microbes in cloud water in comparison to radical chemistry, artificial cloud solutions (marine), containing the substrate studied (formate or acetate) at various concentrations, were incubated with microorganisms at 17°C and at 5°C. The purpose of these experiments was to determine the kinetic parameters of the Michaelis-Menten model, parameters obtained via a linearization of the experimental data. The biodegradation rates of acetate and formate were determined and values obtained are approximately 10-18 mol s-1 cell-1. No significant effect of temperature was highlighted for these two compounds. These rates were then compared with those obtained by radical chemistry process with values from the literature and from modelling. It appears that the rates are in the same order of magnitude and that the microbial contribution prevails at night.

Regarding the case of hydrogen peroxide, previous studies carried out with natural cloud samples revealed that the biodegradation rate is about the same order of magnitude as the photochemical process. Biodegradation experiments for hydrogen peroxide are currently under assessment in our laboratory. The phenomenon has been observed at both 5°C and at 17°C, without actually delivering accurate values.

Results show that microorganisms have the ability to change the carbon budget in the aqueous phase of cloud and also to interact with oxidant species through their anti oxidative stress metabolism, and could revolutionize atmospheric chemistry.

#### P-ATMO - 5

## Particles size trend and chemical speciation of PM2.5 in bakery indoor air

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In the laboratory of a bakery, indoor air monitoring has been performed using a Silent sequential sampler and an OPC Monitor (Fai Instruments s.r.l., Italy) from 7th to 19th April 2013. In the bakery, two ovens are powered by gas and wood, respectively. By Silent sampler, PM2.5 indoor samples have been collected every six hours, with following hourly sampling ranges: First: 03:00 – 09:00; Second: 09:00 – 13:30; Third: 14:00 – 21:00; Fourth 21:00 – 03:00). In total 40 PM2.5 samples were collected. For each daily sampling four PM2.5 samples have been collected. On each sample OC (Organic Carbon), EC (Elemental Carbon), LG (Levoglucosan) Cl<sup>-</sup> (Cloride), NO<sub>2</sub><sup>-</sup> (Nitrite), NO<sub>3</sub><sup>-</sup> (Nitrate), SO<sub>4</sub><sup>2-</sup> (Sulphate), C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (Ossalate), Na<sup>+</sup> (Sodium), NH<sub>4</sub><sup>+</sup> (Ammonium), K<sup>+</sup> (Potassium), Mg<sup>2+</sup> (Magnesium) e Ca<sup>2+</sup> (Calcium) and the following PAHs: BaA(228), Bb,kF (252), BaP (252), BgP (276), Ip (276), DbA (278) were determined [1].

The aim of the paper has been the investigation of size trends of the aerosol particles during the bakery working activities and the indoor PM2.5 chemical speciation in the same time.

The finer particles monitored by OPC (particle sizes ranging between 0.28 and 0.50  $\mu$ m) have shown a bigger concentration during the first hourly sampling range, in particular during the time in which the ovens were switched on. By OPC data mean ratio PM2.5/PM10, PM10 mass density and peak values (numerical and volume distributions) of fine and coarse modes have been obtained. The bigger mean concentrations of OC (36.01  $\mu$ g/m3), EC (1.08  $\mu$ g/m3) e Levoglucosan (0.76  $\mu$ g/m3) have been obtained during the first hourly sampling range. The mean PAHs concentrations per sampling hourly range have shown in the first and last sampling range higher values than the other two hourly ranges.

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## CHARACTERIZATION OF NATURAL AND AFFECTED ENVIRONMENTS

## Spectroscopic characterization of Technofossils encrusted on the cemented matrix of beachrocks

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Beachrocks are considered coastal sedimentary formations resulting from the early intergranular calcium carbonate cement precipitation in the intertidal zone. The studied beachrocks, in particular, are part of the geological record of the Industrial Revolution in the Nerbioi-Ibaizabal estuary. Furthermore, they also constitute a remarkable example of the geological epoch called the Anthropocene, which would enclose the current period of geological history characterised by the radical transformation of planetary ecosystems as a result of human activity [1]. Nowadays, some authors define such materials as technofossils, the preservable material remains of the technosphere driven by human purpose defining a new kind of stratigraphy termed technostratigraphy [2].

Recently, the beachrocks object of study have been considered to illustrate the inclusion of technofossils in the coastal sedimentary system [3]. Indeed, it is remarkable the wide variety and quantity of slag, authigenic sedimentary conglomerates, reworked wastes from iron mining and metallurgical activities, as well as other anthropogenic artefacts like firebricks or refractory materials and glassy vestiges. The erratic materials include also slag from diverse Basque, Scottish and Brittish industrial enterprises dating back to 1920, evidenced by the stamps of brands, acronyms, numbers and logos commonly seen.

In order to identify the composition of the mentioned compounds, Raman spectroscopy and SEM/EDX analyses were performed. As a result, compounds like anatase ( $TiO_2$ ), crocoites (PbCrO<sub>4</sub>), linarite (PbCuSO<sub>4</sub>), bonattite (CuSO<sub>4</sub>•3H<sub>2</sub>O), cristobalite (SiO<sub>2</sub>), tephroite (Mn<sub>2</sub>SiO<sub>4</sub>) and wollastonite (CaSiO<sub>3</sub>) were identified. That information was complemented with the elemental distribution of the materials, confirming the presence of the main elemental constituents. Thus, through this study, an analytical method for the compositional characterization of technofossils has been succesfully accomplished.

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### Cobalt in bark of holm oak (Quercus ilex L.) in urban environments

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Cobalt is found in small amounts in most rocks, soil, water and living organisms. It is present in vitamin B12, thus it is essential to humans, but an increased exposure (e.g. dietary supplements, medical devices and occupation) may represent a serious health threat [1]. For this reason, cobalt acute toxicity and treatment of poisoning have been extensively studied; however, little is known about long term exposure to low levels and scarce data about Co levels in urban areas are available.

As biomonitor for metals, tree bark has been widely used [2], because it accumulates many atmospheric contaminants, providing large amounts of material for the analyses at low cost. Among the tree species, holm oak, Quercus ilex L. (Fagaceae), being widely distributed in the Mediterranean areas and present also in urban and industrial environments, is a suitable bioindicator, able to cover a period of exposition of years. These characteristics are very interesting, because, even if it is not possible to trace back the concentrations measured today to a well-defined time of exposure in the past, they surely reflect the contamination to which the population in the studied area has been exposed during part of its life-time.

Holm oak bark samples were collected in a reference site (on the hill behind the small town of Rapallo, 30 km east of Genova) characterized by sparse human activities, and in two areas of Genova, representing two different urban environments. The first (eastern part) is a residential area with vehicular traffic, while the other (western part) is a mixed industrial-residential area, with very intense port activities (oil and container terminals), transport infrastructures (airport, railway, roads, highways), small and medium-sized industries and a coal power plant; an important steel smelter was dismantled 10 years ago.

The Co concentration in the bark samples was measured using atomic emission spectrometry with inductively coupled plasma source (ICP-OES).

In both urban environments the Co concentrations are significantly higher (2 to 4 times) than in the reference site; western area shows Co levels which are 2 times higher than those in eastern area. Our data allow to map Co deposition in the studied area, identifying the sources of pollution.

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### Metal concentrations in regions with different environmental impact

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Metals in the environment can be of natural or anthropogenic origin. Anthropogenic sources of pollution can be different: industry, traffic, urban development, intense agriculture, etc. One of the results of these processes is increasing metal concentrations in soil, water, air and other elements of the environment [1]. In our previous work honeybees (Apis mellifera) were used to determine metal concertations in the environment. We have concluded that they serve as a good bioindicator that can detect trace element present in the environment and are capable to significantly distinguish concentrations of metals in different foraging regions [2].

The aim of this study was to compare metal concentrations between two regions characterized by different environmental impacts. The studied metals were Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Ni, Pb, Sr and Zn. The first sampling region is around city of Pančevo, which is characterized with heavy industry, mainly petrochemical. The second sampling region is near city of Vršac which has no industrial facilities, but is surrounded with land used for agriculture. Mineralization of the samples was done using microwave digestion and quantitative analysis was done using ICP-OES.

Values of metal concentrations at sampling stations in the region burdened by heavy industry were compared to the values from sampling stations that are not burdened by industrial pollution. The data shows that each region has specific pollution associated to anthropogenic activities that take place in it.

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## "Jonico-Salentino" project: next generation risk assessment on the Apulia area including the provinces of Taranto, Brindisi and Lecce

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The large number of industrial activities in Taranto and Brindisi, high levels of air pollutants near plants, as well as epidemiological data showing excesses of mortality and high incidence of diseases in these areas, have led to a higher subjective perception of risk in local communities. ARPA, AReS and ASL of Taranto, Brindisi and Lecce developed a research project to meet that need. The project aims to identify the risk profiles of the citizens in three areas as function of their "actual" exposure to all pollution sources (industrial sources, biomass combustion, road traffic, naval and airport, and natural sources). In detail, the air quality in three provinces will be evaluated basing on real data from the air quality monitoring stations and on estimates of release to land from diffusion models. The assessment of the toxicity of particulate matter will be performed using both in vivo assay, based on the determination of angiogenesis induced on chorioallantoic membranes (CAM) of chick embryo in ovo, and in vitro assay, using human epithelial cell lines and fibroblasts exposed at air-liquid interface to atmospheric airflows. Moreover, a deepening on maternal and child health will be performed by monitoring indoor and outdoor air quality, lifestyle and exposure of children of school age. This study will integrate the CCM project coordinated by the ISS in Taranto and MAPEC-LIFE project in Lecce. Using new generation instruments it will possible to monitor the main air pollutants in real time, identify emission sources and assess events of short term and/or wind-selective. Specific survey will provide information about activities and eating habits of the children involved in the study. The assessment of the exposure levels to air pollutants will be performed through the study of cellular, biochemical and molecular alterations in tissues, cells and biological fluids of children. Moreover, concentrations of metals with neurotoxic properties and of persistent organic pollutants will be monitored in the blood and urine, while nitric oxide will be measured in exhaled air. The high number of information obtained will allow performing an accurate assessment of the risk of exposure both for children and for exposed people. Health risk (carcinogenic and non-carcinogenic) assessment will be evaluated considering a lapse of attention (1x10<sup>-5</sup> - 1x10<sup>-4</sup>) and a threshold of acceptability (1x10<sup>-4</sup>).

## Risk evaluation for the presence of glyfosate and its metabolite AMPA in the main waterways of northwestern Lombardy region (Italy).

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The National Report on pesticides over the years 2011-2012, published by I.S.P.R.A. (Institute for the Protection and Environmental Research) on 2014, recognized Glyphosate (a common herbycide), and its metabolite AMPA (aminomethylphosphonic acid), as water pollutants of emerging concern [1]. The present work aims to investigate the risks associated to the presence of these derivatives in the main waterways of the northwestern district of Lombardia Region (Italy). The concentrations of pollutants were measured in different sampling points placed along the monitored water streams. The data were analyzed following the method developed by Van Straalen and Denneman [2] based on the determination of the Species Sensitivity Distribution (SSD). This approach allowed to determine the Risk Factor (RF) values for Glyphosate and AMPA. Interestingly, in all the investigated water streams, RF values lower than 1 were obtained. Therefore, according to guidelines established by European Committee [3], it is possible to exclude any risk caused by this herbicide for the aquatic ecosystem of the northwestern district of Lombardia Region.

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### "Cleaning" the environment – the occurrence of cosmetic ingredients in the Danube surface water

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Personal care products (PCPs) include a large group of organic compounds such as disinfectants, fragrances, insect repellants, preservatives and UV filters. The widespread use of soaps, lotions, toothpaste and sunscreen is followed by the continuous release of large quantities of PCPs into the aquatic environment. In developed countries PCPs have received increasing attention as emerging chemicals of concern, due to their possible adverse impact on human health and environment. Therefore, a screening analysis of the Danube surface water in the area of Novi Sad, Serbia is needed to gain insight of PCPs contamination for both research and regulatory needs.

