BOOK OF ABSTRACTS
and
CONFERENCE PROGRAM

Organizers:
CNRS
Université de Pau et des Pays de L'Adour
LCABIE, équipe de recherche de l'IPREM UMR 5254,
European Virtual Institute for Speciation Analysis (EVISA)
International Association of Environmental Analytical Chemistry (IAEAC)
Objectif Congrès

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UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

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and
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Table of Contents

1. PREFACE : Welcome to Pau

The **CNRS**, the **University of Pau** (France), the **European Virtual Institute for Speciation Analysis** (EVISA) and the **International Association of Environmental Analytical Chemistry** (IAEAC) invite you to take part in the ***13th Workshop on Progress in Trace Metal Speciation for Environmental Analytical Chemistry***. Sustainable development needs to rely on accurate information. In this respect, it has long been understood that the occurrence, fate and translocation of metals in the environment including effectiveness in industrial processes is directly controlled by chemical formulation and relative reactivity. Despite of this long term fact recognition, metal speciation has only slowly evolved in our everyday life. At present, considerable progresses have been made so that analytical accessibility of metal species identification can become "routine" for some aspects, as well as the scope to topic and domains to be assessed has broaden, illustrating some maturity. New efforts and trends are emerging with advances in "in-situ' using electrochemistry approaches or direct synchrotron beam determination. Isotopic information either used via isotopic dilution as a quantitative method or now moving into the determination of novel isotopic signatures using plasma mass spectrometry techniques are opening up new doors of the matter structure and related information. "Speciation analysis" is at the crossroads of new intersections and has an array of novel paths to explore, including facilitation and integrating metal species determination in our daily life for improvement of the quality of life. Speciation has now gone a long way, some aspects are now of routine for environmental assessment and are integrated in legislation aspects. The techniques and overall analytical strategies allow now to tackle new frontiers and open up new dimensions (e.g. molecular isotopic signatures, molecular structures, nanoparticles). Further, in situ speciation approaches (electrochemical sensors, chemical probes) have seen considerable development addressing a more refined understanding of spatial distribution and reactivity of metal species.

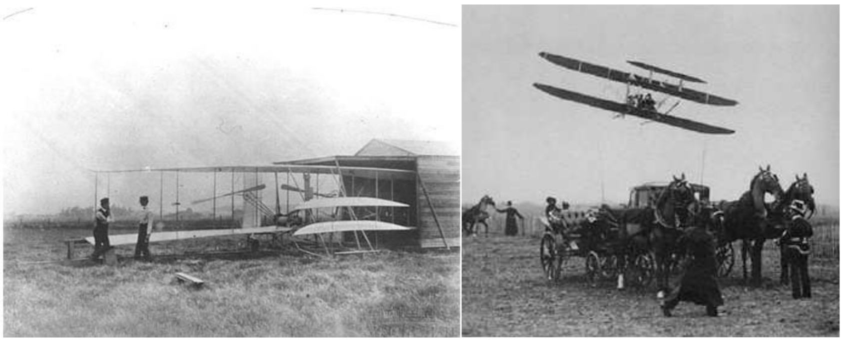
The objectives of this 13th Workshop is to position the major advances made in the field on analytical strategies for trace metal and metalloids speciation in the environment and to discuss the enhanced information value for an understanding of their impact, cycling and fate. Beyond bringing the state of the art in various aspects of speciation in solids, sediments, soils, biological tissues, water and air, this workshop will open up the new horizons in the field of speciation analysis. These aspects will be discussed in the following sessions:

1°- Speciation, lability, bioavailability and transformations;
2° - Direct and in-situ speciation analysis;
3° - Speciation of metal species in colloidal and nano-materials;
4° - Metal speciation in the environment and legal aspects,
5° - Speciation in industrial applications;
6° - New analytical strategies for metal speciation including isotopic information.

The « Laboratoire de Chimie Analytique Bioinorganique et Environnement » in the framework of the new « Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux », promoting this meeting, would like to welcome you in the city of Pau in the "Béarn" close to the Pyrenees. Pau is the "Gateway to the Pyrenees", and has the motivation to play a major role in key challenges of the 21rst century, together with its neighboring cities of Spain.

A strong pioneering spirit is link with the history of Pau. Pau has promoted and seen many novel developments overtime. The strong development of Pau started in the beginning of the 19th century. Its excellent climate and quality of life has attracted many including our UK neighbors. Their legacy resulted in the promotion of the first and oldest golf course of the continent and also a flourishing economy based on horse racing.

Low winds and the quality of the climate have also attracted the Wright brothers and Pau has seen the take off the aeronautic adventure. Indeed, in January of 1909, Wilbur Wright discovers Pau where sport in a premier activity (golf, polo...). At this time, Pau was "the hub of the Sporting world!" according to the international Herald Tribune. Following to their first flights in the US, the Wright brothers settled for some time in Pau, confirmed advance and established the first flying school in Pau.



http://pauwright.free.fr/

Pau is also closely associated with aeronautic developments. In 1938, a polish engineer, Joseph Szydlowski, moves his emerging industry building compressors in the close vicinity of Pau (Bordes). Years later, they developed some of the first gas turbines promoting the development of helicopters. . At present, Turbomeca is a flourishing industry of more than 6 000 employees and equips more than 50 % of turbines of helicopters worldwide.

