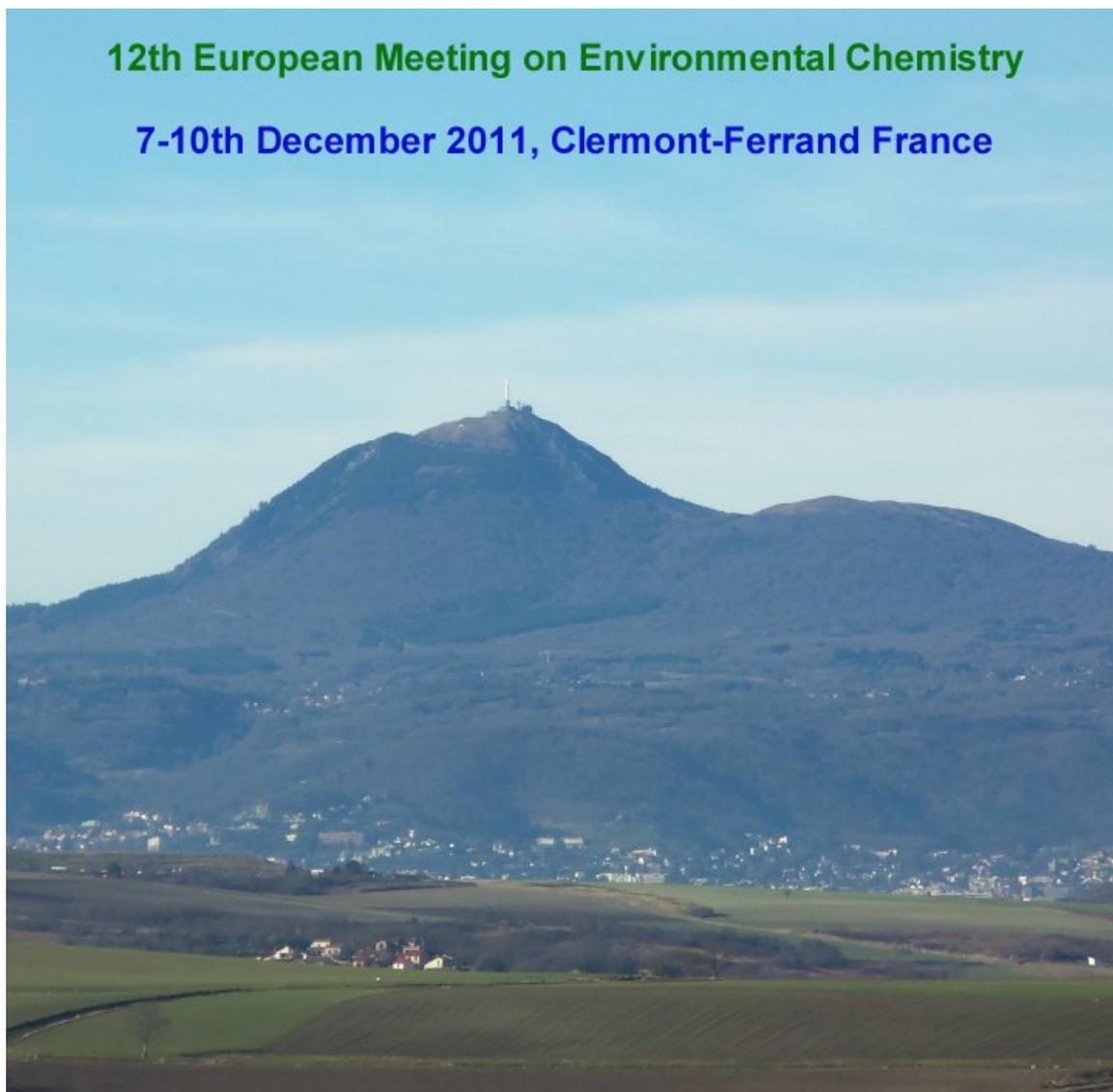


EMEO12

12th European Meeting on Environmental Chemistry

7-10th December 2011, Clermont-Ferrand France



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Welcome and General informations

Welcome

The organizing committee welcomes you to the EMEC 12. EMEC12 continues the tradition of eleven previous annual meetings providing a forum for the exchange of ideas on recent advances in research and development in environmental chemistry and technology for people from industry, research and academia concurrently.

The conference theme is Chemistry for the Environment which gives emphasis to the fields of research on development and application of new materials and clean technologies, particularly where chemistry plays a significant part in current environmental issues.

We wish you a great meeting and that you have the opportunity to visit Clermont-Ferrand and the Auvergne Region.

Registration

Upon arrival, please register at one of the three congress registration desks in the hall n°8. Collect your congressist pack and your name badge. You are requested to have your name badge at all times. The registration desk will be open on Wednesday December 7th between 16h00 and 18h00. On Thursday December 8th, the registration desk will be open between 8h00 and 9h00. On Friday December 9th and Saturday December 10th, the registration desk will be open between 8h00 and 8h30. The registration desk will also be open during the coffee breaks.

Oral presentations

Conferences are scheduled to last 1 hour including 15 minutes for questions. Oral communications are scheduled to last 15 minutes, 12 minutes of presentation and 3 minutes for discussion. Chairs of sessions will be asked to fit strictly to the published schedule. Speakers should deposit their oral presentations 30 minutes before the start of the sessions or during the coffee breaks. Oral presentations should be in PDF format and on a USB stick exclusively.

Poster presentations

Posters should be prepared in A0 format (119 x 814 cm, portrait presentation). The posters will be displayed continuously throughout the congress. The posters can't be installed until the morning of December 8.

Meals

The registration fees include 3 lunches (8, 9 and 10 December), the Gala dinner (9 December) and all the coffee breaks.

The Gala dinner will be held at the restaurant "Brasserie Delille" – Place Delille – Clermont-Ferrand at 20h30.

Guided tour of Clermont-Ferrand

The registration fees also include the guided tour of Clermont-Ferrand. Meeting point at 14h15 in the hall n°8 or at 15h00 at the Tourist Office, Place de la Victoire, Clermont-Ferrand.

Acknowledgments

It would not have been possible to organize the EMEC 12 without the strong financial support and the logistical help provided by many sponsoring institutions:

Sponsors



Fédération Recherche **Environnement**

Exhibitors



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Davide VIONE, Department of Analytical Chemistry, University of Torino

EMEC12 is organized in cooperation with

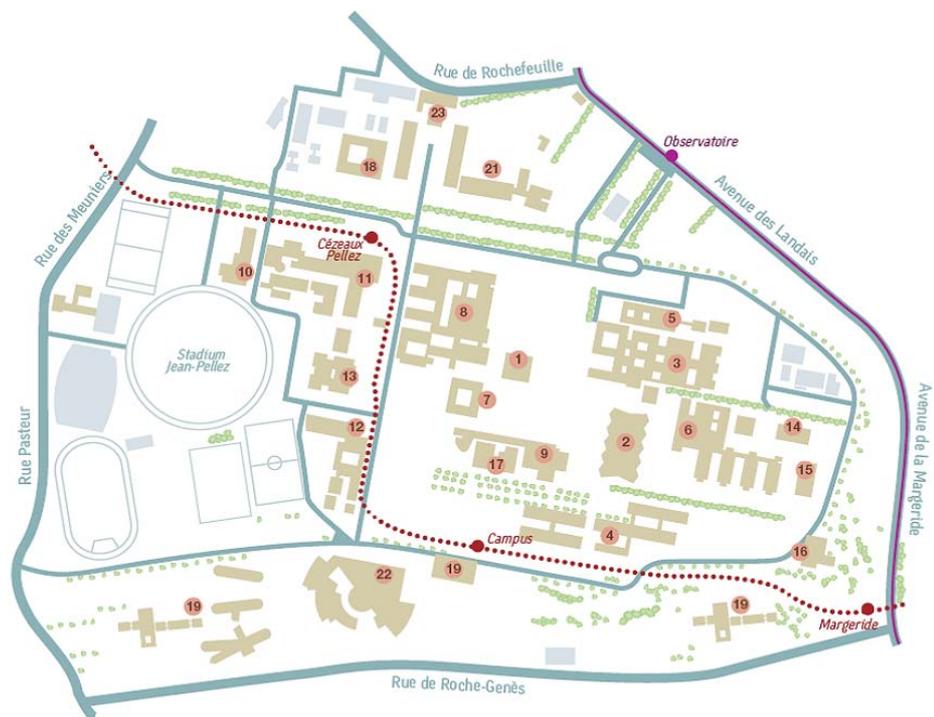


Congress venues and map of Campus "Les Cézeaux"

The congress will take place on the Campus "Les Cézeaux" (University Blaise Pascal Clermont II). The registration will be held in the Hall of the "Pôle de Physique" (n°8). The open ceremony will be held in the Amphitheatre of the "Pôle de Physique" (n°8). All the oral communications will be given in the Amphitheatre to the "Pôle de Physique" (n°8). The coffee breaks will be held in the Hall (n°8). The posters should be installed in two rooms 9105 and 9107 (n°8). The posters can't be installed until the morning of December 8. Lunches will be served at the place n°17 ("Salle Polyvalente").

Plan du Campus des Cézeaux

- 1 - Administration Sciences
 - 2 - Amphithéâtres Sciences
 - 3 - 1er cycle Sciences - SCLV
 - 4 - Biologie Végétale/Animale
 - 5 - Biologie Végétale Recherche
 - 6 - Chimie
 - 7 - Mathématique
 - 8 - Pôle Physique / OPGC
 - 9 - BMIU Sciences
 - 10 - STAPS
 - 11 - Polytech'
 - 12 - ISIMA
 - 13 - Pôle commun CUST / ISIMA
 - 14 - École de Chimie
 - 15 - Pôle chimie
 - 16 - CNEP
 - 17 - Maison de la Vie Étudiante
 - 18 - IUT Clermont I
 - 19 - Résidence Étudiante
 - 20 - Restaurant Universitaire
 - 21 - CEMAGREF
 - 22 - IFMA
 - 23 - CIRI
- Bus - Ligne 13
 - Arrêt de bus
 - Tram
 - Arrêt de Tram



Program

➤ Wednesday December 7th 2011: first day

16h00 Registration

18h00 Opening ceremony

19h00-22h00 Welcome reception

➤ Thursday December 8th 2011: second day

Opening Conference : Metabolomics and Environment (*Chairwoman: A.-M. Delort*)

9h00 *Pr Philippe SCHMITT-KOPPLIN (C1)*

Metabolomics and Environment; a unified approach in Environment and Biology research

Session 1 Analytical chemistry Part 1 (*Chairpersons: M. Filella, J. Schwarzbauer*)

10h00 Conference (C2):

Dr Branislav VRANA

Passive samplers: towards a better characterization of water quality

11h00 *Coffee break / Posters session*

11h30 Oral communication (O1):

G. BONDOUX, A. GLEDHILL, J.-M.-JOURMIER

Using UPLC/QToF and UPLC/Ion Mobility/TOF for the determination of pollutants and transformation products in environmental samples

11h45 Oral communication (O2) :

O. POLYAKOVA, D. MAZUR, K. SOROCHKINA, M. BOLSHOV, I. SEREGINA, A. LEBEDEV

Pollution of Moscow air: Study of snow samples

12h00 Oral communication (O3):

J. COTTON, M. MARIE, G. MADALINSKI, V. SABARLY, S. MASCLET, J. PEROT, C. JUNOT, B. CORMAN

Current status assessment of the quality of Underground waters by metabolomic approach based on high resolution mass Spectrometry

12h15 Oral communication (O4) :

E. PARASKEVAS, K. BOYD, S. GIBB

Multivariate optimization of HPLC-TOF/MAS for determination of pharmaceutical residues in the environment

- 12h30 Oral communication (O5):
N. CIMETIERE, I. SOUTREL, M. LEMASLE, A. LAPLANCHE, F. BELARBI, A. CROCQ
 Standard addition method for the determination of pharmaceutical by SPE-LC-MS/MS in drinking water
- 12h45 Oral communication (O6):
N. MORIN, C. MIÈGE, J. CAMILLERI, C. CREN, M. COQUERY
 Determination of uptake kinetics and sampling rates for 56 polar organic micropollutants and evaluation of 5 potential PRCs using "pharmaceutical" pocis
- 13h00 *Lunch*
- Session 2: Atmospheric chemistry** (*Chairpersons: M. Leriche, M. Brigante*)
- 14h30 Conference (C3):
Dr Ulrich POSCHL
Multiphase Processes Connecting the Atmosphere and the Biosphere
- 15h30 Oral communication (O7):
J. BESSE, B. DAVID, J.-L. BESOMBES, E. NAFFRECHOUX
 Volatilization of svoc from mountain soils, computational and experimental data
- 15h45 Oral communication (O8):
T. NUNES, B. MARQUES, S. ABREU, A. LILLEBØ
 Contribution of salt marsh vegetation to the mobilization of Hg between sediment/water column to the atmosphere
- 16h00 Oral communication (O9):
A. LUPASCU, K. SELLEGRI, E. FRENEY, J. BOULON, G. FORET, G. SIOUR, A. COLOMB, J. M. PICHON, W. WOBROCK
 The influence of emissions database and nucleation schemes on mesoscale modeling of aerosol physical and chemical properties
- 16h15 Oral communication (O10):
L. DEGUILLAUME, M. VAITILINGOM, M. JOLY, Y. LONG, T. CHARBOUILLOT, N. CHAUMERLIAC, M. LERICHE, M. SANCELME, P. AMATO, V. VINATIER, M. BRIGANTE, G. MAILHOT, A.-M. DELORT
 Understanding biological and photochemical impacts on cloud multiphase chemistry: an interdisciplinary approach
- 16h30 Oral communication (O11):
Y. DUPART, B. D'ANNA, C. GEORGE
 Mineral dust photochemistry induces particle nucleation in presence of SO₂.

16h45 Oral communication (O12):
D. VIONE, V. MAURINO, A. BEDINI, D. BORGHESI, C. MINERO
 Phenol transformation upon irradiation of atmospherically relevant
 quinoid compounds

17h00 *Coffee break*

17h30-19h30 Poster session

➤ Friday December 9th 2011 - third day

Session 3 : Chemistry in the aquatic compartments (*Chairpersons: P. Trebse, C. Richard*)

8h30 Conference (C4):
Pr Kristopher McNEILL
"Environmental photochemistry of proteins, peptides and amino acids"

9h30 Oral communication (O13):
Š. MECHORA, M. GERM, V. STIBILJ
 Effect of selenite on three water plants

9h45 Oral communication (O14):
J. DECOONINCK, M. BAUDU, J.-P. BASLY, M. I. VILLAESCUSA GIL
 Preparation of composite biopolymers/adsorbent or oxidant materials
 for the removal of inorganic and organic pollutants

10h00 Oral communication (O15):
D. PUJOL, F. DE LA TORRE, J. POCH, N. FIOL, I. VILLAESCUSA
 Cr(VI) removal from Cr(VI)-Cu(II) binary mixtures using grape stalks
 packed columns

10h15 *Coffee break/Posters session*

11h00 Oral communication (O16):
M.-H. DÉVIER, N. TAPIE, A. BELLES, K. LE MENACH, M. GONZALEZ-REY,
 M. BEBIANNO, B. ECHAVARRI ERASUN, J. ANTONIO JUANES DE LA PEÑA, H.
 BUDZINSKI
 Monitoring of organic pollutants in marine and estuarine harbour areas
 using passive water samplers

- 11h15 Oral communication (O17):
B. OURSEL, C. GARNIER, G. DURRIEU, S. MOUNIER, Y. LUCAS
 Marseille agglomeration (SE, France) inputs to coastal waters:
 contaminant behaviour study in the wastewaters/ rivers mixing with
 sea
- 11h30 Oral communication (O18):
E. LAURENT, L. MONDAMERT, J. FRÈRE, J. LABANOWSKI
 Impact of urban pollution on water and biofilm composition along the
 Vienne river watershed
- 11h45 Oral communication (O19):
**A. ITURREGI, N. ARRIETA, G. ARANA, A. SARMIENTO, I. MARTÍNEZ-
 ARKARAZO, J.M. MADARIAGA**
 Characterization of the materials trapped in a beachrock of the Nerbioi-
 Ibaizabal estuary (Arrigunaga Beach, Bay of Biscay)
- 12h00 Oral communication (O20):
**F. TEMUSSI, M. DELLA GRECA, M. ROSARIA IESCE, L. PREVITERA, A.
 ZARRELLI, M. LAVORGNA, M. ISIDORI**
 Transformation of xenobiotics during chlorine disinfection
- 12h15 Oral communication (O21):
H. LIPŠOVÁ, V. SVÁTA, J.V. DATEL, J. JIRKOVSKÝ
 Novel photochemical procedure for remediation of contaminated
 groundwaters
- 12h30 *Lunch*
- Session 4 : Chemistry in the terrestrial compartments** (*Chairpersons: I. Villaescusa,
 V. Prévot*)
- 14h00 Conference (C5):
Pr Colin BROWN
Transport and transformation of xenobiotics in soil
- 15h00 Oral communication (O22):
D. FANGUEIRO, S. RODRIGUES, E. PEREIRA
 Potential Nitrogen mineralization in soils contaminated with
 potentially toxic elements
- 15h15 Oral communication (O23):
**M. C. AFFHOLDER, F. PEREZ, P. PRUDENT, I. LAFFONT-SCHWOB, B.
 COULOMB, V. MASOTTI, J. RABIER**
 Heavy metals and metalloids tolerance of Rosemary: contamination
 levels and stress biomarkers
- 15h30 Oral communication (O24):
P. ŠTREKELJ, I. KREFT, V. STIBILJ
 Impact of selenium treatment and differences in heavy metals uptake
 by tartary and common buckwheat grown in contaminated soil from
 Mežica Valley

- 15h45 Oral communication (O25):
MC HERNANDEZ-SORIANO, A SEVILLA PEREA, MD MINGORANCE
 Fingerprinting of soil organic matter pools upon soil amendment with waste materials
- 16h00 Oral communication (O26):
J. SCHWARZBAUER, P. RIEFER, T. KLAUSMEYER, A. SCHÄFFER, B. SCHMIDT
 Formation of bound residues in soil derived organo-clay complexes and its relevance for the assessment of pesticide contamination in soils
- 16h15 Oral communication (O27):
B. S. JOVANČIĆEVIĆ, M. ANTIĆ, T. ŠOLEVIĆ-KNUDSEN, V. BEŠKOSKI, G. GOJGIĆ-CVIJOVIĆ, M. M. VRVIĆ
 The influence of bioremediation conditions on the degradation of phenanthrene and its methyl isomers in petroleum-type pollutants
- 16h30 *Coffee break/Posters session*

Analytical chemistry Part 2 (Chairpersons: C. Mousty, A. Lebedev)

- 17h00 Oral communication (O28):
O. GÓMEZ-LASERNA, N. PRIETO-TABOADA, H. MORILLAS, M. OLAZABAL, J. M. MADARIAGA
 Multianalytical measurements to assess the impacts of acidic infiltration waters and atmospheric pollution.
- 17h15 Oral communication (O29):
S. BUDAL, M. FRANKO
 Highly sensitive and rapid flow injection assays for detection of ammonium and biogenic amines in environmental and related samples
- 17h30 Oral communication (O30):
L.A. KARTSOVA, E.A. BESSONOVA, A.A. SIDOROVA, A.V. ALEKSEEVA
 Complexation processes in chromatographic and electrophoretic determination of bioactive compounds
- 17h45 Oral communication (O31):
H. DEMEY, M. RUIZ, A. CANADELL, J. BARRÓN-ZAMBRANO, A. M. SASTRE
 Batch adsorption of boron onto composites of alginate gel beads and alumina
- 18h00 Poster session
- 19h00 ACE general assembly (Association of Chemistry and the Environment)
- 20h30 *Gala dinner*

➤ Saturday December 10th 2011 - fourth day

Session 5 : Sustainable chemistry (Chairpersons: M. Costa Gomes, P. Stepnowski)

- 8h30 Conference (C6):
Dr Stefan STOLTE
(Eco)toxicity and biodegradation of ionic liquids- progress in designing inherently safer chemicals
- 9h30 Oral communication (O32):
Y. DENG, P. BESSE-HOGGAN, M. COSTA GOMES A.-M. DELORT, **P. HUSSON**, M. SANCELME
Oxygen-functionalized ionic liquids: candidates for a sustainable chemistry?
- 9h45 Oral communication (O33):
G. CHATEL, C. GOUX-HENRY, **N. KARDOS**, E. NAFFRECHOUX, J. SUPTIL, B. ANDRIOLETTI, M. DRAYE
Smart approach for enantioselective alkene epoxidation by hydrogen peroxyde using combination of ultrasound, ionic liquid and porphyrin.
- 10h00 Oral communication (O34):
R. KOURIEH, D. STOSIC, V. RAKIC, S. BENNICI, A. AUROUX
Influence of the acid-base properties of oxide catalysts in fructose dehydration to 5-HMF
- 10h15 Oral communication (O35):
J.M. FONTMORIN, S. HUGUET, F. FOURCADE, D. FLONER, F. GENESTE, A. AMRANE
Electrochemical oxidation of 2,4-D: analysis of degradation by products and improvement of the biodegradability
- 10h30 Oral communication (O36):
K. BARTHÉLÉMY, S. NAILLE, C. RUBY, M. MULLET
Iron(III) oxyhydroxycarbonate, ferric green rust, as a new material for phosphate removal
- 10h45 Oral communication (O37):
A. M. HERNÁNDEZ-MARTÍNEZ C. PADRÓN-SANZ
Determination of heavy metals on the Mediterranean endemic plant *Posidonia oceanica* using the green extraction method: "Microwave assisted micellar extraction" and gfaas
- 11h00 Coffee break/Posters session
- 12h00 Oral and poster presentations awards
- 12h30 Closing ceremony
- 13h00 Lunch
- 15h00-17h00 Guided tour of Clermont-Ferrand

ABSTRACTS: ORAL PRESENTATIONS

Opening Conference:

Metabolomics and Environment

METABOLOMICS AND ENVIRONMENT; A UNIFIED APPROACH IN ENVIRONMENT AND BIOLOGY RESEARCH

Philippe SCHMITT-KOPPLIN et al.

¹*Department of BioGeoChemistry and Analytics, Institut für Ökologische Chemie, Helmholtz Zentrum Muenchen, Ingolstaedter Landstrasse 1, 85764 Neuherberg, Germany*

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<http://www.helmholtz-muenchen.de/ioec/biogeochemie-und-analytik/index.html>

From a traditional definition in the field of human health, metabolomics measures the concentrations of the large number of naturally occurring small molecules (called metabolites), that are produced as intermediates and end-products of all metabolic processes. They are measured from biological samples and body fluids such as urine, saliva, blood plasma, tissue sample; even the simple breath (exhaled breath condensates) can carry the information about the state of health.

In environmental issues the same approach can be followed looking holistically to all small molecules detectable in a given systems in various scales, integrating thus metabolites from living organisms and all their biotic/abiotic transformation products.

The total number of different organism metabolites is still unknown; some estimation ranges from a few thousands, up to 200,000 to about 1,000,000, but even this latter estimate may be conservative. Including plant and bacterial metabolites that are not necessary to keep the organism alive, also referred to as secondary metabolites, the number is enormously larger.

Modern analytical tools enable rapid and sensitive investigations using molecular *targeted* or *non targeted* approaches to diagnose status and to monitor therapies within health and environmental sciences. Metabolomic, as the comprehensive study of metabolic reactions is growing very rapidly and integrates the knowledge of earlier developed omics-branches such as *genomics*, *transcriptomics* and *proteomics*.

Further reading:

Gougeon, R.D., Ph. Schmitt-Kopplin et al. *PNAS*, 2009 vol. 106(23) 9174-9179.

Jansson, J.K., Schmitt-Kopplin, Ph. et al *PLoSone* 2009, 4(7) e6386.

Leon, C., Schmitt-Kopplin, Ph. et al *Journal of Chromatography A*, 2009, 1216(43), 7314-7323.

Liger-Belair, G., Schmitt-Kopplin, Ph. et al. *PNAS*, 2009, 106(39) 16545–16549

Rosselló-Mora, R., Schmitt-Kopplin, Ph. et al. *Nature – ISME Journal*, (2008), 2 242-253.

Schmitt-Kopplin Ph. et al. *PNAS*, (2010), 107(7), 2763–2768

Schmitt-Kopplin Ph. et al. *Anal Chem.* (2010), 82, 8017–8026

Suhre, K. and Schmitt-Kopplin, Ph. *Nucleic Acid Research*, 2008; doi: 10.1093/nar/gkn194

Session 1: Analytical chemistry
Conference

PASSIVE SAMPLERS: TOWARDS A BETTER CHARACTERIZATION OF WATER QUALITY

Branislav VRANA

Water Research Institute, Bratislava, Slovakia

branovrana@gmail.com

Passive samplers represent an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in water and sediment. Passive sampling technology is proving to be a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. These devices are now being considered as a part of an emerging strategy for monitoring a range of priority and emerging pollutants.

Passive sampling is based on the deployment in-situ, or use in the laboratory, of nonmechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of timeweighted average (TWA) concentrations in water or equilibrium pore water concentrations in sediment.

This presentation discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it lists the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of priority and emerging aquatic contaminants and availability of calibration data that enable estimation of TWA concentrations.

Session 1: Analytical chemistry – Part 1

Oral communications

USING UPLC/QTOF AND UPLC/ION MOBILITY/TOF FOR THE DETERMINATION OF POLLUTANTS AND TRANSFORMATION PRODUCTS IN ENVIRONMENTAL SAMPLES

Gérard Bondoux¹, Antonietta Gledhill², Jean-Marc-Joumier¹

¹*Waters European headquarters, Guyancourt, France gerard_bondoux@waters.com*

²*Waters Corporation, Manchester, UK*

New developments in LC/MS open multiple new possibilities for environment analysis. For routine targeted analysis, the combination of UPLC with the latest generation tandem quadrupoles instruments brings increased sensitivity, faster analysis and the possibility to continuously monitor the matrix contribution, while minimising the sample preparation. However, there is a growing demand for screening methods, which are able to find and quantitate known contaminants, from an extensive list of compounds, and simultaneously provide information to identify unexpected compounds

These needs are well covered by using high resolution instrument, like UPLC/QToF served by advanced software tools. This approach will be detailed and illustrated with surface water and waste water examples.

When working on transformation products, one of the challenges is to propose or to confirm the structure corresponding to a given elemental composition. Ion mobility spectrometry separates species according to their shape, mass or charge state. This technique, implemented in a QToF geometry instruments opens different possibilities including the separation of isomers, conformers as well as isobaric species which can aid the confirmation of a proposed structure and overall the simplification of data interpretation. The approach will be illustrated with pesticides and pharmaceutical molecules transformation products.

POLLUTION OF MOSCOW AIR: STUDY OF SNOW SAMPLES

Olga Polyakova, Dmitry Mazur, Khristina Sorochkina, Mikhail Bolshov, Irina Seregina,
Albert Lebedev

Chemistry Department, Moscow State Lomonosov University, Moscow, 119991, Russia

Moscow is the largest European city with population about 15 millions and hundreds of enterprises. More than 4 millions cars are registered in Moscow. However just the most common pollutants are monitored in the city at the regular basis. To propose a list of priority pollutants for the atmosphere of Moscow 8 snow samples were collected along the perimeter (109 km) of the Moscow belt road at the end of March 2011. Mass spectrometry was used as an analytical tool to identify individual organic compounds (gas chromatography/mass spectrometry, GC/MS) and the most environmentally relevant chemical elements (inductively coupled plasma with mass spectrometric detection, ICP-MS). Sample preparation was carried out according to US EPA 8270 and 200.8 Methods procedures, while LECO Pegasus IVD and Agilent 7500c instruments were used correspondingly. Both target and non-target approaches were used. As a result more than 500 organic compounds belonging to various classes were identified in each sample. Besides classic pollutants like PAH, PCB, phthalates several classes of other anthropogenic contaminants including, organophosphates, esters of N,N-diethylcarbomodithioic acid antioxidants, and some others were represented by a notable number of compounds. The confirmation of the identification was obtained by consecutive analysis of all the samples with LECO Pegasus GC-HRT instrument with the resolving power exceeding 25000. Several valuable issues concerning reliability and new possibilities for the identification of new compounds were discovered when dealing with a high resolution instrument.

The levels of organic compounds using internal standards as well as the levels of chemical elements were quantified. The data obtained allow estimating atmospheric pollution in Moscow in the period between December and March 2011 and proposing a draft list of priority pollutants for the atmosphere of Moscow.

CURRENT STATUS ASSESSMENT OF THE QUALITY OF UNDERGROUND WATERS BY METABOLOMIC APPROACH BASED ON HIGH RESOLUTION MASS SPECTROMETRY

Jérôme Cotton¹, Mylène Marie¹, Geoffrey Madalinski¹, Victor Sabarly¹, Sébastien Masclet², Jean Perot², Christophe Junot³ and Bruno Corman¹

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Industrial wastes, phytosanitary compounds and drugs often pollute environmental water resources at the origin of drinking water. The presence of all these chemicals at different concentration levels in environment is a real public health issue. Thereby, the monitoring of water quality by a global metabolomic approach was performed in this study. The presence of xenobiotic compounds was researched by acquiring chemical fingerprints from 15 underground water springs spread on the French territory. This work was led in collaboration with the company SAUR, one of the main operators for local authorities in the fields of water and waste management in France. Experimentally, after a thousand-fold concentration step of the samples performed by solid phase extraction (SPE), fingerprints were acquired by LC/FTMS on an ultra-high resolution Orbitrap mass spectrometer after electrospray ionization (Thermo Fisher Scientific, San Jose, CA, USA). This method enabled the recovery of fingerprints comprising between two and three thousand peaks per sample in each of the two ionization polarities. This comprehensive approach highlighted many chemicals including drugs, pesticides, fungicides and industrial compounds. Multivariate statistical treatments allowed the discrimination of water springs on the basis of several criteria such as geographical localization or the environment of the channeling wells. In one hand, these results will contribute to achieve drinking water quality beyond the French and European regulatory frameworks. In another hand, they will guide SAUR for its prevention policy in terms of environmental pollution.

Keywords: Underground waters, micro-pollutants, LC/FTMS, Orbitrap technology, global analysis, metabolomics.

MULTIVARIATE OPTIMISATION OF HPLC-TOF/MS FOR DETERMINATION OF PHARMACEUTICAL RESIDUES IN THE ENVIRONMENT

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In the last decade, human pharmaceuticals have been measured at ng/L to µg/L levels in waste and natural waters in many countries. However, given the large number of pharmaceuticals currently licensed for use and their diverse structural and chemical properties, development of a sensitive analytical methodology with broad utility, sensitivity and applicability is an extensive and highly challenging process.

Statistical tools like Box-Behnken Design (BBD) or Central Composite Design (CCD) with Response Surface Methodology (RSM) have been shown to be effective in reducing the number of experiments needed for optimisation processes (in comparison to a univariate approach) and in identifying complex interactions between experimental factors. In this work we apply CCD and BBD with RSM to the optimisation of a HPLC-TOF/MS protocol for quantification of pharmaceuticals from therapeutic classes including beta-blockers, antifungals and antidepressants.

Optimisation was conducted in four stages. Firstly, optimisation of ion formation inside the ion-source (capillary exit and skimmer voltages), secondly ion-transfer into the TOF/MS (capillary voltage, drying gas flow rate and drying temperature). The third step was to optimise HPLC elution conditions and the last was to address the SPE parameters.

The result, achieved with a low number of experiments, was an analytical methodology optimised for nineteen priority pharmaceuticals from seven pharmaceutical classes. LOQ values ranged from 4 ng/L for Amphetamine to 40 ng/L for Ibuprofen. The study demonstrated that statistical tools like BBD and CCD with RSM can be used to promote the performance of analytical methodologies for the determination of low-level environmental contaminants.

STANDARD ADDITION METHOD FOR THE DETERMINATION OF PHARMACEUTICALS BY SPE-LC-MS/MS IN DRINKING WATER

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Human and veterinary use of pharmaceuticals compounds leads to the releasing of bioactive compounds in aquatic environment. Some pharmaceuticals compounds are not completely removed during waste-water treatment, and can be detected in surface and drinking waters. Some recent studies show that pharmaceuticals are generally less eliminated than other micro-pollutants by conventional sewage treatments and pharmaceuticals concentrations up to 100 ng L⁻¹ can be detected in the effluent.

Determination of 29 pharmaceuticals in the nanogramme per liter range has been performed by solid phase extraction (SPE) with a concentration factor equal to 1000. Acid and neutral SPE steps are necessary in order to reach acceptable yield of extraction for all of the 29 compounds. Aliquots were then analyzed using ultra performance liquid chromatography (UPLC)/tandem mass spectrometry detection.

Most of the analytes can be quantified under ESI + mode with water/acetonitrile mobile phase. Some compounds (hydrochlorothiazide, hydroxyibuprofène, pravastatin, β -estradiol, ethinyl estradiol, estrone, ibuprofen) were poorly quantified under acid conditions. The determination of these molecules was carried out with a neutral water / acetonitrile eluent with ESI- mode. Quantification limit, obtained with this method in pure water, ranges from 1 to 5 ng L⁻¹. Standard addition method was performed in order to solve the matrix effect problems. In addition to a reliable quantification of samples in complex matrix, this method allows to highlight the matrix effect for the 29 selected molecules, even if the molecules are not initially present in the samples. This method was used to study the fate of these molecules in raw water and throughout the drinking water treatment process.

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DETERMINATION OF UPTAKE KINETICS AND SAMPLING RATES FOR 56 POLAR ORGANIC MICROPOLLUTANTS AND EVALUATION OF 5 POTENTIAL PRCs USING “PHARMACEUTICAL” POCIS

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POCIS (Polar Organic Chemical Integrative Sampler) is a recent integrative sampler made for sampling polar organic micropollutants in water. It is still in development concerning its domain of validity (e.g., molecules sampled, type of water studied, optimal exposure duration) and its performances (molecules sampling rates, repeatability, accuracy of the evaluation of time-weighted average concentrations - TWAC).

In order to obtain *in situ* TWAC, POCIS needs to be calibrated in laboratory for each molecule of interest. In this work, we performed laboratory calibration of POCIS for 5 alkylphenols, 9 hormones, 11 pesticides, 27 pharmaceuticals, 3 phenols and 1 UV filter in a flow-through system. The system is composed of 2 aquaria (50 L) containing: i) spiked tap water (circa 3 µg/L for each studied molecule) and non-spiked POCIS, for the determination of accumulation kinetics or ii) non-spiked tap water and spiked POCIS, for the determination of desorption kinetics.

We present results for the different studied molecules, including the duration of linear accumulation phase, sampling rates and possible performance reference compounds (PRCs). The accumulation phase was curvilinear for almost all molecules; so, we obtained the duration of optimal linear accumulation phase using $t_{1/2}$ criteria. Concerning the desorption experiments, 5 compounds showed a good potential as PRC; they enable to decrease the effect of variable environmental conditions, so they can be used to obtain more reliable TWAC *in situ*. At last, we checked isotropic exchange for these molecules comparing the exchange constant k_e in accumulation and desorption experiments.