The surface water samples were collected at eight representative locations along the Danube during winter, spring and summer under comparable meteorological conditions. After the liquid-liquid extraction of samples with the mixture of methanol and dichloromethane (1:5), the extracts were analyzed using gas chromatography coupled with mass spectrometry detection. The most frequently detected compound in the analyzed surface water samples was methyl dihydrojasmonate that is widely used in fragrances. Isopropyl myristate occurred in almost all samples collected during the winter. This popular cosmetic ingredient is used as an additive in wide range of PCPs such as shampoos, antiperspirants, various creams and lotions. Ethylene brassylate, a member of the synthetic fragrances in the musk family, was detected in few samples. Although as a food additive, 2-phenylphenol is no longer permitted in the European Union, this disinfectant was identified during the screening analysis. Nowadays, it could be found in low concentrations in some household products. Among other preservatives, butylated hydroxytoluene and benzyl benzoate were identified in water samples.

The obtained results confirmed the surface water pollution by PCPs and underline the indispensable need for the wastewater treatment plant in Novi Sad, where municipal wastewaters are directly discharged, without any treatment, into the Danube. Having in mind that most of PCPs are bioactive and persistent, the potential ecological and health risks associated with the concentration levels of PCPs in the aquatic environment deserve more attention.

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## Environmental assessment of heavy metals around the largest coal fired power plant in Serbia

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Anthropogenic activities can lead to increased levels of heavy metals in the soil environment and reduced environmental quality. In this study were analyzed heavy metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) concentrations measured by Shimadzu 7000AA atomic absorption spectrometer in soil samples collected in the vicinity of the largest coal fired power plant in Serbia. The soil pollution status was assessed and heavy metal enrichment at some sampling sites was revealed. Enrichment factors for the investigated metals ranged from 0.3 to 15.5, but mean values indicated deficient to minimal enrichment in the investigated area. The highest contamination factor was determined for Ni, followed by Zn, Co and Cd. Cluster analysis identified associations between heavy metals and soil properties. Significant positive correlations were found between: (1) Cd and Mn, Ni, Pb, Zn; (2) Cr and Cu, Fe, Ni, Pb; (3) Zn and Cu, Ni, Pb; and (4) Fe and V. Spatial distribution maps of heavy metal contents based on geostatistical analysis indicated similar patterns of spatial distribution for Co, Fe and V as well as for Cd, Mn, Ni and Pb. Hot spots for Co, Cr, Cu and Zn occurred between two blocks of the coal fired power plant. The distribution pattern indicated that the highest metal concentrations corresponded with the predominant wind directions. From the results obtained it can be concluded that operation of the coal fired power plant had no significant negative impact on the surrounding environment with regard to contamination by the investigated heavy metals.

# Artificial neural network modeling of the groundwater quality (case study: Zahrez basin in Algeria)

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The Zahrez basin is one of the endorheic basins of the vast steppes region in the central northern part of Algeria. The Zahrez hydrological basin covers approximately 8,989 km2. The catchment lies between longitudes 2° 15' to 4° 08'E and latitudes 34° 35' to 35° 30'N. Artificial neural networks (ANNs) model are widely used in water resources applications to predict and forecast water resources' variables. The objective of this study is to investigate the abilities of an artificial neural networks' model to predict the total dissolved solid (TDS) and electrical conductivity (EC). Water quality variables such as pH, calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>),sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) were used as the input data to obtain the output of the neural network(TDS and EC). Performance of the ANN model was evaluated using correlation coefficient (R), Nash-Sutcliffe coefficient of efficiency (NASH), root mean square error (RMS), Normalised Root Mean Square Error (NRMSE) and Mean absolute error (MAE) computed from the measured and model computed values of the dependent variables.

The results of this study reveals that the ANN- MLP (9, 9, 1) model gives the best estimates for the TDS prediction. The results of neural network modeling to predict electrical conductivity (EC) indicate that the ANN- MLP (9, 12, 1) model showed better predictive ability in the determination of EC. The identified ANN model can be used as tools for the computation of groundwater quality parameters in Zahrez basin.

# An evaluation system of surface water quality in Algeria (Application on the western Algerian catchements)

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Easily accessible surface waters remain very fragile and very vulnerable to various types of pollution. Chellif, Macta and Tafna Basins are considered as the main water resources feeding the North West of Algeria however, protection and conservation of theses water resources become the major concern of Algerian government. The evaluation of the quality of waters and the follow-up of the impacts of the anthropological activities on the natural environment is based on the measure of physic-chemical parameters of the surface water and sediments. It is often based on an estimation of the quality with regard to the grid quality according to the uses of the water: drinkable waters, industrial waters, agricultural waters. This conception is the basis of all the systems of water evaluation agencies worldwide. The principle of the evaluation of the quality of waters is a comparison of the chemical analysis to the borders of grid established and distributed in five quality class; this grid does not contain all the physic-chemical parameters, only parameters able to describe water pollution and degradation of the water quality. In this work we have proceeded to an application of this system to all the surface waters on the west of Algeria, physic-chemical analysis realized by the National Agency of the Hydraulic Resources (NAHR) are used for this study for a period of 3 years (2012-2014) and several points chosen on the catchments of Macta, Cheliff and Tafna are taken into account. This tool is going to supply the administrators of the water an easy simple information and especially precise the state of the quality of waters for a better resource management and control of the pollution. In this communication, we will expose the theoretical model, the experimental results, and the validation of this model by the experimental results. We will also try to see the applicability of this model for the other regions of Algeria, and why not over North Africa.

Keywords. Water quality, Physic-chemical parameters, uses of water, quality grid.

### Monitoring and Management of Sulfide induced Acidity in Northern Ostrobothnia

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There are two common types of sulfide rich soils in Finland: sulfide-bearing marine sediments emerged from the former Baltic Sea due to postglacial isostatic land uplift, and coastal and inland black schist areas. When excavated or drained, the oxidation of sulfides produces extremely acidic soils with increased acidity and metal loads flushing to the recipient streams. Results from 2 projects; SuHE focused on peat extraction fields underlain by sulfide soils, with e.g. aims to develop new methods for prediction and rapid detection of acidic discharge and passive treatment methods for acidic runoff neutralization and MaHaKala that focused on surveillance of occasional acid pulses in river Kalajoki region, are presented. Both projects were mainly funded by European Regional Development Fund. In SuHE the runoff from 7 peat extraction areas was monitored continuously for pH, EC and groundwater level in 2012-2013. Water samples were also collected and field meters used bi-weekly during frost-free periods. Various neutralization tests (in pilot scale and full scale) were performed on 2 peat extraction areas during summer periods 2013 and 2014. In MaHaKala project the surveillance was conducted in 15 places (2013) by water sampling to assess the spatial variation in water quality and in 7 (3 in 2013, 4 in 2014) places by continuous pH monitoring and water sampling (e.g. alkalinity and sulfate) to assess the temporal variation. Sulfate concentrations in peat extraction runoff varied substantially (0.6-2400 mg/L). pH varied between 3 and 6.5. The groundwater level in peat extraction areas can be used for predicting acidic pulses. After the ground water level had dropped below a certain site specific point an acidic pulse would appear during the next rain event. In Kalajoki area sulfate amounts varied (1-120 mg/L) indicating that sulfide bearing sediments are present but no decrease in pH values was observed. The alkalinity of the waters observed was on excellent level which was considered a main reason for the stability of the pH. The tipping bucket system was found to be the most effective method for neutralization. Neutralization occurred from pH 3-4 up to pH 10-11. The steel slag drain also increased the pH about 0.5-2 units from an initial pH of 3-6, but with limestone drain problems occurred. In well tests neutralization occurred i.e. the pH increased 1-2 or 7-8 units from an initial pH of 3-4 depending on the material used.

## Bioaccumulation and depuration processes of polyclorobiphenils in bivalve molluscs

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Polychlorinated biphenyls (PCBs) levels were evaluated in bivalve molluscs Mytilus galloprovincialis by means of bioaccumulation experiments conducted in a "Contaminated Site of National Interest" located in the Mar Piccolo of Taranto (Ionian Sea, Southern Italy). Contaminated sediments of the Mar Piccolo of Taranto have an important role in the diffusion of these pollutants to marine organisms. Because of the risk posed to man via farmed mussels caught in the area, extended remediation program are necessary to safeguard marine ecosystem human health and, not less important, farmed activity, in the Taranto area.

Field experiments were conducted with a periodic re-suspension forced processes of sediments conducted over the time (45 days).

The sediments were characterized by pelitic fraction >70%, low redox potential (< 300 mV, anoxic sediment) and high levels PCBs as reported by previous study. [1]

Mussels, purchased from Apulian aquaculture farm located in a clean site on the coast, were put into net cages suspended at 9 m depth and 3 m away from the bottom in the contaminated selected site. Every fifteen days a pool of mussels were sampled for laboratory analysis. For depuration experiment, wild mussels, sampled in the study area, were transferred into a clean site (Mar Grande of Taranto, Ionian Sea) and keep for a 45 days.

The results showed the increase of PCB concentrations over time. After 45-days PCBs target congeners (PCBs 28, 52, 101, 138, 153 and 180) increased from 1.8 to 98.5 ng g-1 w.w. showing high bioaccumulation capacity.

When mussels were transferred in clean water, target PCBs levels showed at the end of the experiment a significant decreasing respect to the initial concentrations (from 155.7 to 74.5 ng g-1 w.w.).

Results of this research has allowed us to verified PCBs mobilization from sediments and the kinetic of bioaccumulation/depuration in mussels.

Results are useful to design mussels depuration plants in order to safeguard the product and human health.

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### Linear and Macrocyclic Musk Compounds in Waste Water

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Synthetic musk compounds are artificial organic compounds with a smell similar to that of a natural musk. The most recently used and also the least studied group of synthetic musks represents linear and macrocyclic musk compounds. Due to their widespread applications they enter aquatic ecosystem, where they could show negative effects owing their persistence. There has been a big focus on studying of these compounds, their properties and fate in different environmental compartments in the last years.

The first part of this study was focused on the analysis of twelve linear musk compounds (linalool, 2-cyclohexylethanol, fresco menthe, citronellol, HSA, isobornyl acetate, arocet, aroflorone, allyl cyclohexyl propionate, lilial, isoamyl salicylate and hexylcinnamic aldehyde) in waste waters. The samples were taken at inflow and outflow of three different waste water treatment plants (WWTP) in South Moravian region (WWTP Brno-Modřice, WWTP Luhačovice and WWTP Hodonín). These WWTPs use similar technology but differ in size (equivalent number of inhabitants).

The second part of this study deals with five macrocyclic musk compounds (habanolide, exaltolide, ambrettolide, musk MC4 and ethylene brassylate). These compounds were analysed in waste water samples from influent and effluent of three water treatment plants (WWTP Brno-Modřice, WWTP Lednice and WWTP Mikulov).

In both cases, Solid Phase Microextraction (SPME) was used for the extraction of analytes. Gas chromatography–mass spectrometry (GC/MS) was then employed for identification and quantification of target compounds. Finally, the removal efficiency of cleaning process in all WWTPs was assessed.

At the inflow of WWTP Brno-Modřice three macrocyclic musk compounds were identified, i.e. habanolide, exaltolide and ethylen brasylate, at levels of units or tens of ng/L. From the group of linear musks linalool and citronellol were detected at similar concetrations, whilst levels of cyclohexylethanol, fresco menthe, isobornyl acetate, arocet, aroflorone were one or two order lower. Concentrations at outflow were mostly below LODs. At WWTP Mikulov and Lednice only habanolide was found at levels higher than LOD. Removal efficiency for macrocyclic musks was found to be within the range of 76 – 88 % and for linear musks from 69 to 96 %.