B. Parmentier, aviafrance.com

Pau has also seen the development of the French oil industry, some 40 years ago with the gas field of Lacq. Advanced technology was developed at this time to extract and purify the gas. These major developments have given rise the development of the French oil industry now represented by Total. Pau now hosts the Total major research and development center with more than 2 500 engineers and technicians working on a worldwide basis.

http://www.abban.fr/

Welcome to Pau, a land of innovation.

Dr. Olivier F.X. Donard
Chairman of the Conference

2 General Information

CONFERENCE VENUE

Themeeting will be held in the Palais Beaumont which is the Palais des Congrès of the City of Pau.It is located in the center of Pau within walking distance to the town center and conveniently located close to major hotels:

Le Palais Beaumont
Centre de Congrès Historique
Office de Tourisme et des Congrès
Parc Beaumont - 64000 Pau - France
Tél.: +33 (0)5 59 11 20 00 - Fax : +33 (0)5 59 11 20 01

REGISTRATION

The Registration Desk is located in the Conference Secretariat on the ground floor. All participants are kindly requested to go to the Conference Secretariat upon arrival, to receive the conference material and check their payments.

NAME BADGES

All registered participants receive a name badge together with their registration documents. Please make sure to wear your badge at all times while attending the meeting, exhibition and social events.

LANGUAGE

The official language will be English. All Abstracts, Posters and Oral Presentations have to be prepared in English. There will be no simultaneous translation.

INTERNET ACCESS

Unlimited and free of charge wireless LAN access is available.

CLOAKROOM

A cloakroom is located next to the Conference Secretariat where coats can be deposited during the congress center's opening hours.

INVITED LECTURES AND ORAL PRESENTATIONS

Invited Lecturers are allocated up to 25 minutes time, with 5 additional minutes for discussion. Oral presentations must be a maximum of 15 minutes long, followed by 5 minutes for questions and discussion. Time limits will be strictly enforced to avoid program delays.

All rooms are equipped with data projector and a PC for Microsoft Power Point presentations. Microsoft Power Point will be available for presentations exclusively (formats compatible with 2003 version are recommended). Presenters should provide their presentations on a USB drive or CD/DVD to the organizers the day before to their sessions and check their presentation well in advance. Presentations will always be removed from PCs at the end of the corresponding session. Presentations on own laptops are not allowed. If the presentations contain video sequences, presenters should pack them with a standard codec and not store them in QuickTime format, since this may not be compatible with Power Point presentations

POSTER INSTALLATION AND POSTER VIEWING

The Poster exhibition takes place at the ground floor Hall. Six Poster Sessions have been scheduled throughout the Conference during coffee breaks. Posters have to be placed before 10:00 AM on the first day and removed after 17:00 PM on the second one; otherwise, they will be removed and disposed off by the organizers. Materials will be available onsite for mounting posters. Authors are requested to be present next to their posters during the poster sessions for discussion.

The poster size is A0 (portrait format, 119 cm high x 84 cm wide).

Publication of the contribution

Novel research work can be presented in the 2 following journals. They will undergo the normal reviewing process. Information for the manuscript can be found on the following WebPages.

The deadline for submission is the end of June 2011:

- International Journal of Environmental Analytical Chemistry

  http://www.tandf.co.uk/journals/titles/03067319.html

- Environmental Chemistry

  http://www.publish.csiro.au/nid/188/aid/2351.htm

3 Committee

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5 Scientific Program

Wednesday, May 18

8:30 **REGISTRATION**

9:00 **OPENING CEREMONY**

SESSION 1 SPECIATION, LABILITY, BIOAVAILABILITY AND TRANSFORMATIONS

CHAIR: DAVID AMOUROUX

Invited Lectures

9:15 **IL-001. *Metal speciation and bioavailability to periphyton in natural waters.***
Laura Sigg (Dübendorf, Switzerland)

Oral Contributions

9:45 OC-001. *Speciation of nickel in a sandy aquifer.*
Erwin J.M. Temminghoff (Wageningen University, NL)

OC-002. *Determination of labile copper in environmental solutions by using two different techniques, electrochemistry and DGT.*
Sandrine Mongin (Lleida, Spain)

OC-003. *Uranium distribution in crayfish Procambarus clarkii- Approach of its speciation in digestive gland and gills.*
Sandrine Frelon (St Paul Lez Durance, France)

10:45 **Poster session - coffee break - vendors exhibition**

Invited Lecture

11:15 **IL-002 *Biomethylation of metal(loid)s in methanoarchaea: A novel multi-metal(loid) methylation mechanism directly coupled to methanogenesis.***
Roland A. Diaz-Bone (Essen, Germany)

Oral Contributions

11:45 OC-004.*Microbial biotransformations of tributyltin and mercury: the interest of the use of stable isotope tracers.*
Romain Bridou (Pau, France)

OC-005.*Bio-accessibility of arsenic species and of toxic and non-toxic elements in seafood by combination of a simple continuous on-line leaching method and inductively coupled plasma mass spectrometry.*
Axelle Leufroy (Maisons-Alfort, France)

OC-006. *Characterization of Cu-, Mn-, Zn- and Fe-glycinates and development of an analytical methodology for their determination in premixtures.*
Véronique Vacchina (Pau, France)