Session 2: Atmospheric Chemistry
Conference

MULTIPHASE PROCESSES CONNECTING THE ATMOSPHERE AND THE BIOSPHERE

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Gas-particle interactions are relevant for many key processes in the Earth system linking the atmosphere, biosphere, and public health. General features of multiphase chemical kinetics will be outlined, and recent results of laboratory, field, and model studies investigating the chemical aging of organic aerosols, the formation of clouds, and the influence of air pollutants on allergies will be discussed.

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Session 2: Atmospheric Chemistry

Oral communications

VOLATILIZATION OF SVOC FROM MOUNTAIN SOILS, COMPUTATIONAL AND EXPERIMENTAL DATA

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An organic pollution of mountain soils from Bauges (Revard) in the French Alpes has been experimentally evidenced by registering the corresponding PAH and PCB levels in environmental matrixes (air, soil, snow, water). The volatilization of semivolatile organic compounds (SVOC) from soils towards the atmosphere is not yet extensively studied in the literature whereas this phenomenon can be of health concern, especially during summer period. In this work, the quantification of PAH flows volatilized from two different mountain soils, rich and poor in natural organic matter, has been studied by means of computational models developed by the Centre for Environmental Modelling and Chemistry (Level I and SOIL[®] - 2011) and by experimental analyses. Level I is based on the prediction of the partition of SVOC in the air, aerosols, soil, water, suspended matter, sediments and fishes whereas SOIL model focuses on the partition of SVOC within the soil: organic and mineral matter, gaseous phase, soil solution and roots. Level I gives results for a stabilized system and allows to access to the preferential compartment of accumulation of the pollutant of interest without taking into account the degradation reactions, the advection processes or the intermediate ways of transport of the pollution (wet and dry depositions). The SOIL model leads to the identification of the main ways of SVOC transfer especially towards the volatilization and degradation. Results computed with both previous models are then compared to experimental data got on the site, where PAH concentration levels are measured in the air (1.5 m above the soil), at the soil surface (3 cm above, corresponding to the volatilization), in the soil itself and in waters (infiltration water and soil solution) leading to the corresponding mass balance of compounds studied.

CONTRIBUTION OF SALT MARSH VEGETATION TO THE MOBILIZATION OF Hg BETWEEN SEDIMENT/WATER COLUMN TO THE ATMOSPHERE

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Past releases of mercury have created a “global pool” that constitutes a legacy of this priority pollutant in the environment. Mud flats in estuarine systems have been acting as sinking traps retaining contaminated fine sediments and confining large amounts of mercury. This mercury legacy is a today’s issue of concern and a potential source of dispersion to the atmosphere and surrounding compartments. Climate changes and global warming tend to increase both surface sediment temperature and period of sunlight exposure affecting in this way mercury volatilization processes, and consequently increasing transference rates of mercury to the atmosphere. Therefore, past contaminated surface sediments, that are already a today’s problem, may exacerbate its role enhancing mercury dispersion processes, including additional inputs to the global atmospheric circulation. Mercury can be transported globally to regions far from its source, meaning that some pollution of a local character, viewed in the short term, adds to the global pool in the long term, leading to contamination of regions with few or no mercury sources; therefore mercury deposits are a “heavy” legacy where each spot has to be assumed and taken into account.

In this study, we evaluate the re-emission of Hg in a contaminated area of Ria de Aveiro, a inner basin called Laranjo where more than 25 tonnes of mercury are estimated to be stored in the sediments after years of industrial chlor-alkali discharges (e.g. Abreu *et al.*, 1998; Pereira *et al.*, 2009). In order to distinguish sediments and biota Hg export in the interface biosphere/atmosphere a set of mesocosmos experiments were performed under controlled conditions with mud and mud + vegetation (*Scirpus maritimus* and *Juncus maritimus*) cores taken from one of the most contaminated basin area (Marques *et al.*, 2011). Parallel experiences with the two types of cores were performed, using a dynamic box technique to measure Hg fluxes. The results showed that vegetation has a strong impact in the exportation of Hg to the atmosphere during day period, which could achieve more than twice the fluxes of a similar area without vegetation cover.

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THE INFLUENCE OF EMISSIONS DATABASE AND NUCLEATION SCHEMES ON MESOSCALE MODELING OF AEROSOL PHYSICAL AND CHEMICAL PROPERTIES

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The ability of chemistry-transport models (CTMs) to accurately simulate aerosols at high altitude stations is still to be demonstrated due to the small number of monitoring sites and difficulties to take into account the complexity of the air parcels dynamics in mountainous areas. Input information, such as emissions, has a strong influence on model results. The objective of this study is to evaluate the ability of the regional air-quality model CHIMERE coupled with WRF meteorological model to simulate the atmospheric composition as a function of altitude, with a focus on aerosol properties, for two sets of emissions: EMEP and MACC European emissions.

An intensive campaign was organized from February 24 to March 9, 2009 at the Puy de Dome station in France using an Aerosol Mass Spectrometer and a Scanning Mobility Particle Sizer, which provide the size distribution and the source-apportioned chemical composition with high temporal resolution. The high altitude measurements were used together with ground based measurements in the boundary layer in order to assess the performances of model simulations for gaseous and aerosol pollutants. Because particle nucleation has been shown to significantly contribute to the aerosol number concentration in the boundary layer, but its impact on the adjacent free atmosphere is quite uncertain, we also investigated the role of different nucleation schemes on the aerosol size distributions.

Keywords: Air pollution; Chemistry-transport models; Emissions; Aerosol size distribution; Number concentration; Nucleation

UNDERSTANDING BIOLOGICAL AND PHOTOCHEMICAL IMPACTS ON CLOUD MULTIPHASE CHEMISTRY : AN INTERDISCIPLINARY APPROACH

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The atmosphere is a complex multiphase compartment which contains basically 3 phases connected through thermodynamical and microphysical processes: gas, liquid and solid particles. Historically, the field of atmospheric chemistry has focused on gas-phase oxidations as the primary fate determining processes of chemical substances in the troposphere. However, aqueous phase chemical and photochemical transformations in atmospheric water drops (cloud, fog and rain drops) can significantly affect the chemical composition of the atmosphere. Clouds favour the development of “multiphase chemistry” since they are an ideal reaction medium for this. Multiphase cloud chemistry strongly perturbs homogeneous gas phase chemistry and also modifies physico-chemical properties of aerosol particles that nucleate or/and are scavenged by impaction. Formation of clouds is consequently modified and this action remains one of the main uncertainties about the climate models assessing the Earth's radiative balance.

In this context, photochemical processes have to be considered due to their high efficiency in clouds. Multiple radicals produced in clouds oxidize pollutants but their sources need to be better estimated. The recent concept of biocatalysed reactions induced by microorganisms has also to be investigated in details and confronted to photochemistry. Finally, the coupling of the two processes and their integration in cloud chemistry numerical models are essential to go further.

In this talk, we will present how biological and photochemical impacts on multiphase cloud chemistry are studied in our research team by combining laboratory experiments, field measurements, and modelling studies. Major results will be presented.

MINERAL DUST PHOTOCHEMISTRY INDUCES PARTICLE NUCLEATION IN PRESENCE OF SO₂

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Every year an estimated one to three thousand teragrams of mineral dust are emitted into Earth's atmosphere, largely through the action of wind erosion over arid and semi-arid regions. The residence time of mineral dust particles in the atmosphere of up to several weeks and the thousands of kilometers over which they may be transported allow ample time and exposure for dust particles to interact with other atmospheric constituents. In the present work, we report the interaction of mineral dust proxies with gaseous SO₂ and the dependence of this heterogeneous reaction on ultraviolet irradiation and availability of water vapor. We find that the interaction under irradiation leads to the formation of new ultrafine particles. Our proposed mechanism for the observed particle nucleation suggests that the metal oxides present in mineral dust serve as photocatalysts that promote the production of OH radicals, which initiate the conversion of SO₂ to sulfuric acid. Sulfuric acid is a proven precursor in the nucleation of atmospheric particles, and this finding may shed new light in the current effort to demonstrate sulfuric acid particle formation rates as high as those needed to explain atmospheric concentrations. Our conclusions are supported by ambient measurements, where a relationship between the formation of new particles and the concentration of dust particles has been observed.

PHENOL TRANSFORMATION UPON IRRADIATION OF ATMOSPHERICALLY RELEVANT QUINOID COMPOUNDS

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Photochemical processes taking place at the surface of atmospheric particulate matter are potentially important pathways for the transformation of organic and inorganic compounds. Some of the cited reactions are sensitised by photoactive molecules such as aromatic carbonyls, furans and quinones. Radiation absorption by quinones causes the formation of the excited singlet states and of the triplet states by a usually efficient inter-system crossing. Quinone triplets are reactive transients that can induce the transformation of other compounds by transfer of electrons, hydrogen atoms or energy. Here the degradation of phenol as model organic compound has been studied in aqueous solution in the presence of 2-ethylanthraquinone, benzanthracene-7,12-dione, 5,12-naphthacenequinone, 9,10-anthraquinone and 2,6-dihydroxyanthraquinone, which have all been detected on atmospheric particulate matter. 9,10-Anthraquinone and 2-ethylanthraquinone showed the highest quantum yields for phenol transformation, while 2,6-dihydroxyanthraquinone had the lowest one. We carried out a DFT study of electron spin distribution in the triplet state, showing that the most effective compounds have the spin density concentrated on the carbonyl groups, while 2,6-dihydroxyanthraquinone has most of the spin density on the aromatic ring. The reaction kinetics between phenol and 2-ethylanthraquinone suggests that the quinone triplet state would abstract an electron or a H-atom from phenol. Involvement of $^1\text{O}_2$ or $\bullet\text{OH}$ could be excluded. The main phenol transformation intermediates were phenoxyphenols and dihydroxybiphenyls, suggesting that phenoxy radicals are being produced in the reaction. The formation of phenol dimers indicates that quinones could potentially contribute to the generation of humic-like substances, which are thought to be formed in the atmosphere from precursors with lower molecular weight.

Session 3: Chemistry in the aquatic Compartments
Conference

THE ENVIRONMENTAL PHOTOCHEMISTRY OF PROTEINS, PEPTIDES AND AMINO ACIDS

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Amino acids, oligopeptides and proteins are central building blocks of life and of key importance in the biogeochemistry of aquatic systems. In these systems, amino acids at different levels of structural organization are susceptible to oxidation by photochemically generated reactive oxygen species. While photochemical transformation therefore plays a key role in the environmental fate of amino acids, oligopeptides and proteins in surface waters, there are as of yet only few systematic studies on this topic. We have undertaken experiments to address this knowledge gap. Specifically, results from experiments on the photochemistry of individual amino acids, oligopeptides, and fully intact proteins will be presented. The goals of these experiments are to determine the dominant environmental processes responsible for the degradation of amino acid-based molecules in natural waters and to assess the effect of protein structure on the photochemistry of its photolabile amino acid residues.

Session 3: Chemistry in the aquatic compartments

Oral communications

EFFECT OF SELENITE ON THREE WATER PLANTS

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The effect of Se (VI) on *Myriophyllum spicatum* L. and *Ceratophyllum demersum* L. and the ability of accumulation of Se in these plants were already investigated (Mechora et al., 2011). In the present study we wanted to investigate the effect of Se (IV) and its accumulation in same aquatic plants - *M. spicatum*, *C. demersum* and additional plant with a larger leaf surface *Potamogeton perfoliatus* L. Plants were cultivated outdoors in semi control conditions in 10 mg Se/L in the form of Na selenite. Applied dose of Se negatively affected photochemical efficiency of photosystem II of all three species. There was no clear effect of Se on electron transport system activity in mitochondria. The climate conditions had a greater impact on the amount of pigments in *C. demersum* and *P. perfoliatus*, while in *M. spicatum* addition of Se affected amount of chlorophyll *a* and anthocyanins.

The duration of Se treatment depended on ability of plants to cope with Se. When half of the plants died, plants were replanted. Every group of replanted plants was given a successive number. *P. perfoliatus* from group 2 was exposed for 5 days (not the longest period) and contained the highest concentration of Se (661 µg Se/g DM). Group 5 of *C. demersum* and *M. spicatum* was exposed for the longest period (11 days) and contained 988 µg Se/g DM and 839 µg Se/g DM, respectively.

Findings showed that all three species took up a great amount of Se. In treated plants, the amount of soluble Se in enzymatic extracts was 30% in *M. spicatum*, 49% in *C. demersum* and 36% in *P. perfoliatus*. Soluble Se species in extracts will be separated and detected using HPLC (anion and cation exchange column) coupled to ICP-MS.

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PREPARATION OF COMPOSITE BIOPOLYMERS/ADSORBENT OR OXIDANT MATERIALS FOR THE REMOVAL OF INORGANIC AND ORGANIC POLLUTANTS

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The use of renewable bioresources allows the development of low cost adsorbents/oxidants that are versatile. It is the reason that physically reactive (adsorption) and chemically reactive (oxidation) materials were prepared in a grain form encapsulated in alginate. In the present work, the affinity and the removal capacity of activated carbon/alginate beads for an hydrophobic organic pollutant (4-Nitrophenol) and an inorganic pollutant (Copper) were evaluated. This capacity was linked with the mechanical properties of the microcapsules for an implementation in such filtering bed reactor. Those properties were investigated under different encapsulation's conditions: introduction of a second polymer (Carboxymethylcellulose: CMC), modification of the cation, dehydration, alginate viscosity. The impact of encapsulation on the material's reactivity was also studied (kinetic and diffusion studies). The introduction of a variable ratio of CMC increased the resistance of the beads and decreased the adsorption capacity and the intraparticle diffusion coefficient. The dehydration/rehydration process could be an interesting way by increasing by 1000 the mechanical properties.

Key Words: Sodium alginate, activated carbon, encapsulation, adsorption, paranitrophenol, copper, mechanical properties, kinetic.

CR(VI) REMOVAL FROM CR(VI)-CU(II) BINARY MIXTURES USING GRAPE STALKS PACKED COLUMNS

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In order to decrease wastewaters treatment costs, sorption processes by using low cost sorbents are being studied for metal removal. In previous works, grape stalks resulted to be efficient for metal ions removal from aqueous solutions and particularly for the elimination of Cr(VI)[1].

Electroplating industries wastewaters usually contains mixtures of Cr(VI) and Cu(II) at high concentrations in their exhausted chromium baths. It's well known that Cr(VI) is the most toxic chromium species, for this reason is important find an efficient treatment for eliminate Cr(VI) in mixtures with others metals. Taking into account these facts we studied the simultaneous removal of the mixture Cr(VI)- Cu(II) by using grape stalks as sorbent.

Adsorption experiments were carried out by pumping a equimolar Cr(VI)-Cu(II) solution through a fixed bed column packed with grape stalks with particle size between 1-1.5mm. The effect of operating parameters such as flow rate, initial metal concentration and bed depth were evaluated. Results showed that the sorption capacity of grape stalks increases with the flow rate decrease. The best results were obtained for a flow rate of 1.5 mL/min, therefore this flow rate was selected to perform the subsequent experiments. The obtained breakthrough curves obtained at different operating conditions were modeled by using Adams-Bohart, Thomas and Yoon-Nelson models. As modeling has an important role in technology transfer from laboratory to industrial scale, the bed depth service time model (BDST) has been applied to predict the column service time.

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MONITORING OF ORGANIC POLLUTANTS IN MARINE AND ESTUARINE HARBOUR AREAS USING PASSIVE WATER SAMPLERS

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The Interreg PORTONOVO project intends to standardize a methodology for the water quality management in port areas all along the Atlantic Area. The interconnected activities of the project, leading to the installation of a tool allowing a balanced management of activities in harbour waters, will be briefly presented. A particular focus will be then on the monitoring of the chemical quality in harbours, notably using passive sampling techniques which represent a promising complementary approach relevant to the Water Framework Directive (WFD).

Knowledge on the presence of organic pollutants, in particular emerging contaminants, in coastal and transitional waters is very limited. In this project, POCIS (*Polar Organic Contaminant Integrative Samplers*) have been deployed in three harbour areas for the monitoring of about 50 pesticides and 20 pharmaceutical substances in water. Numerous target compounds were detected, more particularly in the Gironde estuary. The most frequently detected pesticides in harbours were the priority substances, some biocides also used in antifouling paints, and the herbicide metolachlor, as well as some of their metabolites. Among pharmaceuticals, mainly non-steroidal anti-inflammatory drugs were also frequently found. The passive samplers also allowed the detection of numerous other target compounds at very low concentrations (<0.1 ng/L).

MARSEILLE AGGLOMERATION (SE, FRANCE) INPUTS TO COASTAL WATERS: CONTAMINANT BEHAVIOUR STUDY IN THE WASTEWATERS/RIVERS MIXING WITH SEA

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Coastal ecosystems in the Mediterranean Sea are known to be strongly influenced by continental inputs from large rivers but also small coastal ones. Inputs of urban areas, such as Marseille city (~ 1.7M Ha), should be investigated. The objectives of the GIRAC-PACA and MARSECO projects are (1) to quantify the contaminants brought to the sea by the Marseille city, (2) to study their impact on the coastal zone and (3) to characterize the relationships between pollution levels, contaminant distribution between dissolved and particulate fractions and type of particles, in order to evaluate contaminant net fluxes to the marine environment. Sampling campaigns were carried out during dry periods in the main tributaries upstream and downstream of the Marseille sewage treatment plant and in the freshwater/seawater mixing zone. Dissolved/particulate metals and organic carbon contents were determined after samples lab filtration. Results showed a conservative trend of the studied elements in the salinity gradient. To assess such behaviour, a remobilization experiment was carried out in lab by mixing unfiltered tributaries water with filtered seawater at different mixing ratios, followed by dissolved metal analysis. The results showed a different trend with a time-dependant metal desorption at low salinities. To clarify this contradiction, a new sampling campaign was realized along the salinity gradient: an aliquot of each sample was immediately filtered; the rest was treated using the classical protocole (storage and lab filtration after 4h). Results showed that dissolved/particulate metal distributions were not at equilibrium in the wastewater/river inputs resulting in an important and rapid metal desorption in the salinity gradient. Such a phenomenon, completely undetectable using the classical sample treatment protocole, indicates that contamination of organisms along the coast can be higher than expected.

IMPACT OF URBAN POLLUTION ON WATER AND BIOFILM COMPOSITION ALONG THE VIENNE RIVER WATERSHED

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Nowadays, the preservation of water resource is one of the main concern of public health. Policies and action plans are regularly implemented to protect the quality of natural waters. Physical pressures (water uptake) and chemical pollutions (urban wastewaters, agriculture, industries...) on these water resources have, in the past, led to their deterioration. From many years, scientists interest in the fate and behavior of chemical pollutants (heavy metals, organics) released by human activities. Now, it is well accepted that the watershed approach is the most effective framework to address the highest priority problems (within hydrological-defined geographic areas), taking into consideration both source of pollution and surface water flow. Recent works suggest that monitoring some water quality bio indicators (like microorganisms living in a matrix adhered into submerged surfaces, *e.g.* rocks) provide useful information (Montuelle *et al.*, 2010). Indeed biofilms widely interact with aquatic pollutants (degradation, fixation, biological response).

This study deals with the Vienne river watershed (372 km). This basin is occupied by two main towns (50.000 and 150.000 inhabitants), several industries (paper mill industry, porcelain factory...) and agricultural practices. From the Vienne river source to confluence with the Loire river, water quality may change with geomorphology of landscape, land-use and pollution. The objective is to determine the effect of urban pollutions on the evolution of water quality and biofilm through the drainage basin. In July 2011, 47 sites were sampled (water and biofilm) from source to confluence. Global physic-chemical parameters (pH, conductivity), total nitrogen and inorganic carbon contents were followed and mineral composition was determined by ICP-OES. Specific organic matter characterization was performed by Pyrolysis-GC/MS. Results are then discussed according to the specificities of the sampling point (localization through the drainage basin, nature and source of pollution).

Montuelle, B., Dorigo, U., Bérard, A., Volat, B., Bouchez, A., Tlili, A., Gouy, V., Pesce, S., 2010. The periphyton as a multimetric bioindicator for assessing the impact of land use on rivers: An overview of the Ardières-Morcille experimental watershed (France). *Hydrobiologia* 657, 123-141.

**CHARACTERIZATION OF THE MATERIALS TRAPPED IN A
BEACHROCK OF THE NERBIOI-IBAIZABAL ESTUARY
(ARRIGUNAGA BEACH, BAY OF BISCAY)**

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Arrigunaga beach is some of the few sites located in high latitudes where beachrocks are present. These structures are formed in the intertidal zone when beach grains are cemented together due to carbonates precipitation. During the cementation process, many kind of materials can get trapped in them, such as bioclasts, sediments and anthropogenic wastes. The deterioration of the Nerbioi-Ibaizabal estuary due to wastes received during the last century, lead to promote a cleaning-up programme that started in 1979. Nonetheless, the contaminated sediments are still being transported to the mouth of the estuary, especially to Arrigunaga beach where there is a net flux induced by ocean currents. The aim of this work was to identify the grain size fraction in which metals are more concentrated in order to establish their possible sources. Most of the analysed samples belonged to a stratigraphic column of cemented sand. A granulometric separation of the samples of different strata and the subsequent examination of each grain size with a magnifying glass, allowed the recognition of the most interesting ones to characterize the metal content. The analysis performed by inductively coupled plasma-mass spectrometry (ICP-MS) revealed that the highest metal concentration (including heavy metals), belongs to the grains sized between 75 and 250 μm , in comparison with those of <75 μm . Regarding the composition, ICP-MS analysis, complemented with Raman spectroscopy and SEM-EDX, corroborated that the analysed samples are mainly composed of iron minerals as well as iron and calcium silicates enriched with aluminium and magnesium.

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TRANSFORMATION OF XENOBIOTICS DURING CHLORINE DISINFECTION

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Chlorination is by far the most used process in the disinfection step in wastewater treatment plants (WWTPs). Chlorine is often added to wastewater as a sodium hypochlorite solution and this is still the most commonly used disinfection treatment in Italy. The mixture HOCl/OCl⁻, known as free available chlorine (FAC), is a powerful non-specific oxidant, capable of inducing transformation of different micro-pollutants to products which are chlorinated, oxidized and/or to fragmentation by-products that are potentially more toxic than the parent compounds.^{1, 2} In this framework we decided to study the transformation induced by hypochlorite treatment on different xenobiotics. Selection of the products was based on the presence in the molecular structure of potentially reactive groups, on the literature data about the detection of pollutants (mainly emerging pollutants) in WWTP effluents, and on the environmental load. The experiments were performed mimicking conditions of a typical wastewater treatment process. The main transformation products were isolated by chromatographic techniques (TLC, CC, HPLC) and fully characterized employing NMR techniques and mass spectrometry experiments. The transformation pathways will also be discussed. Furthermore, in order to evaluate the environmental effects of the parent compounds and the transformation products, an overall toxicity approach was adopted considering aquatic acute and chronic toxicity testing on different organisms, mutagenesis and genotoxicity on bacterial strains.

- 1 Pinkston K. E., Sedlak D. L.; "Transformation of aromatic ether- and amine-containing pharmaceuticals during chlorine disinfection" *Environ. Sci. Technol.* (2004), 38, 4019-4025.
- 2 Della Greca M., Iesce M.R., Pistillo P., Previtiera L., Temussi F.; "Unusual products of the aqueous chlorination of atenolol" *Chemosphere* (2009), 74, 730-734.

NOVEL PHOTOCHEMICAL PROCEDURE FOR REMEDIATION OF CONTAMINATED GROUNDWATERS

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The continuing extensive occurrence of old environmental burdens in the territory of the Czech Republic is one of the historical remains of more than sixty years of government by totalitarian regimes (1938-1989) that were not greatly concerned with protection of the environment and management of harmful substances in industrial and other production. It was only after democracy was introduced in 1990 that systematic efforts have been made to remedy these old environmental burdens to a greater degree.

This work is focused on the design, technical implementation and practical realization of *in-situ* reactive barriers. In parallel, suitable contaminated sites for their application have been searched and explored as well as a novel photochemical method for the environmental remediation has been developed and tested.

Based on hydrogeological conditions and chemical contamination, four suitable sites in the Czech Republic were proposed for application of the permeable reactive barriers. Finally, an old industrial area near Ostrava in North Moravia was chosen as the most appropriate. It is located on quaternary gravel-sand deposition of the Odra river that represents a highly permeable collector. The main contaminants are aromatic hydrocarbons and their derivatives as well as inorganic substances, namely sulphate and ammonium ions.

A novel photochemical method has been developed and tested for the continuous remediation of contaminated groundwater streams. It is based on the direct photolysis of hydrogen peroxide upon intensive ultraviolet irradiation. Under such experimental conditions, majority of the molecules of hydrogen peroxide is split into hydroxyl radicals that attack unselectively all organic substrates including microorganisms. These OH-attacks initiate an oxidative degradation of the present organic molecules that are finally completely transformed into harmless inorganic products such as carbon dioxide, water and corresponding mineral acids.

Special flow-through photoreactors has been designed and constructed in different scales for laboratory experiments as well as field tests. The photoreactor consists of a quartz tube surrounded by low pressure mercury lamps, which dominantly emit at 254 nm. The continuous dosing of hydrogen peroxide was optimized as a function of flow rate, concentration of pollutants and other reaction conditions.

For laboratory experiments, 2-butoxyethanol was chosen as a representative model pollutant. Kinetics of its photoinduced degradation and oxidative mineralization in the laboratory photoreactor was followed employing UV/Vis absorption spectroscopy, liquid chromatography as well as determination of the total organic carbon. For comparison, a real contaminated groundwater was also purified under analogous reaction conditions. The results showed that the photoinduced mineralization under optimized conditions proceeds fast enough to be successfully applied in the reactive barriers.

Session 4: Chemistry in the terrestrial compartments
Conference

TRANSPORT AND TRANSFORMATION OF XENOBIOTICS IN SOIL

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Soil systems receive inputs of a range of potential pollutants including pesticides from direct application in agriculture, pharmaceuticals from spreading of sewage sludge to land, and industrial chemicals from a range of historic and current processes. Mechanistic understanding of the fate of xenobiotics is central to quantifying potential for adverse effects, remediating contamination and protecting other environmental compartments such as ground- and surface waters. The behaviour of xenobiotics in soil is a function of properties of the chemical as well as those of soil and weather. Sorption to soil particles is a primary control on transport through soil and bioavailability. Known mechanisms for sorption include non-specific hydrophobic interactions and van der Waals forces as well as specific binding mechanisms such as charge transfer and cation bridging. Nevertheless, the evidence base for specific binding processes is very sparse and considers relatively few organic chemicals. Sorption is now known to be strongly-time dependent with strength increasing markedly over time in many instances. Process-based experiments suggest that diffusion into soil organic matter and the internal micropores within soil aggregates is an important control on the kinetics of sorption.

Transformation of xenobiotics is most frequently mediated by soil microorganisms and there has been significant progress in isolating strains able to degrade specific compounds. This raises the possibility of purpose-designed inoculants aimed at remediating contaminated matrices. An ultimate goal is to quantify how fate of xenobiotics varies in space and time in order to target management of environmental contamination. Here, mathematical models are a key tool to integrate the complexity of interacting factors and processes. This presentation will review current state of knowledge on the transport and transformation of xenobiotics in soil, identify opportunities through application of this understanding, and propose priorities for the future.

Session 4: Chemistry in the terrestrial compartments

Oral communications

POTENTIAL NITROGEN MINERALIZATION IN SOILS CONTAMINATED WITH POTENTIALLY TOXIC ELEMENTS

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Nitrogen (N) is essential for plant growth in terrestrial ecosystems and consequently N availability controls the development, persistence or decline of plant species in many areas. Nitrogen is mainly present in the organic form in the soil-plant system and N mineralization has to occur prior to plant uptake (Nannipieri and Eldor, 2009). Nitrogen mineralization is performed by different microbial species and depends on different physical and chemical conditions of soil. Several elements are known to be toxic to soil organisms, even at low concentrations, and can influence the soil N mineralization (Baath, 1989). Hence, N dynamics in soil may be used as indicator of quality and productivity of contaminated soils.

In the present work, 80 soils contaminated with variable ranges of potentially toxic elements (As, Cd, Cu, Hg...) were sampled in four distinct areas (urban, rural, industrial and mines) in North and Southwest Portugal (Rodrigues et al., 2010) and their potential of N mineralization (PNM) was assessed using an anaerobic incubation (Lober and Reeder, 1993).

The PNM varied from 0.21 to 4.40 % of total N and higher variability was observed in Mines soils with values ranging from 0.27 to 4.40 % of total N. The PNM is well correlated with As and Hg concentration in industrial and Mines whereas in urban and rural soils (lower metal concentrations) poor correlations were observed (Table 1).

Table 1: Pearson correlation between As and Hg concentration and PNM values

	Industrial		Mines		Urban		Rural	
	<i>r</i>	<i>P</i>	<i>r</i>	<i>P</i>	<i>r</i>	<i>P</i>	<i>r</i>	<i>P</i>
As	-0.772	0.0001	-0.73	0.0003	-0.395	0.0847	-0.232	0.3246
Hg	-0.833	0	-0.547	0.0126	-0.474	0.0349	-0.242	0.304

Our results provide an indication that anthropogenic soil contamination with potentially toxic elements such as As and Hg has a significant relationship with N mineralization which may affect plant nutrition.

HEAVY METALS AND METALLOIDS TOLERANCE OF ROSEMARY: CONTAMINATION LEVELS AND STRESS BIOMARKERS

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Heavy metals and metalloids (HMM) pollution is one of the major environmental issues because of numerous areas impacted by past and current industrial activities. In the future National Park of Calanques (South East of Marseille, France), the former smelting factory of L'Escalette led to a diffuse HMM pollution in this area. This study aimed to understand the tolerance of an autochthonous plant species, rosemary (*Rosmarinus officinalis*), to HMM soil contamination and stresses generated by these pollutants.

Thus 4 experimental plots were chosen around l'Escalette, along a pollution gradient. HMM (mainly As, Pb, Sb and Zn) were measured by ICP-AES and GF-AAS after acid mineralization of plant samples and respective mycorrhizospheric soils collected on each experimental plot. Rosemary biomarkers of HMM stresses like some amino acids (proline, methionine, cysteine) and a peptide (glutathione) were determined using acidic extraction and ion chromatography analyses.

The pollution gradient was well established with total As, Pb, Sb and Zn soil concentrations varying from 302 to 52.8, 3031 to 515, 112 to 10, 1017 to 310 mg.kg⁻¹, respectively. Root HMM accumulation ranged from 21.9 to 1.88, 626 to 27.3, 15.1 to 1.69 and 156 to 49.0, respectively for As, Pb, Sb and Zn. Determination of stress biomarkers clarified part of rosemary tolerance mechanisms towards HMM. For example, according to contamination gradient, decrease of glutathione, a phytochelatin precursor, in roots may reveal the occurrence of resistance mechanisms in rosemary.

IMPACT OF SELENIUM TREATMENT AND DIFFERENCES IN HEAVY METALS UPTAKE BY TARTARY AND COMMON BUCKWHEAT GROWN IN CONTAMINATED SOIL FROM MEŽICA VALLEY

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Upper Mežica valley has been exposed to active lead and zinc ore mining and smelting activities (lead and zinc smelter at Žerjav) since the 1665. That affected soil pollution with Pb, Cd and Zn. Values of Pb and Zn in region of vegetable gardens and courtyards in soil exceed Slovenian limit of critical immision values for 10 times. Using plants that accumulate specific metals in cleanup efforts is one of the method used for soil remediation.

The aim of this study was to determine the effect of selenium foliar spraying on Cu, Zn, Cd and Pb uptake by Tartary (*Fagopyrum tataricum* Gaertn.) and Common buckwheat (*Fagopyrum esculentum* Moench.), grown in plastic pots with contaminated soil from Mežica valley. In the beginning of flowering, plants of one half of pots were foliary sprayed with 10 mg Se/L in the form of sodium selenate solution. Sampling was done when grains were developed. Roots, stems, leaves and grain were collected each separately, lyophilized and milled. The concentration of metals were determined using ICP-MS (Aglient 7500ce).

Results for tartary buckwheat shows that roots have the highest concentrations of heavy metals, and that treatment with selenium solution slightly increased the metal uptake. Roots accumulated 1075 mgPb/kg, which could classified tartary buckwheat as a Pb hyperaccumulator. In the research we wanted to compare heavy metal concentration in green and red leaves, because senescence can influence the metal allocation. Foilar spraying increased concentration of Cu, Zn in green and red leaves, and decreased concentration of Pb in both cases. It was no impact of selenium spraying on Cd concentration. Content of heavy metals are the lowest in husks and flour. 100 g flour contains 92.9 µgCd without selenium treatment and 96.8 µgCd with foliar spraying of selenium. Therefore such flour is not suitable for human diet, because maximum tolerable daily intake (60 µg/day) could be exceeded. Concentrations of Cu, Zn and Pb are lower than the highest tolerable daily intake.

The concent of metals in common buckwheat is under investigation and will be discussed.

FINGERPRINTING OF SOIL ORGANIC MATTER POOLS UPON SOIL AMENDMENT WITH WASTE MATERIALS

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Restoration of soil organic matter is essential for soil structure, to promote soil biodiversity and support phytoremediation. Soil from an abandoned mine tailing (Granada, Spain) was amended at 3 and 5% with a mixture of sludge and pruning wastes (SPW) supplied by Biomasa del Guadalquivir.

Samples of non-amended and amended soil were incubated for one week at field capacity and the soil solution extracted and analyzed by luminescence spectroscopy.

Excitation-emission matrix spectroscopy (EEMS) provides the sensitivity to examine subtle changes in dissolved organic matter (DOM) fluorescence (Figure 1) and provide insight into alteration of DOM pool composition. Results indicate a substantial increase in the fraction of UV (Ex/Em 260/400-460) and visible (Ex/Em 320-360/400-460) humic-like organic matter, which provides a pool of highly stable, low degradation rate organic matter.

Moreover, the strong increase in fluorescence intensity suggest that the added organic matter might complex metal ions in solution, therefore reducing the potential leaching of soluble trace metals.

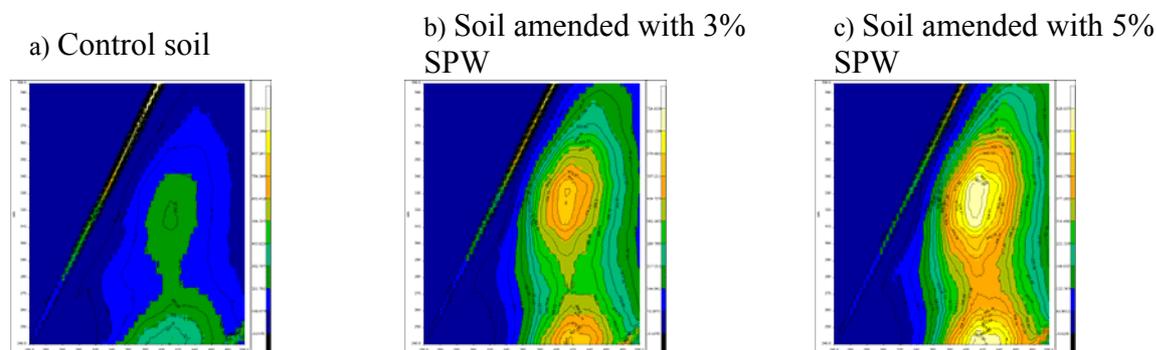


Figure 1. Fluorescence spectra of DOM in the soil solution for a) control soil, b) soil amended with 3% SPW and c) soil amended with 5% SPW.