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# Quantitative measurement of 17 β-estradiol and Ethinyl estradiol in some Central-European rivers

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An LC-MS method for the determination of  $\beta$ -estradiol (E2) and ethinyl estradiol (EE2), which are estrogen type steroid hormones, has been developed. We validated and used it for measuring these analytes in july and august 2015 from freshwater. Samples were collected in 5 Central European rivers (Danube, Sava, Mur, Drava and Zala). They were extracted on solid phase and derivatised using dansyl-chloride. Separation of the derivates was performed on a Kinetex XB-C18 column with a mobile phase of 0.01%(v/v) formic acid in water (A) and 0.01% (v/v) formic acid in acetonitrile (B) in gradient composition. Detection was achieved with a benchtop orbitrap mass spectrometer using targeted MS/MS analysis for quantification.The used transitions were 506.24-171.10 by E2 and 530.24-171.10 by EE2. We found E2 in most of our samples. EE2 was less abundant, but it was also present in some of the samples. A relative high amount of EE2 was found in river Zala, in the catchment area of Lake Balaton (Hungary).

#### P-CHAR\_ENV - 14 Surfactants in waste and surface water

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Surfactants are surface-active agents lowering the surface tension between liquid and solid or between two liquids. They could be used in detergents (surfactants or mixture of surfactants with cleaning properties in dilute solutions), as wetting agents, emulsifiers, foaming agents and dispersants. From the chemical point of view surfactants could be categorized into three basic classes: anionic, cationic and non-ionic.

Due to their widespread use in households and in industry these compounds represent risk for the environment. After application they are transported via waste water to WWTP, where could cause problems in technology (excessive foaming) and due to incomplete removal in treatment process they can enter surface water and cause negative effects on aquatic biota.

This study was focused on the occurrence of 5 frequently used anionic surfactants (sodium butanesulphonate, sodium hexanesulphonate, sodium decanesulphonate, sodium octylsulphate, sodium dodecylsulphate) and one non-ionic surfactant (Triton X-100) at inflow and outflow of 3 waste water treatment plants (Brno-Modřice, 630 000 EI; Hodonín, 90 000 EI; Břeclav, 55 000 EI) and from surface water in Litava River and Tvaroženský Stream. Liquid chromatography with mass spectrometric detection and electrospray ionization was used for determination of target compounds.

The highest levels in waste water at inflow of all three WWTP were found for sodium butansulfonate and for sodium dekansulfate (in tens of ng/L). Presence of the first mentioned compound was also proved in both surface waters.

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FOOD AND AGRICULTURE

## Non target approach for the identification of degradation products of herbicides used in rice cultivation

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Nowadays pesticides of recent formulation are designed to offer higher selectivity and lower persistence in the environment than the formulations used in the past. However a lower persistence in the environment does not necessarily correspond to a lower toxicity since the pesticides undergo natural degradation reactions in the environment and new species potentially more toxic can be formed [1-4]. In this study some of the most important herbicides used in Italy in rice cultivation (imazamox, oxadiazon and profoxydim) were undergone to degradation studies simulating natural environmental conditions. To this aim: a) aqueous solutions of the species were exposed to simulated sun light irradiation in a solarbox; b) hydrolysis processes were studied preserving the solutions at dark. At prefixed times, the solutions were analyzed by using a micro liquid chromatography system interfaced to a quadrupole-time of flight (QTOF) high-resolution mass spectrometer. LC-MS/MS analyses of the samples undergone to sunlight irradiation showed a decreased intensity of the herbicide signals. Instead, no hydrolysis effect was evidenced in samples stored at the dark for two months. Moreover, solutions prepared in ultrapure water showed different degradation rates with respect to those prepared in paddy water. The LC-MS/MS analyses were carried out by using a non-target approach without any a priori knowledge of the possible species formed during the degradation process of the herbicides. All the MS/MS spectra were recorded without prefixed criteria with the help of the SWATHTM (Sequential Window Acquisition of all THeoretical Mass Spectra) acquisition method, and were used to elucidate the chemical structures of the predominant degradation products.

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### Cleanup of fatty food matrices prior to chromatographic analysis using zirconia-based SPE sorbents

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Analysis of compounds in fatty food samples continues to be an obstacle for food chemists. Lipid interferences can produce elevated detection limits, contaminate LC and GC systems, and ultimately decrease instrument and column lifetime. Because traditional solid phase extraction (SPE) cleanup techniques often provide insufficient fatty matrix removal for analysis, a new approach using zirconia-based sorbents has been developed for selective lipid removal.

Novel zirconia-based sorbents employ Lewis acid/base interactions as well as hydrophobic interactions to selectively retain unwanted lipid interferences. In SPE and/or dispersive SPE (QuEChERS) formats, these sorbents may be combined with traditional phases such as C18 and/or Florisil, to further enhance fatty compound removal. Recently, these innovative sorbents have been shown to remove more fatty matrix interferences than traditional cleanup sorbents, including PSA/C18 and silica. A comparison of zirconia-based sorbents to traditional cleanup sorbents for fat removal in meat and oil matrices will be illustrated. Background removal, analyte recovery, and reproducibility of the different cleanup techniques will be compared herein.

### HPLC–DAD determination of insecticide thiacloprid residues in paprika grown in greenhouse

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The behavior of the neonicotinoid insecticide thiacloprid was investigated in greenhouse production of paprika fruits. Thiacloprid was applied at a concentration of 0.2 l/ha, recommended by the manufacturer for aphid control. Degradation of thiacloprid in paprika samples was evaluated in the period from the moment of insecticide application to the stipulated pre-harvest interval (PHI) of seven days. Samples were collected at eight intervals – immediately after thiacloprid application, 2, 3, 4, 5, 6, 7 and 10 days after pesticide application. The analytical method applied for determination of residues was developed to provide a rapid, accurate and efficient method for the determination of thiacloprid residues in paprika. Dissipation rate was studied utilizing liquid chromatography with diode array detection and Agilent Zorbax SB C18 column (250 mm × 4.6 mm, 1.8 µm). Mobile phase used was acetonitrile/1.5% CH3COOH (30/70) with flow rate 1.0 ml/min, column temperature 25 °C and detection wavelength at 225 nm, while the extraction and clean-up procedure was performed using QuEChERS-based method. The method was validated in accordance with SANCO/12571/2013 document. To evaluate the accuracy and the precision of the analytical procedure, paprika samples were fortified at 0.1, 1.0 and 2.0 mg/kg. The obtained mean recovery value was 83.69%, with relative standard deviation (RSD) of 5.05%. Intraday precision, expressed as RSD, was 3.21%. In the concentration range of  $1.0-20.0 \ \mu g/ml$ , thiacloprid showed linear calibration with correlation coefficients (R2) of 0.999%, while the limit of quantification of the method was 0.01 mg/kg. With the aim to check impact of paprika matrix on determination of thiacloprid by described method, matrix effect was calculated and it was 96.03%. The results of the field trial showed that in the first two days after the application, thiacloprid dissipated rapidly from 1.136 mg/kg to 0.321 mg/kg, with a loss of 72%. Throughout the experimental period, thiacloprid residue in the paprika fruits basically remained at a stable low level, and in the terminal residue experiment, no higher residue than 0.198 mg/kg was detected, which was below MRL of 1.0 mg/kg. The half-life of thiacloprid in paprika fruits obtained in this study was 4.95 days. Finally, the PHI for thiacloprid, which has been established by Serbian authorities, is proved to be safe enough for application of this insecticide in greenhouse production of paprika.

## Inorganic content in hazelnut: an important marker for quality and authentication

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Thanks to the diffusion of the concept of "healthy foods", we have assisted to a growing interest toward nuts fruit. The present work take part to a wide project based on comprehensive untargeted studies focused to obtain a chemical food fingerprint of hazelnuts and their semiand finished products, with particular interest on those compositional characteristics whose significance are mainly related to nutritional properties, botanical and geographical origin, technological impact and sensory quality. In addition, the advantages deriving from new markers profiling will be especially evaluated in view of the possible implementation of rapid methods and screening procedures for routine sample authentication and quality assessment. Markers with a relevant informative content (in terms of differentiation and qualification) will be adopted as Analytical Decision Makers. Hazelnuts contain abundant amounts of biologically active compounds such as antioxidants, fiber components, and several nutrients: carbohydrates, fats, minerals and vitamins. In this study, we focused our attention on the inorganic elements. The concentration and the distribution of these nutrients in vegetal foods depend on a number of variables, such as climate, soil characteristics, transportation, storage, transformation and it can be used for geographical assessment. A complete inorganic profile has been obtained from two set of experiments: 1. The shell of hazelnuts, from two different cultivars monitored during growth, were analysed to evaluate the guali-guantitative distribution of the essential micronutrients as a consequence of the soil/plant interaction. The nutrients content could be naturally unaffected by exogenous surface contamination originating from airborne aerosols and soil dusts. 2. The nutrients distributions during the whole product life (from raw nuts to food-end products) were evaluated and their dependence on the species, origin, post harvest treatments and storage processes was investigated. We have quantified the presence of diagnostic inorganic elements even at trace levels using Inductively Coupled Plasma Optical Emission Spectroscopy. Multivariate chemometric analysis applied on the analytical results highlighted similarities or dissimilarities among samples and correlations among the different considered nutrients, soil, origin and processing.

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## Simple methodology for determination of mycotoxins in rice collected from Serbia: occurrence and risk assessment

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Mycotoxins are harmful substances produced by fungi in several commodities with a widespread presence in foodstuffs. Human exposure to mycotoxins occurs mainly by contaminated food. Nowadays the interest and consumption of cereals is increasing due to their nutritional properties. The quantitation of mycotoxins in cereal and cereal-based food, highly consumed by different age population, is of concern. Thus, a sensitive, simple and rapid method for determination of eleven mycotoxins in rice (aflatoxins B1, aflatoxin B2, aflatoxin G1, aflatoxin G2, zearalenone, deoxynivalenol, T-2, HT-2, ochratoxin A, fumonisin B1 and fumonisin B2) has been developed and validated by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). Simple sample preparation technique with only one-step of extraction (acetonitrile/water/acetic acid-79:20:1, v/v/v) was chosen to be used in order to allow fast analysis of selected mycotoxins. Matrix-matched calibration curves were used and limits of quantification were below the maximum content established by EU regulation in rice or other cereals. The obtained recoveries of the developed method were satisfactory between 96%-126% with relative standard deviation lower than 12%. The applicability of the method was successfully demonstrated on real samples of rice collected randomly from different supermarkets within Novi Sad in the capitol of the Vojvodina Province, Serbia. In addition, mycotoxin intakes through consumption of rice will be estimated for adults and children based on Serbian market basket and then compared with the tolerable daily intake (TDI) proposed by relevant authorities. This is the first report to study the presence of several mycotoxins in rice from the Serbia, estimate the intake of mycotoxins and evaluate the risk assessment.

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### Determination of 8 polyphenols and pantothenic acid in extra-virgin olive oil samples by a fast, high-throughput and sensitive UHPLC-MS/MS method

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Extra virgin olive oil (EVOO) is obtained from the first cold pressing of the fruits of olive trees only through a mechanical process. Its importance has grown in years because of its relevance in the Mediterranean diet, due to its medical, nutritional and cosmetic benefits. Those advantages are mainly due to its minor components, polyphenols, also used as an index to evaluate the quality of the EVOO. This work deals with the identification and quantification of 8 polyphenols (hydroxytyrosol, catechin, epicatechin, epigallocatechin gallate, oleuropein, quercetin, rutin, tyrosol) and panthotenic acid through a new ultra-high performance liquid chromatography coupled with tandem mass spectrometry method. To be suitable for the analysis, the samples are extracted through a liquid-liquid method using ethanol/water 70/30 and hexane in order to remove the fatty component. The method was validated considering LOD and LOQ, linearity range, intra- and inter-day precision, recovery and matrix effect [1]. The developed UHPLC-MS/MS method is characterized by a high sensitivity due to the correct combination of the stationary phase and mobile phase. Moreover, the required time for the entire analysis is only ten minutes, taking into account the column equilibration time. The separation of the nine analytes is satisfactory and further advantages are provided by the complete absence of the matrix effect and by the good recoveries, all greater than 73.7%. Those tasks make the method attractive for routine analysis.