12:45 **Lunch – poster session**

SESSION 2 DIRECT AND IN-SITU SPECIATION ANALYSIS

CHAIR: RICHARD ORTEGA

Invited Lecture

14:30 **IL-003. *Physical techniques based on X-rays and electrons to study the speciation of trace metal(loids) in biological and environmental samples.***
Geraldine Sarret (Grenoble, France)

Oral Contributions

15:00 OC-007. *The ID21 beamline at the European Synchrotron Radiation Facility: an ideal tool for sub-micrometric 2D speciation analyses.*
H. Castillo-Michel (Grenoble, France)

OC-008. *Titration, EXAFS and Molecular Dynamics Modeling Study of Cu(II) Ions Sorbed on the Model Biopolymer Xanthan.*
L. Spadini (Grenoble, France)

OC-009. *Direct arsenic speciation in SPION loaded cellulose sponge by XAS.*
Manuel Valiente (Barcelona, Spain)

16:00 **Poster session - coffee break - vendors exhibition**

Invited Lecture

16:30 **IL-004. *Dynamic trace metal speciation using Scanned Stripping Chronopotentiometry.***
José Paulo Pinheiro (Faro, Portugal)

Oral Contributions

17:00 OC-010. *In situ determination of free trace metals and labile complexes in Pyrenees rivers by using screen-printed electrodes.*
Corinne Parat (Pau, France)

OC-011. *Metal speciation dynamics in soft ligand thin-films probed by dielectric relaxation spectroscopy: a theoretical analysis.*
Jenny Merlin (Vandoeuvre-lès-Nancy, France)

17:40 **Round Table : « Is it worthwhile to perform speciation analysis ? »**

Thursday, May 19

SESSION 3 *SPECIATION OF METAL SPECIES IN COLLOIDAL AND NANO-MATERIALS*

CHAIR: JOANNA SZPUNAR

Invited Lectures

8:30 **IL-005. *Reactivity of engineered and natural nanomaterials: status of the metals in and on the nanoparticles.***
Armand Masion (Aix en Provence, France)

Oral Contributions

9:00 OC-012. *Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by ICP-MS.*
E. Bolea (Zaragoza, Spain)

OC-013. S*tudy of natural colloids as environmental nanovectors of toxic elements in contaminated soils by asymmetric flow field-flow fractionation (AsFlFFF) coupled to ICP-MS and x-ray absortion spectroscopy.*
M.A. Gómez-González (Zaragoza, Spain)

OC-014. *Size characterization and quantification of silver nanoparticles by asymmetric flow field-flow fractionation (AsFlFFF) coupled to ICP-MS.*
J. Jiménez-Lamana (Zaragoza, Spain)

OC-015. *Metal association with the colloidal fraction in highway stormwater analyzed with Field-Flow Fractionation coupled to Inductively Coupled Plasma Mass Spectrometry (FFF-ICPMS).*
Kajsa Baumann (Gothenburg, Sweden)

10:20 **Poster session - coffee break - vendors exhibition**

SESSION 3 *METAL SPECIATION IN THE ENVIRONMENT AND LEGAL ASPECTS*

CHAIR: JOSE BROEKAERT

Invited Lecture

10:50 **IL-006. *The use of models to understand the speciation of actinides.***
Pierre Vitorge (Evry, France)

Oral Contributions

11:20 OC-016. *Geogenic Se speciation and distribution in French soils : influence of organic matter content and land use.*
Julie Tolu (Pau, France)

OC-017. *Local coordination and speciation of arsenic in the root-soil interface of the desert plant Prosopis juliflora.*
H. Castillo-Michel (Grenoble, France)

OC-018. *Speciation and analysis of bioavailability of* ^{90}*Sr,* ^{210}*Pb,* ^{210}*Po and Ra isotopes in marine macroalgae from the Bulgarian Black Sea zone.*
Zornitza Tosheva (Luxembourg)

12:20 **Lunch – poster session**

Oral Contributions

14:20 OC-019. *Verification of the success of restrictions for tributyltin by retrospective monitoring of archived biological samples from North Sea and Baltic Sea by SID-GC/ICP-MS.*
Burkhard Knopf (Schmallenberg, Germany)

OC-020. *Mercury species in Austrian fish samples.*
Birgit Vallant (Vienna, Austria)

OC-021. *Arsenic speciation in freshwater plankton*.
Guilhem Caumette (Kingston, Canada)

OC-022. *Cu and Zn speciation in the Zenne River, Belgium.*
A. Magnier (Brussels, Belgium)

15:40 **Poster session - coffee break - vendors exhibition**

Oral Contributions

16:10 OC-023. *Reaching European regulatory levels of priority PBDEs in water samples: Isotope dilution GCMS using 81Br-labelled standard.*
Jose Ignacio Garcia Alonso (Oviedo, Spain)

OC-024. *Physico-chemical and Metal Speciation analysis of vegetable field soils and its Correlation studies.*
Uzaira Rafique (Pakistan)

OC-025. *Application of kinetic catalytic method for the determination and speciation of selenium in environmental water.*
Surendra Prasad (Fidji)

17:10 **Vendors exhibition**

20:00 **Gala Dinner**

Friday, May 20

SESSION 5 *SPECIATION IN INDUSTRIAL APPLICATIONS*

CHAIR: MICHAEL SPERLING

Invited Lectures

9:00	**IL-007 *Challenges in commercial environmental and industrial applications of speciation analysis.*** Hakan Gurleyuk (Bothell, USA)