FORMATION OF BOUND RESIDUES IN SOIL DERIVED ORGANO-CLAY COMPLEXES AND ITS RELEVANCE FOR THE ASSESSMENT OF PESTICIDE CONTAMINATION IN SOILS

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Primary domains for interactions of organic pollutants at biogeochemical interfaces in soils are the organo-clay complexes. Hence, studies on the fate of xenobiotics in soils needs to address in particular to this soil subfraction. Further on, major environmental properties of organic pollutants are related to the type of speciation. For instance, the bioavailability of soil contaminants are closely connected to the accessibility of the particle associated contamination. Strong interactions or incorporation mechanisms on soil particles lead to a decreasing bioavailability and, consequently, to a reduction of the risk potential.

Following these aspects, a comprehensive study on the environmental fate of selected soil contaminants, comprising two pesticides (MCPA, Metalaxyl) and one pesticide additive (nonylphenol), was performed with a special focus on the incorporation behaviour and the mode as well quality of binding to the organo-clay complexes.

Basically, incubation experiments on soils, isolated natural as well as artificial organo-clay complexes have been conducted with ¹³C- /¹⁴C-labelled and unlabelled substances under microbial active and sterile conditions. The incorporation behaviour has been followed for a prolonged time up to 180 days and the distribution of radioactivity into grain size fractions and, additionally, humic subfractions have been followed. Further on, invasive (chemical degradation, pyrolysis) and non-invasive analytical techniques (NMR) have been used to characterize the mode of binding especially of covalent bound moieties.

Briefly, organo-clay complexes have been characterized as major accumulation domain for covalent bound residues. Interestingly, incorporation processes have been initiated exclusively by extensive microbial assistance. The biotic assistance was confirmed by the identification of a stereoselectivity of the incorporation. Dominant incorporation linkages were hydrolysable bonds, in particular ester bonds, related to humic acids. These results allow a more differentiated evaluation of soil contamination by pesticides and additives.

THE INFLUENCE OF BIOREMEDIATION CONDITIONS ON THE DEGRADATION OF PHENANTHRENE AND ITS METHYL ISOMERS IN PETROLEUM-TYPE POLLUTANTS

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In this paper, the changes in the distribution of phenanthrene and its methyl-, dimethyl- and trimethyl-isomers during bioremediation of soils contaminated with petroleum type pollutants under different conditions were investigated. Firstly, the laboratory experiment of the simulated oil biodegradation with aerobic zymogenous microorganisms in soil (Danube alluvium, Pančevo, Serbia) was conducted (75 days period). The changes in the distribution of phenanthrenes were investigated also during *ex situ* bioremediation of soils (6 months period). On the one hand, experiments were conducted in which biodegradation was stimulated (re-inoculation, biostimulation, the addition of sawdust and biosurfactants). On the other hand, experiments were conducted in which bioremediation was not stimulated. A considerably high bioremediation potential was confirmed in the biodegradation of phenanthrene and methyl phenanthrenes with aerobic zymogenous microorganisms. During the process of *ex situ* “natural” microbial degradation similar trend was observed: the relative concentration of phenanthrene is reduced relative to methyl-, dimethyl- and especially relative to trimethyl-phenanthrenes. However, during the process of “stimulated biodegradation” a different sequence was observed: there was a uniform increase in the relative abundance of phenanthrene compared to its methyl isomers. Results obtained from these studies indicate that biodegradation of phenanthrene and its methyl isomers is not unambiguous and that largely depends on the conditions under which the degradation takes place.

Analytical chemistry – Part 2

Oral communications

MULTIANALYTICAL MEASUREMENTS TO ASSES THE IMPACTS OF ACIDIC INFILTRATION WATERS AND ATMOSPHERIC POLLUTION

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The original materials of the buildings are subjected to the action of external agents which determine their evolution over time. Among these, the environmental factor, including water, determines the transformations experienced by those materials and can cause formation of soluble salts. These salts cause damage when crystallize within the pores and produce internal fractures when solubilised ions, coming from others salts, recrystallize as another salt or the same but with different number of hydrate waters.

This work proposes a multianalytical methodology in order to identify degradation compounds as well as the chemical reactions between atmospheric pollutants, infiltration waters and original material. The procedure was applied, in the Basozabal Palace (Gipuzkoa, Spain). For this purpose, a combination of Raman and XRay spectroscopies was used to perform a complete characterization. After checking the condition of the building, quantitative analysis of the soluble salts was carried out by Ion Chromatography in addition to a Chemometric treatment, in order to assess the extent of the impact suffered by the building.

A variety of carbonate, nitrate and sulphate salts were found as CaCO_3 , Na_2CO_3 , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3(\text{HCO}_3)(\text{CO}_3) \cdot 2\text{H}_2\text{O}$, KNO_3 , NaNO_3 and Na_2SO_4 . The distribution of the salt on the wall depends on the solubility and ionic mobility and likely, the sources are the infiltration of waters charged with NH_4NO_3 and the impact of atmospheric SO_2 . Finally, the multianalytical methodology identified the compounds, demonstrated the origin of the problem and evaluated the behaviour of each material against the infiltration waters and SO_2 acid gas. (Acknowledgements: project IMDICOGU (ref. BIA 2008-06592) of MICINN and the predoctoral grants of University of the Basque Country and MICINN).

HIGHLY SENSITIVE AND RAPID FLOW INJECTION ASSAYS FOR DETECTION OF AMMONIUM AND BIOGENE AMINES IN ENVIRONMENTAL AND RELATED SAMPLES

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The need for sensitive, selective and rapid analytical methods in environmental monitoring and research has recently resulted in development of novel techniques and methods, which rely on application of bioanalytical assays and their combination with flow injection analysis and highly sensitive laser-based methods such as thermal lens spectrometry. In this paper the most recent applications of thermal lens spectrometry (TLS) in assays for detection of ammonia and biogenic amines in environmental and related samples will be presented.

Ammonium concentrations at levels below 10 ng/mL (LOD \approx 1 ng/mL) can be reliably detected by TLS. This was accomplished by exploiting the Berthelot reaction and TLS detection of the indophenol blue complex after only 10 min. reaction, following the excitation by a Kr laser (647 nm, 200 mW).

Ammonium can also serve as a marker for the presence of biogenic amines (BAs) in food due to environmental pollution and inappropriate hygienic conditions. Application of transglutaminase (TG) enabled indirect detection of BAs by monitoring the ammonia released in enzymatic reaction between BAs and TG. BAs were detected with LODs of 1.5×10^{-8} M for putrescine and cadaverine, 5×10^{-8} M for histamine and 1×10^{-7} M for tyramine. This represents improvements in LODs of over hundred times compared to a previously reported method relying on application of TG and transmission mode spectrophotometric detection of ammonia in batch mode.

Additional attempts for improvements in specificity and sample throughput were made by performing the described reactions in a FIA system with a TLS detection unit, which enables analysis of 8-10 samples/hour. This is a significant improvement in comparison to existing HPLC methods which require one hour just for derivatization of the sample.

COMPLEXATION PROCESSES IN CHROMATOGRAPHIC AND ELECTROPHORETIC DETERMINATION OF BIOACTIVE COMPOUNDS

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One of the main scientific directions is the development of the separations of acidic, basic and neutral species of biomolecules (antioxidants, drugs, steroids hormones, neurotransmitters, sugars and others) in natural objects. In recent years the methods of CE have been widely used for determining biologically active compounds due to their high efficiency. Considering the small reagent and sample requirement, as well as the rapid analysis times associated with the application of high fields it is clear that CE has tremendous potential for the solution of different biomedical problems. Nevertheless there are some problems: poor detection limits, insufficient selectivity separation, the concentrations of analytes in the biological system are usually very small or extremely different. We have developed some decisions.

Introduction into the mobile phase, background electrolyte (BGE) or sample matrix the ion-pair agents, macrocycles, metal cations as complexing additives can change electrophoretic mobilities of analytes. The effect of addition of organic additives (modifiers of the surface of fused-silica capillary, complexation agents (18-crown-6, 4,13-diaza-18-crown-6, β -cyclodextrin, sulfo- β -cyclodextrin), surface activity substances (SDS) to the BGE on selectivity and efficiency of electrophoretic resolution of the steroids, polyphenoles, biogenic amines, neurotransmitters amino acids, water- and oil-dissolved vitamins was studied. The quantitative estimation of complex formation in the system “*analyte-macrocycle*” has been done.

One of the promising electrophoretic versions for analyzing mixture of natural compounds is ligand-exchange CE. The formed complexes differ in stability, which causes the difference in their electrophoretic mobilities. We have observed on mixture of standards sugars (*glucose, fructose, sucrose*), hydroxyl- and aminoacides, which was not adsorbed at UV-light, that the use of ligand-exchange mechanism during the electrophoretic separation (the BGE was copper-ammonium solution $[\text{Cu}(\text{NH}_3)_4]^{2+}$) enable us to determine these substances in the complex forms.

All this allow to improve selectivity, to decrease the detection limits and to observe the analytes without UV-absorption. It let us to determine individual components and obtain the characteristic profiles of real samples. To reduce detection limits we also used on-line strategy for sample preconcentration in a flow: different variants of stacking (in zone CE) and sweeping (in micelle EKC).

BATCH ADSORPTION OF BORON ONTO COMPOSITES OF ALGINATE GEL BEADS AND ALUMINA

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Water contamination by boron is one of the most widespread environmental problems, during the production of boron compounds (in chemical, pharmaceuticals, and mining industries) much of these are introduced into the environment in the form of waste. Although this element is essential in plants growth and small amounts can even be beneficial for humans, high levels are toxic in reproduction systems of human beings ($> 1\text{mg/L}$). The goal of this study is to establish a possible process for recovery of boron compounds from waters. Batch adsorption was studied for boron adsorption from aqueous solutions and the adsorbents proposed for this, are composites beads of calcium alginate gel and alumina. pH studies were carried out, and results confirm that a better adsorption capacity is obtained under basic medium with alginate beads while alumina improves removal of boron in acidic pH. Composites of alginate/alumina presented better adsorption capacity in acidic medium. Adsorption percentage increases lightly in acidic conditions when alginate/alumina composites are used. The adsorption with alginate gel beads increase when pH is increased reaching a maximum at $\text{pH} = 11$. Adsorption isotherm study was made, Langmuir and Freundlich isotherms models were applied and the experimental data was found to conform to the Langmuir isotherm model. The maximum sorption capacity obtained was 73 mg/g at $\text{pH} 11$ using alginate gel beads. Results of kinetics studies showed that experimental data is fit better to the pseudo-second order model.

Session 5: Sustainable chemistry
Conference

(ECO)TOXICITY AND BIODEGRADATION OF IONIC LIQUIDS - PROGRESS IN DESIGNING INHERENTLY SAFER CHEMICALS

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Green chemistry and its 12 principles - defined and described by Paul Anastas and John C. - represent an essential prerequisite for a sustainable chemistry, sustainable chemical products and a sustainable and hence responsible chemical industry. “Inherently safer chemical products”, the “design” of new and “environmentally benign substances” all these keywords are closely linked to green chemistry and they are gaining more and more importance following the Agenda 21 process and – probably more important - in the light of the European chemical legislation for the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

But how can we reach the goal of a real sustainable chemical, which has to be on the one hand non-toxic, readily biodegradable and its synthesis leaves a small ecological footprint – the key issues owing to green chemistry - but on the other hand meets all technological and economical needs? Using the case of ionic liquids as an example for a promising group of industrial chemicals, which bear a high potential for a sustainable design process the above mentioned issues and related questions will be discussed. Since ionic liquids represent a highly diverse group of chemicals, they serve as an ideal model to demonstrate the problems and challenges chemical and biological complexity pose on the way towards sustainable chemical substances. But the case of ionic liquids also shows how these problems can be addressed and how subsequently the goal of tailor-made sustainable substances can be realised by an integrated approach based on an interdisciplinary and tiered strategy, in which academic and industrial research closely cooperate.

This presentation critically reviews the state of the art in the fields of ionic liquid (eco)toxicology and biodegradability. The latest developments in both fields will be presented in a brief discussion of the most relevant literature in each. Then, it will point out existing data gaps and further research needs with the aim of providing a framework for future research initiatives leading to an effective and sustainable hazard and risk assessment of ionic liquids.

Session 5: Sustainable chemistry

Oral communications

OXYGEN-FUNCTIONALIZED IONIC LIQUIDS: CANDIDATES FOR A SUSTAINABLE CHEMISTRY ?

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Ionic liquids are often presented as chemicals environmentally friendly mainly because of their negligible vapor pressure. However, recent studies^a have underlined their potential toxicity for living organisms and persistence in the environment. Oxygenated ionic liquids have been suggested as better candidates than non-functionalized ionic liquids for a sustainable chemistry^b.

In this work, we have focussed on a selection of oxygenated ionic liquids with different cations (fig.1) and studied (i) their toxicity (MIC), (ii) their biodegradability (biodegradability tests with pure strains and identification of the degradation products) and (iii) their behaviour in the environmental compartments (partition coefficients, transport). The presence of oxygenated functions in the side-chain limits the toxicity of the ionic liquids studied, the imidazolium-based ones remaining the most toxic. The presence of ester and alcohol functions is in favour of an increased biodegradation but the aromatic rings remain persistent. The measured octanol-water partition coefficients, related to the risk of bioaccumulation in environment, decrease in the presence of ester and ether functions.

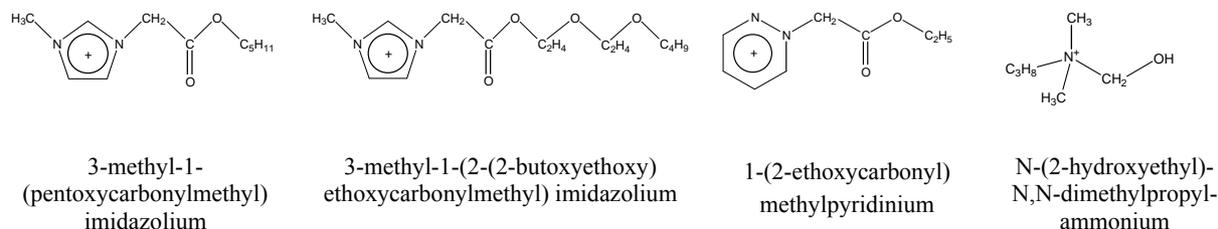


Figure 1. Examples of oxygenated cations studied in this work

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SMART APPROACH FOR ENANTIOSELECTIVE ALKENE EPOXIDATION BY HYDROGEN PEROXYDE USING COMBINATION OF ULTRASOUND, IONIC LIQUID AND PORPHYRIN

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Ionic liquids exhibit many properties which make them very attractive for catalysis. In these almost vapourless, air and moisture stable solvents, catalysts displaying polar or ionic character can be immobilized without any post functionalization. Nevertheless, mechanisms involved in ionic liquids are still poorly described and their reactivity needs to be apprehended.^[1,2]

Ultrasound-promoted synthesis has attracted much attention during the past few decades.^[3] Ultrasound is known to enhance some processes through a physical phenomenon called cavitation, which is the formation, growth and collapse of bubbles in an elastic liquid. By imploding, these bubbles create locally high pressure and high temperature that can lead to high-energy radical mechanisms but also generate some interesting physical effects that can improve catalyst activity.^[4]

Alkene epoxidation with bicarbonate-activated hydrogen peroxide leads to good yields and reaction times without the need of adding metal catalyst, in acetonitrile as solvent.^[5] In our work, the advantageous properties of both H₂O₂/NaHCO₃/imidazole/Mn(TPP)OAc oxidation system and MOPyrroNTf₂ ionic liquid have been combined under ultrasonic irradiation to give an exceptionally favorable environment for Mn(TPP)OAc catalyzed olefin oxidations.^[6] The results suggest that the use of ultrasonic irradiation for olefins epoxidation by metalloporphyrins in an ionic liquid proceeds via a mechanism that involves an oxo-manganyl intermediate, allowing us to consider chiral epoxidation via design of catalyst.^[7] Moreover, the effect of ultrasound in ionic liquids was investigated and for the first time, some typical parameters of sonochemistry were determined in this solvent to better understand the powerful combination ionic liquids / ultrasound in organic synthesis.

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INFLUENCE OF THE ACID-BASE PROPERTIES OF OXIDE CATALYSTS IN FRUCTOSE DEHYDRATION TO 5-HMF

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Recently, saccharides have attracted much attention as biomass for substituting petroleum resources, and their conversion to appropriate chemicals useful in so-called biodiesel synthesis has actively been investigated. In this work we report the results concerning the investigation of aqueous phase dehydration of fructose on various solid materials such as tungstated zirconia and ceria-niobia mixed oxide catalysts and the correlations between catalytic activity and surface acid-base features.

Series of $\text{WO}_3\text{-ZrO}_2$ and $\text{CeO}_2\text{-Nb}_2\text{O}_5$ mixed oxides with various W/Zr or Ce/Nb ratios were prepared by incipient wetness impregnation and coprecipitation. The catalysts were characterized by XRD, BET, XPS, Raman spectroscopy and TPR method. In order to characterize their acid-base properties, the differential heats of NH_3 or SO_2 adsorption were measured by microcalorimetry. The aqueous phase dehydration of fructose was carried out at 120°C under self-pressure in an autoclave. The conversion of fructose and the yield of 5-HMF were determined by ^1H NMR. Figure 1 represents the fructose conversion as a function of time for some of the samples, including the corresponding bulk oxides. As can be seen $\text{WO}_3\text{-ZrO}_2$ mixed oxide displays the highest fructose conversion.

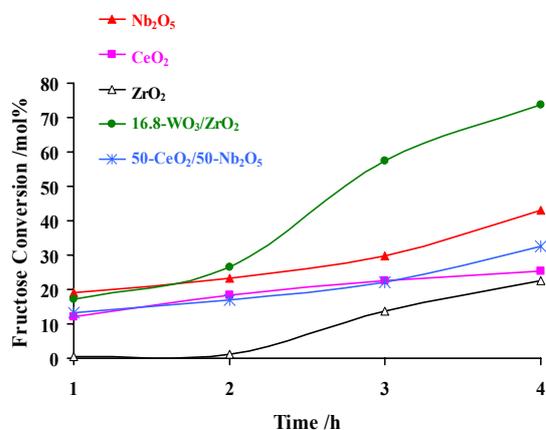


Fig.1. Fructose conversion as a function of reaction time for some catalysts

ELECTROCHEMICAL OXIDATION OF 2,4-D: ANALYSIS OF DEGRADATION BY PRODUCTS AND IMPROVEMENT OF THE BIODEGRADABILITY

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A promising electrochemical pre-treatment was implemented to improve the biodegradability of the 2,4-Dichlorophenoxyacetic acid (2,4-D), prior to a classical biological treatment. This pre-treatment was based on a home-made flow cell and a bare graphite felt was used as a working electrode. The electrolyte solution (500 mg L⁻¹ 2,4-D in 0.1 M Na₂SO₄) percolated the porous electrode at a constant flow rate of 1 mL min⁻¹. Preliminary cyclic voltammetry studies helped setting the potential of electrolysis at 1.6 V/SCE.

After the electrolysis, HPLC and Dissolved Organic Carbon (DOC) measurements revealed that 96 ± 3% of the 2,4-D were degraded whereas 34 ± 4% of the initial organic carbon were mineralized. Degradation by-products were identified by LC/MS/MS or GC/MS and then more precisely quantified by HPLC. LC/MS/MS results showed the presence of Chlorohydroquinone and 4-Chlorocatechol as the main products in the oxidized 2,4-D solution, and other species such as 2,4-Dichlorophenol or glycolic acid were also detected. The biodegradability of 2,4-D and of the electrolyzed solutions were subsequently estimated by means of BOD₅ and COD measurements. The biodegradability was significantly improved, as it increased from 0.04 for the 2,4-D to 0.25 after the pre-treatment step. This improvement in the biodegradability is thus a promising result in view of the combination of the electrochemical process with a biological treatment.

IRON(III) OXYHYDROXYCARBONATE, FERRIC GREEN RUST, AS A NEW MATERIAL FOR PHOSPHATE REMOVAL

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Phosphorus is essential to the growth of algae and other biological organisms. However, its presence in large amount can have critical consequences such as eutrophication. For instance, the bluish-green algae proliferation in Brittany is an environmental problem and combined phosphate and nitrate removal methods have to be found out. In order to answer to this problematic, iron oxides, which are well-known to adsorb anions, seem to be appropriate candidates.

In this work, a ferric oxyhydroxycarbonate, commonly called Ferric Green Rust (FGR), of formula $\text{Fe}^{\text{III}}_6\text{O}_{12}\text{H}_8\text{CO}_3 \cdot 3\text{H}_2\text{O}$, is studied. FGR was prepared by the coprecipitation of iron(II)-iron(III) salts to obtain a mixed iron (II) iron (III) hydroxide, called green rust (GR), followed by a controlled oxidation step. Special attention was first devoted to determine the influence of syntheses conditions (aging, oxidation kinetics...) on the crystal morphology and structure of FGR using Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD), respectively. Aging of GR appears as the most influent parameter controlling crystal size of FGR. Then, experiences of phosphate ions sorption were achieved in batch experiments using the different FGR prepared. In particular, kinetic measurements, adsorption isotherms and pH effect were determined from solution analyses by Ionic Chromatography (IC). Finally, the amount of phosphate ions adsorbed ranges between 35 and 45 $\text{mg}\cdot\text{g}^{-1}$ depending on crystal size of FGR.

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**DETERMINATION OF HEAVY METALS ON THE MEDITERRANEAN
ENDEMIC PLANT *Posidonia oceanica* USING THE GREEN
EXTRACTION METHOD: "MICROWAVE ASSISTED MICELLAR
EXTRACTION" AND GFAAS**

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Heavy metals are listed as priority pollutants by the Environmental Protection Agency and may pose a high risk for environment and human health.

Due to the extremely low concentration of these elements in the marine environment, a very interesting tool for the detection of the environmental pollution due to the presence of heavy metals is the use of bioindicators. In this sense, *Posidonia oceanica*, an endemic plant of the Mediterranean Sea, has demonstrated its potential as bioindicator of heavy metal pollution in the marine environment. It is employed as well as bioindicator of the ecological quality as regulated by the Directive 2000/64/CE of the European Parliament.

The traditional methods used for the extraction of heavy metals are the "acid digestion" and "microwave assisted extraction" (MAE) that usually employ strong acids as extractants, which are highly toxic and corrosive.

Therefore, it is necessary to develop alternative extraction and analysis methods to determine as many pollutants as possible, at the lowest concentration, in a quickly and easily way, with the minimum impact on the environment.

In this sense, it has been optimized a new method for the extraction of the heavy metals: Ni, Cu, Cr, Pb, Cd, from *Posidonia oceanica*. This method is based on the use of a mixture of biodegradable micellar media (SDS, Triton X-100) as extractants, and GFAAS. Results show satisfactory recovery percentages for the metals under study. The optimized method has been validated with the Certified Reference Material BCR-060, *Lagarosiphon major*, and applied to real samples with satisfactory results as well.

ABSTRACTS: POSTERS

Session 1: Analytical chemistry

Posters

PARTICULATE CONTAMINANTS ANALYSIS: ASSESSMENT AND COMPARISON OF SAMPLING TECHNIQUES

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The European Water Framework Directive came into force in 2000, taking the 1976 Barcelona Convention into account and thus encouraging the contracting parties to evaluate pollution discharge to the Mediterranean Sea. Under the umbrella of the Rhone Sediment Observatory a monitoring station was set up upstream from Lyon in order to measure hydrophobic organic compounds and mercury contents of particles and to evaluate fluxes. To analyse those various contaminants several grams of dried suspended particulate matter (SPM) are required – which can be challenging considering low SPM levels in the Rhone river during base-flow regime. To face that problem several sampling techniques have been implemented: manual or automatic sampling, a continuous centrifuge running during several hours and an integrative sediment trap. For the sake of data homogeneity, we must assess and compare these different sampling techniques. The particle size distribution analysis of SPM sampled manually in the Rhone river showed two main peaks: one around 0.25 μm (10% volume) and another around 8 to 15 μm (90% volume). In contrast, the particle size distribution analysis of SPM collected with the continuous centrifuge and the sediment trap highlighted that finest particles were not successfully sampled. These results were confirmed by detectable SPM concentrations for water collected at the outlet of the continuous centrifuge and of the sediment trap. Thus, we investigated SPM contaminant contents according to the particle size classes. Particulate mercury analysis revealed that finest particles are the most contaminated ones. Therefore, all particulate contaminant contents should be normalized using particle size distribution data especially when comparisons are needed between contaminants content of particles sampled with different techniques, or sampled in bed deposits.

CAGED GAMMARIDS TO IMPROVE THE CHARACTERIZATION OF CONTAMINATION LEVELS IN CONTINENTAL WATERS - TOWARD THE DETERMINATION OF THRESHOLD VALUES

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Chemical biomonitoring (i.e., monitoring contamination in biota) is often proposed as a relevant approach to characterize the contamination of aquatic systems. Indeed, biota is an integrating matrix that enables measurements of hydrophobic substances, representative of the bioavailable fraction. Active chemical biomonitoring (i.e., using transplanted organisms from a reference site) allows controlling several parameters such as variability in exposure time, age and size of sampled organisms, therefore providing comparable results. Such active approaches are well developed in the marine environment (e.g., the French “Rinbio” network) but they are still an emerging issue for continental waters. Hence, we investigated the suitability of an active biomonitoring approach to assess trends of metals and hydrophobic organic substances contamination in continental waters. The amphipod *Gammarus fossarum* was selected as the test organism as i) it is a highly ecologically relevant species and ii) it allows controlling easily several biotic factors. Gammarids, sampled from a known unpolluted site, were translocated into cages to 27 sites, in the Rhône-Alpes basin (France) during early autumn 2009. Study sites represented different physico-chemical characteristics and various anthropic pressures. To avoid the influence of biotic factors, only male gammarids with the same average body length were exposed, and gammarids were fed during the experiment. After one week of exposure, concentrations of 5 metals and 28 hydrophobic organic substances, chosen with reference to the Water Framework Directive (WFD), were measured in the organisms. *G. fossarum* accumulated most of the investigated substances and the proposed caging methodology is a relatively simple tool for chemical biomonitoring of continental waters. To improve the discrimination between anthropically impacted and non-impacted sites, we investigated a statistical approach and a model fit to define threshold values of contamination in gammarids, assuming that any concentration under such a threshold would be assumed as the “background” concentration.

THE POSSIBILITIES OF HYPERBRANCHED POLYMER PEI-MAL AS AN ADDITIVES IN MOBILE AND STATIONARY PHASES IN ELECTROPHORETIC DETERMINATION OF BIOACTIVE ORGANIC COMPOUNDS

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One of the great importances in the analysis of original objects is the selective and sensitive determination of trace amounts of bio-active substances: steroids, biogenic amines and amino acids, polyphenoles, vitamins, protein.

In recent years, the method of capillary electrophoresis (CE) has been widely exploited as a powerful separation tool for the analysis of a large variety of complex samples. However, it suffers from low separation selectivity and adsorption of multypositively charged molecules to the inner wall of fused-silica capillary. Using additives so called organized systems (such as surfactant micelles, cyclodextrines, crown ethers and et.) can improve the separation selectivity in CE.

In recent time to improve the separation of complex mixtures have been proposed new additives: surfactants and dendrimers. The interest in dendritic macromolecules originates from their unique chemical and physical properties.

In our study we have investigated the potential of using hyperbranched polymers (hbp) polyethylenimins, functionalized with maltose (PEI-Mal), with different molecular weights (5 and 25 kDa) and degree of modification with maltose, as a components of the mobile or stationary phases in electrophoretic and chromatographic separation of bio-active substances. Electrophoretic and chromatographic methods may, moreover, be convenient methods of studying the interaction of dendrimers with bio-active analytes of different nature.

We have obtained that these polymers can modify the separation selectivity of small (vitamins) and large (peptides, proteins) molecules, mask the silanol groups at a low pH as a consequence of forming the dynamic coating and eliminate analyte-wall interactions. The last fact is very important in CZE analysis of biological compounds because it enhances separation efficiency and resolution.

PEI-Mals have been shown to be potential pseudo-stationary phases for electrokinetic chromatography. PEI-Mals have been also successfully employed as dynamically and covalently bonded capillary coating in the determination of proteins. In this case it was realized a capillary electrochromatography. It has provided higher efficiency (600000 t.p./m) and improve in the selectivity and sensitivity of proteins more than 50 folds due to presence of *on-line* concentration of the sample zone (pH 2.2).

DETERMINATION OF β -BLOCKERS AND β -AGONISTS IN WASTEWATER BY GC-MS

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β -blockers (cardiovascular drugs) and β -agonists (antiastmatic drugs) are one the most frequently detected drugs in wastewater influents, effluents and river waters. Thus, at the end their life cycle large quantities of these pollutants enter the environment where possibly they can pose relatively high risk. β -blockers are known to effect health of fish in a similar way as observed in humans (impact on heart rate, metabolism and growth). More often these drugs are administrated in ground and drinking water. For example metoprolol is detected in Netherlands in concentration of 2.1 $\mu\text{g/L}$ and atenolol in USA is found at 0.47 ng/L . Important environmental source of these pharmaceuticals are hospital wastewater effluents, where concentration of three most frequently found β -blockers – atenolol, metoprolol and propranolol, is in the range from 0.1 to 250 $\mu\text{g/L}$.

Wastewater matrices however are very complex and variable if trace analytics is concerned. Efforts must be made to minimize the level of interfering substances during extraction and pre-concentration steps, since matrix components may cause several analytical problems within quantitative and qualitative analysis of polar analytes. Solid phase extraction is one of the most useful extraction method. Properly optimized SPE procedure ensure good recovery of analytes and reduction of matrix interferences. Gas chromatography coupled with mass spectrometry is one of the most used technique for determination of pharmaceuticals in environment, because EI ion source is less sensitive for interfering components than ESI ion source in LC-MS system.

Presented work, demonstrate optimized SPE-GC-MS(SIM) method for determination of β -blockers and β -agonists in wastewater samples. Two-stage washing step ensure good absolute recovery of target drugs. Results of analysis of real wastewater samples collected in WWTP 'Wschód' in Gdańsk are presented.

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ACCUMULATION OF PAHS AND METALS BY SPMDs AND DGTs WHEN FACING VARIATIONS OF CONCENTRATION IN TIME

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Over the last twenty years, several passive samplers have been developed to improve the monitoring of contaminants in aquatic systems. Not only passive sampling allows improving the analytical procedures, but also most passive samplers give access to Time-Weighted Average (TWA) concentrations during the deployment period. It is a big advantage contrary to grab sampling which only delivers a spot image of the pollution. For this purpose, the Semi-Permeable Membrane Devices (SPMDs) and the Diffuse Gradient in Thin Film (DGT) are already widely used and studied. However, few experimental studies have focused on their behaviour when facing important variations of concentration in time and on their ability to reliably evaluate a TWA concentration.

In this study, passive samplers were deployed for 21 days in artificial rivers provided by Total, in Lacq, France (64). These mesocosms allow performing exposure under realistic hydrological conditions, with a controlled contamination. Three scenarios were studied: 1) a mix of standards was continuously injected in river water; 2) the contamination was periodic and 3) an accidental contamination was mimicked during the first three days of the sampler exposure. In all experiments, the accumulations of Ni, Zn and Pb in DGTs and the accumulation of anthracene, chrysene, and benzo(a)pyrene in SPMDs were followed. For continuous injections, linear accumulation in DGTs and first-order kinetic accumulation in SPMDs were verified. TWA concentration of labile metals were reliably estimated with DGTs in the two others experiments, whereas the estimation of TWA labile PAH concentrations with SPMDs could be biased.

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**ANALYSIS OF 25 ENDOCRINE DISRUPTORS AND 13
PHARMACEUTICALS IN SURFACE WATER AT THE LOWER NG/L
USING A VALIDATED ON-LINE SPE-LC-MS/MS METHOD**

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Analysing various Endocrine Disruptor Compounds (EDCs) and Pharmaceuticals in environmental matrices like surface water is challenging for the analyst as they display a wide spectra of physic and chemical properties, and they occur in the environment at very low levels. Many multi-residue methods focusing on one or two families of EDCs or pharmaceuticals have been developed with offline sample preparation steps to allow their monitoring in surface water at the sub ng/L level. In this study, 38 molecules of interest including 5 different EDCs families have been selected. Often used in pharmaceutical analysis to allow better wash steps of complex matrices, on-line SPE have been applied to environmental samples looking for automation, increased limits of detection and decreased human interferences during the concentration steps.

An automated on-line SPE-LC-MS/MS method has been developed and validated for the quantification of 38 emerging pollutants in surface water. Comparison of percolated volume and overfilling enabled to choose the best compromise between optimising the signal and increasing the noise. The influence of particles sizes varying from 5 to 30 μ m of five different SPE cartridges filled with PS/DVB sorbent (PolyStyren/DiVinylBenzen) have been evaluated.

The combination of low particles size of SPE cartridge and 1.7 μ m core-shell LC column technology enabled to obtain good pre-concentration and separation within 28min of run. Good linearity ($R^2 > 0.9$) and good repeatability and reproducibility enabled to validate this method calculating intraday and interday relative standard deviations over 3 days for calibrations with 7 levels of concentration. Limits of quantification for all the molecules ranged from 0.1 to 18ng/L.

**CALIBRATION OF 29 ENDOCRINE DISRUPTORS AND
20 PHARMACEUTICALS ON C18 CHEMCATCHER
TO MONITOR SURFACE WATER WITH 3 POTENTIAL PRCs**

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In response to the growth of organic pollutants identified in surface water many multi-residue analytical strategies using enrichment steps have been used for the analysis of grab sampling. Recently, sampling systems more realistic of environmental exposition have been designed to measure mean concentrations of those xenobiotics to estimate their toxicological effects on the environment and populations.

The ability to use one of these integrative samplers for the monitoring of Endocrine Disruptors and pharmaceuticals has been evaluated. Chemcatcher with C18 SPE disks and PES diffusion membrane have been rigorously calibrated for 49 emerging organic pollutants but also investigated for the Performance Reference Compounds (PRCs) approach. Samplers have been exposed for 28 days in 50L tanks with continuous renewal of spiked tap water for the adsorption study and spiked samplers for the desorption experiment.

Most of the compounds of interest accumulate with relative good linearity (R^2 from 0.90 to 0.99) over 7 to 21 days on the Chemcatcher. Sampling rates were calculated for the C18 Chemcatcher (0.02 to 0.16 L/d) after confirmation of the maximal exposure time using the half time of equilibrium criteria. 3 molecules showed accumulation and desorption consistent with first order kinetics with similar half time of equilibrium and thus almost verifying all the criteria for the use of PRCs on passive samplers.

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ANALYSIS OF HPA ON A NEW HPLC BONDED LIQUID CRYSTAL

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A new HPLC bonded liquid crystal stationary phase (BLCSP) is presented. Characterization of BLCSP needed different methods: proton NMR, DSC, ¹³C NMR and elemental analysis. The surface area was determined by the BET method.

This new material can successfully be used to separate mixtures that are commonly done by both reversed and normal phase materials.

Thermal and analytical chromatographic behaviors of the phase were investigated in normal and reversed phases (figure 1). Separation of polyaromatic hydrocarbons (PAHs) is described in figure 2. Bonded material exhibits a liquid crystal-like behavior and molecular shape recognition toward geometric isomers. The more retained solute is the more stretched solute. Using acetonitrile/water, satisfying resolutions are obtained in separation of aromatic hydrocarbons.