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## Extraction and Analysis of Essential Oils from Mentha spicata and Rosmarinus officinalis

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Due to the carcinogenic potential of synthetic antioxidants, extraction and purification of natural organic compounds are being studied as an alternative [1]. Mentha spicata (spearmint) and Rosmarinus officinalis (rosemary) are widespread in Portugal. For instance, spearmint essential oil (EO) is among the ten most traded EOs in the world, finding a variety of applications such as in pharmaceuticals, cosmetics, food processing and chemicals [2]. Rosemary EO has been traditionally used to relieve muscular pain and spasm and improve memory. Furthermore, its antioxidant activity is considered to be of high interest for the cosmetic industry [3]. Phytochemical compounds potentialities are numerous and one way to explore its valuable properties their by extraction from plants [4].

In this work, fresh and dry leaves of spearmint and rosmary were extracted by simultaneous distillation-extraction (SDE) employing chloroform or n-pentane. GC-FID was used to assess high-value volatile compounds in the extracts. Chloroform showed a slightly better extraction capacity, although at cost of a higher variability. Comparing fresh and dry leaves, no significant differences in extract compositions were noticeable. In spearmint, main identified compounds were pulegone, (S)-(-)- $\alpha$ -terpineol and 1,8-cineol, while Rosmary showed high concentrations of 1,8-cineole, borneol, bornyl acetate and (S)-(-)- $\alpha$ -terpineol. Antimicrobial activity of the extracts was evaluated by disc diffusion method. Extracts showed antibacterial activity against the B. cereus, although no activity against P. fluorescens was verified.

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## Assessing the impact of storage temperature on the stability and biocidal activity of essential oils formulated. Case tribolium castaneum (Herbst)

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Cereals like other stored food currently experiencing serious health problems during storage. The offending agents are primary pests such as Sitophilus oryzae and secondary pests among other Tribolium.Sp. This study focused on the evaluation of the biocidal effect of the essential oils of thyme and made the citrus, against adults of red flour beetle (Tribolium castaneum) under different temperature regimes.The results of this study showed that different molecules have made a late effect (12h-14h-16h-18h) on the populations of Tribolium castaneum at the storage temperature of 20°C. The same results show an early striking effect of thymol and carvacrol on individuals Tribolium castaneum compared to limonene. The toxicity of thymol and carvacrol are much more active than limonene at 12h and exercise a very remarkable as limonene expresses its toxicity that from 14h deadly effect. At temperatures under 20 °C and 25 °C, thymol showed a greater degree of efficiency followed by carvacrol and limonene which has a low. However at 28 °C, carvacrol expresses a very significant biocidal effect compared to the other two formulations thymol and limonene.

Keywords. Thymus fontanesii, bio-efficacy, formulation, temperature, Tribolium castaneum.

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## Determination of organochlorine pesticides adsorbed on plastic pellets

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In the past years, several studies have revealed the presence of organic contaminants at concentrations from sub ng g-1 to mg g-1 on/in plastic pellets found in coastal environment worldwide [1,2,3]. Plastic pellets are actually industrial raw material, typically in the shape of small granules with a diameter of a few mm. They are categorized as microplastics (< 5 mm). They can be unintentionally lost in the environment during manufacturing and transport. They can subsequently reach the marine and coastal compartments. Due to their environmental persistence, they are widely distributed in the oceans and on beaches [1]. Organic pollutants associated to pellets are either additives (e.g. PBDEs) that are incorporated into plastics during production processes or hydrophobic chemicals (e.g. PCBs, organochlorine pesticides) which adsorb from the surrounding environment (e.g. seawater). Among these chemicals, some are recognized as POPs (Persistent Organic Pollutants) because of their persistence, bioaccumulation and potential adverse environmental and health effects. Thus, in order to better assess the impact of plastic pellets in coastal environment, it is necessary to determine the level of associated organic pollutants.

The present study was carried out in the frame of DeFishGear project, which focuses on marine litter and microplastics issues in Adriatic region. This investigation aimed at developing an experimental protocol allowing the quantification of 11 organochlorine pesticides. Plastic pellets, sampled on beaches located in the Adriatic region, were first sorted by colour. Pesticides were extracted from the plastic matrix (c.a. 0.5 g) in a pressurized fluid extractor (50°C, 100 bar). Prior to evaporation, the extract was cleaned on Florisil sorbent through solid-phase extraction (SPE). The concentrated extracts were quantified on gas chromatography equipped with a micro electron capture detector (GC- $\mu$ ECD). Preliminary results revealed the presence of DDT transformation products.

Acknowledgements. The DeFishGear project (http://www.defishgear.net/) is co-funded by the European Union, Instrument for Pre-Accession Assistance (IPA) Reference.

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GEOLOGY

#### P-GEOLOGY - 1

## Biogeochemical investigation of NSO fraction in lignites from the Smederevsko Pomoravlje field, Kostolac Basin (Serbia)

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In order to clarify precursor compounds and source of organic matter, polar fraction which contains nitrogen, sulphur, and oxygen compounds (NSO fraction) was analysed in ten lignite samples from eight boreholes of the Smederevsko Pomoravlje field (Kostolac Basin, Serbia). Contents of fatty acids (FAs) and neutral lipids (NL) ranged from 0.4-4.8 mg and 0.2-1.3 mg, respectively. All analyzed samples are richer in the extent of FAs than NL class. In samples from depth interval 35-50 m a noticeable sharp rise in concentration of both classes of compounds is observed. On the other hand, the shallowest and the deepest samples have approximately the same amounts of both groups of compounds, regardless to the fact that they originate from different coal seams (I and III). The most obvious feature is predominance of compounds with even chain-lengths in both fractions, n-alkanoic acids and n-alkanols, which originated from vascular plants. It is interesting that this difference becomes less obvious with depth (from 19.8 m towards 112.2 m). FAs present in examined lignite samples have a range  $C_6$ - $C_{30}$ . Enrichment in long-chain compounds ( $C_{12}$ - $C_{28}$ ) is observable, with hexadecanoic acid ( $C_{16}$ ) as the highest peak. This type of distribution of FAs with the prevalence of even over odd-carbon number FAs is inherited directly from FAs present in cuticular waxes of terrestrial vascular plants being the main biological source of investigated lignites [1]. The fatty alcohols range is  $C_{12}$ - $C_{28}$  with the predominance of long-chain fatty alcohols (C22-C28) indicating terrestrial plant waxes as their source. Distribution of steroidal alcohols is dominated by  $C_{29}$  homologues,  $\beta$ -sitosterol and stigmastanol. Cholesterol, C27 steroidal alcohol is also found in minor quantity and it is usually ascribed to terrestrial vascular plants. The distribution of FAs and alcohols indicates that the main precursor compounds are originated from higher vascular plants which were the dominant source of organic matter, particularly gymnosperms. This conclusion is in accordance with the results of analysis of saturated fractions of our samples, which characterized by notable domination of diterpenoids with  $16\alpha(H)$ -phyllocladane, indicator of the gymnosperm families, Taxodiaceae, Podocarpaceae, Cupressaceae, Araucariaceae and Phyllocladaceae, as the main compound.

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### Assesment of possible perylene precursors in the organic matter of Upper Miocene lignite from the Kovin deposit, Serbia

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Kovin deposit is divided in two exploration fields "A" and "B" with three coal seams ranging in depth from 24.25 to 116.5 m. The aim of this study was to examine possible natural precursors of perylene in 24 samples from the "B" field. The concentration of perylene ranges between 0.01 to 55.55  $\mu$ g/gTOC (average, 12.10  $\mu$ g/gTOC). It has been discussed that the natural precursors of pervlene could be structurally related to pervlene guinones and their derivatives, which are kinds of black pigments widely present in modern plants, fungi, as well as crinoids [1]. On the basis of the structural similarity of perylenequinones and perylene, several authors have suspected a fungal origin of perylene. The correlation between perylene and funginite contents in investigated lignites is only barely positive (r = 0.22; p = 0.30), which could imply that only minor amounts of perylene are derived from fungi. In case of our samples, reducing environment, that is required for the preservation of guinone structures is confirmed both, by Pristane/Phytane ratio (averaging at 1.43) and by Gelification Index values (averaging at 3.46). Therefore, perylene is considered a paleo-environmental marker for syn- and post-depositional anoxia [2]. Concerning that biomarker distributions clearly indicate that organic matter of investigated lignite is predominantly of terrestrial origin, we presumed that there would be some correlation between terrestrial sources and perylene. Since odd long chain n-alkanes (C27- $C_{31}$ ) are mainly derived from leaf waxes of higher plants we used  $C_{29}$  n-alkane as a representative of odd long chain n-alkanes originated from forest, to avoid possible influence of grasses and herbs on the abundance of  $C_{31}$  n-alkane [3]. The perylene vs.  $C_{29}$  n-alkane correlation is fairly positive (r = 0.67; p = 0.00), indicating certain coherence between perylene and forest leaf waxes. Perylene concentrations as a function of depth are structured and vary between the coal seams. It might reflect fluctuations in input of a precursor and/or changes in depositional conditions.

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## GREEN CHEMISTRY AND SUSTAINABLE USE OF RESOURCES

## Inorganic constituents in biochars from woody biomass gasification and pyrolysis

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Woody biomass is gaining attention as a potential source of alternative energy to increase energy independence on fossil fuels and reduce environmental pollution. The use of biomass does not increase carbon dioxide and does not contribute to the risk of global climate change.

Biomass can be converted into more valuable energy carriers (biooil and syngas) via thermochemical conversion technologies (pyrolysis and gasification). During these processes, a solid residue (biochar) is formed. This carbonaceous residue can find different uses, e.g. as soil amendment in agriculture. Therefore, elemental analysis of this byproduct is important in consideration of its potential uses.

Biomass is characterized by a variable composition and in particular its inorganic constituents deserve special attention. They will find in the biochar or will be partly entrained by the gas stream causing problems in the plant operation or to the environment.

The aim of this work is to identify the fraction of elements that remains in the biochar and of that one which follows the syngas stream in relation to the initial contents in the biomass after pyrolysis and gasification.

To this end, the concentration of major and minor elements was determined on char from a pyro-gasification industrial plant fueled with wood pellets. Furthermore, the same determinations were made on biochar samples of six kinds of biomass (beech, chestnut, pine, spruce, poplar and pellets) produced by laboratory pyrolysis using a tube furnace at different conditions (temperature, residence time and presence/absence of oxygen).

The analyses of the biomasses and biochars were made by ICP-OES (AI, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si and Zn), CVAAS (Hg) and HGAAS (As).

Preliminary results showed that the amount of produced biochar is approximately a quarter of the initial biomass, although this ratio is in relation with the temperature. Thus, the considered element concentrations in the biochar will be about four times higher. Nevertheless, the concentrations of the metals harmful to the environment (Hg, Pb ...) already were low in the biomass. The contents of Ca, K, Mg, P and S vary appreciably between the considered biomasses.

### Catalytic oxidation of D-glucose over supported noble metal catalysts

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Catalytic oxidation of saccharides performed with air under mild condition is taking interest because it is more environmental friendly than stoichiometric oxidation with mineral oxidizing agents. With this approach, it is possible to obtain fine chemicals and intermediates for further transformations in cheaper and cleaner processes. The present investigation focused on the formation of gluconic acid and D-saccharic acid as products of glucose oxidation; gluconic acid presents wide applications in both food and pharmaceutical industry [1], while D-saccharic acid has used as key intermediate in the formation of adipic acid [2]. Platinum was selected as the active phase for the supported catalyst while several types of support were investigated for the conversion of glucose. Platinum on silica, zirconia, alumina, titania and carbon were prepared with wet impregnation method in order to obtain maximum an amount of metal equal to 5 wt%; their surface areas and total pore volumes were determinates with a Tristar II (Micrometrics Instrument Corporation).

Catalytic wet air oxidation of glucose water solution (1 wt%, Sigma-Aldrich) was tested in a 300 ml batch stirred reactor (Berghof, BR300) at 353 K. The temperature was selected as described in published works, while the effect of time of reaction, air pressure and frequency of rotation were investigated [3]. In all cases were established a metallic charge of 1 mol%.