Oral Contributions

9:30	OC-026. *A closed cycle for removing and recovering selectively chromium, copper, nickel and zinc from real electroplating effluents.* Manuela D. Machado (Porto, Portugal)
	OC-027. *Arsenic bioaccumulation and speciation in different plants species from two highly polluted mining areas.* Raquel Larios (Madrid, Spain)
	OC-028. *Mercury characterization in contaminated soil and tailings using sequential extraction and thermal desorption.* Pavel Coufalik (Jihlava, Czech Republic)
10:30	**Poster session - coffee break - vendors exhibition**

Oral Contributions

11:00	OC-029.*Speciation of Gd-Based MRI Contrast Agents in Wastewater Treatment Plants*. Michael Sperling (Münster, Germany)
	OC-030. *Metal speciations in environmental and clinical applications.* Kelvin Sze-Yin Leung (Hong Kong, China)
	OC-031. *New analytical approach for silicon speciation in petroleum products.* Fabien Chainet (Solaize, France)
12:00	**Lunch – poster session**

SESSION 6 *New analytical strategies for metal speciation including isotopic information*

CHAIR: JOSE IGNACIO GARCIA ALONSO

Invited Lecture

14:00 **IL-008. *The use of enriched stable isotopes to study the species-specific environmental reactivity of metals.***
Pablo Rodriguez (Oviedo, Spain)

Oral Contributions

14:30 OC-032. *Species-specific isotope ratio of mercury in biological tissues.*
Vladimir N. Epov (Pau, France)

OC-033. *Lead speciation and isotopic composition as an indicator of anthrogenic contamination: comparison of buried and modern soils.*
Tatiana Pampura (Russian Federation)

OC-034. *A metrological approach for the assessment of selenium status in humans.*
Petru Jitaru (Paris, France)

OC-035. *Detection and characterization of Se-binding proteins in wheat by gel electrophoresis and laser ablation-inductively coupled plasma-mass spectrometry*
Espen Govasmark (Aas, Norway)

OC-036. *Analysis of Selenoneine, Se-methylselenoneine and their sulfur analogs in human urine and blood samples by parallel coupling of bidimensional liquid chromatography with ICP-MS and ESI-LTD Orbitrap MS detection.*
Laurent Ouerdane (Pau, France)

Saturday, May 21

9:00 - 13:00 **Short course: Free Registration**
Trace metal speciation for food, industry and environmental applications.
Olivier Donard (Pau, France)
Visit of the laboratory

6. Abstracts
6.1 Invited Lectures

1°- Speciation, lability, bioavailability and transformations

IL - 001

Metal speciation and bioavailability to periphyton in natural waters

Laura Sigg, Philippe Bradac, Renata Behra

Eawag, Swiss Federal Institute of Aquatic Science and Technology, P.O. Box 611, CH-8600 Dübendorf, Switzerland

Metal speciation is a key parameter for the bioavailability of trace metals to algae under freshwater conditions. Laboratory experiments and theoretical derivations have demonstrated that either the free metal ion concentrations or under certain conditions the labile metal species determine the uptake of metals by freshwater algae. Periphyton, the algal biofilm growing on solid substrates in natural waters, is of high ecological interest and may be influenced by the natural polymer matrix with respect to metal uptake.

Our studies aim at investigating cadmium, copper and zinc accumulation in periphyton under natural freshwater conditions, as related to measured speciation parameters. DGT (diffusion gradients in thin films) has been selected as a convenient method, by which the labile metal concentration in natural waters may be measured as a time average over hours to days. Labile metal concentrations obtained by DGT were compared to modelled speciation on the basis of characterization of natural organic matter by size exclusion chromatography / organic carbon detection. Accumulation of metals in periphyton (algal community growing on solid substrate in natural waters) was determined either in microcosms with varying speciation conditions, or under field conditions by making use of the concentration variations in streams during rain events (1,2). Intracellular cadmium in periphyton was related to DGT-labile Cd under conditions where speciation was varied by adding NTA (nitrilotriacetate) to natural waters. In a similar way, copper accumulation in periphyton was related to labile Cu, whereas zinc accumulation was best related to free ion concentrations (3). Under field conditions, Cd concentrations in stream water were elevated during rain events, probably due to increased inputs from sewage treatment effluents and from sediments. Cd content in periphyton closely followed the Cd concentration variations in water. Labile metal concentration may be determining metal uptake by periphyton if diffusion of metals through the embedding matrix is the rate-limiting step.

1. Bradac, P.; Behra, R.; Sigg, L., Accumulation of cadmium in periphyton under various freshwater speciation conditions *Environ. Sci Technol.* 2009, 43, 7291-7296.
2. Bradac, P.; Wagner, B.; Kistler, D.; Traber, J.; Behra, R.; Sigg, L., Cadmium speciation and accumulation in periphyton in a small stream with dynamic concentration variations. *Environ. Poll.* 2010, 158, 641-648.
3. Meylan, S.; Behra, R.; Sigg, L., Influence of metal speciation in natural freshwater on bioaccumulation of copper and zinc in periphyton: a microcosm study. *Environ. Sci. Technol.* 2004, 38, 3104-3111.