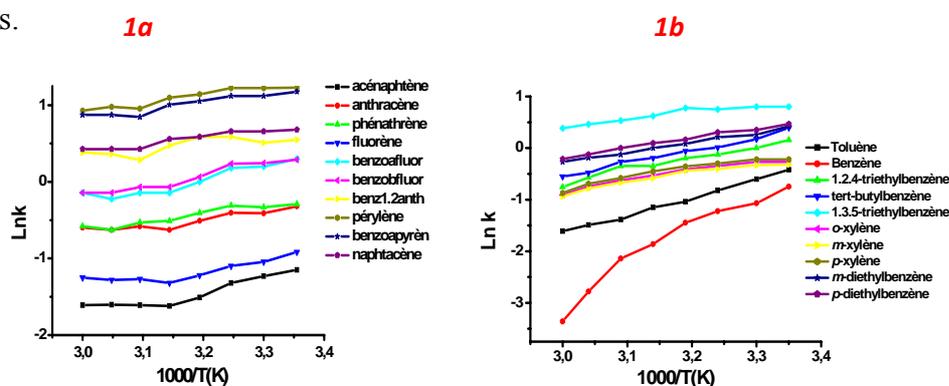
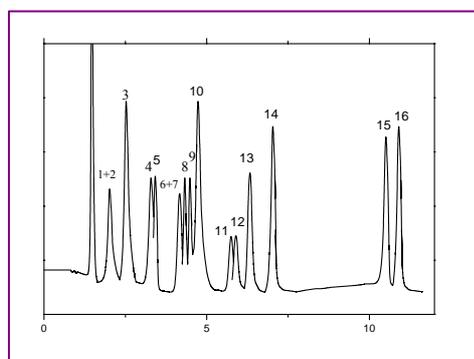


Figure 1: Thermal study of BLCSP in normal and reversed phases (1a, 1b)

Figure 2: Separation of HPA. Mobile phase: isooctane / Chloroform (97.5 / 2.5) (V/V), 1 ml/min ; λ 254 nm.
1: Acenaphtene ; 2 : Acenaphtylene ; 3 : fluorene ;
4 : Anthracene ; 5 : Phenanthrene ; 6 : Benzo-a-fluorene ;
7 : Benzo-b-fluorene ; 8 : Pyrene ; 9 : Fluoranthene ;
10 : 1,2-benzanthracene ; 11 : Chrysene ; 12 : Naphtacene ;
13 : Perylenee ; 14 : Benzo-a-pyrene ; 15 : Dibenzo-a,c-anthracene, 16 : Dibenzo-a,h-anthracene.



**DETECTION AND MEASUREMENT OF ENGINEERED
NANOPARTICLES IN NATURAL SYSTEMS:
LOOKING FOR A NEEDLE IN A HAYSTACK?**

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Nano-sized particles have always been present on Earth and have been used by mankind for thousands of years. Recently, however, particles in this size range have attracted a lot of attention because of our increasing ability to synthesize and manipulate them. Close to 1000 consumer products that contain nanoscale materials are claimed to be on the market and the development and commercial production of nanomaterials is expected to continue to grow rapidly.

Nanomaterials have been under public scrutiny since the first nanoparticles became available and the discussion about their safety has increased steadily in recent years. A high number of studies have so far been devoted to the toxicology and health implications of nanoparticles, with their behaviour in the environment and their ecotoxicology having received slightly less attention.

A point that is often overlooked is the fact that we are not yet capable today of detecting and measuring engineered nanoparticles in the different environmental compartments. In fact, the awareness about the possible deleterious effects of nanoparticles in the environment has grown in a fundamentally different way from organic micropollutants, where advances in analytical techniques and detection of compounds in the environment were the starting point for scientific and public discussions. In the case of nanoparticles the public discussion has largely preceded the possibility of detecting them in nature. Nevertheless, since “a material can be hazardous but still be classified as low risk if there is little chance of exposure”, the development of the necessary analytical techniques remains a key issue.

DETERMINATION OF AZITHROMYCIN IN WASTER WATER USING RP-HPLC AND ELECTROCHEMICAL DETECTION AFTER SOLID PHASE EXTRACTION

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Azithromycin is a broad spectrum antimicrobial agent that is approved to be used in humans. Due to azithromycin's low rate of metabolism it is likely to be found in wastewater treatment plants, where its broad spectrum of antimicrobial activity could lead to development of resistance in bacteria. In this work, a solid-liquid extraction using Oasis HLB cartridge was developed to extract azithromycin from 50 ml aliquots of wastewater. Cleaning of the cartridge was made by suction of 10mL of methanol (HPLC grade), conditioning with 10 mL of water (HPLC grade). Then, the cartridge was dried under vacuum. 50 ml of the polluted water was applied to the cartridge by suction at 0.5 atmosphere. Azithromycin was elated by 2 ml of methanol (HPLC). The extract was evaporated to dryness and reconstituted with 0.2 mL of mobile phase; 100 μ L were injected into the chromatograph. Liquid chromatography was performed using a X-Terra RP 18 (25mm \times 4.6 mm) column The mobile phase was a mixture of 20 mmol·L⁻¹ KH₂ PO₄ solution(pre-adjusted to pH 7.37 with 1 mmol·L⁻¹ KOH solution) and methanol(mixed in the ratio of 47 to 53 by volume) with flow-rate of 1.0 mL·min⁻¹. Detection was measured by electrochemical detector at 1.2mV and 10 nA range. The method was completely validated and allowed to quantitate azithromycin in wastewater still 5ng/L.

SILVER-AMALGAM BASED ELECTRODE FOR VOLTAMMETRIC MONITORING OF SELECTED NEONICOTINOIDS INSECTICIDES

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A sensitive square-wave voltammetric (SWV) method has been developed for the characterization and determination of selected neonicotinoid insecticides by using a silver-amalgam electrode (Hg(Ag)) in aqueous Britton-Robinson buffer solution as supporting electrolyte. Before the measurements, the electrode was subjected to electrochemical activation by potential cycling in the range from -0.20 to -1.50 V vs. reference SCE in the supporting electrolyte. In the investigated pH range between 2.0 and 9.0, the reduction peaks of the nitroguanidine compounds (imidacloprid and thiamethoxam) were obtained in an interval of approximately -0.8 to -1.4 V. Silver-amalgam electrode exhibited the best analytical characteristics at pH 7.0, both in respect to the peak shape and signal intensity. The optimal measuring parameters were as follows: pulse amplitude, 25 mV; and polarization rate, 100 mV/s. The developed SWV method was used to determine thiamethoxam in honey and river water samples. Additionally, the developed method was applied for the monitoring of the imidacloprid concentration during its photolytic and photocatalytic degradation. It can be concluded that the developed method can be used to obtain rapid information on the concentration of selected neonicotinoids in various complex samples.

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**COMPARISON OF FOUR EXTRACTION METHODS FOR THE
ANALYSIS OF TRIAZIN AND ORGANOPHOSPHORUS PESTICIDES
IN SOIL SAMPLES WITH GAS CHROMATOGRAPHY COUPLED
WITH MASS SPECTROMETRY**

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Four different extraction methods were compared regarding the analysis of the pesticides in soil samples. Simazine, atrazine, promethrin, chlorpyrifos, fenitrothion and diazinon were extracted from the soil with physico-chemical properties as follows: pH 7.64, organic matter content of 3.96%, sand content 49.80%, silt content 33.40% and 16.80% of clay. The methods used for the pesticide extraction were the liquid-solid extraction – LSE (extraction with methanol/acetone and the clean-up over florisil cartridge), the QuEChERS method, ultrasonic extraction (Method 3550 C, USEPA) and Soxhlet extraction followed by silica gel cleanup. The pesticides were analyzed with GC-MS. All the substances were observed to be linear in the range of 10-300 ng/g, with the recoveries from 64.2 to 103.7%. The relative standard deviations (RSD) were from 0.3 to 10.1%. The limits of detection (LOD) were between 0.3 and 6.9 ng/g.

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WATER AND SEDIMENT QUALITY ASSESSMENT USING AGRICULTURAL PLANTS AS BIOINDICATORS

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Monitoring of water and sediment quality in watercourses of Serbia gained in importance in last few decades. The Great Bačka Canal occupies the special attention as it is considered to be the most polluted canal that is intensively used in agriculture production. This study presents the results of comparative study of chemical analysis of water and sediment and their biological effects on test plants. Heavy metal and organic pollutant contents were determined according to EPA 7000B method, and biological effects evaluated using physiological (germination) and morphological (root and shoot length) responses of cucumber (*Cucumis sativus* L.) and barley (*Hordeum vulgare* L.) by standard method on filter paper (ISTA Regulations book, 2011 and Regulation of the quality of seed of agricultural plants (Official gazette 58/2002)). Assay comprised the samples of water and pore water (obtained in process of sediment precipitation) from the canal, while as control variant distilled water was used. Chemical analysis indicate elevated levels of Cd (exceeding MAC-EQS according to Directive 2008/105/EC) in water while the sediment was slightly contaminated with Cu. Regardless of chemical composition, seed germination was at the same level of significance between all treatments for both plant species, and was within the norms stipulated by mentioned Regulation book. However, water and pore water from the canal inhibited root growth of cucumber and barley expressing highly significant difference compared to control variant. Shoot growth was stimulated in water and pore water samples and was significantly higher compared to the control. Given indicates that more reliable assessment of water and sediment quality can be achieved only with comparative analysis (chemical and evaluation of plant responses). Accordingly, cucumber and barley showed good potential as bioindicators of quality of these systems.

OCCURRENCE OF PHARMACEUTICAL COMPOUNDS IN THE FRENCH DEPARTMENT OF DORDOGNE

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Third largest french department (french division) by area, the Dordogne remains a fairly rural area characterized by a wide and diversified aquatic network (with a linear of 6 000 km). Although its aquatic ecosystems exhibited good ecological and chemical status during last years (according to the Water Framework Directive), some areas could suffered from chemical hazards like downstream of the main city: P erigueux (approx. 30 000 inhabitants in 2008) which is crossed by the river Isle.

In relation with the Water Framework Directive screenings, samples were taking every months for one year (2011) in the 6 major Dordogne's rivers to determine ecological and chemical status. In parallel, a characterization of pharmaceutical contamination of water was done for 15 sampling stations through the departement. The investigation of pharmaceuticals was carried out with a list of 40 compounds including lipid regulators, antibiotics, β -blockers, non-steroidal anti-inflammatories, anticancer drugs, etc. The different campaigns have shown a seasonal effect and correlations between pharmaceutical concentrations with other parameters (ammonium, DOC and suspended materiels) were established. Results of the survey will be presented and discussed in relation with potential sources and analyzed in terms of impact.

ANALYSIS OF HIGH MOLECULAR WEIGHT PHTHALATES IN SEDIMENTS USING ATMOSPHERIC PRESURE GC COUPLED TO A TIME OF FLIGHT MASS SPECTROMETER

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The analysis of phthalates in environmental samples is an important application as some phthalates are considered to be potential endocrine-disrupting chemicals (EDCs). Most classical methods for this application are based on GC/MS. Attention has recently turned to the analysis of di-isononylphthalate (DiNP) and di-isodecylphthalate (DiDP) but their analysis by GC results in an unresolved cluster of peaks that all predominantly fragment to the phthalic anhydride ion at $m/z = 149$. Consequently, quantification of DiNP and DiDP using the most abundant ion is impossible and the same sensitivity as for the single isomer phthalates cannot be reached.

Atmospheric pressure ionisation has primarily been used to interface MS with LC, but it is also a powerful ionisation method that can be applied to GC. APGC is a novel atmospheric pressure ion source for MS instruments that allows laboratories to switch rapidly between LC and GC applications. It can be used to analyse compounds traditionally analysed by dedicated vacuum GC/MS instruments.

Ionization of a GC eluent at atmospheric pressure is a softer process, giving molecular weight information for compounds which are extensively fragmented in traditional Electron Ionization (EI). Another key advantage is that GC separations can be optimized as the carrier gas flow and column dimensions are not limited by the pumping capacity of the MS.

In this work, APGC coupled to a quadrupole time-of-flight mass spectrometer was used to analyse the high-molecular-weight phthalates. DiNP and DiDP were successfully ionized in proton transfer mode yielding spectra that contained the molecular ion as the base peak. The method was also applied to measure DiNP and DiDP in a sediment extract at relevant levels for environment samples.

DETECTION AND QUANTIFICATION OF UNKNOWN CONTAMINANTS DURING TOF SCREENING FOR PESTICIDES IN RIVER WATER USING AN INTEGRATED SOFTWARE APPROACH

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The use of Time-of-Flight (ToF) screening approaches has steadily increased in both food safety and environmental monitoring laboratories. ToF screening can either be used for targeted screening activities – where an extensive database is used to target key compounds of interest after the screening acquisition stage, or it can be used in a non-targeted way – using deconvolution software to identify all peaks present in a sample after non-targeted data acquisition.

When analysing environmental waters, pesticide contamination screening is one of the most important analyses carried out. However, other contaminant species, such as veterinary drugs or human pharmaceuticals and their metabolites, may also be present at similar ultra-trace levels as pesticides and could be equally as harmful to the aquatic ecosystem.

Discovery of a non-targeted, unexpected compound subsequently entails the confirmation and identification of that compound. The ToF instrumentation must be sufficiently sensitive and accurate to ensure that the unknown compound is correctly detected and identified, while at the same time maintaining exact mass accuracy for components at very low concentrations. Accurate and precise exact mass data on both the low energy precursor ion and the MSE high energy fragment ions, together with an integrated, multi-component software approach, provide increased confidence in the identification of the non-targeted species.

This talk describes the non-targeted screening of water samples using OASIS HLB cartridges for SPE clean-up and pre-concentration, followed by analysis using Waters ACQUITY UPLC coupled with Xevo G2 QTof. Three non-targeted contaminant species were detected and successfully identified in river water using ToF screening and a structural elucidation workflow.

COMPARISON OF SELECTED EXTRACTION METHODS FOR DETERMINATION OF CLOTHIANIDIN INSECTICIDE IN HONEY SAMPLES USING LIQUID CHROMATOGRAPHY EQUIPPED WITH DIODE ARRAY DETECTOR

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Neonicotinoid insecticides are intensively used for crop protection because of their excellent systemic properties, but are unfortunately suspected as major cause of observed massive killings of honey bees.

The aim of this work was to develop a method based on liquid chromatographic determination of selected neonicotinoid insecticide clothianidin in honey samples by diode array detector (HPLC-DAD). The chromatographic separation was carried out using reverse phase column with isocratic conditions of mobile phase consist of water (with 0.2% phosphoric acid) and acetonitrile (7:3, v/v). Due to the complexity of the sample matrix several sample preparation procedures were tested including dichloromethane extraction, ethyl acetate extraction, extraction based on their combinations with solid-phase (with Discovery-18 column) extraction and QuEChERS AOAC Official Method 2007.01. From the obtained results it can be concluded that neither one separated step of extraction is providing sample with satisfactory pureness for further HPLC-DAD analysis. For this reason this method proposes a procedure of sample purification based on combination of two clean-up steps: dichloromethane extraction for the first step and purification using solid phase column for the second one providing satisfactory extraction recovery yield. Furthermore, commercially available extraction kit for implementing the QuEChERS method has showed a low extraction recovery yield for quantities of clothianidin less than 1 ppm.

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EXTRACTION METHODS RESIDUES OF METRONIDAZOLE FROM BIOLOGICAL SAMPLES – PRELIMINARY ASSESSMENT

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The biologically active substances referred to as pharmaceuticals are not used exclusively to protect human health: significant amounts of these compounds are also produced for husbandry and veterinary applications. Hence, there are many ways in which these drugs can be discharged into the environment. One of the major fraction of environmental polar pollutants are pharmaceuticals used in aquaculture. This is due to the fact that aquatic organisms are usually treated with therapeutic agents added to feed or directly to fresh water baths. Thus, it is likely that these drugs will bioaccumulate in animal tissue but also will concentrate in waters and sediments. .

Metronidazole belongs to the group of nitroimidazole antibiotics. It is commonly used in treatment of diseases caused by anaerobic bacteria and protozoa. It is also employed in fish farms.

The present work has been aimed to selection of the best possible method of isolation and enrichment of metronidazole from fish tissue. It is a matter of urgency to investigate the most appropriate sorbent type, because it can control such parameters as selectivity, affinity and capacity. This choice depends strongly not only on the target analytes, but also on the kind of sample matrix (e.g. fish tissue) and its interactions with both the sorbent and the analyte.

COMPARISON OF COLUMN AND BATCH TEST ELUATES DERIVED FROM PAH- AND TPH-CONTAMINATED SOILS

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Laboratory leaching tests are important tools for the risk assessment of contaminated soils and waste materials on the soil-groundwater pathway. They allow for the determination of the source term as an expression of release potential of water soluble contaminants during the use or disposal of waste materials. With the designated establishment of a new Ordinance on Waste Utilization and the amendment of the German Ordinance on Soil Protection and Contaminated Sites, the German Federal Ministry for the Environment will allow for column and batch tests as preparation methods for aqueous eluates at a liquid-to-solid ratio of 2 L/kg. Whereas column tests provide a more realistic simulation of field conditions, batch tests might be prone to excess finding of analytes due to particle release caused by friction during the test. Thus we tested several polycyclic aromatic hydrocarbon (PAH)- and total petrol hydrocarbon (TPH)-contaminated soils and soil materials with both leaching methods to check for their comparability.

The low standard deviations of the triplicate column and batch tests results indicated a good reproducibility of both methods. For PAH, we found a correlation between batch and column tests results, with a slight tendency to excess findings with batch tests (up to 50 %). With increasing organic matter content in the test materials, less PAH were released with both methods. In case of TPH, there were partly large excess findings with batch tests. Whereas the column tests led to 328 µg/L at most, the highest amount detected in a batch test was 3494 µg/L. Contrary to PAH, the highest TPH amounts were leached from soils with the highest organic matter content.

LDH-BASED SENSORS FOR ENVIRONMENTAL MONITORING

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Layered double hydroxides (LDH) are synthetic solids with positively charged brucite-like layers of mixed metal hydroxides separated by interlayer hydrated anions, defined by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} [(A^{n-})_{x/n}, y H_2O]$. They are used as electrode surface modifiers for the properties of the layered structures, including their adaptable anion exchange capacity and their electrocatalytic properties. Moreover, these materials are often used as immobilization matrices of enzymes. All these properties make the LDH interesting materials for the fabrication of sensors and biosensors, in particular for the detection of water pollutants. For instance, an efficient electrochemical detection of herbicides (glyphosate and glufosinate) can be done at redox active NiAl-LDH modified electrodes and offers a valid alternative to UV or fluorescence detections for which organic tagged procedures are needed [1]. Highly sensitive LDH-based biosensors have been also developed for the direct detection of phenols [2] and nitrite [3] with immobilized tyrosinase or nitrite reductase. Finally, LDH-biosensors based on the principle of enzyme inhibition processes were applied to a wide range of significant pollutants such as cyanide [4-6], nitrite [7], arsenate [8] and mercury [9]. An overview of all these sensor concepts based on LDH modified electrodes will be presented.

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EXTRACTION AND CHARACTERIZATION OF SOIL ORGANIC MATTER FROM BLACK SOIL OF LIMAGNE

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Soil organic matter (SOM) plays a key role in soil major biogeochemical. It is known to provide an analytical challenge to individuals seeking molecular-level information. This is mainly due to its extreme complexity. In this work we have been interested to black soil of Limagne which shows similarities with chernozem, according to French soil taxonomy; they contain a large amount of organic matter and are fertile soils.

Our work is focused on the water extractable organic matter (WEOM) and on its photochemical properties. The first objective was to extract it. For this, we used different extraction procedures by varying the water temperature and the time of extraction. The efficiency and selectivity of these processes were compared in terms of total organic carbon recovered, spectroscopy properties (UV-Vis and fluorescence) of the extracts, chemical composition (HPLC analysis) and photosensitizing activity.

The comparative evaluation of three extracts obtained in (20°C, 24 h), (60°C, 30 min) and (80°C, 20 min) conditions highlighted significant differences among them. In particular, the TOC content, the SUVA₂₅₄ value, the E₂/E₃ ratio and the humification index varied in the following order:

WEOM (20°C, 24h) < WEOM (80°C, 20min) < WEOM (60°C, 30min).

The fluorescence analysis of the three samples showed the presence of common fluorophore units associated with simple aromatic structures, while HPLC analysis showed the presence of three fractions of distinct polarity. WEOM (60°C, 30min) presented the strongest photosensitizing potential.

RISKY LEACHATES, A CHRONIC PROBLEM OF ABANDONED MINES

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Acid Mine Drainage (AMD) and the contamination associated with it has been described as the largest environmental problem facing the worldwide mining industry. AMD is primarily a function of the mineralogy of the rock material and the availability of water and oxygen. Because mineralogy and other factors affecting the potential for AMD formation are highly variable from site to site, predicting this kind of phenomena is currently difficult, costly, and of questionable reliability. In addition to the acid contribution to surface and ground waters, AMD may cause metals such as arsenic, copper, silver, lead, and zinc to leach from mine wastes. According to some researches, the metal load causes environmental damage and is of greater concern than the acidity in environmental terms (i.e. groundwater pollution, diseases in human beings).

AMD prediction tests are increasingly relied upon to assess the long-term potential of acid generation. The purpose of this research was to evaluate the ability of soil and rock samples to both generate acid formation and increase the mobility of metals from an abandoned lead-zinc mine. The mobility tests carried out in lab, showed highly polluted acid leaches enriched in soluble metals (i.e. Zn, Cu, Pb, As, Cd), phosphates, nitrates, sulphates, etc. Considering that the mine is located in a karstic area where the pollution may leach in both horizontal and vertical directions, such results may be an important sign of a chronic pollution of the groundwater, a hot spot that will require urgent action.

IN SITU RAMAN SPECTROSCOPY APPLIED TO THE ANALYSIS OF CONCRETE MADE URBAN BUILDINGS

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Urban environments present diverse pollutants such as atmospheric acid gases, which are in constant interaction with building materials. These pollutants produce several decaying due to the generation of harmful compounds often in form of weathering salts. Besides, the portability has taken a great importance in the last years due to the advantages that a nearly immediate diagnosis can offer. Ultramobile Raman spectroscopy is an ideal technique to perform an in-situ characterization of these compounds since it allows the identification of salts under similar efficiency as conventional spectrometers.

In this work the viability of the in-situ technique in the determination of the conservation state of building materials is demonstrated. The analyses were performed by an ultramobile Raman Spectrometer (785nm laser, B&WTEK_{INC}) on a scaffolding installed in a concrete made urban building under restoration. Calcite was the main compound identified as a consequence of the so called concrete carbonation. The analysis of the steel of the reinforced concrete reveals the formation of several oxohydroxides by the action of infiltration water. Thenardite, which is one of the most harmful sulphate salts due to the reversible transformation into mirabilite, was found as decaying salt. Moreover, the identification of nitrate evidenced the action of NO_x gases on the carbonated concrete. With regard to gypsum, although it is sometimes added during the preparation, the high amounts found suggested a contribution of atmospheric SO₂ attack on building materials. In conclusion, in situ analyses evidenced that they provide valuable information on the conservation state of building materials without decreasing or even avoiding sampling.

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A NEW EXTRACTION METHOD TO DETERMINE SOLUBLE SALTS IN BUILDING MATERIALS: AN ALTERNATIVE TO EUROPEAN STANDARDS

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Cracks and losses of material are the most serious effects that soluble salts can produce in buildings materials, especially in carbonate based stones such as limestone. Nowadays, different standard protocols are used to determine the content of soluble salts in building materials. The Italian recommendation NORMAL 13/83, later replaced by the UNI 11087/2003 in Italy or CENT/TC 346/WG 2 in Europe, has been used as standard for years. These norms are based on long-time stirring (72, 2 and 2 hours, respectively) of the sample in deionised water. Therefore, the aim of this work was to reduce the extraction time by using ultrasound energy. Two protocols are proposed to treat samples with high pollution level (>8% of weight in soluble salts including up to the 4% of sulphate): ultrasound bath and focused ultrasound. The extraction by both methods was optimized using experimental design and the results were statistically compared with those obtained by the standards.

Using the same sample mass and water volume, the optimal extraction time for the ultrasound bath was found to be of two hours. Although the extraction time was equal to the standards, the obtained extraction was better. The focused ultrasound system achieved even better efficiencies for some analytes in only one hour treatment.

Parameter	NORMAL 13/83	CEN/TC 346	Ultrasound bath	Focused ultrasound
Weight (g)	0,1	0,1	0,1	0,1
Water volume (ml)	100	100	100	45
Time (h)	72	2	2	1

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OPTIMISING THE REMOVAL OF PHARMACEUTICALS FROM AQUEOUS MEDIA USING BIOSORBENT MATERIALS

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Globally, the use of human pharmaceuticals is increasing each year. However, studies conducted in countries including Germany, USA, UK and France have demonstrated the presence of pharmaceutical residues in wastewater effluents, rivers, lakes and seawaters. Conventional methods for removal of xenobiotics such as pharmaceuticals from water are generally expensive and there is need for development of alternative approaches. Biosorption has been shown to have potential as a low-cost effective alternative for the removal of some contaminants from aqueous media, but has not been extensively evaluated for pharmaceuticals. Furthermore the application of mixed biosorbents for the removal of pharmaceuticals has not been reported.

In this work, mixtures of the biosorbents crab carapace, peat and seaweed were evaluated for the removal of pharmaceuticals from seven therapeutic classes including beta-blockers, anti-fungals and anti-depressants and the efficiency of biosorption determined by HPLC-TOF/MS. The use of Simplex-Lattice Mixture Experimental Design (SLMED) was applied to assess the efficiency of biosorbents of constant mass, but variable composition. This process allowed the identification of synergistic or competitive actions between biosorbents and allowed determination of optimum mixture composition.

Results demonstrated that pharmaceuticals which were analysed in positive mode TOF/MS were more efficiently removed (from 45% for Paracetamol to 97% for Terbinifine) than those in negative mode (from 16% for Pravastatin to 29% for Diclofenac). The evaluation of the experimental models revealed synergistic actions between biosorbents and that a mixture of 53% peat, 37% seaweed and 10% crab was optimum for the removal of pharmaceuticals from test solutions.

SORPTION OF Pb^{2+} ION BY a-BAUXOL

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The aim of this paper is to present the investigation of the sorption capacity of the activated red mud as an alternative sorbent for the removal of lead from water solutions. The influence of various parameters has been investigated: solution concentration, contact time and sorbent mass on the sorption process.

The time necessary for the equilibration is 60 minutes, regardless of the initial solution concentration (Fig. 1). The experimental results have been in accordance with Langmuir theoretical model, used to determine the maximum sorption capacity of 0.62 mg/g.

The calculated values of separation factors and Gibbs function change indicate that the sorption process is favoured and spontaneous.

The sorption efficiency has been shown to decrease with the increase of the sorbent mass.

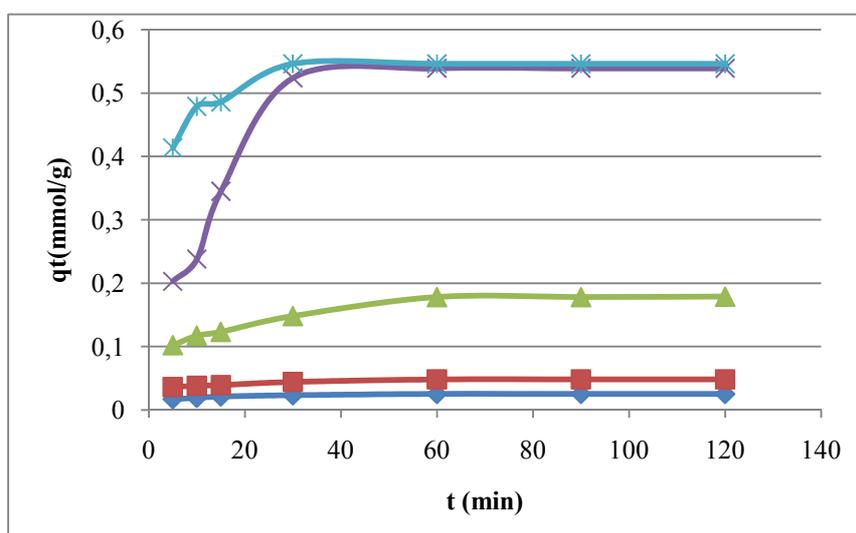


Fig.1 The sorbed amount of Pb by a-Bauxsol in the function of time. The initial solution concentrations (mol/dm³):(◆) 5×10^{-5} ; (■) 10^{-4} ; (▲) 5×10^{-4} ; (x) $2,5 \times 10^{-3}$; (x) 5×10^{-3}

DETERMINATION OF POLYCHLORINATED BIPHENYLS IN HUMAN COLOSTRUM AND INFANT FORMULAS

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The objective of this study was to determine concentrations of eight EPA PCB congeners, as the typical representatives of persistent pollutants, in early human milk and its supplement – infant formulas of artificial milk, as a measure of exposure of breast fed newborn babies born to mothers living in Novi Sad and its surrounding. PCBs in 3rd day colostrums were monitored in South Bačka since 1982. Healthy mothers expressed colostrums into specially prepared glass containers. Samples were frozen at -20°C until analyzed. n- Hexane and conc. sulfuric acid were added to milk samples, cooled and stood overnight at room temperature. The hexane layer was separated and cleaned up twice with conc. sulfuric acid and through the Florisil column, and the eluate evaporated and analysed by GC-ECD (HP 5890 supplied with a Quadrex fused silica column 5% Ph for PCBs).

No correlation was found between the PCBs concentrations and age of mothers. Birth weights also did not influence of PCBs concentrations on human milk burden. Concentrations of PCBs in infant formulas were below average values in human colostrums. Formula manufactured in Serbia did not contain any of PCB congeners. In other four imported formulas PCB congeners 153, 138 and 180 were detected in a concentration range from 0.05 to 0.07 ng/g ww. Mean value for the concentration of 8 PCBs showed exponential decrease from 1982 (40.08 ng/g ww) to 2009 (1.06 ng/g ww), with half time of decrease of 6.7 years.

Higher exposure of babies to PCBs was estimated for human milk samples than for infant formulas of artificial milk. However, breastfeeding should be encouraged since human milk presents the indispensable food for infant's development and growth.

REMOVAL OF MERCURY FROM AQUEOUS SOLUTIONS BY UNMODIFIED RICE HUSK SORBENT

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In the last two decades, new approaches based on the sorption properties of natural materials have been developed to remove metal ions from waters. Several materials have been proposed and a special attention has been given to low cost sorbents, since in many cases they represent either a by-product or waste material from industry and are usually available in large quantities. The objective of this work was to develop an economical method for the removal of mercury from waters and to characterize and explore an inexpensive, highly available, effective sorbent. Rice husk, a by-product of rice processing that comprises 23% of the rice grain and regarded as a waste disposal problem, was the sorbent selected. The structural and morphologic features of unmodified rice husk were evaluated and parameters such as contact time, initial metal concentration and sorbent mass were studied. Moreover, the kinetic and equilibrium behaviour was evaluated.

The results reveal that the maximum Hg^{2+} removal rates were 83 and 92% for an initial Hg^{2+} concentrations of 50 and 500 $\mu\text{g/L}$, respectively, and a sorbent mass of 1 g. The Hg^{2+} concentration was reduced to values lower than 8 $\mu\text{g/L}$ after the remediation procedure and for a initial Hg^{2+} concentration of 50 $\mu\text{g/L}$, which can be considered a satisfactory result, but not adequate to obtain a clean water with drinking quality ($C_{\text{Hg}^{2+}} < 1 \mu\text{g/L}$) [1]. The results obtained for a starting Hg^{2+} concentration of 500 $\mu\text{g/L}$ where lower than 50 $\mu\text{g/L}$, that represents the actual maximum value for Hg discharges from industrial sectors [2]. This way it was shown that unmodified rice husk can be successfully applied to remove Hg^{2+} from waters.

[1] Council Directive 98/83/EC on the quality of water intended for human consumption.

[2] Council Directive 84/156/EEC on limit values and quality objectives for mercury discharges by sectors other than the chlor-alkali electrolysis industry.

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BORON REMOVAL FROM AQUEOUS SOLUTIONS USING SiO₂ AND TiO₂ HYBRID GELS

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Boron is widely used many industries such as chemical, ceramic, metal welding and pharmaceutical manufacturing. The discharge of boron containing wastewater to the environment causes several pollution and health problems. The attachment of organic functional groups to inorganic oxides allows the synthesis of new materials with specific sorption properties. In this work, boron removal from aqueous solutions by adsorption with SiO₂ and TiO₂ hybrid gels functionalized with *N*-methylglucamine groups was investigated. Borate esters are produced by reaction of boric acid with alcohols groups presents in the *N*-methylglucamine moiety of the hybrid gels. The effect of initial pH, initial boron concentration, time of contact and type of inorganic oxide on the adsorption was investigated. The characterization of the hybrid gels was conducted using the FTIR technique before and after the boron adsorption. Boron adsorption is a pH dependent process. The adsorption increases when de pH increases, reaching a maximum at pH = 6 for the SiO₂-based hybrid gel, and at pH = 10 for the TiO₂-based hybrid gel. Maximum boron removal obtained were 9.73 mg/g and 29.96 mg/g for the SiO₂ and TiO₂ hybrid gel respectively. Kinetic results fit better to the pseudo-second-order adsorption model suggesting that the overall rate of boron adsorption is controlled by the chemical process. In the isotherm studies, Langmuir and Freundlich isotherm models were applied. The experimental data conformed to Langmuir isotherm model in the case of the SiO₂ hybrid gel, while the Freundlich model better describes the experimental data obtained with the TiO₂ hybrid gel. These results suggest that the type of oxide has a great influence onto the sorption mechanism.

ADSORPTION OF FUMONISINS ONTO ALGINATE GEL BEADS

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Fumonisin is a group of mycotoxins mainly produced by *Fusarium verticillioides*. Mycotoxins are toxic chemical compounds that are produced by several fungi. There are different physical, chemical and biological processes for the reduction of mycotoxins in animal feed. The most applied method for protecting animals against mycotoxicosis is the utilization of adsorbents mixed with the feed, especially clay products such as bentonites, zeolites and aluminosilicates, which not being digestible have problems during the digestion process. The aim of this work is to provide an alternative to the use of clays as adsorbents of mycotoxins. A calcium alginate gel beads is the adsorbent proposed in this study. Fumonisin solutions necessary to carry out the experimental study were prepared from pure fumonisins and contaminated grain with an initial concentration of 3 mg/L and 6 mg/L, respectively. The adsorption has taken place by batch system, adding to each of the solutions given amount of adsorbent (0.005–1.5g). Residual mycotoxin concentrations of the different samples were analysed by enzyme linked immunosorbent assay (ELISA). The applicability of the Langmuir and Freundlich isotherms for the present system was evaluated. The parameters obtained by these equations show high affinity between fumonisins and calcium alginate. The maximum adsorption capacity was 2.7 and 2 mg fumonisins/g calcium alginate when the samples were prepared from pure fumonisins and contaminated grain, respectively.