Liquid products were characterized by high performance liquid chromatography (Shimadzu Corporation) equipped with a Rezex ROA H<sup>+</sup> organic acid column; organic acids were quantified with a Photodiode Array Detector.

The best operative conditions were 5 hs, an air pressure of 5 bar and 400 rpm; the highest conversion of glucose was obtained with Pt on carbon and it was equal to 61,3%. Nevertheless, better selectivities toward the desired compound were achieved using metal-oxides supporting platinum; silica and alumina showed the highest selectivities to gluconic acid and D-saccaric acid respectively (41,3% and 22,3%). Titania and zirconia exhibited similar selectivities to the desired compounds of Pt/C with the advantage of a lower degree of poisoning; less poisoning also occurred to the other metal-oxide based catalysts tested.

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### Energy storage from renewable sources: a green solution to energy supply problems in remote areas

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In off-grid areas the most popular solution for electricity production is still the use of diesel generators, this electricity production option is not only environmentally unfriendly, but also expensive to run. [1]

The use of renewable energy in such areas would be ideal; however, the intermittent production by renewable sources makes it necessary to store this energy in order to use it when the source does not produce it. Stand-alone photovoltaic (PV) and fuel cell (FC) systems can play a strategic role in this case especially with the use of hydrogen, which can be considered an eco-friendly fuel when extracted from water using the electricity obtained from renewable energy sources [2]. On the other hand, stand-alone PV and battery systems are already widely used [3].

These main alternatives have been considered in this study. The two power systems, designed for off-grid applications, were sized on the basis of load curves created starting from possible appliances in use of a family house, and the photovoltaic energy production in the area of Turin, Italy. They have to provide 3 kW maximum power, with an average daily consumption of 10.25 kWh in winter, 8.96 kWh in spring and autumn and 8.62 kWh in summer. The two systems were compared from a technical and economical point of view and a preliminary Life Cycle Assessment analysis (LCA) was performed, in order to give an idea of the environmental impact of the systems.

Being the fuel cell and the electrolyzer niche products from a commercial point of view, their costs are higher with respect to Li-ion batteries, therefore, power system based on the hydrogen technology results to be more expensive. From the environmental point of view however the preliminary LCA results show that electrolyzer and fuel cell have lower impacts than other components of the systems, for example the solar panels. Moreover, battery packs have a high environmental impact on the integrated system if compared to the other components, like the solar panels.

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# Investigation of some properties of olive mill wastewater in olive oil industry: characterization and economic usability

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Many Mediterranean countries have a strong market place in the world with huge amounts of olive oil production. As a result of the olive oil production in these countries; such as Italy, Spain, Greece and Turkey, olive mill wastewaters (OMW) are produced and represent a serious environmental problem. OMW have an organic matter matrix with a wide spectrum of organics, solid matter, oil and grease, acidic pH. This high polluting and phytotoxic organic load, which resists biological degradation, causes harmful effects on the flora and fauna of disposed areas [1-2]. Recently, there is a rising interest in natural antioxidants as currently used synthetic antioxidants have been suspected to cause or promote undesirable effects on human health. OMW is an excellent source of natural antioxidants, e.g. phenolic compounds, which are considered to be the main antioxidant compounds in OMW [3-4].

In this study, firstly, characterization of olive mill wastewater is studied which is from olive oil production facility located in Balikesir, Turkey. Chemical oxygen demand, suspended solid content, oil and grease, pH, total organic carbon content, total nitrogen content and total phenolic contents were determined. After characterization of olive mill wastewater, extraction was performed and qualitative and quantitative analysis of the phenolic compounds was carried out.

Finally, it was determined that the antioxidant effects of olive mill wastewater known to exhibit high antioxidant capacity. Antioxidative properties of OMW samples such as reducing power, total antioxidant activity, DPPH radical and ABTS<sup>•+</sup> radical scavenging activities were investigated and results were compared to some standard antioxidants (BHT, Trolox,  $\alpha$ -tocopherol). As a result, OMW showed antioxidant activity as high as the standard antioxidants. Therefore these natural antioxidants can isolated from OMW and can be used in various industries.

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### P-GREEN - 5

## Study of the possibility for agricultural reuse of by-products from the treatment plant of Médéa (Algeria)

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The rationalization of the use of conventional water resources has become an imperative management. In this, and in the context of sustainable development, agricultural reuse of treated wastewater and sludge generated by the treatment appears to be an alternative for the preservation of water resources and the environment and the promotion of agriculture sector. It is around this axis as revolves this work, based primarily on the aptitude of treated wastewater and sewage sludge of WWTP of Medea to the reuse in agriculture. To do this, analysis of these by-products were made at the laboratory level.

The results, projected and compared to the recommendations of FAO and WHO standards, revealed that the treated waters of the WWTP of Medea, despite their high salinity, are reusable for irrigation of certain salt-tolerant species. The high concentration of faecal coliforms revels that these waters can not be used without chlorination. The sewage sludge, by the relatively low amount of organic matter it contains is considered a fertilizer, more than organic amendment. In addition, the C/N presents an important availability and rapid nitrogen mineralization.

Keywords. treated wastewater, sewage sludge, standards, reuse, irrigation.

#### P-GREEN - 6

## Use of vegetable wastes to remove nickel ions from exhausted electroplating baths

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The ability of vegetable wastes such as grape stalks and exhausted coffee to remove metal ions from synthetic aqueous solutions has been demonstrated in various studies performed by our research group [1, 2]. In this work, the performance of these wastes to remove nickel ions from an exhausted electroplating bath of a metal finishing industry from Barcelona (Spain) has been investigated. The experiments were carried out at room temperature in packed bed flow-up columns of 250 mm of length and 25 mm internal diameter using grape stalk (GS) and exhausted coffee wastes (EC) particle size 0.5-1.0 mm and 0.8-1.0 mm, respectively. In all experiments nickel concentration was kept constant about 5500 mg dm-3 and pH, flow rate, and bed height were varied in order to predict nickel ions transport in the column. Breakthrough curves were successfully described by Bed depth service time (BDST), Thomas and Yoon Nelson models [3]. Desorption studies were performed by using 0.1 mol dm-3 HCl as elution solution at the same flow-rate used for sorption experiments. The results obtained demonstrated that, in the studied experimental conditions, variation of initial pH, flow rate and bed height did not lead to significant differences on sorption capacity. The sorbent sorption capacity was higher for GS (20 mg g-1) than for EC (12 mg g-1) and metal recovery from the column was close to 50% and 10% for GS and EC, respectively.

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### PHOTOCHEMISTRY AND PHOTOCATALYSIS

### Р-РНОТО - 1

## Imidazolium-based ionic liquids in water: Assessment of photocatalytic and photochemical transformation

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lonic liquids (ILs) are a subject of active research in the field of alternative solvents, being promoted as "green chemistry" replacements to traditional solvents used in industry. The great interest toward these compounds relies on their attractive properties such as low vapor pressures and flammability, chemical and thermal stability, high ionic conductivity, wide electrochemical potential window and ability to behave as catalysts.

Only a few environmental data for these new "green solvents" are presently available, but the low biodegradability and ecotoxicity of some ILs are a potential risk to aquatic and terrestrial ecosystems. Recently, they were included in the list of the so-called "contaminants on the horizon" [1].

For these reasons it is necessary to prevent their leakage and to develop effective means of removal and recovery from wastewater, as well as to minimize their occurrence in such a matrix. In this work we studied two ILs, 1-methylimidazole hydrogensulfate (HMIM) and 1-ethyl-3-methylimidazole bisulfate (EMIM), by investigating the feasibility of their advanced oxidative removal by employing heterogeneous photocatalysis.

We evaluated substrate disappearance, evolution of transformation products (TPs), degree of mineralization and toxicity of the irradiated systems. Acute toxicity measures suggested that the transformation of both compounds yielded TPs with higher toxicity than the parent molecules. A total of five TPs were identified from HMIM and nine from EMIM, all characterized via HPLC-HRMS. The identification of the TPs is a crucial aspect because, in addition to providing important information on the mechanism of degradation, they may have a very different impact on the environment compared to the parent molecules. Complete mineralization and stoichiometric release of nitrogen was achieved for both compounds within 4 h of irradiation. The photochemical transformation kinetics and pathways in surface waters (direct photolysis and indirect photoreactions) were studied for EMIM, to assess its persistence in sunlit water bodies such as rivers or lakes. Environmental phototransformation is predicted to be dominated by direct photolysis, with half-life times of up to one month under fine-weather conditions.

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P-PHOTO - 2

## Triplet-induced oxidation of organic contaminants: inhibition by dissolved organic matter and model antioxidants

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One of the major photochemical pathway for the degradation of micropollutant in surface waters is their interaction with excited triplet state of dissolved organic matter (DOM). Recently an inhibition mechanism of the excited triplet state reaction, involving reduction of the oxidation intermediate of a micropollutant by the phenolic antioxidant moieties of DOM, was discovered.

Investigations on the dual effect (photosensitization vs inhibition) of DOM on the degradation of micropollutant will be presented, as well as the influence of DOM source (autochthonous vs allochthonous) and characteristics (phenolic content and electron donating capacities) on the photosensitization and on the inhibition mechanism, the comparison between the use of phenol as model antioxidant and the inhibitory effect of DOM.

This work should clarify the role of DOM in the triplet-sensitized degradation of micropollutant.

### Р-РНОТО - З

### Phototransformation of new oral anticoagulants in river water

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Drug residues are of particular concern due to their biological activity (they are created for that), their continuous introduction into the environment through wastewater treatment plant effluents and finally the confirmed toxicity of some of them. New Oral AntiCoagulants (NOACs) such as apixaban, rivaroxaban and dabigatran are used since five years in France [1]. They still have not been monitored regarding their environmental fate. Human metabolism studies show that these three compounds are eliminated in urine as unchanged forms at levels between 27 and 85% of the dose delivered [2]. Moreover, if these NOACs currently represent a small amount of ingested anticoagulants, it is expected that their prescriptions increase in the near future. The probability of the presence of these compounds and their by-products in wastewater and in surface waters will thus increase. Therefore, the environmental fate of these contaminants needs to be better documented. Currently, to our knowledge, the data relative to their abiotic degradation are still scarce.

The goal of this work was to determine rates of abiotic degradations (hydrolysis and photolysis) of the anticoagulants in purified water and environmental matrices (river water and mineral water) and to identify the structures of the compounds formed. Results show that, after one month, no hydrolysis is observed. Photolysis is one of the main way of degradation for rivaroxaban and dabigatran. At the opposite apixaban is almost not impacted by solar light after two days of irradiation. Finally, LC-MS experiment lead to a first identification of the photoproducts. At longer time scale, the toxicity of these products will need an assessment.

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#### Р-РНОТО - 4

### Oxidation of bisphenol A in the photo-iron-sulfite-O2 system at circumneutral pH

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BPA belongs to the group of endocrine disrupting chemicals (EDCs) and has been widely found in various environments globally as an extensively used substance. However, conventional treatment techniques are not effective enough for the removal of the majority of EDCs. In this work, we preliminarily investigated the photochemical degradation of bisphenol A (BPA) in aqueous solutions containing iron(III)-sulfite complex under ultraviolet irradiation. The effects of factors such as light intensity and initial concentrations of sodium sulfite and BPA were examined. The presence of various radicals was confirmed through quenching experiments using tert-butyl alcohol and ethanol as radical scavengers. The results indicated that BPA could be efficiently photooxidized by using the iron(III)-sulfite complex system, and the degradation follows pseudo first order kinetics. Under the same conditions, the iron(III)-sulfite system and iron(II)-sulfite system had nearly the same capability for BPA degradation. The optimal ratios of iron(III) to sodium sulfite ranged from 1:10 to 1:15, and the corresponding reaction rates resulting from these ratios were almost the same. However, the smaller reagent dosage is more economical. Under the same concentrations of iron(III) and sodium sulfite, stronger light intensities led to higher efficiencies of BPA removal. Identification of primary radicals through quenching experiments using tert-butyl alcohol and ethanol confirmed that BPA degradation was mainly due to the action of sulfate radicals. Through LC-MS, the products of BPA degradation were identified as catechol and quinone derivatives.