1°- Speciation, lability, bioavailability and transformations IL - 002

Biomethylation of metal(loid)s in methanoarchaea: A novel multi-metal(loid) methylation mechanism directly coupled to methanogenesis

Dr. Roland A. Diaz-Bone

Instrumental Analytical Chemistry and Microbiology I, University of Duisburg-Essen, Universitätstr. 3-5, 45141 Essen

Biomethylation of Group 15 and 16 metals and metalloids by microorganisms are widespread phenomena in anaerobic habitats including sewage sludge, soils and, as recently shown, the gut of mice and man. The fundamental mechanisms of biomethylation are under intensive research, as both bioavailability and toxicity of metal(loid)s are strongly modulated upon methylation. However, biochemical details are only available for arsenic, which is methylated by S-adenosylmethionine (SAM) dependent methyltransferases expressed in response to elevated arsenic concentrations. For identification of alternative metal(loid) methylation mechanisms, we focused on *Methanoarchaea*, since, in contrast to other physiological groups, the capability to volatilize a broad spectrum of metal(loid)s (As, Sb, Bi, Te and Se) was observed for almost all methanogens studied.

Here, we studied the methyltransferase MtaA from *Methanosarcina mazei*, which catalyses the methyl group transfer from methylcobalamin to coenzyme M in the course of methylotrophic methanogenesis. We demonstrate that the same metal(loid)s (As, Se, Sb, Bi, Te), which are methylated by *Methanosarcina mazei in vivo*, are also methylated by *in vitro* assays with purified recombinant MtaA, thereby revealing the first mechanism capable of multielement methylation of metal(loid)s. In the presence of methyl transferase MtaA, a 100 to 10000 fold acceleration of the methylation reactions was observed. In addition to methylation, formation of hydride As, Se and Sb species was observed.

For mechanistic investigation of the methyl transfer from methylcobalamin to the metal(loid), a range of methods was applied. Demethylation of methylcobalamin was followed by use of UV-VIS spectroscopy. Formation of volatile and non-volatile species was analyzed by GC-ICP-MS with additional identification of unknown compounds by GC-EI-MS/ICP-MS. For investigation of carbon isotope fractionation during methyl transfer to the metal(loid)s, a newly developed method based on GC-IRMS (isotope ratio mass spectrometry) was used.

With this methodology, we studied the role of MtaA and methanogenic cofactors in the methyl transfer from methylcobalamin to metal(loid)s. Possible methylation mechanisms *in vitro* and in methanogenic archaea *in vivo* are discussed. These results provide interesting insights towards the cause for the remarkable capability of methanogens to methylate a broad range of metal(loid)s.

2° - Direct and in-situ speciation analysis IL –003

Physical techniques based on X-rays and electrons to study the speciation of trace metal(loids) in biological and environmental samples

Géraldine Sarret[1], Beate Bersch[2], Gaëlle Uzu[3], Sophie Sobanska[4], Camille Dumat[3], Marie Pierre Isaure[5], Pierre Saumitou-Laprade[6], and Jacques Covès[2]

[1] ISTerre, UMR 5275, Université J. Fourier & CNRS, BP. 53, 38041 Grenoble Cedex 9, France

[2] Institut de Biologie Structurale-Jean-Pierre Ebel, UMR 5075 CNRS-CEA-UJF, 41, rue Jules Horowitz, 38027 Grenoble Cedex, France

[3] UMR 5245 CNRS-INP-UPS; EcoLab (Laboratoire d'écologie fonctionnelle); 31326 Castanet-Tolosan

[4] LASIR UMR 8516, Université Lille 1, Bâtiment C5, 59655 Villeneuve d'Ascq Cedex, France

[5] IPREM, UMR 5254/LCABIE), Université de Pau et des Pays de l'Adour, Hélioparc, 64053 PAU Cedex 9 France

[6] Génétique et Evolution des Populations Végétales, UMR 8016, CNRS, Univ. Lille 1, F-59655 Villeneuve d'Ascq, France

Determining the speciation of trace elements is essential to evaluate their toxicity, obtain insights on their biogeochemical cycle in the environment and better understand the mechanisms developed by living organisms to cope with metal toxicity. Physical techniques using X-rays and electron beams are non destructive and allow a direct determination of metals speciation in any type of sample, inorganic or biological. Examples of studies on plants and microorganisms will be presented.

The speciation and localization of zinc in a Zn hyperaccumulating model plant, *Arabidopsis halleri* and the progenies obtained from an interspecific cross presenting contrasted Zn accumulation capacities were studied by extended X-ray absorption fine structure (EXAFS) spectroscopy and micro X-ray fluorescence (µXRF). Results obtained were consistent with an enhanced xylem unloading and vacuolar sequestration in the leaves in the stronger accumulators.

The foliar transfer of Pb-rich particles in leafy vegetables (lettuce) was studied. Plants were exposed to the atmospheric fallouts of a smelter recycling lead batteries. The speciation of Pb in the original particles was determined by X-ray diffraction and raman spectrometry. The observation of the leaves by µXRF, SEM-EDX and Raman microspectrometry showed that particles were present on the leaf surface, in the stomatal openings and beneath the leaf tissue, and evidenced secondary species. Based on these observations, several routes for the foliar uptake of contaminants were proposed.