CHARACTERIZATION OF DISSOLVED ORGANIC MATTER RELEASED DURING ALKALINE PEROXIDE BLEACHING PROCESSES

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The pulp and paper industry is under pressure to reduce its environmental impact, particularly chemical oxygen demand (COD) in released effluents. With this in view, alkaline peroxide bleaching was successfully carried out using magnesium hydroxide or carbonate in place of the strong alkali sodium hydroxide, which is responsible for the dissolution of organic compounds.

The characterization of the dissolved organic matter (DOM) present in NaOH-based bleaching effluents showed that lignin, measured by ultraviolet (UV) spectrometry at 280 nm on aqueous samples pretreated with MTBE, was the main constituent, at the high concentration of 1025 mg.L⁻¹, compared with only 167 mg.L⁻¹ of polysaccharides as shown by ionic chromatography analysis. All the compounds identified in the NaOH-based bleaching were also present in the effluents of the Mg-based process, but in smaller amounts. For example, analysis of silylated samples by gas chromatography coupled with a flame ionization detector (GC/FID) showed that there were 24% and 43% less extractives generated during Mg(OH)₂ and MgCO₃-based processes, respectively, compared with NaOH-based bleaching.

DOM was also characterized by high performance size exclusion chromatography (HPSEC) coupled with sequential on-line detectors consisting of UV at 254 nm, fluorescence and quantitative dissolved organic carbon (DOC) measurement. Excitation-emission wavelengths of the fluorescence system were set at 280-330 nm for lignan-type substances such as secoisolariciresinol and 330-440 nm for lignin based on excitation-emission matrix (EEM) spectra of NaOH-based peroxide bleaching effluents and reference samples. The analysis of NaOH-based bleaching effluent by HPSEC showed that lignan-type substances had an apparent molecular weight (MW) of about 325 g mol⁻¹ and that lignin had apparent MWs of 1140, 900 and 300 g mol⁻¹. Also, the DOM fraction in the high apparent MW range (> 220 000 g mol⁻¹) consisted of lignin-carbohydrate complexes (LCCs). EEM spectra of NaOH- and Mg-based bleaching effluents displayed similar major peak values. However, the apparent MW peaks on HPSEC were less intense, demonstrating that all DOM fractions are reduced when using Mg-based alkali during peroxide bleaching.

APPLICABILITY OF ION CHROMATOGRAPHY FOR IONIC LIQUID CONSTITUENTS ANALYSIS IN WATER AND WASTEWATER

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In this study ion chromatography (IC) was tested to verify its applicability in analysis of ionic liquid constituents in environmental matrices. Firstly the suppressed IC method for analysis of $[(F_3CSO_2)_2N]^-$, $N(CN)_2^-$, $B(CN)_4^-$, $C(CN)_3^-$, $[(C_2F_5)_3PF_3]^-$ and $[H(C_2F_4)SO_3]^-$ anions in the presence of inorganic anions were developed. Mobile phase contained the carbonate buffer modified by acetonitrile. In the next stage of research the reliable and sensitive method was proposed to separate mixture of imidazolium entities together with typical inorganic cations, usually found in various matrices, in the one run. Nitric acid with acetonitrile used as eluent was suitable for analysis of cationic constituents. Proposed methods were validated and applied for the analysis of those compounds from waste water plant sludge samples during assessment of ionic liquids biodegradation. The limit of detection was in the range 0,1 – 0,3 μM , the repeatability for various analytes vary between 0,5 – 9,0 %. Developed methods was optimized and validated with good analytical performance parameters. Limits of detection were about 3 – 5 μM , and the repeatability lay in the range of 1.06 – 5.59 %. These methods were evaluated for their applicability to the analysis of soil samples and freshwater contaminated with ionic liquids.

ANALYSIS OF ALACHLOR RESIDUES IN DIFFERENT TYPES OF WATER

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Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide] is chloracetanilide based herbicide, used in row crops at application rates 1.4-2.9 kg a.i./ha. According to EU Directive 2000/60/EC (Annex X) it is classified among 33 most important water pollutants. This study assessed the possibility of alachlor detection in samples of tap, river and groundwater. Prior to analyzing, river water was filtered. Extraction was performed using ENVI C18 SP disc (47 mm; Supelco No. 57171), conditioned with 5 ml ethyl-acetate, 5 ml methanol and 5 ml deionized water prior to extraction, and afterwards vacuumed (10 ml/min) through model solution: 1000 ml of sample (tap, river and groundwater) with addition of 1 ml of standard alachlor solution (conc. 0.01 µg/ml, 0.1 µg/ml and 1 µg/ml). Disc had been dried for 24h at 30 °C, after which, alachlor was eluted with 5 ml of ethyl-acetate/isooctan (10/90, v/v) mixture. Eluent was steamed at the evaporator until totally dry, and then diluted in 3 ml of acetone and homogenised with ultrasound. Alachlor content was analyzed using gas chromatograph (HP 5890 series II) with EC Ni⁶³ detector (column SUPELCO 24048, SPBTM-5, 30m x 0.32mm, 0.25µm FILM; gas carrier N₂). Injected volume was 2 µl. Conditions for detection were: t °C of column 200 °C with an increase of 30 °C/min up to 240 °C, t °C of injector 230 °C and t °C of detector 250 °C. Results represent average values obtained from three assays repeated under the same conditions. Linearity of detected response was determined by injecting standard alachlor solution in concentrations 0.01-1 µg/ml. Correlation coefficient was 0.997 %, regression equation $y=15221x+37.27$, and the limit of quantification (LOQ) 0.01 µg/l. The average recovery for tap water was 89.1 % (79.3-95.9 %), for river 79.6 % (75.2-84.5 %) and for groundwater 87.1 % (81.5-93.4 %), with coefficient of variation (CV) less than 10 %. The research was funded by the grant of the Serbian Ministry of Education and Science (III 43005).

ON-LINE MONITORING OF TRACE METAL IN AQUATIC SYSTEM WITH AN ADAPTABLE VOLTAMMETRIC SYSTEM

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An Automatic Trace metal Monitoring System (ATMS) was assembled and deployed in the field using a hanging mercury drop electrode. Concentrations of metals (electroactive at natural pH and acid-leachable fractions of Mn, Zn, Cd and Pb) were measured by anodic stripping voltammetry and dissolved oxygen and reduced sulphur species concentrations were estimated by cathodic stripping voltammetry. The dynamic behaviours of these parameters as well as pH, conductivity and turbidity were then recorded on two sites: Le Quesnoy pond where occur regularly eutrophication processes and the Deûle River where sediments are heavily contaminated in Pb and Zn and are regularly resuspended because of intense barge traffic. Preliminary results show a dependence of metal concentrations in time with turbidity and luminescence i.e. day-night cycles. Metal concentration values were also compared with European Environmental Quality Norms and USEPA recommendations. The system enables easy adaptation of procedures according to the analyst of interest and can be used for the task of early warning.

LAND-BASE ORGANICS POLLUTION EVIDENCE IN MARINE SEDIMENTS OF CORTIOU, MARSEILLE

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Organic pollutants such as aliphatic (n-alkanes), polyaromatic hydrocarbons (PAHs), Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) were measured in sediments collected from 12 sampling sites (C1-C12) of sewage discharge to the sea from the wastewater treatment plant of Cortiou-Marseille. This study aims to determine the extent of these compounds in the sediments and to establish the possible sources of these contaminants. Total n-alkane and PAH concentrations ranged from 34 to 2155 $\mu\text{g.kg}^{-1}$ dw and 696 to 10700 ng.kg^{-1} , respectively. Total pesticides in the sediments ranged from 1.2 to 190.6 ng.g^{-1} dry weight of sediment while the PCBs concentrations, expressed as equivalent to Arochlor 1260, varied from 9.1 to 226.9 ng.g^{-1} . Specific hydrocarbon indexes suggest that terrestrial biogenic inputs were predominant compared to marine sources, and both pyrolytic and petrogenic sources contributed to PAHs in the surface sediments. Concerning

OCs, we showed the long term contamination input of these compounds (DDT, endosulfan, HCH and heptachlor cases) rather than a recent release resulting from degradation and long-term weathering (dieldrin, aldrin and methoxychlor cases) whilst, occurrence of PCBs might be due to their resistance to degradation processes or/and chronic inputs.

EFFECT OF CHALCONE SUBSTITUTION ON PHTHALOCYANINE PHOTOSENSITIZATION

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Metallated phthalocyanines are sensitizers generating singlet oxygen with a high yield. Their photophysical and photochemical properties are highly dependent on molecular aggregation which is itself function on solvent, substituents and sensitizer concentration, in particular. This work is devoted to the substitution effect. A chalcone derivative was chosen as a substituent. Chalcones, 1,3-diphenyl-2-propene-1-ones, belong to the largest class of plant secondary metabolites. Hydroxy and methoxy substituted chalcones are known to possess antioxidant character at various extents, singlet oxygen quenching being one of the possible mechanism.

In this preliminary study, we compared the quantum yield of singlet oxygen production (Φ^{Δ}) of the tetraethyleneglycol phthalocyanine **1** with that of the chalcone substituted counterpart **2** in air-saturated acetonitrile. **1** populates its triplet excited state efficiently, the quantum yield ranges between 0.24 and 0.72 depending on the solvent (1). Sensitizers were excited selectively at 630 nm using a xenon lamp equipped with a monochromator. The scavenging technique was employed for Φ^{Δ} measurement using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen scavenger and methylene blue as a reference ($\Phi^{\Delta} = 0.55 \pm 0.3$). **1** and **2** were found to generate singlet oxygen with close quantum yields.

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A SURVEY OF WATER QUALITY IN THE TUTONG DISTRICT OF BRUNEI DARUSSALAM

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Brunei Darussalam is a small country located on the north west part of Borneo island. Most of the country is still pristine tropical rainforest. At the same time, Brunei Darussalam is an exporter of oil and natural gas. Thus far, production has been confined to the southernmost Belait district, both on- and off-shore. The Tutong district is the central part of the country; it consists mainly of primary rainforest together with farming and urban development on the coastal plain. This area is still undeveloped industrially. There are plans to explore the area for its oil and natural gas potential.

Before this could come to pass, we carried out a survey of the quality of the surface water at several sites to establish a baseline prior to any possible perturbations by exploration. The parameters assessed were: temperature, acidity, dissolved oxygen, conductivity, suspended solids, metal and anion content and bacteria.

THE INVESTIGATION OF SILVER ABSORPTION TO DITHIZONE COATED PARTICLES

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Three different supports were investigated in order to determine differences in coated and uncoated samples of material. The three different supports investigated were titanium (TiO₂), alumina (Al₂O₃) and silica (SiO₂). The coating investigated was dithizone in ethyl alcohol. The coated and uncoated material was characterized using gas sorption. The results showed that coating titanium produced a 7% increase in surface area, whilst coating silica caused a 10% decrease in surface area. Due to their surface area, the particles contain a large amount of reactive surface. In general, a larger surface area material has greater reactivity towards adsorption of metal ions.

Session 2: Atmospheric chemistry

Posters

HETEROGENEOUS REACTION OF NO₂ ON ILLUMINATED URBAN GRIME

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Condensed matter can be found in form of films coating of urban surfaces (e.g. buildings and roads), also called "urban grime". These films are composed of a mixture of organic and inorganic compounds. Recent laboratory studies have involved the uptake of some trace gases (ozone, nitrogen dioxide, NO₃) on organic samples, as liquid or solid coatings under dark conditions while a very few investigations focus on the effect of solar radiation on this heterogeneous chemistry, they confirm that the presence of UV-A/Visible can allow photosensitized processes.

The present study focuses on the heterogeneous reaction between gaseous NO₂ and solid films simulating "urban grime" where nitrate and iron oxides were mixed to pyrene. The potassium nitrate was chosen as an inorganic compound, iron oxide as metal and pyrene representing the fraction of organic compound in the deposit. This reaction was investigated under simulated atmospheric conditions with respect to relative humidity, NO₂ concentration and irradiation using a coated wall flow tube reactor. The results suggest that the photo-induced uptake coefficients when pyrene/KNO₃, pyrene/Fe₂O₃, pyrene/Fe₂O₃/KNO₃ films are exposed to 50 ppbv of NO₂ are approximately two times higher under near-UV irradiation (300-420 nm) than under dark conditions and decreased with the increase NO₂ concentration. The NO₂ removal is linearly dependent on the light intensity and a release of gas-phase NO and HONO is observed, the nitrous acid can rapidly photodissociates to form OH in the troposphere. The outcomes of this study imply that urban "grime" containing PAHs may be a key player in urban air pollution.

MODELING ATMOSPHERIC GASES AND AEROSOLS : IMPACT ON CLOUD AND PRECIPITATION FORMATION

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Clouds droplets are directly dependent on aerosols that are present in the atmosphere and on their probabilities to act as cloud condensation nuclei (CCN). As observed at the Puy-de-Dôme monitoring site, if the atmosphere is poor in aerosol particles, the vapor condensation on aerosols leads to the formation of clouds droplets which reach easily the critical size to precipitate. Therefore, it is necessary to improve aerosol characterizations: physical (concentrations, size distributions...), chemical (volatility, hygroscopicity, chemical composition...) and optical (absorption coefficient, diffusion coefficient...) properties. Moreover, aerosols particles properties are directly link to gas species present in the atmosphere. In fact, gas species can condense over a pre-existing aerosol particle or can lead to the formation of a new particle. So, it is firstly necessary to study conversion between gas species and aerosols in order to understand clouds droplets formation. Sensitivity tests, using WRF-chem (Weather Research and Forecast), should allow an improvement in the knowledge of gas species, aerosol properties and their impacts on clouds droplets and precipitation. From this perspective, a comparison between WRF-chem and WRF coupled with the CHIMERE chemistry-transport model has been tested. The WRF-CHIMERE model has been chosen because it is widely used in the international scientific community. The aim of that comparison was to valid WRF-chem outputs. The chemical mechanism RADM2 (Regional Acid Deposition Model second generation; Stockwell et al., 1990) associated with MADE/SORGAM aerosols (Model Aerosol Dynamics Model for Europe; Ackermann et al., 1998) has been used. MADE dissociates aerosols into 3 modes: Aitken, accumulation and coarse modes. That study allows to quantify gases (O_3 , CO, CO_2 , NO, NO_2 , ...) and the proportion of various chemical components (ammonium, nitrate, sulfate, sodium, chloride ...) in aerosol chemical composition.

MINERAL DUST PHOTOCHEMISTRY INDUCES PARTICLE NUCLEATION IN PRESENCE OF SO₂

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Every year an estimated one to three thousand teragrams of mineral dust are emitted into Earth's atmosphere, largely through the action of wind erosion over arid and semi-arid regions. The residence time of mineral dust particles in the atmosphere of up to several weeks and the thousands of kilometers over which they may be transported allow ample time and exposure for dust particles to interact with other atmospheric constituents. In the present work, we report the interaction of mineral dust proxies with gaseous SO₂ and the dependence of this heterogeneous reaction on ultraviolet irradiation and availability of water vapor. We find that the interaction under irradiation leads to the formation of new ultrafine particles. Our proposed mechanism for the observed particle nucleation suggests that the metal oxides present in mineral dust serve as photocatalysts that promote the production of OH radicals, which initiate the conversion of SO₂ to sulfuric acid. Sulfuric acid is a proven precursor in the nucleation of atmospheric particles, and this finding may shed new light in the current effort to demonstrate sulfuric acid particle formation rates as high as those needed to explain atmospheric concentrations. Our conclusions are supported by ambient measurements, where a relationship between the formation of new particles and the concentration of dust particles has been observed.

SUPPORTED LIQUID MEMBRANE EXTRACTION OF DICARBOXYLIC ACIDS FROM ORGANIC AEROSOLS AND SUBSEQUENT GAS CHROMATOGRAPHIC MASS SPECTROMETRIC ANALYSIS

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Aerosols are climatically important because of their impact on scattering and absorbing solar and thermal radiations [1]. Organic fraction of aerosols contains a major constituent of water-soluble organic compounds (WSOCs) that may account for up to 50 % of organic fraction of particulate matter [2]. (WSOCs) involve a variety classes of compounds and carboxylic acids are the most important because they may alter the properties of aerosols because of their hydrophilic and hygroscopic character [3]. Dicarboxylic acids have been found the most abundant among organic acids in aerosols.

There are various analytical methods that have been used for extraction and analysis of dicarboxylic acids. All these methods not only require a lot of time, laborious work, and extra careful handling during all the steps, but also result in loss of analytes during these pre-analytical steps and introduce an extra uncertainty factor. Also individual dicarboxylic acids from (C3-C9) are found at trace level (from $< 1 \text{ ng.m}^{-3}$ to around 100 ng.m^{-3}). So analysis of dicarboxylic acids require a more selective extraction and enrichment step prior to the analysis.

We applied for the first time the concept of supported liquid membrane (SLM) to the aerosols for extraction of analytes. SLM extraction involves a three-phase system (aq/org/aq), an aqueous phase (donor phase) is separated from another aqueous phase (acceptor phase) by means of an organic liquid immobilized in a porous hydrophobic membrane support. Different parameters like selection of organic phase solvent, stirring speed, time of extraction acceptor and donor phase pH were optimized. And optimized method was successfully applied to real aerosol samples for extraction of dicarboxylic acids (C3-C9). After extraction acids were derivatized using BSTFA and analyzed with gas chromatography mass spectrometry (GC-MS).

6-undecanone was found as optimum organic phase solvent. With this method we obtained maximum enrichment factor ranging 15000 – 28000 for different dicarboxylic acids. And limits of detection were reduced to pg/m^3 range for all studied dicarboxylic acids. All studied dicarboxylic acids were analyzed from real aerosol samples and all nine dicarboxylic acids were found in aerosol samples collected in south of Sweden.

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MESO-SCALE MODELLING OF SOA PRECURSORS FROM CLOUD PROCESSES

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Atmospheric aerosols play a major role in environmental issues related to global and regional climate, atmospheric chemistry and human health. A number of studies have indicated that organic aerosol (OA) plays an important role in both the direct and the indirect aerosol forcing. The majority of the organic fraction of aerosols is suspected to be of secondary origin. However, the sources, chemical composition and formation mechanisms of secondary organic aerosols (SOA) remain one of the least understood processes relevant to the atmosphere. A few studies have considered the existence of a new route for the formation of SOA via the condensation of the low volatile organic products of aqueous phase reactivity during cloud evaporation.

In this framework, this work presents the development of a new condensed chemical mechanism in aqueous phase for soluble organic compounds including isoprene and its oxidation products. This new mechanism is implemented in the meso-scale Meso-NH model. Using the puy de Dôme station database, a scenario is elaborated to perform an idealized 2D simulation of an orographic cloud observed at the station. An assessment of the formation of SOA precursors formed by aqueous phase reactivity during this simulation is realised. In particular, the roles of isoprene and of aqueous phase reactivity are evaluated using some sensitivity tests.

10-YEAR MONITORING OF CLOUD CHEMICAL COMPOSITION AT THE PUY DE DÔME STATION

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Long-term monitoring of the chemical composition of clouds sampled at the puy de Dôme (pdD) station. Around 200 cloud events have been sampled between 2001 and 2011. Physico-chemical parameters, as well as the concentrations of the major organic and inorganic constituents, were systematically determined and associated with 3-days back-trajectories. Three different categories of air mass reaching the summit of the pdD were identified, based on the abundance of organic and inorganic compounds and on physico-chemical characteristics (pH, conductivity, redox potential and total organic carbon): polluted, continental and marine. Trends of the cloud water chemical composition in direct relation with environmental factors were then extracted for each air mass categories. These typical cloud chemical compositions corresponding to particular air mass histories will allow the creation of “standard chemical scenarios” that will serve for modelling purposes on multiphase cloud chemistry.

EMISSIONS OF CO, CO₂, HYDROCARBONS AND PM_{2.5} FROM THE RESIDENTIAL COMBUSTION OF SPANISH TREE SPECIES

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Residential biomass burning has been pointed out as one of the main sources of wintertime atmospheric pollutants, including in Mediterranean countries. Emission factors are required not only for international reporting obligations, but also for applying source apportionment methodologies and for implementation of mitigation measures. As in other countries, in Spain there is a lack of information concerning the characteristics of emissions from biomass combustion systems. The aim of this study was to characterise the emissions from the combustion in a fireplace and in a woodstove of three common woods grown in this Mediterranean country: black poplar (*Populus nigra*), Pyrenean oak (*Quercus pyrenaica*) and European beech (*Fagus sylvatica*). The gas sampling was carried out in the exhaust ducts of both combustion systems. Particles were collected under isokinetic conditions in a dilution tunnel that was directly coupled to the chimney. Emissions of CO, CO₂, total hydrocarbons (THC) and fine particles (PM_{2.5}) vary significantly among the different combustion stages. Globally, CO and PM_{2.5} emissions from the fireplace are higher than those from the woodstove, while the opposite is observed for CO₂ and THC. The comparison of emissions from this study with literature data showed significant differences between the various types of combustion equipments, especially old-type residential appliances versus modern woodstoves and boilers with higher combustion efficiency.

PREDICTION OF GAS-PARTICLE PARTITIONING OF POLYCHLORINATED BIPHENYLS (PCBs) BASED ON M5' MODEL TREES

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Numerous approaches to modelling the distribution and fate of PCBs in the environment have evolved in response to few dominant characteristics of these substances. First of them is presence of PCBs in virtually all environmental phases and the ease with which they move from one to the other. Describing transport across phase boundaries and type of partitioning becomes as, or even more, important as quantifying transport within the phases. Since PCBs may persist in the environment for many decades, processes such as equilibrium partitioning and steady-state are very important for their fate. Measuring PCBs is difficult and expensive. The paper evaluates the applicability of multivariate piece-wise-linear M5' model-tree models to the problem of gas-particle partitioning. Experimental values of particle-associated fraction, obtained for 129 ambient air samples collected at 24 sites, were compared to the prediction results obtained using M5' and the Junge-Pankow (JP) model. The M5' approach proposed and models learned are able to achieve good correlation (correlation coefficient >0.8) for PCB28 and PCB153 compounds, when the target is to predict the concentration of gas phase based on the particle-associated phase. When converted to particle-bound fraction values, the results, for selected compounds, are superior to those obtained by JP model. Statistical significance of the differences between the predictions obtained by JP and the proposed models has been tested using two-tailed t-tests, which returned significance levels below 10^{-6} for all compounds tested. The values are well below the 0.05 significance level usually used to test for distribution difference, and prove that the error characteristics of the two models are indeed different.

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LIVING MICROORGANISMS IN CLOUDS

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The viable microbial community that exists in cloud water sampled from the summit of the puy de Dôme Mountain (1465 m.a.s.l; France) is described, along with its qualitative and quantitative variability, based on 41 independent cloud water samples (2003-2010). The total microbial counts determined by microscopy reached about $\sim 10^5$ cells per mL of cloud water, of which less than 1 % were cultivable under aerobic conditions and in the absence of light. However, the global ADP/ATP concentrations and ratios measured in cloud water samples were compatible with the existence of a metabolic activity in the cloud droplets.

More than 500 bacterial and yeast strains were isolated and identified by 16s or 26s rRNA gene sequencing; Most frequent genera included *Pseudomonas*, *Sphingomonas* and *Frigoribacterium* for bacteria and *Udeniomyces*, *Dioszegia* and *Cryptococcus* for yeasts. They presented high similarities with those originating from vegetation, soil and aquatic environments. Interestingly, most of *Sphingomonas* strains isolated from clouds were phylogenetically located in a small and specific cluster that gathered a few species found in the atmosphere.

BIOTRANSFORMATION OF METHANOL AND FORMALDEHYDE BY BACTERIA ISOLATED FROM CLOUDS. COMPARISON WITH RADICAL CHEMISTRY

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The kinetics of biodegradation of methanol and formaldehyde, major atmospheric VOCs by 4 bacterial strains (*Pseudomonas* spp., *Bacillus* sp. and *Frigoribacterium* sp.) isolated from cloud water at the puy de Dôme mountain have been investigated using ¹H and ¹³C NMR spectroscopy at 5 °C and 17 °C, respectively average and summertime temperature at this site.

Metabolic intermediates were identified, with notably production of C3 compounds (glycerol, 1,2- and 1,3-propanediol) from formaldehyde by the strain *Bacillus* sp. It shows that in addition to classical oxidative pathways leading to CO₂, compounds with higher molecular weight can be produced from C1 compounds.

In order to evaluate to which extent microbiological oxidation of organic compounds has to be considered as an alternative route to radical chemistry in cloud water, the biodegradation rates measured were compared with rates related to the reactivity of organic species with free radicals [•]OH (daytime chemistry) and NO₃[•] (nighttime chemistry) under two cloud situations (urban and remote cases).

Clearly, measured biological and chemical reaction rates were in the same range of magnitude and their relative contribution varies according to the scenarios we tested, including the temperature of the clouds (5 or 17 °C), the category of the clouds (urban and remote) and the diurnal cycle (day and night time). Except for the degradation of methanol at 5°C in remote clouds, our results show that biotransformation processes could be the main sink for C1 compounds in liquid clouds (warm cloud) during the night and both in polluted and non polluted clouds.

CHEMICAL CHARACTERISATION OF ORGANIC AEROSOLS IN ALGIERS CITY AREA: SEASONAL VARIATION AND SIZE DISTRIBUTION

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The water-soluble fraction of organic aerosols suspended in different atmospheres of Algiers city area was qualitatively and quantitatively characterised through several monitoring campaigns. This includes polar and non polar species comprising n-alkanes, n-alkanoic acides, ketones, polycyclic aromatic hydrocarbons (PAHs) and their oxygenated and nitrate derivatives (OPAHs and NPAHs, respectively), caffeine, nicotine and some psychotropic substances. These air pollutants containing in particulate phase were reconciled to their emission sources by combining the diagnostic tools and molecular markers. Seasonal modulations of these organic aerosols were studied and showed that most of particulate organic compounds peaked in winter-times while those of photolytic origin presented higher concentrations in summer-times. Carcinogenic and mutagenic potencies associated to PAHs were evaluated by multiplying the concentrations of “active” compounds times the corresponding potency factors normalized vs. benzo(a)pyrene (BaP). The distributions of organic species in different particle size fractions were also investigated and revealed that high molecular weight organic compounds were preferentially present in fine particles. Finally the aerial concentrations of the relevant particulate organic compounds determined in Algiers were compared to those reported for other Mediterranean and European cities.

Session 3: Chemistry in the aquatic compartments

Posters

PHARMACEUTICAL RESIDUE LEVELS IN RIVER GARONNE: COVERAGE OF A RAW WASTEWATER BYPASS EVENT

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Pharmaceuticals have now been clearly identified as emerging contaminants of the water compartment. Since wastewater treatment plants are unable to fully remove these micropollutants, the discharge of treated wastewaters is a source of contamination of aquatic systems. However, removal rates of pharmaceuticals in Waste Water Treatment Plants (WWTP) are compound dependent in such a way that it is to some extent possible to determine a more or less specific pattern of both influent and effluent with specific tracer molecules. For instance, paracetamol is a typical molecule present in WWTP influent. In a classical WWTP, running on conventional activated sludge, its quasi-total removal from the effluent could make it a untreated water WWTP discharge tracer. On the other hand, carbamazepine and diclofenac, hardly removed, could trace a discharge of treated WWTP effluent. The screening of these molecules in the water compartment makes possible the tracking of the origin of the pollution.

This study focuses on the coverage of a raw wastewater bypass event due to work on sewers. 21 pharmaceuticals have been screened in the influent and effluent of Bordeaux main WWTP prior to this study. These 21 compounds have then been studied in the receiving compartment, the Garonne river, before, during and after the four days bypass event on a full tide cycle (four sampling times), at two depths and along a transect. At the same time, POCIS passive samplers have monitored the event one week before, the week during and one week after, upstream and downstream the discharge.

The results reveal a local impact of the treated wastewater discharge on the river water. The importance of the tide cycle on the concentrations has been shown. The use of influent tracers such as paracetamol and global WTP discharge tracers such as carbamazepine, has also been validated.

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ASSESSMENT OF ECOTOXICOLOGICAL POTENTIAL OF SELECTED SULFONAMIDES

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Sulfonamides are a group of antibiotic drugs widely used in veterinary medicine. The contamination of the environment by these pharmaceuticals has raised concern in recent years. However, knowledge of their (eco)toxicity is still very basic and is restricted to just a few of these substances. Even though their toxicological analysis has been thoroughly performed and ecotoxicological data are available in the literature, a systematic analysis of their ecotoxicological potential has yet to be carried out. To fill this gap, twelve different SAs were chosen for detailed analysis with the focus on different bacteria as well as non-target organisms (algae and plants). A flexible (eco)toxicological test battery was used, including enzymes (acetylcholinesterase and glutathione reductase), luminescent marine bacteria (*Vibrio fischeri*), soil bacteria (*Arthrobacter globiformis*), limnic unicellular green algae (*Scenedesmus vacuolatus*) and duckweed (*Lemna minor*), in order to take into account both the aquatic and terrestrial compartments of the environment, as well as different trophic levels. It was found that SAs are not only toxic towards green algae ($EC_{50} = 1.54 - 32.25 \text{ mg L}^{-1}$) but have even stronger adverse effect on duckweed ($EC_{50} = 0.02 - 4.89 \text{ mg L}^{-1}$) than atrazine – herbicide ($EC_{50} = 2.59 \text{ mg L}^{-1}$).

HOMOGENEOUS FENTON AND PHOTOFENTON PROCESSES: IMPACT OF IRON COMPLEXING AGENT ON THE REACTIVE SPECIES FORMATION

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Chemical oxidation processes has been the subject of increased interest for the treatment of toxic and biorefractory contaminants in soils and waters. Modified Fenton's reagent is an important *in-situ* chemical technology that has evolved from the standard Fenton reaction (the iron(II)-mediated decomposition of dilute hydrogen peroxide (H₂O₂)), leading to the formation mainly of hydroxyl radical, a powerful and relatively non-selective oxidant that reacts rapidly with organic constituents, to a Fenton like process from Fe(III) species. However, a low efficiency of such systems was observed under neutral pH condition mainly due to the insoluble forms of Fe(III) in this condition.

In the present work we investigated the homogeneous reactivity of Fe(III)-EDDS (Ethylenediamine-*N,N'*-disuccinic acid) complex, which is a stable Fe(III) complex between pH 3.0 and 9.0, in Fenton and photo-Fenton processes. The first part of our research work was focused on the formation of reactive species and more particularly on the detection of hydroxyl (HO•) and superoxide (O₂•⁻) radicals.

Main results underlined the very positive effect of the Fe(III) used in the presence of an organic ligand (EDDS) in Fenton and Photo-Fenton processes. In the presence of such complex, we observed an important increase of Bisphenol A (BPA) degradation under neutral pH condition in aqueous solution.

ALTERNATIVE SILYLATION AGENT – DIMETRIS (DIMETHYL(3,3,3-TRIFLUOROPROPYL)SILYLDIETHYLAMINE)

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Increasing interest in gas chromatography for the determination of polar pharmaceuticals in the environmental compartments demands research into new derivatization techniques. Employed derivatization agent should ensure sufficient selectivity and sensitivity for final determination of analytes, that occur in the environment at the very low level. Depending of the nature of derivatization reagent selective (ECD, MS/MS) or universal (FID, MS) detectors may be applied. One of the most selective and sensitive GC detector is an electron capture detector (ECD), which is sensible to halogen atoms. From this reason perfluorinated acylating reagents seems to be the best choice for analysis of drugs by ECD detector, but they are highly corrosive and unsuitable for the derivatization of a wider group of analytes. Silylation is a milder reaction, but the products do not contain fluorine atoms. The reagent that may combine the advantages of both types of derivatization technique is DIMETRIS (dimethyl(3,3,3-trifluoropropyl)silyldiethylamine) proposed in this study (Fig. 1).

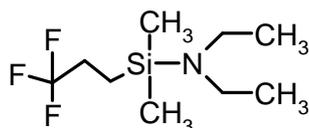


Fig. 1. Chemical structure of DIMETRIS.

There are no reports on its use in the analysis of pharmaceuticals, but its properties are very promising. In this work, preliminary study of derivatization of pharmaceuticals by DIMETRIS are presented. The test kit of analytes comprised of selected β -blockers and β -agonists, for which previously silylation reagent (BSTFA) was used. Mass spectra of BSTFA and DIMETRIS derivates of β -blockers and β -agonists are showed and compared.

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BORON REMOVAL FROM AQUEOUS SOLUTIONS USING SiO₂ AND TiO₂ HYBRID GELS

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Boron is widely used many industries such as chemical, ceramic, metal welding and pharmaceutical manufacturing. The discharge of boron containing wastewater to the environment causes several pollution and health problems. The attachment of organic functional groups to inorganic oxides allows the synthesis of new materials with specific sorption properties. In this work, boron removal from aqueous solutions by adsorption with SiO₂ and TiO₂ hybrid gels functionalized with *N*-methylglucamine groups was investigated. Borate esters are produced by reaction of boric acid with alcohols groups presents in the *N*-methylglucamine moiety of the hybrid gels. The effect of initial pH, initial boron concentration, time of contact and type of inorganic oxide on the adsorption was investigated. The characterization of the hybrid gels was conducted using the FTIR technique before and after the boron adsorption. Boron adsorption is a pH dependent process. The adsorption increases when de pH increases, reaching a maximum at pH = 6 for the SiO₂-based hybrid gel, and at pH = 10 for the TiO₂-based hybrid gel. Maximum boron removal obtained was 9.73 mg/g and 29.96 mg/g for the SiO₂ and TiO₂ gel respectively. Kinetic results fit better to the pseudo-second-order adsorption model suggesting that the overall rate of boron adsorption is controlled by the chemical process. In the isotherm studies, Langmuir and Freundlich isotherm models were applied. The experimental data conformed to Langmuir isotherm model in the case of the SiO₂ gel, while the Freundlich model better describes the experimental data obtained with the TiO₂ gel. These results suggest that the type of oxide has a great influence onto the sorption mechanism.

PHOTOPHYSICAL CHARACTERIZATION OF THE PLANT GROWTH REGULATOR 2-NAPHTHOXYACETIC ACID

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Fresh water is crucial for sustainable development. However, the quality of surface waters is being prejudiced by pollution arising from a variety of sources, including agricultural pesticides. Therefore, knowledge of pesticide behaviour in the environment is essential to have a more accurate understanding of the hazard that these compounds may or may not possess. In this study we report the photophysical characterization of 2-Naphthoxyacetic acid (2-NOA), a plant growth regulator hormone with auxin activity that has been used on several crops to promote the growth of roots, early fruit setting and to prevent fruit from falling prematurely. 2-NOA excited states were studied in aqueous solution and in some representative organic solvents (methanol, acetonitrile, chloroform and 1,4-dioxane) by UV-visible absorption, fluorescence and phosphorescence spectroscopies, time-resolved fluorescence, nanosecond laser flash photolysis and singlet oxygen measurements. The quenching of 2-NOA fluorescence by various substrates has also been studied to obtain insights into the importance of electron transfer and other routes in 2-NOA photodegradation under environmental conditions. The triplet excited state was characterised by its absorption at 430 nm in water and in organic solvents. This is quenched by molecular oxygen at diffusion controlled rates. A comparison will be made between the results obtained in water and in organic solvents, and the relevance of this to the photostability in environmental conditions will be assessed.

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Eliana S. Da Silva thanks FCT (Portuguese Foundation for Science and Technology) for the PhD grant (SFRH/BD/43171/2008).