#### Р-РНОТО - 5

### Photocatalytic activity of Zr and Mn co-doped TiO<sub>2</sub> in aqueous media

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Photo initiated oxidative degradation of organic pollutants on the TiO<sub>2</sub> surface is a perspective approach in modern environmental technology which can be used for water and air purification. Various strategies are used to improve the photocatalytic efficiency of TiO<sub>2</sub>, one of which is modification with transition metals. The most resent research in this area is devoted to the investigation of co-doped TiO<sub>2</sub> systems. The present study reports the synthesis of Zr and Mn co-doped TiO<sub>2</sub>. The spectroscopic characterization of the TiO<sub>2</sub>–(10-x)%Zr–x%Mn photocatalysts and their photocatalytic activities are also discussed.

All samples were prepared using a sol-gel method from metal alkoxides as Ti/Zr precursors. As Mn precursor, its acetylacetonate was used. Experimental results show that the anatase is the major crystal phase for all of the samples and Zr can be incorporated into the TiO<sub>2</sub> matrix in a substitutional mode, while Mn can exist as a surface species. It was found that the porosity and surface area were influenced by the doping materials. The surface area of pure TiO<sub>2</sub> was 15.81 m2g-1, which is lower than Mn and/or Zr doped samples. Particularly Zr/Mn co-doped samples exhibited the largest surface area. Moreover, it was shown that Zr/Mn co-doping causes significant changes in the optical properties of the samples. In comparison with pure TiO2, Zr doping induces a blue shift of the band–band transition. The band absorptions of the Zr,Mn codoped TiO<sub>2</sub> samples are gradually shifted to longer wavelengths with the increase of Mn content. The photocatalytic activity tests show that the  $TiO_2-10\%$ Zr sample has better photocatalytic performance than the pure TiO<sub>2</sub>. Introduction of Mn decreases the photocatalytic efficiency in nonadditive manner. Moreover, with increase of Mn concentration the inhibition effect became stronger. To explain this effect, it was suggested that in the oxidation process, catalysed by Zr/Mn-TiO<sub>2</sub>, a competitive side reaction between hydroxyl radicals and Mn ions takes place, which was shown using the decoloring process of commercial dye "Bezaktiv Blau" in reaction with Fenton's reagent as a source of OH. The obtained experimental results clearly indicate that Mn ions effectively scavenge the hydroxyl radicals, and as a results the whole oxidation process is inhibited. However the mechanism of binding to these free radicals is not known.

**QSAR** 

#### P-QSAR - 1

## A QSAR study on the toxicity of halogenated organophosphorous compounds

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Organophosphorous compounds (OP) constitute an important class of pesticides. These compounds have a high acute toxicity and a wide range of biological activities[1]. The increasing amount of use is significantly increasing the risks of environmental contamination of groundwater, food, plants, water resources and human beings [2]. These compounds are released into the environment and due to their physicochemical properties, they can disperse in various environmental media, provoking serious health problems [3]. An increased understanding of the physicochemical and electronic properties involved in the reactions of OP compounds with potential destructants could lead to superior pesticides with greater safety margins. Therefore, there is a need for certain molecular descriptors to predict the toxicity of OPs.

Quantum-chemical descriptors have become quite popular recently and are widely used to the reliability and accuracy, as well as capability to characterize electronic properties of the molecules. In this study, the structures of 30 halogenated organophosphorous pesticides were investigated theoretically with the intention of finding certain molecular descriptors to predict the toxicity for both gas and aqueous phases. Conformational analyses and geometry optimizations of all the structures were performed to determine the most stable structures. Modeling of the molecules was performed with DFT at B3LYP/6-31G\* level. The solvation effects were computed using COSMO as the solvation model.

Based on the quantum mechanical calculations, charge densities, frontier orbitals, energetic parameters and thermodynamic properties of molecules were determined. These results were used to calculate the chemical reactivity indicies; hardness, chemical potential, and electrophilic indicies of the molecules. The relationship between the experimental LD50 (lethal dose) of the molecules and the calculated descriptors was examined through lineer regression in order to determine the best descriptor showing the toxicity of the molecule.

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### SOIL, SEDIMENTS AND REMEDIATION

### Implementation of a biological degradation process to eliminate PAHs from contaminated marine sediments

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The introduction by man, directly or indirectly, of substances or energy into the environment can cause deleterious effects such as harm to living resources, hazards to human health, hindrance to marine activities, including fisheries, deterioration of sea water quality and reduced opportunities in the field of entertainment. The most contaminants for the marine environment are those that show a persistence in the environment, an ability to be transported over long distances, a tendency to bioaccumulate and vis-à-vis toxicity of non-target organisms. The identification of environmental contamination by PAHs often requires the implementation of effective analytical techniques. Among the listed PAHs benzo (a) pyrene (the most studied for its toxicity) and fluoranthene (most common in the environment). PAHs are relatively recalcitrant compounds to biological degradation. The last thirty years, research on the degradation of PAHs have allowed the isolation of many species of bacteria capable of fungi and algae degrade the small molecular weight PAHs (2-3 benzene rings). The biggest PAHs are generally recalcitrant to microbial attack, some fungi and algae are able to transform them. In order to enhance the polluted sediment PAH, a method for processing and degradation was developed, the PAHs have been treated with chemical and biological knowledge for reuse in other business areas such as construction.

Keywords. Marine sediments, Pollution, PAH contamination, treatment, degradation.

## Removal of hexavalent chromium from soil and deep water; chemical vs bio-mediated approach.

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The contamination of natural ecosystems by hexavalent chromium is of a major concern worldwide, since Cr(VI) has been recognized as highly toxic, mutagenic and cancerogenic for living organisms. When present in sediments Cr(VI) could be naturally reduced to Cr(III), but the capacity of soil is not enough to operate this reduction in reasonable times. Indeed Cr(VI) can persist in soils and because of its high mobility, it can easily leach and contaminate ground waters. The present work deals with the in vitro study of Cr(VI) removal from a water-sediment system in different condition of water saturation, in order to simulate different possible occurring real scenarios. For the Cr(VI) removal two different approaches were compared: i) the use of sugars as organic nutrients for a bio-mediated approach, since sugars can promote the growth of microorganisms naturally present in soils and stimulate their reductive capability; ii) the chemical Cr(VI) reduction, testing different reducing agents such as sodium sulphite, sodium metabisulphite, sodium dithionite and ascorbic acid. The results demonstrated that both approaches can yield to the total abatement of Cr(VI) from a contaminated soil-water system. Among the organic nutrients the best performances can be ascribed to the glucose while the best chemical reducing agent has been demonstrated to be the ascorbic acid. Despite the similar performance in term of efficiency, the chemical system is much simplified compared to the biomediated one and allows to obtain good results in very short times (up to 24 hours) compared to the bio-ones (up to above 30 days). In addition, the chemical system allows a better control of the process parameters, not involving the action of microorganisms. Under an economical point of view the higher cost of ascorbic acid compared to glucose is compensated by the much lower amount necessary to attain the 100% of Cr(VI) reduction. In case of in-situ remediation of groundwater, the spreading also on soil of ascorbic acid would therefore contribute to reduce the leaching of Cr(VI), helping the overall site remediation.

### Oil pollution in the vicinity of a heating plant in New Belgrade (Serbia) – influence on the quality of the surrounding soil and sediments

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Petroleum products have been used for decades in the plants for district heating in Belgrade (Capital of Serbia). The most used derivative for this purpose is a heavy oil fuel. Additionally, raw petrol and ecodiesel are in use as well.

During the months of May and June 2015 an extensive investigation of the pollution of the soil and sediments in the vicinity of a heating plant in New Belgrade (Serbia) was conducted.

According to the geologic and hydro geologic characteristics, the research area is located in the alluvial plains of the Sava River, close to its confluence to the Danube. Because of that, the significance of this research is not only local but also regional.

The soil and sediments were sampled in a zig-zag pattern, from 20 micro locations and 5 different depths making in total 100 of samples.

The results showed that the whole investigated area was contaminated with diesel and a heavy oil fuel which have been used for decades in this heating plant. Although the results did not indicate a significant contamination, the presence of these oil pollutants in the investigated samples indicates that this area should be under continuous monitoring.

### Oil pollution in the vicinity of a heating plant in New Belgrade (Serbia) – influence on the ground water quality in alluvial plains of the Sava River

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The district heating plants in Belgrade (Capital of Serbia) have been using petroleum products as fuel for decades. The most used derivatives are heavy fuel oil, raw petrol and ecodiesel.

One of the largest heating plants in Belgrade is a heating plant in New Belgrade. Within the area of this facility, there are several storage tanks of petroleum products and a decanter.

Being located in the alluvial plains of the Sava River, close to its confluence to the Danube, this heating plant represents potential source of the oil pollution for the whole alluvial area.

During the months of May and June 2015 an extensive investigation of the pollution of the ground water in the vicinity of a heating plant in New Belgrade (Serbia) was conducted. The samples were analyzed from the system of the 13 existing piezometers and from the 3 new wells.

The results proved that the whole investigated area was contaminated with diesel and a heavy oil fuel which have been used for decades in this heating plant. Additionally, the results showed that the contamination of surrounding soils and sediments was transferred to the ground waters. In this way the pollution of the solid phase of the investigated aquifer left a "fingerprint" of its composition in the neighboring ground waters.

Although these results did not indicate a significant contamination of the investigated ground waters with oil pollutant, presence of this contaminant in the aquifer means that this area should be under continuous monitoring.

## Removal of dibenzothiophene and its alkyl homologues during ex situ stimulated bioremediation of contaminated soil

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Dibenzothiophene (DBT) and its alkylated homologues are common sulfur heterocyclic constituents of crude oils. In oil pollutant biodegradation studies they keep attracting great concern due to their environmental persistence but also due to their toxicity. Additionally, they seem to be more resistant to aerobic microbial degradation then polycyclic aromatic compounds (PAHs) of similar weight.

The aim of this research was to investigate the changes in the distribution of DBT and its C1 and C2 alkyl homologues during ex situ stimulated bioremediation of a soil contaminated with heavy residual fuel oil. The results of this experiment were compared with the results of natural biodegradation of the same soil that was not subjected to the processes of stimulation.

In the set of naturally biodegraded samples, DBT was more degraded than its alkyl homologues. According to the current knowledge, these changes during the natural biodegradation might be characterized as expected.

In the set of samples exposed to the stimulated bioremediation, the opposite trend was observed. Within the homologue series of DBT and its C1 and C2 alkyl homologues, some of the higher alkylated homologues were more degradable than DBT.

Based on these results, a general conclusion can be drawn that the conditions applied during this stimulated bioremediation process of contaminated soil result in more pronounced reduction in the concentrations of alkyl DBT homologues comparing to their parent molecule. However, the extent and the applicability of this process, as well as the further fate of these persistent pollutants, still remain to be investigated.

## Diclofenac in presence of copper(II) in soils: adsorption and degradation

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Diclofenac is a non-steroidal anti-inflammatory drug widely used for the treatment of inflammatory disorders and painful conditions. Diclofenac together with its human metabolites enter wastewater treatment plants through sewers. The main molecule, diclofenac, has been frequently detected in effluent samples collected of wastewater treatment plants in Europe at concentrations ranging from 0.1 to over 5  $\mu$ g L-1. [2] Widespread use of diclofenac as over-the-counter drug in conjunction with relatively high doses at short dosing intervals and low removals in wastewater treatment plants lead to its continuous discharge into the aquatic environment, making it a pseudo-persistent pollutant therein [3].