Cupriavidus metallidurans CH34 is a microorganism adapted to metal-contaminated media. It is resistant to a variety of metals and metalloids. The fate of selenite and selenate accumulated by the bacteria was studied by EXAFS spectroscopy and analytical chemistry. The metallic center of several proteins involved in the resistance to metals (Cu, Zn, Co) was studied by XRD and spectroscopic techniques. Conformational changes due to the fixation of metals were observed. Such type of information may help to infer possible roles for these proteins whose exact function is still not known.

2° - Direct and in-situ speciation analysis **IL –004**

Dynamic Trace Metal Speciation using Scanned Stripping Chronopotentiomentry

José Paulo Pinheiro

Faculty of Science and Technology, University of Algarve, Faro (Portugal)

A comprehensive knowledge of metal speciation in natural systems is a requisite for understanding the relationships between the different physicochemical forms of the metals and their reactivity, mobility, and bioavailability[1].

It is generally assumed that complex formation reactions in aqueous solutions follow the Eigen mechanism, consisting on the rapid formation of an outer-sphere complex between the hydrated metal ion and the ligand, followed by a slow, rate-limiting dehydration step. Of late, several publications addressed important aspects that were previously neglected, like the reaction/diffusion control in colloidal dispersions[2], and the influence of charge distribution in the complexation[3].

The development of Scanned Stripping Chronopotentiometry (SSCP) for which a known rigorous equation is available for the full wave in the kinetic current regime, provided a tool to experimentally access the dynamic parameters[4]. These are contained in the characteristic parameters of the SSCP wave, i.e., the limiting wave height, τ^*, and the half-wave deposition potential, $\Delta E_{\mathrm{d},1/2}$.

In this presentation the theoretical background for dynamic trace metal speciation in colloidal systems will be detailed followed by the relevant theoretical and experimental aspects of performing and analysing SSCP experiments and finally some examples of applications in model systems will be presented.

1. H.P. van Leeuwen, *Env. Sci. Technol*., 33 (1999) 3743.
2. J.P. Pinheiro, M. Minor, H.P. van Leeuwen, *Langmuir*, 21 (2005) 8635.
3. H.P. van Leeuwen, J. Buffle, *Env. Sci. Technol,* 43 (2009) 7175.
4. J.P. Pinheiro; H.P. van Leeuwen; *J. Electroanal. Chem*. 570 (2004) 69.

3° - Speciation of metal species in colloidal and nano-materials IL –005

Reactivity of engineered and natural nanomaterials: status of the metals in and on the nanoparticles

Armand Masion

CEREGE, UMR6635 CNRS-UPCAM, Europole de l'Arbois,Aix-en-Provence, France

Nanoparticles and nanomaterials have become a part of our everyday life; they are present in over 1000 consumer products and are also found in natural environments. Their sometimes unique properties derive from a surface structure that is different from larger scale phases. To design new materials for specific applications, it is necessary to characterize as precisely as possible these materials, their formation mechanism(s) and their reactivity. This can be achieved by determining the speciation of the nanomaterials but also of the molecules they react with. This will be illustrated be examples showing how nanosized metal oxides can lead to enhanced pollutant removal, and how inorganic nanotubes may stabilize heavy metals.

4° - Metal speciation in the environment and legal aspects IL –006

The Use of Models to Understand the Speciation of Actinoids.

Pierre Vitorge

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The speciations of actinoids and several radionuclides at trace concentration levels in deep groundwaters are studied for the management of radioactive wastes. Modelling of such chemical systems in equilibrium conditions is based on thermodynamics, and on corresponding thermochemical data bases. Such a scientific approach is well established, and accepted. It can be extended to more concentrated solutions (activity coefficients), to solid solutions (co-precipitation) and to surfaces (sorption, ionic exchange, surface complexation), some key phenomena of the migration of pollutants in natural waters, while the scientific bases of their modelling are not so well established or accepted: thermodynamic aspects of their modelling will be addressed, together with the limits of thermodynamic modelling.

The numerical values of equilibrium constants and other corresponding thermodynamic data reflect chemical reactivity. This will be discussed for f-block elements -lanthanoids and actinoids- attempting to use molecular modelling to qualitatively understand, or simulate their chemical behaviours. f-block elements usually form hard cations, their hardness indeed often account for the stabilities of their complexes. Hardness explains the success of simulations based on classical molecular dynamics. Nevertheless, actinoids in high oxidation states can as well form covalent ions, which needs quantum level of modelling. Quantum modelling indeed recently explained the exceptional chemical behaviour of Pa, the actinoid element between Th and U.

Finally chemical behaviours of actinoids will be illustrated with Pourbaix diagrams for equilibrium conditions as typically in deep groundwaters, while differences with non-equilibrium conditions (surface or near-surface conditions, accidental releases...) will be outlined.

5° - Speciation in industrial applications

IL –007

Challenges in environmental and industrial applications of speciation analysis

Hakan Gürleyük

Elemental speciation analysis using hyphenated methods such as GC/LC /IC-ICP-MS have become extremely popular during the last decade. While hundreds of papers are being published related to speciation analysis every year, the main focus seems to be either development of new methods and identification of new species in various matrices. In the US, lack of legislation causes speciation analysis to be regarded mostly as an academic tool. With the exception of methylmercury analysis, there are very few commercial labs that provide routine speciation analysis as a service in the US. With the increased regulatory influence, commercialization of speciation analysis is inevitable. Unfortunately, commercialization of this powerful technology without a good understanding of data quality (both by the analysts and the end user of the data) can cause wrong and costly decisions if these decisions are based on compromised data. While arsenic speciation analysis in a bottled water sample can be very simple, various problems can surface as the sample matrix gets complicated. Therefore, appropriate quality control measures should be implemented to identify and/or solve issues related to the sample matrix. This presentation will focus on the challenges in providing routine speciation analysis in a variety of matrices with tight deadlines and budgets.