ANALYSIS AND MODELING OF ARSENIC DYNAMICS IN COASTAL SEDIMENTS AND FLUXES TO THE WATER COLUMN (TOULON BAY, FRANCE)

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Sediments of the Toulon bay (SE, France) are significantly polluted by trace metals, metalloids and organic contaminants, due to historical events, especially during 2nd World War. Contaminants behavior in sediments and transfer to the water column should be investigated to evaluate the risks linked to such pollution. The presented work focused on As dynamic in the Toulon Bay. Three major processes of As physico-chemical transformations were studied: effect of early diagenesis on As behavior in sediment, subsequent diffusive flux and remobilization during sediment resuspension. Interface sediment cores were sampled at contrasted locations of the bay and at different seasons, followed by analysis of physico-chemical parameters (pH, E_h , DOC), diagenesis tracers (Fe, Mn, S, Ca, DIC, ...) and As species. The hyphenated use of speciation calculation (PHREEQC) and one-dimensional steady-state modeling of dissolved species in depth profiles (PROFILE) led to a better understanding of the phenomena at work. The obtained sediment profiles showed a significant variation of E_h , SO_4^{2-} , DOC and arsenic in porewaters between the two campaigns (June 2009 and April 2011). Such observation could result from different diagenesis activity, linked to inputs of labile organic matter (e.g. plankton bloom). Modeling showed that As depth profiles were strongly controlled by the successive consumption of oxidants occurring in anoxic sediment, leading to changes in As speciation and affinity for solid phases. Additionally, in the deepest layer, As appeared to be significantly correlated to the DOC content, indicating a possible association between As(III) and organic matter. These results allowed the evaluation of As diffusive fluxes at the sediment/water column interface, which should be compared to the As remobilization during surface sediment resuspension events (e.g. storm, boat traffic, dredging).

ARSENIC SORPTION ONTO SYNTHETIZED LEPIDOCROCITE

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Arsenic standard level in drinking water has been lowered to 10 $\mu\text{g L}^{-1}$ in many countries. Efficient As remove from water is always a big challenge, especially for developing countries. During the last decade, zero valent iron (ZVI: Fe^0) was used as an economic material for arsenic removal. Numerous studies showed that arsenite (As^{III}) and arsenate (As^{V}) could be effectively sequestered by the ZVI-applied system.

Since lepidocrocite could be one of important products by the oxidation of ZVI in aerobic conditions, it is worth to investigate the As^{III} and As^{V} sorption by lepidocrocite. Adsorption isotherms of As^{III} and As^{V} onto lepidocrocite were studied as a function of pH. In addition, Langmuir and Freundlich models were applied to simulate the surface complexation of lepidocrocite. As sorption capacity onto lepidocrocite was far higher than values reported in the literature for other iron oxy(hydro)des: at pH 7, As^{III} and As^{V} sorption capacity were respectively 50 and 19 mg/kg lepidocrocite. pH value affects the adsorption efficiency : in the range 5 to 9, As^{III} sorption capacity increased whereas it decreased for As^{V} .

DRY DEPOSITION OF PESTICIDES ON WATER ESTIMATED WITH A LABORATORY SYSTEM

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Pesticides applied to agriculture fields can volatilize and be subsequently dispersed in the atmosphere and contaminate surface water by dry deposition. A French project supported by ONEMA (*Office National de l'Eau et des Milieux Aquatiques*) aims at characterizing pesticides emissions to the atmosphere through volatilization and their dry deposition onto surface water. A laboratory system has been developed to study both emissions and dry deposition processes. It is composed of an emission cell in which a pesticide solution is introduced and a deposition cell which contains water. A regulated air flow circulates between the cells thanks to a pump. A mixture of seven pesticides was selected to cover a large spectrum of physico-chemical properties (vapor pressure, Henry law's constant and water solubility): chlorothalonil, clomazone, fenpropidin, fenpropimorph, metazachlor, S-metolachlor and trifluralin.

The estimation of the quantity of pesticides volatilized and deposited onto water was based on the measurements of their concentrations in air and in water. In air, pesticides were trapped by an adsorbent (Tenax® TA) from which they were eluted with hexane. They were extracted from water by SBSE (Stir Bar Sorptive Extraction) followed by liquid desorption. All these samples, along with the initial pesticide solution placed in the emission cell, and the residue at the end of the experimentation were analyzed by GC-MS. SBSE conditions were optimized for extraction time (40-180 min) and ionic strength (0- 300 gL⁻¹ NaCl). SBSE recoveries were determined and calibration curves (SBSE on spiked water samples) were drawn. Several experiments were carried out and allowed to quantify the volatilized quantity of pesticides together with the deposited one.

GEOCHEMISTRY AND ENVIRONMENTAL EVALUATION OF THE SKADAR LAKE SEDIMENTS

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National Park Skadar Lake is located on the border between Montenegro and Albania. Two thirds of the lake belongs to Montenegro. With an area of 370 to 530 km², depending on water level, it is the largest lake at the Balkan peninsula. It is considered 44 km long and 14 km wide.

Lake sediment probably plays a major role in the transport and storage of heavy metals in the aquatic environment. Except in the natural process, metals could be found in aquatic systems due to anthropogenic factors such as solid and liquid waste nearby factories, discharge of wastewater, usage of biocides on the surrounding farms, etc.

The aim of this study was to estimate possible contamination with heavy metals (Mn, Zn, Cu, Cr, Ni and Pb) of sediment of Skadar Lake, and determine the degree of sediment quality. For this purpose, it was used geochemical parameters: Geo-accumulation Index (GeoI), Pollution Load Index (PLI), Enrichment Factor (EF) and Risk Assessment Code (RAC).

Samples were collected from six locations at the lake between June and September 2010. River influents, places frequently visited by tourists and fishermen and special nature reserve were selected as a sampling points.

The content of metals in the sediment samples was determined by ICP-OES technique after strong acid digestion (HNO₃, HCl, HF).

Geo-accumulation Index (GeoI) shows that Ni is in moderate level of pollution while the other metals are in minor level of contamination.

Pollution Load Index (PLI) among the studied heavy metals in lake sediments showed the following sequence: Ni > Pb > Cu > Cr > Mn > Zn.

Based on the criteria Metal Enrichment Factor (EF), it could be concluded that Ni, Pb and Cu are under the certain influence of anthropogenic sources. EF-values for Mn, Zn and Cr show that presence of this metals does not originate from anthropogenic activities.

Criteria called "Risk Assessment Code (RAC)" shows that the results of Zn content at all sampling points is in the category of no risk. Mn at three sampling points, Cr at five and Ni at two of the selected locations are also in the no risk category. Pb and Cu are at all locations in low-risk category. In the same category are also: Mn at three locations, Cr at one and Ni at four sampling points.

**DISTRIBUTION AND EVOLUTION IN TIME OF TRACE ELEMENTS
CONTAMINATION IN SEDIMENTS, OYSTERS AND WATER FROM
THE BIOSPHERE'S RESERVE OF URDAIBAI ESTUARY (BASQUE
COUNTRY)**

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Several elements, even at the trace concentrations in which they appear in estuaries, are highly toxic, and may cause important damages in these sensitive environments. In fact, metals and arsenic are included in the indicative list of the main pollutants of the Water Framework Directive (2000/60/EC, WFD) of the European Union. Cadmium, lead and nickel, in addition, are classified as priority substances. Urdaibai estuary is a protected area declared Reserve of the Biosphere by the UNESCO in 1984 (Bay of Biscay, Basque Country). However, potentially polluting activities (plastic and paper industry, shipyards, leisure harbours, etc) are still operative in the area nowadays. Water samples, sediments and oysters were collected at different points of the estuary of the Urdaibai during seven sampling campaigns in 2010 and 2011. Samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn. Analysis of the results using basic statistics and different chemometric tools allowed us to draw conclusions on the geographical distribution of pollution in the estuary and its evolution in time.

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LEACHING OF SOME ELEMENTS FROM SLAGS USED IN BASQUE COUNTRY FOREST TRACKS

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Given the similarity of the slags composition with the concrete, these by-products have been used as construction material and as filling in roads. The slags are by-products from the steel production, and according to the moment in which are generated, these can be black or white slags. In this work, the scenario to which we had access was about forest tracks in the Basque Country (North of Spain). It was analysed several slags collected in different stretches of the forest tracks to compare them. Firstly, the slags were measured using Raman spectroscopy. Secondly, the slags were milled and sieved (< 2mm size), and later the metals extraction from the slags was carried out, through (a) ultrasound energy focused in a glass probe, using Milli-Q water, (b) acetic acid and (c) HNO₃-HCl as extractants. Finally, the samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ionic Chromatography. By means of these techniques it could be observed the molecular characterization and the concentration of some elements (Li, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Sr, Mo, Sn, Sb, Ba, W, Tl, Pb, SO₄²⁻ and Ca) of the slags. Compounds like calcite (CaCO₃), magnetite (Fe₃O₄), magnesioferrite (MgFe₂O₄) and hashemite (BaCrO₄) were identified among the samples. On the other hand, it could be appreciated that the highest concentrations of the leachable elements in the slags were found mainly in the lowest areas of the forest tracks. It could be an effect of washout by the rainfalls or the consequences of rain off which would transport the elements from the upper parts of the forest tracks to the lowest ones. Moreover, the majority elements were Mg, Ni, Al and Fe.

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**ASSESSMENT OF SEDIMENT CONTAMINATION BY HEAVY
METALS IN FEZ AND SEBOU RIVERS IN THE REGION OF FEZ
(MOROCCO)**

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Lately, massive economic growth and industrial development in the region of Fez (Morocco) has led to excessive release of wastewaters and effluents into the environment. The uncontrolled release of industrial effluents has negatively affected water quality and aquatic life in the Sebou river. Contaminants, either inorganic (metals, metalloids) or organic (PHA, PCB, pesticides,...), are introduced into the water column under different forms: particulate, colloidal and dissolved. Once in the water column, these pollutants are quickly adsorbed onto particles, deposited and accumulated in sediments. So, sediments can be valuable indicators for monitoring contaminants in aquatic environment. They provide useful information on the modifications in the river quality. Three 30-cm sediment cores were sampled in the Fez river (downstream Fez city) and the Sebou river (upstream and downstream the mixing with Fez river waters), and then 2-cm sliced, frozen and freeze-dried and 2-mm sieved. Each sediment slice was studied for grain size distribution (laser diffraction particle-size analyzer), organic and inorganic content (TOCmeter), mercury (CVAAS), major and trace metals/metalloids (acid mineralization assisted by micro-wave followed by ICP-OES, FAAS or GFAAS analysis). The obtained results showed vertical and spatial variability of these elements as a function of particle size and bearing phases, and allowed the calculation of enrichment factor.

This study has revealed that the Fez river is facing serious metals pollution. Past and current industrial discharges in the Fez river have created significant reservoirs of pollutants. Even if in the future, wastewater and industrial effluents would be treated, decreasing the pollutant input to the ecosystem, these contaminated sediments could act as a secondary source of pollution to the overlying water column, due to diffusive processes or contaminants remobilization during surface sediment resuspension.

**VISCOSITY MEASUREMENTS OF A WATER-ETHANOL BINARY
SOLUTION WITH RHODAMINE 6G BY FLUORESCENCE
CORRELATION SPECTROSCOPY**

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We have attempted to determine the viscosity of an ethanol/water binary solution using fluorescence correlation spectroscopy (FCS). The confocal system is constructed by means of assembling an Optical Block® (purchased from Hamamatsu Photonics K.K.). This method is based on observation of the fluorescent molecules under Brownian motion.

Rhodamine 6G (R6G) as the observation target was employed in the ethanol/water binary solution. A 473 nm semiconductor laser with a single mode optical fiber output (Model 473-5F, purchased from Sumitomo Osaka Cement Co. Ltd.) was used as a excitation light source, and connected to the Optical Block. In the correlation function between fluorescence and time, the diffusion time τ_D was given by $\tau_D = \omega^2/4D$ ---(1) and the diffusion constant, D , was given by $D = k_B T/6\pi\eta r$ --- (2). where ω , k_B , T , and r are the observation volume, Boltzman constant, temperature, and radius of a particle (dye molecule in this case), respectively. Therefore, the observed diffusion time is linearly proportional to the viscosity of the solution (η).

The diffusion time (τ_D) becomes maximum at around χ (ethanol molar fraction) = 0.2 ,which also gives the maximum of physical viscosity. In the FCS, the diffusion time decreases faster for lower χ (<0.2) than for higher χ (>0.2). It can be considered that the bulky structure constructed around the dye molecules increases the apparent volume of dye (r in equation (2)), which then leads to a smaller diffusion time. In contrast, it can be interpreted that the disruption of the water cage decreases the apparent volume of R6G (i.e., smaller value of r in equation (2)), giving a smaller diffusion time in the region of higher χ . At this point, the viscosity measured by FCS reflects the micro-environment of the solution structure (micro-viscosity) in some aspects.

HISTORICAL CONTAMINATION OF THREE FRENCH PERI-ALPINE LAKES SEDIMENTS BY PCBS : INFLUENCE OF LOCAL SOURCES AND WATERSHED CHARACTERISTICS

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Polychlorinated biphenyls (PCBs) are considered as persistent organic pollutants, due to their bioaccumulation and toxicity. They were introduced in France during the 1930s and production has been stopped in the 1970s. They are released in the environment, transported in the atmosphere and deposited and stored in soils, sediments, or glacier's ice. These compounds exhibit a high tendency to adsorb the particles and they accumulate in the lake sediments. Dated sediment profiles have been used to infer deposition of PCBs to lakes. The goal of this study is to reconstruct the historical inputs of PCBs into three French peri-alpine lakes and to distinguish between those impacted mainly by local and regional sources from those affected mainly by atmospheric deposition. Dated sediment cores from lakes Bourget, Annecy and Geneva, covering the last 130 years were analyzed to get an overview of the historical trend of PCBs deposition.

Analyses of sediment cores revealed that concentrations of PCBs started to increase in the 1940s and decrease after the 1980s, due to their interdiction. The concentration-time profile is in good agreement with the available information on global production data. PCB concentrations in lake Bourget are very high and reached a maximum of 1800 µg/kg dw in 1973. Today, the annual flux of PCBs in this lake is about 0.008 µg/cm²/year and has reached 0.451 µg/cm²/year during the 1973-76 periods. For lake Geneva, concentrations of PCB were lower and have reached 50 µg/kg dw during the 1970-76 periods while annual flux was 100 times lower. The identified PCB mainly consisted of highly chlorinated compounds for the lake Bourget, while they consisted of low chlorinated biphenyl for lake Geneva. PCB concentrations in lake Annecy are very low and comparable to the one found in high altitude mountain lakes contaminated by atmospheric deposition (LALLEE, 2009).

These results indicate different origins of the lakes contamination. High contamination of lake Bourget can be attributed to the local industries of PCBs production in the lake watershed (JUNG, 2009). Despite regulations, the PCB concentrations are still high in lake Bourget and could be attributed to the phenomenon of volatilization from nearby polluted soils of bio-resistant highly chlorinated congeners. For lake Geneva, its bigger size and the fact that PCB have never been manufactured in the nearby Switzerland might explain its lower contamination as compared to lake Bourget, while the profiles of PCB congeners support an origin from soil leaching and wastewater treatment plants. In contrast, the very low contamination rate of lake Annecy attests of the absence of any direct local PCB source and can be explained by a much less industrialized watershed such as the limitation of direct sewage water inputs to the lake as soon as the early 1960s.

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APPLICATION OF GCXGC-TOF MS FOR THE ANALYSIS OF DRUG RESIDUES IN WASTEWATERS AND SURFACE WATERS

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Pharmaceuticals and their residues become frequently controlled environmental contaminants in recent years, due to their increasing concentration mainly in aquatic environment. Many of these compounds are excreted from human or animal organism after administration. Unchanged or as various metabolites and conjugates are discharged to the sewer system and enter the wastewater treatment plants (WWTP), where they are only partly removed during the cleaning processes and enter the recipient river water, where they can negatively influence the water organisms.

This study is focused on determination of 10 acidic drugs mainly from the group of non-steroidal anti-inflammatory drugs (NSAID) in wastewater and surface water. Target compounds were follows: salicylic acid, acetylsalicylic acid, clofibric acid, ibuprofen, caffeine, naproxen, mefenamic acid, ketoprofen and diclofenac. Samples of wastewater were collected daily in November 2010 from the influent and effluent of WWTP in Brno – Modřice in Czech Republic. Samples of surface water were collected from two rivers streams in Czech Republic in October 2010. Solid phase extraction (SPE) was used for extraction and preconcentration of analytes. Comprehensive two-dimensional gas chromatography with mass spectrometric detection (GCxGC/TOF MS) was used for final analysis of these compounds. Limits of detection of presented analytical method were ranged from 0.18 to 5 ng.L⁻¹ depending on specific compound. Concentrations of selected pharmaceuticals in wastewater varied from one to several tens of µg.L⁻¹ and in surface water from tens to several hundreds of ng.L⁻¹.

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ASSESSING PARTICULATE CONTAMINANT FLUXES THROUGHOUT RIVER NETWORKS AND THE ASSOCIATED UNCERTAINTIES

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The particulate contaminant flux (ϕ) across a river section is the product of the discharge (Q), the suspended particulate matter concentration (C_s) and the content in contaminant adsorbed on the particles (C_i). High temporal resolution sampling of Q and C_s can provide continuous time series with a controlled uncertainty for both parameters. In contrast, C_i measurements are often infrequent, due to analysis costs and sampling difficulties, resulting in a larger uncertainty in the flux estimation. The influence of the temporal sampling of C_i was studied using a large data set on particles content for many contaminants collected 4 times per year from 2000 to 2009 at 17 sites throughout the Rhône River catchment by the regional water authority. About 300 individual molecules were analysed, however many of them were never quantified. Information about the molecule hydrophobicity and comparison with data collected in the liquid phase may allow to optimize the number of analysis. Then we studied discontinuity over time of the C_i values for some contaminants and highlighted changes in extraction protocols and reported limits of quantification, that were linked with a change of the analytical laboratory. Intercomparison exercises between laboratories and a complete documentation on analytical methods and quality control results are therefore of utmost importance. Finally, we observed that events with the highest C_s values were unsurveyed, which probably leads to an underestimation of the C_i variations. Thus extrapolation of C_i can lead to huge uncertainties on calculated fluxes for the most contributing events. Therefore, the sampling effort should be focused on the most sediment-laden events, relying on an automatic sampler, to estimate C_i variability with the hydrological cycle.

PHOTOCHEMICAL DEGRADATION OF CHLORANTRANILIPROLE

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Chlorantraniliprole is an insecticide with a new mode of action as a ryanodine receptor activator. According to producer's observations, it features high photo stability and high temperature insensitivity, short withdrawal period and high persistence on agricultural crops. However, since there is no independent scientific research made about the chlorantraniliprole's behavior in the environment, its degradation pathways and transformation products into which the pesticide degrades, a question of insecticide's fate in the environment remains.

We studied photostability of chlorantraniliprole in water and organic medium with a use of Suntest simulation chamber and UVC light. We set the Suntest program to simulate a hot summer day, where the irradiation intensity is high. At such settings we studied the degradation of chlorantraniliprole into transformation products. With UVC light we accelerated the photodegradation in order to obtain transformation products in higher quantities. Two main degradation products were identified, isolated and characterized with spectroscopic methods NMR and MS. The first degradation product, compound A, seems to be formed by direct photolysis of chlorantraniliprole in liquid medium. On the other hand, we observed that compound B is probably formed out of compound A spontaneously, when reaction mixture in solution is left in dark at room temperature for some time. Surprisingly, LC-MS analysis shows that compounds A and B are isomers (same m/z value) owning same chemical formula. From the producers list of predicted degradation products and by NMR analysis that allowed us to distinguish between compounds, we were able to suggest the structural formulas of compounds A and B.

MODELLING COPPER BIOACCUMULATION IN *GAMMARUS PULEX* AND ALTERATIONS OF DIGESTIVE METABOLISM

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The metal determination in tissues of organisms enables to integrate their ability to regulate metals and the effects of water chemistry on metal bioavailability. Thus, the construction of bioaccumulation models integrating both physiological and chemical parameters offers promising lines of enquiry for water quality assessment. Among net accumulators of metals, gammarids are widely represented in European freshwaters and known as ecosystem engineers by facilitating the litter decomposition. This study aims at characterizing the mechanisms of Cu bioaccumulation in *Gammarus pulex* and relating this process to biological responses, which could reflect a Cu impact on both the health of organism and its involvement in ecosystem functioning. The organism was exposed to several Cu concentrations (from 0.5 to 100 $\mu\text{g L}^{-1}$) in aquatic microcosms to establish kinetic and binding constants for the construction of two models, commonly proposed in the literature. We showed that the saturation model is more suitable than the biodynamic model to describe the Cu bioaccumulation in *G. pulex* due to a limited number of binding sites for Cu. Then, Cu bioaccumulation was recorded in waters exhibiting various contents in three major cations at environmental levels (Na, Mg and Ca) to assess the influence of water chemistry on metal uptake. Only Ca has an inhibitory effect on Cu uptake. Finally, Cu impact on the metabolism of *G. pulex* was investigated by measuring enzyme activities (β -glucosidase, N-acetyl- β -glucosaminidase, β -galactosidase) involved in the digestion of natural polymers found in litter. Our results indicated that Cu decreases the digestive activities whatever the tested enzyme but with different sensitivities. A high correlation was established between the inhibition of β -galactosidase and the amounts of metal accumulated by *G. pulex* ($R^2 > 0.91$). Thus, these alterations of digestive metabolism could provide early-warning of an impact of bioavailable Cu on environmental health of freshwaters.

**RESONANCE RAMAN IDENTIFICATION OF CAROTENOIDS
PRESENT IN *LECANORACEAE* LICHENS: A NEW BIOINDICATION
STRATEGY RELATED WITH ENVIRONMENTAL STRESS**

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Lichens are photosynthetic organisms which filter air to obtain the proper micronutrients. They are continuously exposed to open air and synthesize extra compounds to protect themselves from UV radiation. One of these groups of photoprotective pigments are carotenoids which include polyenic hydrocarbons known as carotenes and their oxygen derivates so called xanthophylls. This study is focused in the carotenoid type identification by Raman spectroscopy using the green laser (514 nm) to achieve the resonance effect. Under resonance conditions, new signals, overtones and combination bands that allow to uncertainly identify the carotenoid pigment are also observed.

According to the measurements carried out on *Lecanoraceae* specimens collected in locations suffering different environmental conditions, the occurrence of the carotenoid is directly related to the nature and concentration of acid gases of the emplacement: the higher concentrations of acid gases of the emplacement the more oxidized the carotenoids. Therefore, β -carotene is found in non polluted environments, zeaxanthin in moderately polluted and astaxanthin (usually together with scytonemin) in locations with a high pollution level or in areas affected by a direct impact. In this work, a new bioindication strategy based on the cited evidences is proposed.

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QUANTITATIVE ELEMENTAL DATA OF A HIGH-LATITUDE BEACHROCK (TUNELBOKA COVE, BAY OF BISCAY)

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This work is focused on the occurrence of an intertidal carbonate cementation in a sand-gravel cove that has been formed in an unusual temperate climate setting adjacent to the Nerbioi-Ibaizabal estuary (43°N latitude). The coastal sedimentary formation, presents a high amount of slag that were dumped during the XX century in an open sea disposal area located 4 miles north of the cove. Previous works revealed a marine-phreatic diagenetic context. Moreover, the mineralogical composition of the cements was defined by means of Raman microspectroscopy, SEM-EDX and petrographic descriptions: mainly CaCO₃ polymorphs, high-magnesium calcite and iron containing cements.

The aim of this work was to achieve quantitative elemental compositional data of the cemented outcrops to diagnose their relation with the beachrock formation and to determine if the vertical distribution of the elements could evidence arrivals of materials from different provenances. For that purpose, two vertical stratigraphic columns were sampled and each sample was subjected to granulometric separation. The analyses performed under a magnifying glass showed that the highest particulate metal content was apparently associated to 250µm < Ø < 75µm and Ø < 75µm grain-sized fractions. Therefore, these fractions were subjected to a microwave assisted extraction (using *aqua regia* as extractant) and a total number of 25 elements were measured by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The metal concentration raw data of all analysed samples were introduced in chemometric software for a Principal Component Analysis. According to the results, there was a significantly higher amount of metals in the 250µm < Ø < 75µm fraction, belonging the highest concentrations to Fe, Mg, Al, Na, Mn and K.

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PRELIMINARY ECOTOXICITY ASSESSMENT OF SELECTED VETERINARY PHARMACEUTICALS

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The relatively low cost of sulphonamides and tetracyclines and their broad spectrum of antimicrobial activity has made them the usual choice in animal breeding (*i.e.* food additives). Sulphaguanidine, florphenicol and oxytetracycline are registered in Poland as medicinal premixes and for this reason can be used in feedstuffs for the treatment or prevention of animal diseases; they are therefore used very frequently in animal husbandry in Poland, mainly in pigs. However, it has been observed that these animals often do not completely metabolize those substances.

Preliminary sorption studies of sulphaguanidine and florphenicol show rather low sorption potential. They can leach into ground water, drainage water or surface runoff where they may further affect the ecosystem. Furthermore, florphenicol and oxytetracycline are considered as compounds need to be assessed due to their annual sales amount and potential to reach the environment.

The main aim of this study was to determine the range of effective concentrations of florphenicol, oxytetracycline and sulphaguanidine in selected ecotoxicological tests on various levels of biological organization. There were: acetylcholinesterase enzyme-inhibition assay, *Daphnia magna* – immobilization assay, *Lemna minor* – reproduction assay and test of extinction of bioluminescence of bacteria *Vibrio fischeri*. Obtained results indicate that compounds under investigation may pose certain toxicological risk at environmentally relevant concentrations.

APPLICATION OF SOLID PHASE EXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY TO ANALYSIS OF PHARMACEUTICAL RESIDUES IN WATER SAMPLES

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Pharmaceuticals have been lately identified as emerging environmental pollutants. The residues of these compounds can be discharged into the environment in different ways: for example, during their manufacture, during the disposal of unused or expired drugs, with human and animal excretion, including hospital and domestic sewage, or by non effective wastewater management at pharmaceutical plants. Conventional wastewater treatment plants are usually not capable of completely removing this type of pollution, which means that these compounds get into surface water and even drinking water. There is therefore a need to develop procedures for the determination of these compounds in environmental samples.

The main aim of this study was to develop a procedure based on solid phase extraction (SPE) followed by derivatisation and gas chromatography determination of 11 pharmaceuticals including non-steroidal anti-inflammatory drugs (ibuprofen, ketoprofen, flurbiprofen, diclofenac, diflunisal, and naproxen) and hormones (estrone, β -estradiol, estriol, 17 α -ethynylestradiol and diethylstilbestrol). During this study special attention was taken into SPE step. Four commercially available sorbents (Oasis HLB, Strata X, Lichrolut EN, C18) were assayed in order to optimise the simultaneous extraction of the selected analytes. Different conditions of extraction were tested. Recoveries and LODs values of individual target compounds were investigated. The optimized SPE procedure was combined with derivatization step and GC analysis giving the method suitability in surface and wastewater monitoring.

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DESIGN OF EARLY WARNING SYSTEM FOR MONITORING OF DRINKING WATER QUALITY IN NOVI SAD, SERBIA

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Novi Sad municipality faces a specific problem, deriving drinking water either from the Danube River or from several groundwater reservoirs. In the first case, the drinking water abstraction point is located only several hundred meters downstream of the municipality wastewater disposal area. Additionally, all of the groundwater abstraction points are located under dense settled urban areas, while one of them is situated in the vicinity of the oil refinery. The presence of numerous toxic chemicals and pathogens that have been identified in the Danube River alluvion over the last decade (see: <http://www.icpdr.org/jds/>) is also expected in the aquifers used for the abstraction of drinking water. Initial phase of the project ESP.EAP.SFP 984087 includes target and screening analyses for selected compounds and possible contaminants, and prediction of toxicity of the chemical substances using QSAR modelling. The second part of the project consists of the design and implementation of a fully automated multiparameter integrated system equipped with automated sample treatment method and both, an organics analysers and an array of miniaturised electrochemical or possibly immuno-bio-sensors for simultaneous unattended and reliable monitoring of the most relevant hazardous pollutants in raw water in Novi Sad. The system will allow switching among different groundwater reservoirs whenever excessive pollution is detected in one of the drinking water supply streams.

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BIODEGRADATION OF BISPHENOL A BY FUNGI NATURALLY OCCURRING IN FRESHWATER ENVIRONMENTS

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Bisphenol A (BPA) is an environmental contaminant that has recently been under investigation for its detrimental effect on the aquatic ecosystem. In this study, an aquatic fungus, *Heliscus lugdunensis* Saccardo & Therry (live and heat-inactivated by autoclaving) was evaluated for its ability to utilize BPA as a carbon source. Both live and heat-inactivated fungal cells were exposed to 10 mg/L bisphenol A after cultivation in glucose for 3 days. Extraction of BPA in the fungal cultures was carried out using PrepSep™ C-18 mini columns followed by quantification of recovered BPA by high performance liquid chromatography. While heat inactivation sufficiently disrupts the ability of the fungal cells to utilize BPA, the live fungal cells removed over 70 % of BPA after 12 days. Our results suggest that *Heliscus lugdunensis* Saccardo & Therry is capable of biodegrading BPA and utilizing it as an energy source.

**IMPACT OF WATER PHYSICOCHEMICAL PARAMETERS ON
ZOOPLANKTON DYNAMIC IN A SOUTH-SAHARAN RESERVOIR
(BURKINA FASO, WEST AFRICA)**

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From May 2004 to April 2005, the zooplankton of the Loubila reservoir was subject to a 14 days periodicity follow-up. This study attempt to highlight the impact of water quality and quantity on zooplankton diversity, abundance and seasonal dynamic in a south-saharian reservoir. Plankton community was sampled with horizontal tows of a plankton net of 100 μm mesh size. The samples analysis permitted to identify 7 species of Cladocera and 2 species of the Copepoda. The overall Rotifers observed belong to 14 genera. The Cochran's Q test together with various methods of variance analyses and the Redundancy Analysis (RDA) allowed highlighting effect of physicochemical parameters on zooplankton settlement. The most significant factors were "water movement", conductivity, ammonium, nitrate, sulphate and potassium rates. Crustaceans are more sensitive to the season impacts than Rotifers.

Keywords: Zooplankton, Seasonal dynamics, Physicochemical parameters, Burkina Faso.

BEHAVIOUR AND FATE OF URBAN PARTICLES IN COASTAL WATERS: SIZE DISTRIBUTION, SETTLING RATE AND METAL CONTAMINATION CHARACTERIZATION

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From the various contaminant sources of oceans, river inputs are one of the most important especially in coastal zones. In such systems, transport by terrigenous particles is a main pathway, so that the evaluation of contaminant net fluxes to open ocean needs to study terrigenous particles behaviour and fate. This study was conducted as a part of MARSECO and GIRAC-PACA research programs whose objectives are to define the influence of Marseille city (France, 1.7 M inhabitants) to the contamination of coastal seawater. The urban area impacts the watershed of 2 main rivers (Huveaune and Jarret) whose waters are mixed with Marseille's treated wastewater and channelled through 2 outlets which flow into the sea. The aim of this study was to estimate the fate of transported contaminant-bearing particles in the freshwater/seawater mixing zone. An experimental device composed by a 1 m height plexiglass tube filled with 7 L of seawater was developed for determining particles settling rates and size distribution. The particles used were sampled in flood deposits of rivers and outlets during rainy periods and in rivers and outlet waters during dry periods. Wet particles were introduced on the top part of the tube and the bottom 500 mL were successively sampled at defined times (30 s to 5 days), allowing separation of settling particles (rates: $6 \text{ cm}\cdot\text{s}^{-1}$ to $1 \text{ }\mu\text{m}\cdot\text{s}^{-1}$). Organic carbon and metal contents of particles were analysed after filtration. Flood deposits were mainly composed by 50-200 μm size particles with higher metal content in the finest fractions. Dry period outlet particles showed strong influence of wastewater inputs. These characteristics will be implemented in a transport model developed by IFREMER to evaluate the contaminant fate and results will be compared to actual coastal sediment contamination.

INDIRECT PHOTOLYSIS AND DEGRADATION OF XENOBIOTICS IN AQUEOUS MEDIA: ROLE AND IMPACT OF THE HYDROXYL RADICAL

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The release of xenobiotics into all the compartments of the environment (water, atmosphere, soil) is a growing problem and may present ecological risks and consequences to human health. Often the aquatic system is the most contaminated because many pollutants are in urban and industrial STP effluents and wastewaters from roads and agricultural lands. Abiotic and biotic processes could be responsible for the xenobiotics transformation in natural waters. Direct or indirect photolysis are the main processes involving the pollutants degradation. The first one occurs when such compounds are able to absorb sunlight (above ~300 nm), while indirect photolysis in surface waters involves mainly organic matter triplet states, singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($\cdot\text{OH}$) and carbonate radicals ($\text{CO}_3^{\cdot-}$); these species are generated in natural waters after absorption of light by naturally occurring chromophores. In particular hydroxyl radical is the most important oxidant often involved in indirect photolysis processes; it may be produced by irradiation of nitrite, nitrate and hydrogen peroxide as well as iron species. Nitrite and nitrate are naturally present in surface waters and in cloud water while hydrogen peroxide is present generally only in cloud water. In order to predict the environmental fate of pollutants it is therefore very important to know the reactivity of these compounds toward $\cdot\text{OH}$.

In this communication we value the rate of formation of $\cdot\text{OH}$ in natural and synthetic waters and examine the reactivity and rate of degradation of some xenobiotics. We relate components in natural water (concentration of nitrite, nitrate and organic matter) to the formation rate of $\cdot\text{OH}$ (R_{OH}), and finally we try to correlate this value with the degradation rate of some xenobiotics in order to better calculate the half-life time in environment.

ZnCr- LAYERED DOUBLE HYDROXIDE AND DERIVED MIXED OXIDES AS EFFICIENT PHOTOCATALYSTS FOR POLLUTANT DEGRADATION IN WATER

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Layered double hydroxides (LDH), also known as anionic clays and their derived mixed oxides (DMO) have recently attracted much attention due to their specific physicochemical properties. These compounds find interest in many fields of application in particular in catalysis, photodegradation of waste water, dye-sensitized solar cells development and greenhouse gas control emission. Interestingly, in presence of specific metal cations into the layered structure LDH and DMO display semi-conducting properties. For instance, LDH phases containing Ti and Zn were described as highly active UV and visible light photocatalysts for O₂ production and pollutant degradation. In this study, a ZnCr-CO₃ is prepared by classical coprecipitation and thereafter transformed by controlled thermal treatment at different temperatures into mixed oxides with homogeneous interdispersion of the elements. The photocatalytic activities of the different phases are tested in the presence of Acid Orange 7 (AO7) used as organic pollutant of aquatic compartment. In the same time, structural, physicochemical and adsorption properties of LDH and DMO are investigated. Particular attention is paid to the photochemical processes, first of all through the identification of oxidant species responsible of AO7 degradation. Moreover, to optimize and better understand the mechanism, the influence of different physico-chemical parameters are evaluated (irradiation wavelength, pH, concentrations of DMO ...).