Previous studies investigated diclofenac adsorption [5] and the formation of degradation products. [1] However, interactions of diclofenac with other soil pollutants are poorly documented. Among soil pollutants, copper is a ubiquitous metallic trace element. It can form complexes with diclofenac in aqueous media [4] and thus modify the fate of diclofenac in the environment. In this context, knowledge about the influence of copper on diclofenac adsorption and degradation is needed. This study aims to investigate the adsorption and degradation of diclofenac in different conditions: absence or presence of copper(II), dark and light conditions.

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## Reactions at the soil-solution interface control element cycling under alternating redox conditions

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Most soil processes characterizing the biogeochemical cycling of nutrients and pollutants, which have been deeply studied in oxic environments, can be substantially transformed by changing soil redox conditions. Such redox fluctuations may occur naturally or after anthropogenic causes; the latter case is typically represented by paddy rice fields. Alternation of submersion and drying induces subsequent dissolution and precipitation/sorption reactions at the soil solid interface involving redox-sensitive species together with related ones.

Most redox reactions in the biogeochemical cycling of C, N and P, microbially mediated, are strongly related to the processes occurring at the soil-solution interfaces. In particular Fe oxides, which may promptly undergo redox dissolution, represent one of the main phases controlling the immobilization/release and microbially mediated reactions of nutrients in anaerobic environments.

Together with nutrients, also the cycling of contaminants are directly or indirectly affected, so that immobilized forms in oxic soils may become easily bioavailable under reducing conditions and enter the food chain. For instance, paddy rice may become one of the major ways of arsenic intake in human diet. At oxidizing/reducing interfaces with alternating submersion conditions, the composition and equilibria of As forms are strongly controlled by interaction with iron oxides and organic matter dynamics.

Changes in the redox environment can have dramatic consequences on heavily contaminated sites, such as mining sites, industrial and urban environments, where different inorganic and organic contaminants are interconverted from immobilized into available forms, depending on their interaction with soil solid phases.

Thus, the effect of alternating redox conditions on speciation of nutrients and contaminants is strongly related to the soil phase which drives element fluxes through soil, water, plant and/or atmosphere.

### Metal adsorption on biochar: study of pH influence

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Biochar is a solid residue produced by thermochemical degradation of biomass. It has a graphitic-like structure and presents different functional groups that are responsible for its chemical properties. Thanks to these interesting characteristics it can be used in several applications, including water remediation, due to its remarkable adsorption capacity of organic and inorganic pollutants [1]. Recent studies have demonstrated that metal adsorption on biochar is influenced by many parameters, e.g. initial concentration and solution pH. A pH variation, indeed, could affect the surface's charge, metal speciation and, as a consequence, adsorption capacity [2]. All these studies, however, were conducted by setting initial conditions and overlooking the possible pH variations during the tests that could be caused by the adsorption process itself. Aim of this study was the evaluation of the influence of pH and initial metal concentration on adsorption capacity, through Experimental Design approach, for a biochar sample obtained by Miscanthus straw pellets pyrolysis. After a preliminary physical chemical characterization of the sample and determination of its adsorption capacity of Cd2+ and Pb2+, a Central Composite Design was set establishing pH and initial Cd2+ concentration as factors and final metal concentration as response. In order to avoid pH variation during adsorption, pH was maintained steady at the set point chosen by the model.

The test have demonstrated that not only pH and concentration influence the system promoting adsorption at high concentration and basic condition, but also that pH tends to vary during adsorption. This variation could be due to basifying characteristics of biochar and protons exchange that could take place when the metal ion is adsorbed on the surface [3].

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### WATER TREATMENT AND ITS IMPLICATIONS

# Microbusters: an integrated approach for the treatment of micropollutants: oxidation, membrane technologies and new adsorbing materials.

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The present research aims to develop an innovative integrated tertiary water treatment for the removal of micropollutants (MPs) such as pharmaceuticals, personal care products, steroid hormones, etc.... These compounds are actually under study for their potential risks for human and ecosystem health. Wastewater treatment plants are not specifically designed nor optimized for MPs abatement at trace concentrations (from few ng/L to several  $\mu$ g/L). Thus, many of these MPs are still present at the end of wastewater treatment processes and can re-enter the water cycle. The presence of MPs in natural waters has been associated with many negative effects, such as short- and long-term toxicity, endocrine disrupting effects, antibiotic resistance of microorganisms. The present research considers the development of novel materials for optimizing four complementary technologies that have shown promising results in the treatment of MPs, namely membranes, adsorption, biocatalysis and photocatalysis. The research has been divided into specific objectives, including preparation, characterization and application of: i) oxidic and polymeric nanostructured films and membranes obtained from the self-assembly of block copolymer templates; ii) nano-alumina as filter and adsorbing material, pure and/or coupled with other oxidic phases (e.g., TiO2, to generate synergies in the MPs abatement); iii) new adsorbing materials based on cyclodextrin nanosponges with tunable properties (pores size and distribution, hydrophilicity/hydrophobicity and swelling ability); iv) waste-derived biochar and Bio-Based Substances from Green Compost (BBS-GC) as adsorbing materials; v) heterogeneous oxidation biocatalysts easily recoverable after MPs treatment (enzymes fixed on SiO2 and/or Fe3O4 supports); vi) BBS-GC immobilized on supports as heterogeneous photocatalysts. Moreover, based on the preliminary results, the present research has the ambitious goal of creating a consortium of academic and industrial partners for preparing a proposal under H2020, including the Life Cycle Assessment of new materials and proposed technologies in order to evaluate their economic and environmental sustainability and the design of a prototype for MPs abatement in real waters at pilot plant scale. To face these aspects, additional expertise in the field of biology, engineering, economics, environmental and soil chemistry, sub-trace analysis are needed; networking activities will have therefore a key role.

## Continuous-flow system for selective removal of boron by binary mixture of porous adsorbents

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In this study, continuous removal of boron from aqueous solution by selective adsorption was examined using a fixed-bed column packed with binary mixture of polyvinyl (alcohol) functionalized porous eggshell powder (PSP) and glycidol functionalized porous seashell powder (GSP). The effects of solution pH, flow rate, bed depths, and the PSP: GSP ratios in the binary mixture on the breakthrough characteristics were investigated. The breakthrough time increased with increase in the bed depths and decreased with feed flow rate. Experimental results confirmed that the mixture of PSP and GSP adsorbed boron in the form of both boric acid and borate anions via inner-complex mechanism with maximum sorption capacity of 87.5 mg/g at pH 8.5. The breakthrough time increased with increase in the binary mixture and various column kinetic models were fitted to describe the sorption mechanism. Results in this study, suggest that the simultaneous utilization of adsorbents can be adopted for efficient treatment of boron-containing effluents.

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### Applications of Iron Chemistry for Environmental Remediation Technologies: an international collaboration

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This project is situated within the wider concern of environment quality. Indeed, with the increasing of human activities more particularly agricultural and industrial production, the amount of pollutants released to the environment increases. So, a large variety of contaminants are currently found in surface water, groundwater and soil, including organic solvents, hydrocarbons and halogenated hydrocarbons, pesticides, pharmaceuticals, personal care products and heavy metals. The technologies used for environmental remediation consist of conventional phase separation techniques, such as screening, sieving or stripping techniques, adsorption processes and processes designed to destroy the pollutants, mainly biological treatment and more recently chemical treatment based on oxidation/reduction processes.

An appropriate technique seems to be a special class of oxidation methods defined as advanced oxidation processes (AOPs). AOPs are based on the generation of very reactive free radicals, mainly the hydroxyl radical (HO•), which are able to destroy pollutants by oxidation. In the most of Fe-based decontamination reactions, low pH (< 4) is required to avoid the Fe precipitation and formation of iron sludges, which have negative impacts on the overall performance of process. To overcome this limitation, a new class of remediation methods using Fe bearing minerals and/or Feoxyhydroxides has recently appeared to promote Fenton-based reactions at circumneutral pH values.

We will focus on an improved understanding of both formation mechanisms of radical species in aqueous phase and heterogeneous redox reactions taking place at Fe-oxide/water interface under a set of chemical and physical conditions. Using this novel approach we intend to characterize the properties, the dynamics of radical formation, transformation/mineralisation of contaminants and the overall impact of the developed processes. These issues will be addressed using environmental relevant contaminants or emerging compounds typically present in surface waters and wasterwaters such as organochlorinated compounds, pharmaceutical products, pesticides and other anthropogenic organic compounds.

## Identification of performance indicators for better management of WWT of Medea (Algeria)

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Despite the magnitude of the repercussions generated by the wastewater on the degradation of the Environmental medium, on the water shortage and consequently on public health, in Algeria, little importance is given to sanitation compared with the supply of drinking water services. These sanitation problems remain a major concern and require an supported significant by taking appropriate measures, in perspective to safeguarding and respecting the environment. From the collection to treatment, This wastewater route deserves to be diagnosed in order to control the sanitation system and optimize its facies, by prospecting and research performance indicators, that identify gaps and propose technical solutions for better wastewater management.

For this, we have identified the physicochemical parameters most significant in terms of impact on the receiving environment by analyzing 10 physicochemical variables (Temperature, pH, electrical conductivity, TKN, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, COD, BOD5, TSS) for wastewater from the city of Medea . This study defines the values of mean concentrations, ratios and ranges of variations associated wastewater characteristics. Subsequently, we calculated the ratios of pollution indicators that should enable us to highlight the optimizations necessary to the wastewater treatment plant of Medea.

Keywords. Sanitation, treatment plant, ratios, optimization, performance.

### Chemical characterizations of the low-cost biosorbent prepared from cherry/sweet cherry kernels

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Among alternative methods for heavy metal-contaminated wastewater stream treatments, filtration with new-sorbent-based processes have proved to be a promising separation technique in terms of low cost and ease of operation. Thus, great attention is given to the characterization of the sorption properties of alternative low-cost materials. Lignocellulosic materials are one of the most used materials for the production of activated carbons. Lignocellulosic biomass derived from fruit growing by-products has proven to be a promising type of raw material for producing low-cost adsorbents.

Cherry kernels were used to prepare activated carbon (CsCPA) by thermochemical activation with phosphoric acid as the activating agents at 500°C for 2h. Chemical characterizations of the prepared biosorbent were studied by FTIR spectroscopy. FTIR spectra were recorded with a (Thermo Nicolet Nexus 670 FTIR) spectrometer, from 400 to 4000 cm-1 wavenumbers, identifying the functional groups at the surface of the CSCPA.

The numerous chemical functional groups have been identified as potential active sites to be important for binding metallic ions to the biosorbent. The FTIR spectra showed a broad band at 3737.91 cm-1 due to N–H stretching vibration and a peak at 484.91 cm-1 due to O–H bending vibration. The adsorption peaks between the regions 3700 and 3200 cm–1 represented the overlapping peaks of stretching vibrations of O–H and N–H groups. The strong absorption peak at 2922.59 cm–1 and 2852.11 cm–1 could be assigned to –CH stretching vibrations functional groups. Peak at 1565.63 cm–1 correspond to the primary and secondary amide bands. 1436.28–1374.69 cm–1 was the deformation stretching of C–H, –CH3 and –CH2 functional groups. The strong band within 1163.33 – 983.94 cm–1 is due to the C–O group, which are characteristic peaks of polysaccharides.

Based on presented results, it can be concluded that possible mechanism of adsorption of heavy metals ions on the created biosorbent may be due to chemical reactions with active sites, physical adsorption, ion exchange, precipitation and other interactions with functional groups. For the determination of more specific nature of the sorption processes further investigations require FTIR spectrum analysis of metal loaded biosorbent.

### Keywords. fruit stones, FTIR, biosorbent

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## Box-Behnken optimization of the removal of As(III) from aqueous effluents by modified polypropylene nonwovens

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The use of heavy metals, metalloids and their compounds has contributed to enhance the comfort of human being. However, the occurrence of heavy metals and metalloids is a major concern nowadays due to their increasing concentration in both, aquatic systems and sediments. One of the most relevant environmental poisons based on metalloids elements is arsenic. It is mostly found in natural waters due to i.e.: natural weathering process, geochemical reactions, biological activity, combustion of fossil fuels, volcanic eruptions, gold mining, leaching of man-made arsenic compounds, smelting of metals ores, desiccants, woods preservatives, agricultural pesticides. Due to the toxicity of this element and its bioaccumulative potential, the World Health Organization set the recommendation limit as  $10 \mu g/L$  of arsenic in drinking water [1].