6° - New analytical strategies for metal speciation including isotopic information IL –008

THE USE OF ENRICHED STABLE ISOTOPES TO STUDY THE SPECIES-SPECIFIC ENVIRONMENTAL REACTIVITY OF METALS

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The environmental reactivity of metals is extremely dependent on their chemical form. The use of enriched stable isotope tracers offers a great potential to study the species-specific environmental reactivity of metals. First, they can be used as efficient analytical internal standards to correct not only for incomplete recoveries but also for undesired degradation reactions of the endogenous species during the analysis of environmental samples. In this way, it is possible to obtain accurate, precise and reliable data even at background contamination levels. Secondly, isotopically enriched metal species can be added to closed environmental systems to study species-specific reaction pathways. Field incubations of a sample spiked with several isotopically enriched species may provide reliable estimations of specific degradation rates and half-lives of elemental species under different environmental conditions. All these approaches require the implementation of complementary mathematical approaches capable of discriminating or deconvoluting species-specific information from a mixture of endogenous or exogenous compounds when opposite and simultaneous reactions occurr.

Different applications on the use of enriched stable isotopes of Hg and Sn will be presented. Field incubations of seawater and surface sediment samples from different aquatic environments will be employed to evaluate the main factors affecting the persistence and degradation of contaminants such as tributyltin (TBT) and monomethyl mercury (MMHg). Also the potential of isotope dilution approaches will be demonstrated with the study of the influence of tidal cycles on the biogeochemistry and partition of the organometallic pollutants (TBT and MMHg) at sub ng/L levels. It will be also demonstrated that the capabilities of different bacterial strains to degrade Sn and Hg compounds can be studied by means of enriched isotope tracers. Finally, the study of the species-specific isotope fractionation of the elements will be addressed as a powerful tool to track and understand its cycle and pathways in the environment.

6.2 Oral Contributions

1°- Speciation, lability, bioavailability and transformations

OC - 001

Speciation of nickel in a sandy aquifer

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Mining activities and industries have created nickel (Ni) contaminations in many parts of the world and can lead to serious ground and surface water contamination. The objective of this study is to increase our understanding of Ni adsorption and Nickel-Aluminum Layered Double Hydroxide (Ni-Al LDH) precipitation to reduce risks of distribution. A coarse grained sandy soil aquifer with a low iron and aluminum (hydr)oxide content and low adsorption capacity was used. At relatively low Ni concentrations (<0.5 mg/l) Ni adsorption could be predicted well using a multi-surface adsorption model. However, at higher Ni concentrations and pH ? 7.2 also Ni-Al LDH precipitation occurred. The solubility product of Ni-Al LDH was determined experimentally and included in the geochemical model. Results will be shown and discussed. Ni concentrations in batches with a low Ni content (< 100 mg/kg) were in good agreement with the predicted equilibrium concentrations, whereas at higher Ni content Ni-Al LDH precipitation was still rate limited after 56 days. The slow reaction rates are due to a decrease in Al availability over time since already up to 70% of oxalate-extractable Al was taken up in LDH formation. In a long term column experiment we observed that 99% of influent Ni was retained in the soil column at pH 7.5 due to Ni adsorption (? 34 %) and Ni-Al LDH precipitation (? 66 %)., From this retained Ni only a part was leached out at lower pH. Based on reactive transport model calculations we will show that this leaching is largely attributed to desorption.

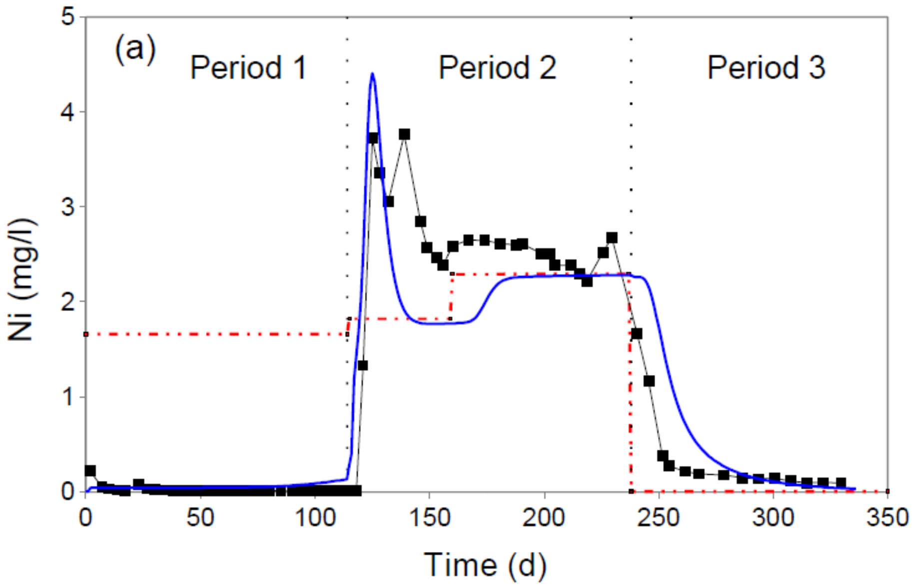

Figure: Experimental and modeling results of the column experiment; Ni influent concentration (– – –); Data Ni effluent concentration (?); Model prediction of Ni effluent concentration (???). Period 1 pH ? 7.2; period 2 and 3 pH ? 6.3.