EVALUATING THE MOBILITY OF ARSENIC IN RIVER SEDIMENTS (ANLLÓNS RIVER, SPAIN) USING AN IMPROVED SEQUENTIAL EXTRACTION PROCEDURE WITH EMPHASIS ON SULPHIDIC PHASES

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The fate and mobility of arsenic (As) in the environment depend strongly of the associations established between As and the different geochemical phases of soils and sediments. The geochemical distribution of As in several As-rich river sediments (containing up to 265 mg As kg⁻¹) from an ancient gold mining area (Anllóns River basin, NW Spain) was studied using a modified sequential extraction procedure (SEP) involving the following pools of As: (1) ionically bound, (2) strongly adsorbed, (3) coprecipitated with AVS, carbonates, Mn oxides and very amorphous Fe oxyhydroxides (4) coprecipitated with amorphous Fe oxyhydroxides, (5) coprecipitated with crystalline Fe oxyhydroxides, (6) As oxides and As incorporated in silicates, (7) As in pyrite and amorphous As₂S₃, and (8) Residual (As sulphides and remaining recalcitrant As minerals). The SEP results were interpreted in terms of As potential mobility. Exchangeable (easily mobile) As ranged between 1.3 and 8.7% of As_{total}. Most As was found in the crystalline Fe oxyhydroxides (23.6–44.3% of As_{total}) and residual phases (20.9–49.3% of As_{total}), which suggests a low mobility of As in the sediments studied. A significant fraction of As (15.0–19.3%) was extracted by 1M HCl in step 3, whereas ligand promoted dissolution (oxalic extraction) released between 2.5 and 9.9% of As_{total}. Arsenic coprecipitated with pyrite, potentially mobile upon oxidation of the sediments, was low (0.14–1.10% of As_{total}). However, As extracted by phosphate (step 2) represented up the 22.7–35.5% of As_{total}, indicating a high mobility of As in the presence of this competing anion. This is especially relevant in terms of risk assessment, considering the high amounts of phosphorous delivered to the Anllóns River from a wastewater treatment plant and a sea-food canning factory.

INFLUENCE OF pH ON THE SORPTION/DESORPTION AND DISTRIBUTION OF ARSENIC AND URANIUM IN SEDIMENTARY ROCKS OF THE KEUPER AQUIFER (FRANCONIA, GERMANY)

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High concentrations of geogenic arsenic (up to $150 \mu\text{g L}^{-1}$) and uranium ($>10 \mu\text{g L}^{-1}$ in 16% of the analysed wells) have been found in groundwater of the *Keuper* sandstone aquifer (Franconia, Southern Germany), which is one of the major sources of drinking water in the region. This study investigates the influence of pH conditions on: (i) the potential mobilisation of As and U from As- ($15\text{--}46 \text{ mg kg}^{-1}$) and/or U-rich ($3\text{--}260 \text{ mg kg}^{-1}$) sandstones from the *Keuper* aquifer, (ii) the sorption and desorption kinetics of both As and U on/from As–U loaded rocks, and (iii) the geochemical distribution of both elements within the rocks, using two sequential extraction procedures. Geochemical modelling (Visual MINTEQ) and XRD–Rietveld analyses were additionally carried out to understand the mechanisms and to identify the geochemical phases controlling the mobilisation process of As and U. Acidic conditions ($\text{pH} < 4$) enhanced greatly the release of both As ($\sim 4\%$) and U ($\sim 8\%$) in the U-rich rocks, whereas the As-rich rocks exhibited a V-shaped release profile, where As ($\sim 3\%$) and U ($\sim 16\%$) release was mainly enhanced under alkaline conditions ($\text{pH} > 8$). The sorption of As(V) and U(VI) was very fast (75% and 90% of the process occurring within the first 15 min). Arsenic desorption was characterized by a readsorption profile at pH 3 (12% As_{total}), whereas a sigmoid pattern was observed at pH 9 (47% As_{total}). Uranium desorption was rapid and experimented less variation with pH and time. Leaching at pH 3 and 9 caused a redistribution of As and U within the rocks, depleting the easily mobile fractions while increasing greatly the contribution of residual fraction (inert phase) from $\sim 50\%$ to $\sim 99\%$. Geochemical calculations revealed oversaturation of some Fe(oxy)hydroxides and strengite, suggesting that Fe minerals play an important role in the control of aqueous As and U concentrations in the systems studied.

MOLECULAR TRANSPORT OF PESTICIDES IN WATER

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Diffusion coefficient is the key property to understand molecular diffusion and describe the transport of a chemical in the aquatic compartment of the environment. However, such data are nearly nonexistent in the case of persistent organic pollutants like pesticides.

Our aim was the determination of this coefficient for some pesticides. Six commonly used were selected (fig 1): a fungicide (tebuconazole), two insecticides (cyromazine and pirimicarb) and three herbicides (chlortoluron, metazachlor and sulcotrione).

First, their diffusion coefficients were experimentally measured at infinite dilution in water using Taylor dispersion technique¹ (uncertainty of 5%) between 5 and 50°C. At 25°C, the coefficients vary from $0.35 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for tebuconazole to $0.75 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for sulcotrione, decreasing with increasing temperature. They are comparable to those obtained for polycyclic aromatic hydrocarbons like anthracene, benzanthracene and naphthalene².

In a second part, a group contribution model based on these experimental results and literature data was developed for simple molecular structures allowing a prediction of

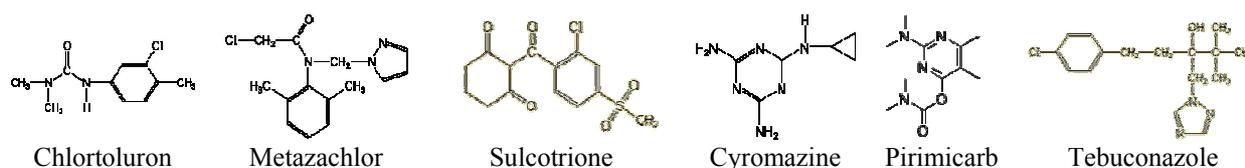


Figure 1

diffusion coefficient of pesticides in water at 25°C with an uncertainty of 10%.

¹ S. Sarraute, M.F. Costa Gomes, A.A.H. Padua, Diffusion Coefficients of 1-Alkyl-3-methylimidazolium Ionic Liquids in Water, Methanol, and Acetonitrile at Infinite Dilution, *J. Chem. Eng. Data* (2009) 54, 2389-2394.

² K.E. Gustafson, R.M. Dickhut, Molecular diffusivity of polycyclic aromatic hydrocarbons in aqueous solution, *J. Chem. Eng. Data* (1994) 39(2), 281-285.

LINKING BIOTIC METABOLISM, FORMATION OF NON-EXTRACTABLE RESIDUES AND ISOTOPIC FRACTIONATION FOR A COMPREHENSIVE ENVIRONMENTAL EVALUATION OF ORGANIC POLLUTANTS AND AN ENHANCED RISK ASSESSMENT– THE EXAMPLE DDT

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For the protection of environmental ecosystems and of human health the risk assessment of individual chemicals is a fundamental instrument. However, substance related risk assessments based either on predicted environmental concentrations in relation to (eco-)toxicological relevant concentrations (e.g. PEC/PNEC approach) or on the monitoring of real ecosystems on a middle to large geographical scale. However, most approaches applied to organic contaminations focussed exclusively on the primary and analytical available pollutants neglecting those environmental processes that lead to an alteration of the original contaminants including their speciation but not necessarily to a reduction of the environmental risk. These processes comprise in particular metabolism and formation of non-extractable residues (NER). Although both aspects are well investigated over decades and much information is available for numerous organic pollutants, the linkage of both processes has been ignored so far.

In this presentation the importance of considering the complementary environmental processes of metabolism and formation of NER will be highlighted by an extended investigation on DDT, a priority pollutant and representative member of the Dirty Dozen. The complex environmental fate of a huge and long lasting contamination (of up to 50 mg/g Σ DDX) in a surface/ground water system near Berlin was studied over 10 years comprising the monitoring of biotic transformation products in the free and bound status, the reversibility of the incorporation processes, the mobility of DDT metabolites at water sediment interfaces and the isotopic signature of relevant DDT derivatives as indicators for microbial alterations. As a major implication of this study, the importance of considering all relevant environmental processes contemporarily and comprehensively in order to get a reliable data base for a pollutant specific risk assessment is clearly evident.

BIOACCUMULATION OF HEAVY METALS IN FISHES FROM TISZA RIVER, SERBIA

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The accumulation of heavy metals in fish has been extensively studied and well documented. In this study, heavy metals were analyzed in liver, gills, gonads and brain of ten individual four fish species (*Abramis brama* L., *Esox lucius* L., *Acipenser ruthenus* L., *Cyprinus carpio* L.) caught from the four sites (3km, 58km, 72km, 153km) Tisza River (Serbia) during October 2010. The concentrations of Al, As, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr and Zn have been assessed by using the inductively coupled plasma – optical emission spectrometry.

The results showed that metals with the highest values in all samples are: Zn, Al, Cu, Sr and Mn. The organisms that adopt the highest concentration of heavy metals are bentivore species, and organs that accumulate the most of them are the liver and gills. The highest concentration of heavy metals measured on the next sites: for Al – on 3rd and 72nd km; for Cu – on 58th km; for Mn and Sr – on 72nd km; and for Zn – on 153rd km Tisza River.

The present state of pollution on Tisza River indicates the potential for deterioration and need for further biomonitoring.

LAND-BASE ORGANICS POLLUTION EVIDENCE IN MARINE SEDIMENTS OF CORTIOU, MARSEILLE

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Organic pollutants such as aliphatic (n-alkanes), polyaromatic hydrocarbons (PAHs), Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) were measured in sediments collected from 12 sampling sites (C1-C12) of sewage discharge to the sea from the wastewater treatment plant of Cortiou-Marseille. This study aims to determine the extent of these compounds in the sediments and to establish the possible sources of these contaminants. Total n-alkane and PAH concentrations ranged from 34 to 2155 $\mu\text{g.kg}^{-1}$ dw and 696 to 10700 ng.kg^{-1} , respectively. Total pesticides in the sediments ranged from 1.2 to 190.6 ng.g^{-1} dry weight of sediment while the PCBs concentrations, expressed as equivalent to Arochlor 1260, varied from 9.1 to 226.9 ng.g^{-1} . Specific hydrocarbon indexes suggest that terrestrial biogenic inputs were predominant compared to marine sources, and both pyrolytic and petrogenic sources contributed to PAHs in the surface sediments. Concerning

OCs, we showed the long term contamination input of these compounds (DDT, endosulfan, HCH and heptachlor cases) rather than a recent release resulting from degradation and long-term weathering (dieldrin, aldrin and methoxychlor cases) whilst, occurrence of PCBs might be due to their resistance to degradation processes or/and chronic inputs.

PHOTOCHEMICAL DEGRADATION OF CHLORANTRANILIPROLE

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Chlorantraniliprole is an insecticide with a new mode of action as a ryanodine receptor activator. According to producer's observations, it features high photo stability and high temperature insensitivity, short withdrawal period and high persistence on agricultural crops. However, since there is no independent scientific research made about the chlorantraniliprole's behavior in the environment, its degradation pathways and transformation products into which the pesticide degrades, a question of insecticide's fate in the environment remains.

We studied photostability of chlorantraniliprole in water and organic medium with a use of Suntest simulation chamber. The Suntest program was set as to simulate a hot summer day, when the irradiation intensity is high. The degradation of chlorantraniliprole under simulated sunlight led to the formation of several products. In order to get more insight into the reaction pathway, also the irradiation with UVC light was performed. In this case, a single product was formed initially (compd A), which was spontaneously transformed into secondary products.

Two main degradation products were identified, isolated and characterized with spectroscopic methods NMR and MS. Analysis shows that compounds A and B are isomers (same m/z value) owning same chemical formula. From the producers list of predicted degradation products and by NMR analysis that allowed us to distinguish between compounds, we were able to suggest the structural formulas of compounds A and B.

VEGETABLE WASTES USED AS LOW COST SORBENTS. DO THEY RELEASE TOXIC COMPOUNDS?

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During the last two decades many non-conventional low cost sorbents coming from different sources have been investigated for their sorption capacity to remove metal ions and other noxious compounds. Although the toxicity of these sorbents is not commonly controlled, it is advisable to check it, especially in wastes that have suffered some kind of processes. These materials might release some toxic compounds as a consequence of the sorption process. In this work, the toxicity of five vegetable wastes (cork bark, grape stalks, yohimbe bark, olive stones and exhausted coffee) used in our laboratories as sorbents for metal ions removal has been evaluated by using the Microtox® test. This test which consists of measuring the decrease of light emission by *Vibrio fischeri* bacteria exposed to noxious chemicals is claimed to be reliable, rapid and sensitive. The influence of critical parameters investigated when optimizing the sorption process such as particle size, contact time, sorbent dose and solution pH on toxicity have been investigated.

Results indicated that cork bark was not toxic in any of the tested experimental conditions while the other four sorbents resulted to be toxic to some extent. Particle size, time of contact and sorbent dose was found to influence on toxicity with a same trend for all the sorbents investigated. A decrease of particle size, and increase of contact time between sorbent and solution and an increase of sorbent dose provokes an increase of toxicity. Concerning the influence of pH an increase of pH resulted in general in a decrease of toxicity. The only exception was yohimbe bark which was found to be more toxic at the highest pH values. HPLC was used to determine the organic compounds released by the materials in the different tested conditions. Though several chromatographic peaks have not yet been identified a direct relationship between the corresponding compounds concentration and the measured toxicity was observed.

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STRATEGIES OF NANOTECHNOLOGY DEVELOPMENT IN WATER PURIFICATION IN RUSSIA ON THE BASIS OF INTEGRATED ROADMAPS

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One of the most urgent for Russian society issues is insufficient water provision system for population and industrial needs. According to Higher School of Economics (HSE) social survey the problem of water quality and related problem of water purification remains the deepest concern of the 35 per cent population of Russia and dominate among other social and domestic/ household problems.

To solve this problem the roadmap «Applying Nanotechnology to Water Treatment» (further – Roadmap) has launched by HSE for the Russian Corporation of Nanotechnologies (Rusnano). The main aim of this document is to identify the most prospective solutions for the sphere of water purification. The concept ‘integrated roadmap’ was used to develop strategy of nanotechnology development in this field.

The Roadmap summarises opinions of expert community members regarding the most important nanotechnologies and interim products made with their help which are used or can be used for water treatment and purification purposes. The roadmap has promising practical application for investment project-making and project appraisal in the field of water treatment as it provides both technological and commercial validation of alternative chains «R&D – technology – product – market». It becomes a basis for development innovation strategies for area development, supports government decision-making in the field allowed improving provision pure water for citizens.

PRESENCE OF PHARMACEUTICALS AND HORMONES IN INFLUENTS AND EFFLUENTS OF DRINKING WATER TREATMENT PLANTS

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The levels of a wide variety of pharmaceuticals and hormones, in source and potable-water supplies of French drinking water treatment plants (DWTP), were determined in order to assess the potential for these compounds to resist to drinking water treatments.

Analytical methodologies based on liquid chromatography coupled to tandem mass spectrometry, sufficiently selective and sensitive to allow their determination at the sub-ng/L levels, were developed and applied to influent (surface waters) and effluent of eight DWTP.

Results obtained in the raw surface waters indicate that 27 of the 51 target compounds were determined at least once. Four of them were quantified in more than 90% of the samples (paracetamol, salicylic acid metformin and carbamazepine). Sixteen other substances were widely found, contaminating between 20 and 70% of the waters. These compounds include analgesics, psychotropic drugs, antibiotics and beta-blockers consistent with the French consumption, as well as natural hormones (estrone, progesterone and androgens) and synthetic progestatives. In drinking water supplies, 27 compounds were also present, acetaminophen being the most frequently detected.

The efficiencies of the eight DWTP were compared. Pharmaceuticals exhibited different reactivity towards the treatments, while progestagens and androgens seemed resistant to most of them.

Finally, a risk assessment was conducted, based on the I70 concept, to evaluate the potential for adverse human effects of the compounds detected.

EFFECT OF MIXING PESTICIDES ON THEIR BIODEGRADATION KINETICS AND METABOLIC PATHWAYS.

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The assessment of pesticide occurrence in the different aquatic compartments shows the presence of a mixture of molecules due to the agronomic standard practices: sequence of herbicide, fungicide and insecticide; several applications in one vegetation season; various crops. Moreover all these compounds are submitted to abiotic and biotic processes leading to the formation of new degradation products in most cases. The presence of multiple potential contaminants has been shown to result in greater toxicity than any of the individual components but the effect on their biodegradability has rarely been reported. The aim of this research work is to compare kinetics of biodegradation and metabolic pathways of a herbicide, Mesotrione, and a fungicide, Tebuconazole, used alone or in combination.

The biodegradation of Mesotrione, a triketone selective herbicide for maize, and Tebuconazole, a systemic fungicide used for disease control on fruit, cereal and vegetable crops, was studied using an isolated bacterial strain (*Bacillus* sp.). The first experiments were carried out on each compound separately. The monitoring of pesticide dissipation showed the complete disappearance of Mesotrione whereas the extent of Tebuconazole degradation did not exceed 50% whatever the initial concentration. The metabolites formed were then identified using LCMS and ¹H and ¹³C RMN as the complete degradation pathway was not described in the literature. Different hydroxylation reactions of Tebuconazole occurred whereas the first steps for Mesotrione degradation were either hydrolysis or reduction of its nitro group. Both pesticides (pure molecules or formulated commercially available preparations) were then combined and comparisons of the dissipation kinetics and metabolic pathways were then carried out.

MONITORING OF DRUG RESIDUES CONTAMINATION IN TWO CZECH RIVERS BY LIQUID CHROMATOGRAPHY

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This study monitors presence of sulfonamide antibiotics, which are widely used in human and veterinary medicine, in two river streams in the Czech Republic. Drugs and their residues are discharged to the sewer systems together with the urine and faeces and enter to the sewage treatment plant, where they are not completely removed. Their further negative impact on the water and soil ecosystem cannot therefore be excluded.

Presence of selected antibiotics (sulfacetamide, sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfamethazine, sulfamethoxazole) was monitored in Svratka and Svitava rivers in Moravia region in the Czech Republic. Samples were collected along the whole river streams in March 2011. Optimized solid phase extraction method (SPE) was used for extraction and preconcentration of analytes. The most suitable SPE method and SPE column were found. For determination of the real samples 300 mL of sample volume without pH adjustment and ENVI-18 SPE Tubes (6 mL; 1 g) were chosen. The recoveries of drugs under these conditions range from 50 to 99 %. HPLC-MS was used for final analysis. Limits of detection were from 0.24 to 2.55 $\mu\text{g}\cdot\text{L}^{-1}$. Sulfonamide antibiotics were found in some of sampling places with concentration range of tenths to units of $\mu\text{g}\cdot\text{L}^{-1}$.

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CHLORINATED BIPHENYLS AND PESTICIDES IN COMMERCIAL BARENTS SEA FISH SPECIES

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The elements of Arctic environmental have been gaining an increasing interest recent years because they are considered as a final sink for many anthropogenic pollutants. Commercial Barents Sea fish (cod *Gadus morhua*, haddock *Melanogrammus aeglefinus*, long rough dab *Hippoglossoides platessoides*, plaice *Pleuronectes platessa*, polar cod *Boreogadus saida*, spotted wolffish *Anarhichas minor*, capelin *Mallotus villosus*) were analyzed to evaluate the presence of α -, β - and γ -isomers hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), cis- and trans-isomers chlordane, trans-nanohlor, o,p'- and p,p'- isomers of DDT, DDD and DDE, and twelve polychlorinated biphenyls (PCBs). Levels found in these species, characterized by different ecological features, were compared in order to evaluate differences in HCH, HCB, chlordanes, DDT and PCB levels. Gas chromatography–mass spectrometry (GC- MS) showed higher contaminant concentrations in liver than in muscle. *A. minor* showed the highest HCB, chlordanes, DDT and PCB levels in muscle (1.76, 28.8, 28.5 and 16.2 ng/g wet wt, respectively); *M. villosus* showed the highest HCH level (5.91 ng/g wet wt). Lowest HCH, HCB, chlordanes and DDT mean concentrations in muscle were detected in *G. morhua* (1.26±0.27, 0.42±0.13, 0.13±0.08, 0.97±0.15 ng/g wet wt, respectively); *M. aeglefinus* showed the lowest PCB level (1.22±0.20 ng/g wet wt). The congeners PCB153>PCB138>PCB118>PCB52 in muscle, and PCB153>PCB138> PCB118>PCB99 in liver were the most abundant in fish from the Barents Sea, confirming a similar profile between the different species. The species with the highest fat content shown higher amount of contaminants than low-fat, in confirm the lipophilic nature of the organochlorines.

Session 4: Chemistry in the terrestrial compartments

Posters

DECONTAMINATION OF DREDGED SEDIMENTS CONTAINING ETM AND PAHs BY ELECTROREMEDIATION

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The maintenance of harbor waterways generates large amounts of dredged sediments which are often rich in organic and inorganic contaminants. These sediments can be inappropriate for disposal at sea and reuse solutions can be proposed if they are treated before. Electrokinetic (EK) remediation is often developed for heavy metals decontamination but is extremely limited for polycyclic aromatic hydrocarbons (PAHs) which are nonionic and have a low aqueous solubility. Deionized or salt water was circulated through an EK system and various processing fluids were tested to improve the decontamination of a model sediment artificially contaminated with cadmium, lead, chromium, copper, zinc and five PAHs. Nitric acid and citric acid were tested to avoid the formation of an alkaline front into the sediment and were circulated under a constant voltage gradient of 1 V/cm for 14 days. The strong inorganic acid was more effective than the weak acid to remove heavy metals but the complexing citric acid was promising for longer treatments. Concerning PAHs, an anionic surfactant (sodium dodecyl sulfate SDS) was tested to mobilize, solubilize and favor their migration. At last, SDS and citric acid were tested simultaneously on a naturally contaminated dredged sediment from a French Norman harbor.

SORPTION AND BIODEGRADATION STUDIES OF THE HERBICIDE SULCOTRIONE IN AN AGRICULTURAL SOIL

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After spreading, herbicides reach the soil where their fate is controlled by different competitive or interactive abiotic (sorption, degradation) and biotic (biodegradation) processes. In order to better understand the mechanisms involved in these transfer/transformation processes, and to identify the role of each soil component in their fate, a multi-scale experimental study was developed.

Sulcotrione, a triketone herbicide, was selected because of its growing use on maize. Agricultural soil samples from the Limagne plane (Auvergne, France), particularly rich in clay and organic matter, were studied. They were separated into 3 fractions depending on their size after physical treatments ($50\mu\text{m} < \Phi < 500\mu\text{m}$; $2\mu\text{m} < \Phi < 50\mu\text{m}$; $\Phi < 2\mu\text{m}$). A particular focus is put on the fine fraction containing mainly clay minerals known for major effect on xenobiotic adsorption. Adsorption isotherms of sulcotrione by the various soil fractions are in progress to quantify the soil response to the pesticide contamination. The effect of organic matter on sulcotrione immobilization is also studied comparing clay and organo-clay fractions.

Sulcotrione dissipation was shown in this soil using microcosm experiments, its rate increasing with the soil moisture. Isolation of sulcotrione-degrading microorganisms was carried out in soil-mineral medium (MM) containing the herbicide. The degradation time decreased dramatically with the number of sulcotrione doses added. Four bacterial colonies were isolated from an agar-MM plate supplemented with sulcotrione and one strain was shown to biotransform the herbicide. Its biodegradative metabolism will be studied in water and in interaction with the various soil fractions.

THE EFFECT OF PIG SLURRY ADDITION ON ANION EXCHANGE MEMBRANE EXTRACTABLE SOIL PHOSPHORUS

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Animal manure is generally used as a soil fertilizer to supply nitrogen (N) to crops, despite the input of readily available phosphorus (P) being also considerable. Consequent environmental concerns gave rise to a shift and nutrient management practices are becoming focused primarily on P rather than on N. Thus, bioavailable P from animal manures must be adequately quantified to match crops' needs and avoid over-fertilization.

To rapidly assess bioavailable P from pig slurry (PS), a short term anaerobic incubation was set up. Portuguese soil samples from Castelo Branco (Cb), Azores (Az), Minho (Mn) and Degracias (Dg), with different factors limiting P availability, were mixed with 100 mg P kg⁻¹ as fresh PS and incubated during 7 days at 25°C in 60mL syringes adjusted to a 25mL volume with deionized H₂O. The syringes were daily shaken for 1 hour. Control soil samples were also prepared accordingly. After the incubation one anion exchange resin in the membrane form (AEM) was placed in each syringe and P extraction was carried out with an overhead rotator shaker during 16 hours. The AEM -P was eluted in 0.5M HCl during 1 hour and determined by the molybdenum-ascorbic acid blue method.

The results reveal that soil samples AEM-P varied from 0.41 to 17.35 mg P kg⁻¹ in soils Dg and Az, respectively. PS addition significantly increased AEM-P in soils Mn and Cb, both sandy loam soils. The highest increase, 24.4 mg P kg⁻¹, was observed in soil Cb, an acidic soil (pH_(H2O) 5.5) with low cation exchange capacity (CEC = 2.23 cmol₍₊₎kg⁻¹) and organic matter content (OM = 14 g kg⁻¹). In soils Az and Dg no significant differences were observed between soil samples with and without added PS, results that could be ascribed to soil P retention and microbial immobilization. Therefore, bioavailable P from PS applied to different soils was not constant and soil characteristics must always be considered.

PREVENTION OF HERBICIDES POLLUTION USING BENTONITE AND ANTHRACITE AS MODIFYING SORBENTS IN ALGINATE-BASED CONTROLLED RELEASE FORMULATIONS

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Important risk of groundwater pollution has been observed as a result of rapid leaching of highly soluble herbicides when used in agronomic practices as conventional formulations. This risk can be minimized through the application of the herbicide at a set rate using controlled release formulations (CRFs). In this research, alginate-based CRFs of chloridazon and metribuzin, identified as groundwater pollutants, have been evaluated in a calcareous soil. The effect of two modifying sorbents (bentonite and anthracite) on herbicide release kinetics from CRFs has been investigated. Using an empirical equation, the time taken for 50% of the active ingredient to be released in soil (T_{50}) was calculated. T_{50} values ranged between 2.87 days for metribuzin-bentonite alginate-based granules and 14.63 days for chloridazon-anthracite alginate-based granules. From the analysis of the T_{50} values, we can deduce that the release rate of the herbicides was controlled by diffusion mechanism being sorption capacity of the sorbents and the permeability of the formulations the most important factors that affect herbicides release. Besides, it was observed that the release rates were higher in metribuzin CRFs than in those prepared with chloridazon, which has lower water solubility. Mobility experiments, carried out in soils columns, showed that the use of CRFs reduces the presence of both herbicides in the leachate compared to the technical grade products; in addition, the amount of herbicide leached can be related to the T_{50} values in soil of the CRFs. The results have demonstrated the capacity of CRFs to control the delivery of mobile herbicides, reducing the amount of active ingredient for leaching, and thus being useful to prevent aquifers pollution by chloridazon and metribuzin.

VOLATILE ORGANOCHLORINE COMPOUNDS EMITTED BY TEMPERATE CONIFEROUS FORESTS

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Chlorine is one of the most abundant elements in nature, which undergoes a complex biogeochemical cycle. Chlorine bound in some substances is partly responsible for atmospheric ozone depletion and contamination of some ecosystems. As due to international regulations anthropogenic burden of volatile organochlorines (VOCl) in atmosphere decreases, natural sources (plants, soil, abiotic formation) are expected to dominate VOCl production in the near future. Examples of plant VOCl production are methyl chloride, and bromide emission from (sub)tropical ferns, chloroform, 1,1,1-trichloroethane and tetrachloromethane emission from temperate forest fern and moss. Temperate forests are found to emit in addition to the previous compounds tetrachloroethene, and brominated volatile compounds. VOCl can be taken up and further metabolized in plants.

The aim of this work is to quantitatively analyze the formed VOCl in temperate forest ecosystems by a cryofocusing/GC-ECD detection method; identify possible unknown VOCl by SPME preconcentration method. The studied mosses and ferns showed stable emissions of chloroform ($5\text{-}367 \text{ pmol day}^{-1} \text{ g}^{-1} \text{ DW}$), tetrachloromethane ($0\text{-}90 \text{ pmol day}^{-1} \text{ g}^{-1} \text{ DW}$) and lower amounts of tetrachloroethene ($0\text{-}54 \text{ pmol day}^{-1} \text{ g}^{-1} \text{ DW}$). The emission of dichloromethane and 1,2-dichloroethane by plants has been indicated.

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LUMINESCENCE OF HUMIC SUBSTANCES AT 77 K PRELIMINARY EXPERIMENTS

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Humic substances are abundant in the environment. Due to their absorption in the visible wavelength range, they show reactivity that has an important impact on the environmental chemistry. Their complex structure makes however, studies quite difficult.

Their photoinductive or photosensitizing properties, i.e. their ability to induce the phototransformation of a variety of chemicals was explained by their capacity to generate reactive species such as triplet excited states, hydroxyl radicals and singlet oxygen [1,2].

To our knowledge, the direct observation of triplet excited states was never reported in the literature.

This presentation gives our first detection of humic substances by luminescence at 77 K. Data seem to confirm the existence of charge transfer complexes already mentioned to rationalize fluorescent emission at room temperature [3,4].

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WATER AND SEDIMENT QUALITY ASSESSMENT USING AGRICULTURAL PLANTS AS BIOINDICATORS

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Monitoring of water and sediment quality in watercourses of Serbia gained in importance in last few decades. The Great Bačka Canal occupies the special attention as it is considered to be the most polluted canal that is intensively used in agriculture production. This study presents the results of comparative study of chemical analysis of water and sediment and their biological effects on test plants. Heavy metal and organic pollutant contents were determined according to EPA 7000B method, and biological effects evaluated using physiological (germination) and morphological (root and shoot length) responses of cucumber (*Cucumis sativus* L.) and barley (*Hordeum vulgare* L.) by standard method on filter paper (ISTA Regulations book, 2011 and Regulation of the quality of seed of agricultural plants (Official gazette 58/2002)). Assay comprised the samples of water and pore water (obtained in process of sediment precipitation) from the canal, while as control variant distilled water was used. Chemical analysis indicate elevated levels of Cd (exceeding MAC-EQS according to Directive 2008/105/EC) in water while the sediment was slightly contaminated with Cu. Regardless of chemical composition, seed germination was at the same level of significance between all treatments for both plant species, and was within the norms stipulated by mentioned Regulation book. However, water and pore water from the canal inhibited root growth of cucumber and barley expressing highly significant difference compared to control variant. Shoot growth was stimulated in water and pore water samples and was significantly higher compared to the control. Given indicates that more reliable assessment of water and sediment quality can be achieved only with comparative analysis (chemical and evaluation of plant responses). Accordingly, cucumber and barley showed good potential as bioindicators of quality of these systems.

MERCURY ACCUMULATION AND TRANSFER IN SOIL-PLANT SYSTEM: ORGANIC VS INORGANIC

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Despite the emissions decrease in the last decades, the production-oriented policies that prevailed before resulted in large input and accumulation of mercury in most soils, some of them agricultural. To establish soil quality criteria that ensure food safety is crucial to understand the major processes leading the transfer and accumulation of Hg from soil to crop. The accumulation of Hg in root and shoot will be the same? It will depend on the degree of soil contamination, on the plant species or on the Hg species present? Information regarding these questions is practically non-existent, although there are several studies on aquatic biota, which indicate bioaccumulation and biomagnification processes [1].

The work presented will focus on the relations between Hg contents (organic and inorganic fraction) in soil and root plant and between root and shoot plant. Besides general soil properties, also total and organic mercury content were successfully determined in several soils and plants (*ryegrass, cotton grass and brassica juncea*) from agricultural fields surrounding a chlor-alkali plant located in Estarreja (Aveiro, Portugal). Results show that total Hg concentrations ranged from 0.08 to 209 mg/kg in soils, from 0.01 to 84 mg/kg in roots and from 0.02 to 6.87 mg/kg in shoots. Average organic Hg contents in root and shoot plants, considered the most toxic fraction [2], represents only 0.58% and 0.66 % of total Hg, respectively, which must not be overlooked since it presents relatively high concentrations. The results will contribute to realise the factors that control the accumulation and transfer of organic and inorganic mercury species from soil to crop.

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EFFECT OF A CYCLOLIPOPEPTIDIC BIOSURFACTANT ON PAHs SORPTION BY SEDIMENTS

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Polycyclic aromatic hydrocarbons (PAHs) are toxic contaminants found on sediments and understanding how they are sorbed in the different mineral and organic fractions of the sediment is critical for performing effective removal strategies. Then fifteen PAHs were studied and their sorption isotherms could be simultaneously obtained, thanks to a chromatographic method combined to a trace concentration procedure. The influence of various factors on the sorption behavior, such as pH, ionic strength and amount of organic matter could be evaluated. Among sediment decontamination methods, electrokinetic (EK) remediation is a promising one but is not adapted for lipophilic nonionic contaminants. Then, the mobilization of PAHs from the sediment to the aqueous fluid by an anionic surfactant was investigated, this step being essential before PAHs electromigration by an EK process. This work demonstrates that PAHs could be desorbed from the highly retentive sediment, even when it is composed of a high fraction of kaolinite or organic matter. An original cyclolipopeptidic anionic biosurfactant (amphisin), produced by *Pseudomonas Fluorescens* DSS73, was used for this purpose and was compared to the conventional synthetic anionic surfactant sodium dodecyl sulfate (SDS).

BIOREMEDIATION ACTIVITY OF ACCLIMATED *STREPTOMYCES* *SP* IN SOLID AND LIQUID WASTE

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In recent years, Uttarakhand has emerged as one of the most attractive industrial destinations in India. The industrial sector of the Uttarakhand state growing day by day and it is very good for the development of state and country also, but we should remember the second phase of industrialization. It is the industrial effluent, disposed by the industries. The industrial effluents have many pollutants including heavy metals. The major environmental problem is the pollution of heavy metals and they cause serious diseases in animals including human. In the present study, the *Streptomyces* strain isolated from sludge contaminated with heavy metal was trained for heavy metal remediation by exposing metal to them and used for bioremediation activity for chromium, copper and lead in the waste. The metal chromium reduction ranged from 0.386-6.42mg/l, which showed maximum reduction in chromium by *Streptomyces sp*, copper reduction ranged from 0.288-1.129mg/l and reduction in lead ranged from 0.063-0.286mg/l. In future, the gram positive filamentous *Streptomyces* strain can be sued for chromium ion reduction as bioremediating agent.

Keywords- Bioremediation, *Streptomyces sp.*, metal tolerance, effluent, bioremediating agent.

STUDY ON SORPTION DYNAMICS OF SULPHAGUANIDINE IN NATURAL SOILS

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Sulphonamides are widely used in intensive livestock rearing for the treatment and prevention of bacterial diseases. When animals graze or manure is applied, these compounds can disperse into the natural environment in an uncontrolled way.

Generally, medicines are excreted as the parent compounds, or as their metabolites including oxidation/hydrolysis products. However, only small amount of sulphonamides are metabolized. Up to 90% of these drugs are excreted into the environment within 2 days of administration.

It is therefore a matter of urgency to assess the potential mobility of these compounds in natural soils and sediments. Sorption and desorption of sulphaguanidine are important processes that influence the amount of this compound retained by the soil and that which is susceptible to runoff or movement in the soil profile.