Conventional processes for treatment of arsenic polluted waters are based on adsorption, coagulation, co-precipitation, ion-exchange and oxidation-reduction process. Among these methods, sorption has demonstrated a good performance, especially when iron-based materials are used [2].

In this study a set of novel materials based on polypropylene (PP) modified nonwovens has been prepared and assessed for As (III) removal. The PP-base material explored in this work was modified with: (a) Zinc Oxide (ZnO), (b) Yttrium (III) oxide ( $Y_2O_3$ ), (c) Multiwall carbon nanotubes, (d) Multiwall carbon nanotubes + akagenite (FeOOH) and (d) Multiwall carbon nanotubes + bernalite (Fe(OH)<sub>3</sub>). A Box–Behnken statistical experiment design has been used to investigate the effects of relevant operating parameters such as initial arsenic concentrations, pH and sorbent doses on the removal of As (III) and to optimize the combination of variables that leads to maximum arsenic removal efficiency.

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## Removal of physical and chemical pollution from run-off rainwater by using cork packed columns

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The use of rainwater and water reuse could be a critical element for improving water resources. Nevertheless, when using water from these sources two aspects must be taken into account: the potential uses and water quality required for each use. Water quality standards are usually fixed according to the assessment of potential health risks [1, 2]. Rainwater runoff could be a good source of water in urban areas but air pollution is especially high there and consequently rain water and runoff rainwater could be highly polluted. Thus, an effective treatment of runoff rainwater must be carried out before its reuse.

This research focuses on the use of a low cost material, granulated cork, for the efficient removal of physical contamination (particulate matter) and heavy metals from runoff rainwater. For this proposal, samples of rainwater from different runoff episodes were collected in different episodes.

The experiments were carried out by using cork packed columns with three different lengths: 5-24 cm. The columns were divided into 2 sections both of them containing cork a different cork particle size (1.00-3.15 mm and 3.15-6.30 mm). Two scenarios of physical pollution, measured as turbidity, were tested: 70 NTU and 30 NTU. So as to test metal ions elimination capacity of the column, the rainwater samples were spiked with chromium (20 mg/L) to simulate metal pollution.

Results showed that the use of a pre-sedimentation step, before filtration through the cork column, can reduce the physical contamination with an average of 51%. The percentage of decrease on turbidity and chromium elimination after passing the cork columns increases as increasing bed lengths. After rainwater cork filtration, water turbidity fitted the quality required for the Spanish regulation (RD 1620/2007) to be used for different proposals (urban services, agricultural, industrial and recreational uses). The maximum percentage of chromium eliminated was around 20%

In conclusion, granulated cork appears as an efficient and economic filter to reduce physical contamination and chromium in solution.

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## Boron-specific porous magnetic adsorbent based on chicken bone ash: economics and modeling

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Boron-specific magnetic adsorbent (BSA) was fabricated through the integration of copper ferrites onto combustion residues of chicken bone, and resulting material modified with polyvinyl alcohol. The Brunauer-Emmett-Teller surface analysis and Vibrating sample magnetometry confirmed that the BSA is porous and had a saturation magnetization of 53.29 emu/g. The BSA showed excellent selectivity towards boron and resulted in 70-89% boron removal in the presence of coexisting ions (Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>). At pH 7.0 in the batch system, the maximum sorption capacity of 80.5 mg/g was achieved, outperforming most of the reported adsorbents. In the fixed-bed system, the breakthrough time increased with bed depths (2.0 -6.0 cm), and relatively higher uptake (103.5 mg/g) observed at the lowest flow rate of 3.0 mL/min. The experimental results confirmed that boron was adsorbed by BSA in the form of boric acid via outer-sphere complex, and also in the form of borate ions via inner-sphere mechanism. The boron-loaded BSA could be effectively regenerated using simple acid solution, adsorption sites reactivated with water at pH 8.0 and repeatedly used. The stability and simple magnetic separation after spent demonstrate the superiority of the BSA in removing boron. The cost-benefit analysis and net profit confirmed that the recovery process is economically feasible.

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## Air plasma induced removal of emerging organic pollutants: green solution to water purification

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Emerging organic contaminants (EOCs) have recently become one of the most important problems related to water and soil systems. EOCs originate from several kinds of products including pharmaceuticals, veterinary medicines and personal care products [1]. The increasing concern about these chemicals as aquatic contaminants is due to their environmental persistence and the impact they may have on ecosystems and human health, even at low concentrations [2].

Novel technologies based on atmospheric-pressure non-thermal plasma (NTP) are emerging as an alternative approach for wastewater treatment. The primary advantage of NTP is the capability to generate hydroxyl radicals, ozone and UV light without chemical additions or UV lamps. This work focuses on the effect of air atmospheric plasma in inducing degradation of persistent organic contaminants in water. Aqueous solutions of, respectively, a sulfa drug, sulfamethoxazole, and an antimicrobial agent, triclosan, were treated in our plasma reactor, previously described [3]. In this case Dielectric Barrier Discharges generate plasma in the air above the polluted water. In this apparatus, ozone and hydroxyl radicals play a key role in the oxidation of organic matter. Experiments were carried out to determine the oxidation kinetics, the reaction site(s), and the intermediates and products arising from plasma treatment. The pHdependence of EOCs depletion and a comparison of their reactivity toward plasma with that of similar compounds were also investigated.

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## The importance of determining the AOC to assess the cleaning efficiency of the Švařec water treatment plant

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Recently, the content of biodegradable organic substances and the possibility of secondary propagation of microorganisms in drinking water have become an issue. The drinking water not allowing propagation of microorganisms even at the minimum residual concentrations of disinfectants is labelled as biologically stable water. Permanganate chemical oxygen demand (CODMn), absorbance at 254 nm (A<sub>254</sub>) and culturable microorganisms are commonly determined as frequently monitored parameters that indicate the presence of organic substances.

This work deals with comparing separation efficiency of individual stages of technological processes of drinking water treatment in the Švařec plant and focuses on the presence of organic substances in treated water and on its biological stability. Determination of assimilable organic carbon (AOC) using the reference strain of Pseudomonas fluorescens (P17) was employed to assess biological stability of water.

The highest values of CODMn and A<sub>254</sub> were found in raw water. During water treatment both indicators decreased gradually. The largest fall was recorded after coagulation with sand filtration. Sanitation and alkalization did not prove a significant impact on the CODMn and A254 indicators. The highest biological recovery was found in July. The water was dominated by the filamentous cyanobacteria of Aphanizomenon genus that subjects to easy disintegration into individual fibres and cell lysis. The results show a gradual reduction in the number of individuals and cells in water surrounding the technological line. Pre-ozonation led to a slight decrease in numbers of organisms probably due to decay of cells after ozone exposure. The measured AOC concentration in raw water ranged between 33 - 58 µg·L-1. The changes in AOC content along water treatment technological line corresponded to literature. The results proved good separation efficiency of coagulation followed by sand filtration that showed a significant reduction in all monitored indicators and removed most organisms from water. The GAC filters that reduced values of majority of analyzed parameters also participated in separation and eliminated organisms. Use of the AOC indicator was monitored, too; it evaluates water quality concerning potential development of microorganisms with secondary reproduction.

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### Treatment and reuse of textile wastewaters by solar photocatalysis in the presence of urban waste extracts and evaluation with fluorescence EEMs

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The effluents generated by finishing textile industries represent an environmental problem because of the high water consumption, heavy contamination of wastewater with an elevated content of complex organic matter, conductivity and intense colour (Sharma 2007).

Homogeneous solar photocatalysis (photo-Fenton) was used in the presence of extracts from urban waste (BOS) for the treatment of industrial effluents from the equalization tank of a textile wet processing company (BOS stands for bio-soluble organic substances, these obtained from a mechanical-biological treatment of wastewater). The presence of BOS has allowed carrying out these processes at a more neutral pH (pH = 5), and thanks to its surfactant characteristics the treated waters could be reused in subsequent dyeing processes of cotton with direct dyes, thus reducing the consumption of water as a natural resource.

These extracts are the isolated humidic fraction of urban wastewater and their chemical composition is very similar to natural organic matter such as humic substances (Fantozzi, 2009). The characterization of the urban waste extracts by fluorescence techniques can be very useful after applying methods based on multivariate analysis (PARAFAC) on excitation-emission matrixes (EEMs) obtained by fluorescence spectroscopy methods (Sikorska, 2005).

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## New technologies for monitoring and treatment of emerging contaminants: MOTREM project

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The MOTREM european project, "Integrated Processes for MOnitoring and TRreatment of EMerging Contaminants for Water Reuse" funded through the joint programming initiative "Water Challenges for a Changing World" (WATER JPI), studies the development of new technologies integrating monitoring and treatment of emerging contaminants, enhancing the efficiency of the removal of these pollutants in urban wastewater treatment plants, especially for water reuse. The project aims to provide new technologies for water treatment and/or improving the existing ones through the development of integrated processes for monitoring and treatment of emerging contaminants (ECs) in the current waterline of municipal wastewater treatment plants, especially focusing on the aspect of water reuse.

Therefore, the general objectives of the project are: a) To develop new processes or modifications of the current biological and disinfection technologies in WWTPs by advanced oxidation and biooxidation processes to achieve the removal of ECs before water reuse or the discharge of the effluents to the environment; b) To develop new technologies for the monitoring of the wastewater treatment plant operation regarding the removal of ECs, including analytical procedures and ecotoxicology assessment; c) To bring the "key enabling technologies (KET)" developed in the previous steps together to test them in an urban WWTP.

To achieve these goals and based on the previous expertise of the different research groups that constitute MOTREM consortium, the research lines developed in the project are:

- Advanced Biooxidation Processes.
- Photochemical Advanced Oxidation Processes.
- Monitoring of Wastewater Treatment Processes.
- Chemical Analysis of Emerging Contaminants.
- Assesment of Ecotoxicology and Estrogenicity.

### Mat4treaT: Enhancing water quality by developing novel materials for organic pollutant removal in tertiary water treatment

CONSORTIUM MAT4TREAT

Università degli studi di Torino (UNITO, Italy), Politecnico di Torino (POLITO, Italy), Universitat Politecnica de Valencia (UPV, Spain), University of Ioannina (UOI, Greece), Aalborg Universitet (AAU, Denmark), Liqtech International A/S (LQT, Denmark), ACEA Pinerolese Industriale (ACEA, Italy), McGill University (McGILL, Canada), La Plata University (UNLP, Argentina), Stellenbosch University (SU, South Africa).

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The MAT4TREAT project consists in a consortium of 8 Universities, 5 of them European (UNITO, POLITO, UPV, UOI and AAU), and the other three from outside the EU (UNLP, McGill, SU), as well as two non academic institutions (ACEA and LQT). These groups are committed to work in the development of novel materials to be used in innovative integrated water tertiary treatments (to remove, for instance, Emerging Pollutants). This ambitious goal will be achieved by world leading research groups in the following fields: (i) graphene-based and other carbon-related materials, (ii) polymeric materials, (iii) oxidic ceramic materials, and (iv) hybrid inorganicpolymeric materials. The new materials will be used as adsorbents, as photocatalysts and as active layers for the fabrication of membranes, and thus tested for the pollutant removal from model aqueous solutions as well as from real water samples. Furthermore, approaches combining different materials and pollutant abatement technologies will be proposed and a demonstrative lab- bench apparatus for the integrated treatment of wastewaters will be builtup with the support of two European non academic institutions, which will directly participate to the project. Chemometric approach will be followed to model photocatalytic processes and to elucidate the effect of experimental parameters on adsorption and/or membrane based water treatments. Life Cycle Assessment of new materials and proposed technologies will be performed in order to evaluate their economic and environmental sustainability. For the implementation of the programme secondments of ESRs and ERs are scheduled (96 secondments for 146 person-months).



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