This study aimed to characterization of sorption dynamics of sulphaguanidine in soils significantly differentiated in their physical and chemical properties such as: pH, organic matter content and cation exchange capacity. The strength and the extent of sorption were determined by sorption coefficient, isotherms and sorption kinetics. To assess the sorption type, the results were further fitted to the Langmuir and Freundlich models. The influence of external factors on the sorption of these pharmaceuticals, such as solution pH and ionic strength were also determined. Initially, the sorption experiments were performed in accordance with the OECD Test Guideline 106 (OECD, 2000). The degree of sorption of this compound to soils was quantitatively assessed using HPLC technique with UV/Vis detection.

USEFULNESS OF QuEChERS PROCEDURE FOR DETERMINATION OF PHARMACEUTICAL RESIDUES IN SOIL SAMPLES

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The presence of pharmaceuticals of high biological activity, even at very low concentrations, may pose a significant risk to the environment. Literature data indicates that increasing number of these compounds are analysed in aqueous environment if compared to the soil and sediment matter. The aim of the study was to develop an analytical procedure for the extraction of non-steroidal anti-inflammatory drugs (NSAIDs) and estrogenic hormones in soil samples based on QuEChERS method. This method is used, *inter alia*, for the determination of polar pesticides with acidic properties, and therefore its adaptation to the determination of NSAIDs and estrogenic hormones seems justified.

In this study solvents such as acetonitrile, ethyl acetate and acetone were tested in order to choose appropriate conditions of extraction. Extract purification was carried out by dispersive solid phase extraction (dSPE), as well as by column extraction to the solid phase (SPE). Since chosen pharmaceuticals are polar compounds before GC determination derivatization step was made using BSTFA + 1 % TMCS with pyridine.

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CONTAMINATION OF SOIL IN THE VICINITY OF THE TRANSFORMER STATION IN SUBOTICA MUNICIPALITY, SERBIA

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Polychlorinated biphenyls (PCBs) are a group of synthetic organochlorines with numerous harmful effects to humans and to the environment. Although the usage of PCBs is banned in many countries, they can be released into the environment by evaporation from the old open systems (paint and wood protecting layers, softeners etc.), dumping sites and waste incinerators, and leaking from operational or dumped transformers, condensers, hydraulic systems and other PCB-containing devices. Polychlorinated biphenyls bind strongly to soil and their degradation is lengthy, from several years to decades. The transformer station 110/20kV "Subotica 1" is located on the periphery of the municipality of Subotica. The station's capacitors which contain pyralene oil have been out of use for some time now but have not been properly removed yet. This situation, combined with weather conditions over time, has resulted in a visible physical damage of the capacitors and a long-range leaking of pyralene oil into the environment. The said conditions have prompted us to take four samples of soil around the capacitors and to analyse the presence of six PCB congeners (28, 52, 101, 138, 153 and 180) using US EPA Method 3540 C, 630 C, 8082. In the course of our research, we have found the presence of OCPs (α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT) in all soil samples by US EPA Method 3540 C, 3630 C, 8081 A. Overall, concentration levels of PCB congeners in collected samples ranged from 1.168 to 2.354 mg/kg, while OCPs concentrations were in the range from 0.077 to 0.315 mg/kg.

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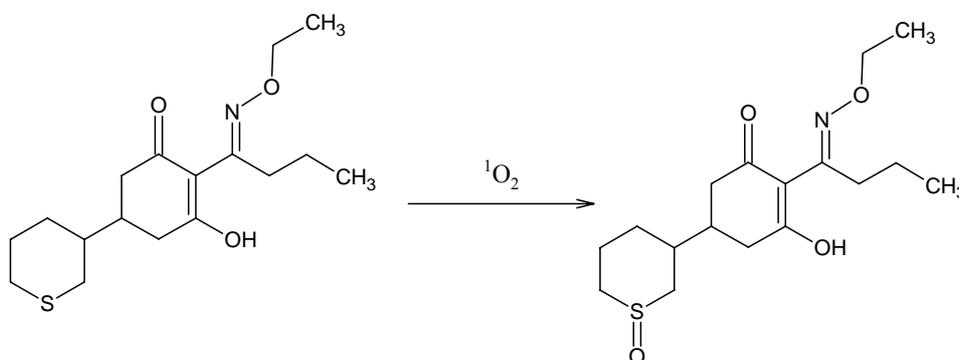
REACTIVITY OF CYCLOXYDIM TOWARD SINGLET OXYGEN

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Cycloxydim (CD) is a systemic cyclohexanedione herbicide that is used for the control of grass weeds of many agricultural and horticultural broad-leaved crops. CD can occur as *E*- and *Z* isomer, depending on the polarity and the pH of the solvent. Besides, keto-enol tautomerism can also occur. The reactivity of CD toward singlet oxygen was studied in acetonitrile in which the stable tautomer is the enol. In these experiments, singlet oxygen was produced using perinaphtenone as a sensitizer ($\Phi_T = 0.97$). Excitation wavelength was set at 365 nm in order to avoid CD absorption. At first we checked that CD reacts negligibly with the perinaphtenone triplet excited state by monitoring the triplet decay in the presence of increasing CD concentrations.



Then, the rate of CD loss was measured for several CD concentrations of air-saturated solutions of perinaphtenone/CD. Plotting the reciprocal of the rate against the reciprocal of the concentration gave a linear relationship from which the bimolecular rate constant of reaction between CD and singlet oxygen could be obtained : $k = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The analytical study by mass spectrometry revealed that a major photoproduct is formed. This is the sulfoxide derivative.

PLANT EXTRACT ACTS AS NATURAL PHYTOSANITARY PRODUCT

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Plant protection has been the major concern in agriculture to improve yields and ensured regular production. Promising molecules have emerged in the 90's with the progress made in plant resistance mechanisms. They are named Plant Defense Inducers (PDIs) (“Stimulateurs de Défenses naturelles”) and trigger a molecular and biochemical cascade mechanisms in the host plant to defend against pests. Unlike any (bio)pesticide control action or most plant biotechnological approaches, the PDI concept is not based on “human” view but try to resolve the problem from the “plant” view. The plant acquired resistance is not limited and restricted to one pest infection and generally covers the entire plant body. Their mechanism of action is based on plant recognition ability of some elicitor molecules that initiate defense reactions (immunity) *in planta*.

Very few PDIs have been patented and/or commercialized by private sector as active ingredient and/or commercial formulation. Our group developed a new class of phytosanitary product extracted from grapes having two combining intransit-flux reduction properties i.e. PDIs (patent submitted-DI/CNRS n°3372-01) and pesticide photoprotectors (patent PCT/IB2008/001007). It promotes plant defense and protects chemical pesticides from sunlight prolonging their half life.

REACTIVE AND AVAILABLE POOLS OF METALS IN DEGRADED SOIL AS AFFECTED BY THE APPLICATION OF ORGANIC WASTES

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The amendment of soil with organic wastes is a common strategy for the recovery of mine tailing. This practice can constitute a source of harmful elements and can alter metals solubility. The assessment of solubility, availability and reactivity for potentially toxic elements within the soil matrix is essential to avoid toxic metal exposures for living organisms but also to water resources. In order to evaluate the chemical forms in which metals occurs in the solid and solution soil phases, several chemical extractions were performed. A soil from an abandoned Fe mine tailing (Granada, Spain) was amended with sewage sludge and a compost consisting on a mixture of sewage sludge and vegetable wastes. The mixtures were incubated for 30 d at 40% of field capacity and 25 ° C. After the incubation period single and sequential extractions were carried out and metals concentrations (Cd, Cr, Cu, Ni, Pb and Zn) were determined by ICP.

Addition of compost did not affect the amount of metals in the more mobile fraction but increased the presence of metals in the bioavailable (EDTA) and reactive (dilute acid) fractions at application rate of 10%. An increase in the fraction of mobile forms of metals was observed for the application of sludge. Besides, metals were redistributed in the soil solid phases after application of the amendments. Additionally, the phytotoxicity was evaluated using a germination test. Application of amendments at low rate (3%) did not affect seed germination but for a higher dose (10%) medium or low toxicity were determined.

DEVELOPMENT OF AN ANALYTICAL METHOD BASED ON QuEChERS-LC-MS/MS FOR THE ANALYSIS OF STEROIDS AND VETERINARY ANTIBIOTICS AT TRACES LEVEL IN SOIL

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Antibiotics are more and more used as growth promoters of farm animals. These compounds can therefore enter in the environment through land application of manure. Steroids are also found in the environment due to animals but also humans wastes. As these compounds can be harmful for human health, their analysis provokes interest.

The aim of the study was to develop a method for the analysis of traces of hormonal steroids or veterinary and human drugs. Therefore, 11 hormonal steroids, 16 veterinary antibiotics and 11 human contaminants, used in this study as pollution tag, were chosen. An analytical method both selective and sensitive based on liquid chromatography-tandem mass spectrometry was developed. The best conditions for the separation and for the detection were optimized.

The analysis of complex matrices such as soil needed a rigorous sample preparation to obtain a repeatable and enough sensitive analysis to achieve the detection limits required. For this purpose, an extraction step using the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was set up. It is a new technique, simple, quick, cheap and particularly innovative for the analysis of environmental matrices such as soil. This technique is based on a liquid-liquid extraction principle with an organic solvent in presence of salts and buffers. Several parameters were optimized (sample weight, solvent nature, water and solvent volumes, buffer type). As soil is a complex matrix, a SPE (Solid Phase Extraction) step was compulsory to reduce matrix effects. Therefore the SAX (Strong Anion Exchange) cartridge was used in tandem with the Strata-X cartridge for the clean-up.

This analytical methodology was successfully applied to soils collected in several areas of France and treated differently (manure and sludge spreading). Some human drugs, steroids and veterinary antibiotics were found.

DEGRADATION STUDIES OF A PESTICIDE ON MODELS OF SOIL AND NATURAL SOIL UNDER LIGHT IRRADIATION

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Given that environmental problems such as water, air or soil pollutions, acid rains or weather warming became great and international concerns, we focused our studies on pesticides' behavior on soil regarding their intensive use in agriculture and presence in soil. Many studies which have been devoted to the pesticides' behavior in aquatic compartments showed that processes like hydrolysis, biodegradation or photodegradation could be responsible of their degradation. In soil, the main part of studies was interested in biodegradation reactions but just a few of them deals with the pesticides' transformation processes at the surface of soil under irradiation.

In this Work, we examine the photodegradation of a pesticide, carbaryl, a carbamate derivative, on three models of soil inorganic moieties (silica, kaolin, Fontainebleau Sand) and a natural soil from Orange agricultural region in south east of France. In order to determine relevant parameters that influence the degradation rate of carbaryl. The natural soil has been modified by different treatments (fractionation, sterilization, organic matter removing). Photodegradation kinetics and constant rates have been systematically determined for all solid matrix and soil fractions. Additionally, their photochemical properties have been evaluated by chemical probes for hydroxyl radical and singlet oxygen. In parallel, physical and chemical characterizations of these solid supports such as particle size, specific surface or chemical composition were found out to potentially establish the relationship between the organic pollutant photodegradability and specific properties of the matrix. Moreover, specific degradation pathways on this support have been elucidated by the photoproducts identification using LC-MS analysis.

Session 5: Sustainable chemistry

Posters

NITRATE REMOVAL BY REVERSE OSMOSIS: APPLICATION TO GROUNDWATER TREATMENT

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Nowadays, industries rejections, human activity and fertilizers used for the intensive agriculture lead to a groundwater pollution by nitrates. Nanofiltration is an adapted technique for drinking water production when nitrate concentration in treated water is about 30 ppm. However this technology is ineffective when the standards qualities are very constraining. For agroalimentary industries, the maximal admissible nitrate concentration is fixed at 10 ppm. In this case, reverse osmosis seems to be an appropriate technique for treating this pollution. The aim of this work is the performance study of reverse osmosis process for the nitrate removal from water which would be used for beverage industry. At first, tests were carried out with synthetic solutions. Two salts, KNO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, were used at various concentrations in a distilled water.

For the experiments, a laboratory-scale cross flow membrane test unit was used. The RO membrane was a commercial thin-film composite denoted TW30-1812-75 by the manufacturer (Dow-FilmTech). In spiral wound configuration, the surface area was 0.96 m² and observed minimum salt rejection was 96%.

Effects of various parameters (transmembrane pressure, initial nitrate concentration, temperature and feed flux) on the removal rate of nitrates have been investigated. The results obtained from experiments indicated that nitrates can be removed effectively by reverse osmosis process.

Keywords nitrates, groundwater pollution, reverse osmosis

ADSORPTION OF PCB 3 ON ORGANOMODIFIED LDHs

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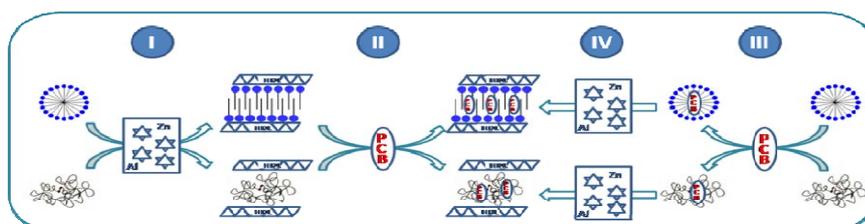
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1200 million ton of Polychlorinated biphenyls (PCBs) have been produced worldwide and about 400 million tons are considered to be spread in the Environment. PCBs are persistent pollutants and highly immunotoxic toxic and carcinogenic. They may concentrate in river sediments and strongly affect ecosystems and biodiversity. Conventional cleaning processes are environmental non-friendly methods and there is still need to look for alternative ways of treating these contaminations. Washing sediments with surfactant solutions offers good results. Layered Double Hydroxides (LDH) are synthetic anionic clays that have proved to be good adsorbant for both surfactant and organic pollutants. Modification of LDH by anionic surfactant or polymer enhances their adsorption properties toward hydrophobic xenobiotics.

This study aims to develop a new cleaning process based on the adsorption of PCBs by organically modified LDH. 4-chlorobiphenyl (PCB 3) was used as a model. Zn_RAl LDH materials with variable anion exchange capacities, intercalated by sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS) or humic acid were tested as new sorbents. PCB 3 adsorptions were processed either by intercalation or direct coprecipitation (scheme). Surfactant modified LDH show a great ability to trap PCB 3, about 97% adsorbed, all the same by coprecipitation with pollutant. Humic acid adsorbed LDH are less efficient, with a maximum of 50% of adsorption.



APPLICATION OF FENTON REACTION FOR REMOVAL OF SULFONAMIDES FROM WASTEWATER

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The chemical oxidation methods present highly effective alternatives to traditional water treatment processes while degrading toxic and biofactory organic pollutants. Fenton process is one of these methods, that presents easy to handle and operate option, where radicals responsible for degradation are produced by catalytic decomposition of hydrogen peroxide in reaction with ferrous ion. In many studies it was shown that Fenton process is an effective method for decomposition of pharmaceuticals, including sulfonamides. Sulfonamides are synthetic antibiotics frequently used in veterinary medicine. They are likely to run off into surface waters and further penetrate the environment. Sulfonamides are characterized with a relatively long lifetime in the environment and are partially resistant to biodegradation. They can be accumulated in various organisms of the food chain. Elimination of these chemicals from wastewaters is therefore crucial for preventing their discharge into the environment.

The present study focused on comparison of degradation patterns of five sulfonamides: sulfathiazole, sulfadiazine, sulfamerazine, sulfamethazine and sulfadimethazine by heterogeneous Fenton system ($[\text{Fe}(\text{II})]$ immobilized on $\text{Al}_2\text{O}_3/\text{H}_2\text{O}_2$) in deionized water and in wastewater. The experiments examined the effect of operating conditions like pH, initial concentration of catalyst and dose of H_2O_2 . Qualitative comparison of the products of degradation and biodegradability of mixtures after oxidation process in different matrix is also presented.

Acknowledgment: Financial support was provided by Polish Ministry of Research and Higher Education under grant Nr 538-8200-0509-1.

ASSESSMENT OF DEGRADATION IMIDAZOLIUM IONIC LIQUIDS BY ELECTROCHEMICAL PROCESS

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Ionic liquids (ILs) have been area of great interest owing to unique properties and unlimited resources for designed properties by variation of cation and anion. Among the several applications foreseeable for ILs in the chemical industry such as solvents in organic synthesis, as homogenous and biphasis transfer catalysts, and in electrochemistry, as extraction media. Concerning the chance of wide applications of ionic liquids in the industry there appears a real risk of finding them soon in industrial wastewater and finally in the environment. Therefore, there is a need to look at effective methods utilization of ionic liquids. Electrochemical conversion is promising as method for removing toxic and non-biodegradable organic pollutants from aqueous solution. Important factors for the application of electrochemical degradation are the electrode materials and the electrolysis conditions. High stability, high activity and low cost are the desirable properties of electrodes.

The presented investigations are focused on electrochemical oxidation of 1-butyl-3-methylimidazolium chloride (IM14Cl) on modified PbO₂ anodes. The effect Co, F/Fe, Co/F, CeO₂ doped on PbO₂ anode on oxidation of IM14Cl efficiency was investigated. Cyclic voltammetry, hydroxyl radicals and hydrogen peroxide measurement were carried out to get a better understanding of IL electrooxidation on prepared anodes.

Acknowledgment: Financial support was provided by Polish Ministry of Research and Higher Education under grant N N523 42 3737.

INFLUENCE OF METALLIC NANOPARTICLES ON THE PHOTOCATALYTIC ACTIVITY OF TiO₂ FOR THE ELIMINATION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTION

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Advanced oxidation processes (AOP) are of considerable interest in water and wastewater treatment for the elimination of organic pollutants. One of the most promising AOP methods used for the degradation of many organic refractory pollutants (such as pesticides, herbicides and dyes) from water and wastewater is the heterogeneous photocatalysis. This is mainly due to its high mineralisation efficiency and low toxicity ideally producing carbon dioxide, water and mineral ions as end products. It involves the presence of a semi-conductor as photocatalyst. Among the available semiconductors, titanium dioxide (TiO₂) is the most popular one.

In recent years, the main challenge of researches is to enhance the photocatalytic efficiency of semi-conductors by depositing transition metals or to extend its light absorption spectra to the visible region.

In the present work, we have investigated the photocatalytic efficiencies of a TiO₂ and a Rh doped TiO₂ photocatalysts for the degradation of two organic compounds in aqueous suspensions under artificial ultraviolet (UV) irradiation conditions. The P500 titanium dioxide (purchased for Millenium Chemicals) was used as reference photocatalyst in this study. For this purpose batch, studies were conducted in the presence of different photocatalysts in order to study the photodegradation kinetics of the target compounds.

EFFECTS OF SEVERAL CO-SUBSTRATES ON THE DEGRADATION OF CARBAMAZEPINE BY AEROBIC NON ACCLIMATED SLUDGE

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Water pollution by organic compounds is one of the leading emerging issues in environmental chemistry.

In recent years several processes, using physical, chemical and/or biological methods, were developed to remove organic micropollutants in the effluents of wastewater treatment plants. Activated sludge is a frequently used technique in this field. It involves microorganisms present in the sludge, for their ability to degrade organic matter through their metabolization as carbon and energy sources. However, some of the most harmful pollutants, the endocrine disruptors, are very recalcitrant during the wastewater treatment.

The aim of the present work was to investigate the main factors involved in the conventional activated sludge process and to optimize them in order to enhance the biodegradation efficiency of endocrine disruptors. The organic compound investigated here is the carbamazepine, known to be resistant to biodegradation. It was repeatedly found in surface waters and has been described as a persistent substance. Batch experiments were carried out using different co-substrates in oxic conditions by using a laboratory scale activated sludge reactors.

PRELIMINARY STUDIES ON 3,4- DICHLORANILINE AND METHYLENE BLUE REMOVAL FROM WATER USING OLIVE POMACE ALGINATE-BASED GRANULES

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In the present study, an olive pomace (OP) and a composite adsorbent have been applied to removal 3,4-dichloroaniline (3,4-DCA) and methyleneblue (MB) from aqueous solution. The composite adsorbent (OPAG) has been obtained by entrapment of OP into calcium alginate gel granules. SEM, FTIR, TGA and physicochemical parameters were carried out to characterize the adsorbents. The sorption study at the solid-liquid interface was investigated using batch experiments. Preliminary results indicate that non-encapsulated OP exhibits a better efficiency in terms of sorption capacities towards the 3,4-DCA(0.919 mg/g) than those obtained for olive pomace alginate-based granules (0.586 mg/g for the granules containing 20% of alginate (OPAG₂₀) and 0.743 mg/g for the granules containing 10% of alginate (OPAG₁₀)). The higher value of sorption capacity obtained for non-formulated olive pomace compared to alginate-based granules might be justified considering that the adsorption process of this organic molecule takes place mainly through a hydrophobic mechanism. On the other hand, it was shown that OPAGs have higher adsorption capacity for MB than non-encapsulated olive pomace, increasing this capacity with the increase of alginate content. The maximum adsorption capacity for MB was found for OPAG₂₀ (789.7 mg/g), which is over 20 and 5 times higher than that obtained for non-encapsulated OP and OPAG₁₀, respectively. These results suggest that the electrostatic interaction between methylene blue positive ions and the negative charge of the alginate chains is the main mechanism involved on removal of this cationic dye.

WASTEWATER TREATMENT PROCESS PLANT PROPOSAL TO REMOVE CHROMIUM (VI) BY LOW COST SORBENTS

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Chromium is used in a wide range of industries. The removal of Cr (VI) from wastewater of these industries is crucial due to its high toxicity. Biosorption, using adsorbent materials derived from low-cost agricultural (grape stalks) and food wastes (crab shells), can be used for the effective removal and recovery of chromium ions from wastewater streams with low cost, high efficiency and minimization of chemical. The biosorption of Cr (VI) with grape stalks produces Cr (III) in solution from Cr (VI) reduction and crab shells have been used as adsorbent to remove the residual Cr (III). Although the efficiency of this biosorption in laboratory scale, some aspects make difficult its industrial application, like solids handling and choose the best contact method. In this communication experimental data are obtained for the sorption of chromium with grape stalks and crab shells to determine the optimal contact process for scaling to industrial application. The operational variables investigated are influence of pH, adsorbent concentration and operation time.

The interest of this communication is to use experimental data to propose a complete plant process for industrial wastewater treatment. In the process the wastewater and the grape stalks are introduced to an agitated tank controlled at about pH=3. A hydrocyclone is used to remove the grape stalks greater than 100 μm being subsequently filtered to remove fine stalks. As the treated wastewater contains residual Cr (III), is introduced to a second agitated tank with crab shells where is removed until the low level required. To remove de solids (crab shells) greater the 100 μm a hydrocyclone is used. In the last step, to clarify the stream water treated it is filtered to remove the fine shells and solids. Treated water with low concentration of Cr (VI) and Cr III, under the limits established by environmental authority is achieved, finally.

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ANTIMICROBIAL AND CYTOTOXIC AGENTS INSPIRED BY NATURE

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Sterols are not only parts of cell membranes, but they are also precursors of different biologically active natural products, including hormones. Phytosterols have been believed to become important plant products with a broad spectrum of application in the near future. Based on that foreseen importance, they have become inspirational natural products in designing novel biologically active compounds by conjugation with polyamines. The use of phytosterols has been investigated for designing novel drugs capable of treating and preventing ailments like inflammation, infectious diseases and cancer.

Polyamines are positively charged at physiological pH value, and, therefore, they play an important role in biological systems. Positively charged polyamines are able to bind to negatively charged DNA macromolecules, which process neutralize negative charge of phosphates.

Lipophilic derivation of polyamines results in obtaining conjugates, the importance of which consists in enabling transportation of biologically active compounds through biomembrane. The objective of this investigation was focused on a synthesis of conjugates of stigmasterol with spermine, piperazine and ethylene diamine, and on subjecting them to microbiological and cytotoxicity tests. The spermine derivative displayed considerable antimicrobial effect ($50 \mu\text{g}\cdot\text{mL}^{-1}$) on *Staphylococcus aureus*, a gram-positive bacterium, and high cytotoxicity ($\text{IC}_{50} = 0.028 \pm 0.006 \text{ mmol}\cdot\text{L}^{-1}$) on mouse fibroblasts Balb/c 3T3.

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ANTHROPOGENIC CONTAMINANTS IN TERRESTRIAL SEDIMENT ARCHIVES OF THE RIVER MAIN (GERMANY): TIME TRENDS

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Within the aquatic system fluvial particulate matter is of major importance within the aquatic environment regarding discharge, transport and transfer (fate) of anthropogenic contaminants. In the river system particulate matter is an important sink for numerous environmental pollutants and therefore it can act as the memory of the river. The deposition of this particulate matter occurs in two parts of the river: (i) subaquatic, in slow flowing areas and behind barriers, as well as (ii) on terrestrial areas, on floodplains and wetlands. In case of undisturbed and continuous sedimentation and accumulation, sediment profiles (particularly dated profiles) can act as ecological archives. Therefore, geochemical and chronological investigations of aquatic sediment archives can be used to assess the extent and effect of human inputs in the past towards the present

In this content, time related differences in the concentration levels of anthropogenic pollutants within a sediment profile are used as distinct information about the origin and strength of the input sources.

The present study sediment profiles from different riparian floodplains of the Main River (Germany) were taken in order to determine concentration trends of “common” or “modern” anthropogenic contaminants. Here we show the quantitative distribution of selected persistent lipophilic contaminants (PAHs, PCBs etc.) characterising municipal as well as industrial input sources.

GEOCHRONOLOGICAL INVESTIGATIONS IN FLUVIAL SEDIMENTS: TIME TRENDS OF ANTHROPOGENIC CONTAMINANTS

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During the last 200 years an increase in concentrations of many anthropogenic contaminants (e.g. persistent organic pollutants, heavy metals) discharged into the aquatic environment by human activities is obvious. Since dawn of industrialization particularly rivers have been affected by anthropogenic activities, recorded by different stages of water quality problems. Numerous studies have reported this impact, as well as the harmful effects on the environment. They have tried to predict variances in the chemical inventory over a broad time interval. Since the beginning of the 1970's and 80's reduction of these negative impacts within the aquatic environment is of particular interest.

Geochronological investigations of anthropogenic pollutants in aquatic sediment archives are a useful tool to predict variances in the contaminant inventory over a broad time interval. In addition, based on a catchment-wide assessment of the historical load of soil and sediment, this method is able to give detailed information about the:

- spectrum of sediment contaminants
- sphere of direct or indirect influence of an emission source, as well as parameters like transport, flow, morphological and geological setting
- classification of polluted areas: areas of low/high/significant pollution, and
- significance of regulatory intervention: areas of high/significantly high contamination.

Here an overview on geochronological investigations on fluvial sediment archives will be given. Although there is only a very limited number of studies on the historical record of organic contaminations, these studies demonstrate convincingly the significance of this analytical approach.

USED BREWERS DRAFF: A LOW-COST SORBENT FOR Cr(VI)

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The use of agricultural byproducts and industrial biowaste materials has been shown to be an attractive technique for removing Cr(VI) from contaminated waste waters. In this study, used brewers draff was investigated as a novel biosorbent for Cr(VI). The material was subjected to acid (2 M H₂SO₄) and alkali (0.5 M NaOH) pre-treatments to remove starch, proteins and sugars before use [1]. Fourier transform infrared rays analysis on solid phase (FTIR-ATR) was used to determine the main functional groups that might control the metal uptake. Batch experiments were performed at different pH values (3, 4.5, 6) and at various initial concentration of Cr(VI) (25–250 mg L⁻¹). Two equilibrium empirical models, Langmuir and Freundlich, were used to describe Cr(VI) adsorption. In order to identify possible reduction processes, ion exchange separation on the AG1-X8 resin was used to separate the anionic Cr(VI) and the reduced cationic Cr(III) from the aqueous phase after biosorption [2]. As expected, Cr(VI) removal was pH-dependent and fitted well both the Langmuir and Freundlich isotherm models. The ion exchange separation showed that Cr(VI) reduction had occurred in the solution during biosorption [3]. The efficiency of draff as a biosorbent was comparable (or even higher) to highly organic materials (e.g., composted peat) showing its potential application for Cr(VI) decontamination.

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IRON-MAGNESIUM SILICATES AS SOLID IRON SOURCES IN FENTON-LIKE PROCESSES

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Oxidative destruction of organic pollutants is considered as an alternative of their biodegradation. Oxidative systems where radical particles are generated from hydrogen peroxide are discussed widely. The most important of the systems are Fenton reagent (a composition of hydrogen peroxide and Fe (II)) and Ruff reagent (hydrogen peroxide with Fe (III)). An important drawback of these homogeneous systems is a necessity of introduction of iron ions in water. Heterogeneous system operating by a similar principle would be very attractive: ions of iron activate hydrogen peroxide but they stay in a solid phase and do not pollute solution. The general requirements for solid sources of iron for oxidative destructive processes are stability in oxidative environment, availability to interact with hydrogen peroxide, which is in a solution, minimal sorption of substrate.

In this work an attempt of constructing of solid source for Fenton process was made. Iron silicates and iron-magnesium silicates with different iron content were tested in oxidation of nonylphenylethoxylate.

Silicates were synthesized by hydrolysis of tetraethoxysilane with water solutions of magnesium sulfate and iron (II) sulfate followed by calcination. Oxidation was carried out in aqueous solution of ethoxylate by hydrogen peroxide in the presence of synthetic silicates. Changes of concentration of substrate were detected by tensiometry. It was established that synthetic iron-magnesium silicates containing 5 - 7% of iron could promote oxidation. Neither iron silicates with similar content of iron nor iron-magnesium silicate with lower iron content could activate hydrogen peroxide. Study of sorption ethoxylate on synthetic materials showed that iron-magnesium silicates possessed poorer sorption properties in contrast to iron silicates.

Acknowledgement. The study was supported by RFBR grant N 09-03-97538-r_center_a.

SORPTION PERFORMANCE OF *QUERCUS CERRIS* AND *QUERCUS SUBER* WITH POLYCYCLIC AROMATIC HYDROCARBONS. ROLE OF CHEMICAL COMPOSITION ON SORPTION CAPACITY

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Quercus cerris and *Quercus suber* are an important oak species. *Quercus suber* forest cover an area almost 2.2 million hectares concentrated mainly in the Mediterranean region. The bark of *Quercus suber* is called cork and is a natural, renewable and biodegradable raw material. Cork is a suitable material for wine bottle stoppers. The production of cork stoppers for wine represents almost 70% of the cork market. *Quercus cerris* is an important oak species extended in large areas of Eastern Europe and Minor Asia that has a thick bark which is not utilized at all.

The potential uses as a biosorbent of both materials was investigated. The sorption performance of cork from two oak trees with four polycyclic aromatic hydrocarbons (PAHs) (acenaphthene, fluorene, phenanthrene, and anthracene) was measured and compared with each other. All isotherms fit the Freundlich model and displayed linear n values. *Quercus cerris* cork exhibited a high efficiency for sorption of PAHs for the studied concentrations (5 to 50 $\mu\text{g/L}$) with 80-96% removal. In relation to *Quercus suber* cork, KF values of *Quercus cerris* are about three times lower.

In addition, two multivariate analysis were performed to establish the relationship between the sorption capacity measured as KOC and the chemical characteristics of *Quercus suber* cork. The results indicate that there is a strong positive correlation between the adsorption capacity and the lignin; otherwise a negative correlation between KOC and phenolic groups was found.

IONIC LIQUIDS AS ALTERNATIVE ABSORBENTS IN GAS CAPTURE PROCESSES

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Since the preindustrial period, global anthropogenic greenhouse gases emissions strongly increased, rising from 28.7 GtCO₂eq in 1970 to 49.0 GtCO₂eq in 2004. Among these gases, carbon dioxide is the one which saw its emissions rise the most in 34 years, due to the development in the use of fossil fuels, mainly for industrial and electricity production purposes.

In order to decrease the emissions of flue gases, interest has been ported on carbon dioxide capture technologies. One of the different ways is the post combustion capture which consists in capturing carbon dioxide directly in the smokes emitted from the combustion or industrial installation. Ionic liquids, due to their tunable properties through the endless combination of cations and anions, are considered as potential substitutes for classical solvents in processes of gas separation and capture by absorption.

Characterization, determination of thermophysical properties and measurements of absorption and selectivity of gases are necessary to decide which ionic liquid is suitable for the separation and capture processes. The ionic liquids studied consisted in an alkylimidazolium, pyrrolidinium or phosphonium cation and a carboxylate or tris(pentafluoroethyl)trifluorophosphate (eFAP) anion. Specific combinations of these cations and anions allowed us to measure the absorption of different gases - carbon dioxide, nitrous oxide, oxygen, nitrogen and ethane - in seven ionic liquids at low pressure and as a function of the temperature. Ionic liquids with the carboxylate anion and in particular alkylimidazolium acetate present a higher absorption than ionic liquids with the eFAP anion. This can be explained by the occurrence of a chemical reaction between carbon dioxide and the alkylimidazolium acetate ionic liquid.

CHEMISTRY AND ENVIRONMENT
AT THE *INSTITUT DE CHIMIE DE CLERMONT-FERRAND*

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We present the main research projects conducted at the *Institut de Chimie* of Clermont-Ferrand in the field of environmental chemistry. The synergy between the different research teams allows integrated approaches in interdisciplinary projects at the interface between physical chemistry, biochemistry and inorganic chemistry.

The ongoing research projects contribute to the understanding of different issues of societal and scientific importance, relevant to the fields of agronomy and food-growth, atmospheric physics and chemistry, and chemical technology. The projects aim at: i) the characterization of the impact of organic contaminants in the different environmental compartments (atmosphere, soil, water and vegetation); ii) the understanding and modelling of biological and chemical processes in the atmosphere and iii) the development of eco-friendly and sustainable processes for limiting pollution.

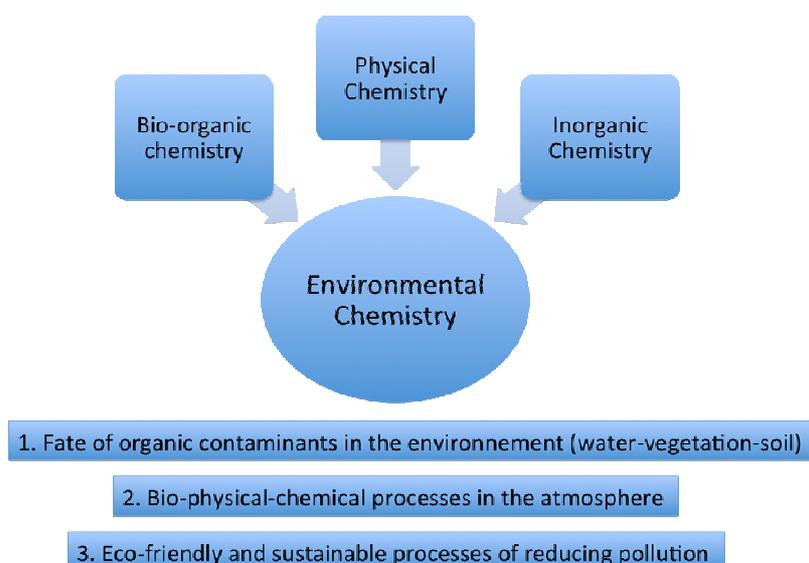


Figure 1. Environmental Chemistry at the *Institut de Chimie* of Clermont-Ferrand

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