OC - 002

Determination of labile copper in environmental solutions by using two different techniques, electrochemistry and DGT

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Copper under Bordeaux mixture is permitted in organic farming as a fungicide and since the end of the 19th century, it is used in Europe to treat downy mildew in vineyard. These treatments induce an accumulation of copper in treated soils and consequently a contamination risk of the rivers draining cultivated areas (1).

Measurements of total copper concentrations provide little insight to the potential ecotoxicological impact. Knowledge of dynamic factors is fundamental for establishing a rigorous quantitative basis for the relationship between metal ion speciation and bioavailability. Different dynamic analytical techniques have been compared in natural freshwater (2). Among theses techniques, two have been considered in this study:

- Stripping chronopotentiometry (SCP) with a Hg-film screen printed electrode (SPE) as a working electrode
- Diffusive Gradient in Thin film (DGT) allowing to reach bioavailable copper; study reported that the bioaccumulation is controlled by weakly complexed copper, measured by DGT (3).

The determination of labile copper by these different techniques is made in the same sample. First, the calibration of both techniques has been carried out in copper solution without any ligands. Then, response is tested in presence of synthetic ligand, in controlled medium. Finally, labile copper concentrations were measured by both techniques in soil solution and the results were compared.

First estimations of copper lability were made in presence of different concentrations of NTA. The results show that electrochemical approach allowed the determination of free and very weakly complexed copper, whereas DGT sensors access to measurement of more stable complexes. This preliminary study highlights the complementarity of the both techniques.

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OC - 003

Uranium biodistribution in crayfish *Procambarus clarkii* – Approach of its speciation in digestive gland and gills

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In aquatic media, relevant information concerning the impact of uranium on biota is scarce. Even though uranium speciation in water column is quite well studied, its speciation within aquatic organisms is poorly described despite a wide coordination chemistry. Besides, recent reports on the topic emphasize the need of studying uranium speciation at the organ and sub-cellular levels in order to better explain uranium bioavailability (direct and trophic transfer), accumulation and toxicity.

Within this problematic, the aim of this study was to better understand the link between distribution of the metal inside the cell and molecular responses (such as evaluation of specific gene expression levels) after acute waterborne exposure. The challenges and the analytical strategy used to understand the fate of uranium within two different organs of crayfish will be described. U biodistribution will be presented and faced to gene expression levels obtained in the same organs.

Groups of crayfish were exposed to 0 (controls), 0.03, 0.6 and 4 mg/L of U for 4 and 10 days. The subcellular distribution of uranium was performed in the gills and the digestive glands of crayfish by ultracentrifugation and uranium ICP-MS measurement. Expression levels of genes involved in mitochondrial metabolism *(cox1, atp6*) were studied in the same organs using real-time RT-PCR. Moreover, the expression level of the mitochondrial gene *12S* was evaluated and used as an indicator of the amount of mitochondria in cells.

Data suggest that (i) the percentage of uranium recovered in the mitochondrial fraction (versus total amount in each organ) is increasing with concentration of exposure and (ii) the level of mitochondrial gene expression is altered in presence of U in the studied organs. Histological damages were also observed in the hepatopancreas. Further investigations on uranium distribution pattern on biomolecules will be performed by HPLC-SEC and ICP-MS measurement to determine more accurately if uranium has specific targets in this specific mitochondrial fraction and better understand the link between exposure, speciation and biological effects.

OC - 004

Microbial biotransformations of tributyltin and mercury: the interest of the use of stable isotope tracers

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Tributyltin (TBT) and mercury (Hg) as well as their organic derivatives are ubiquitous and persistent metallic micro-pollutants present at trace level in aquatic ecosystems. The microbiological alkylation and dealkylation processes of the more toxic organic forms of tin and mercury (tributyltin, methyltin and methylmercury) under oxic and anoxic conditions are still poorly understood. The use of Hg and tin species specific stable isotope tracers methodology coupled to the sensitive GC-ICP-MS detection allowed the systematic study of these co-occurring phenomena. We report the potential of TBT biodegradation and inorganic tin methylation, e.g. Sn(IV), for pure strains of microorganisms isolated from simplified bacterial communities contaminated by TBT as well as for various microorganisms growing under aerobic and anaerobic conditions. These data allowed defining some alkylation and dealkylation pathways for which the environmental implication of microorganisms was solely suspected. Mercury methylation and demethylation capacities of sulphate-reducing prokaryotes - suspected to be the main methylmercury producers in the aquatic ecosystems - were also investigated. The use of Hg stable isotopic tracers allowed the systematic study of this phenomenon in environmental microorganisms under different physiological conditions (fermentation, nitrate respiration, sulphate respiration and substrate starvation). Potential implication of ubiquitous microorganisms isolated from the environment in the production of methyl mercury was determined and emphasises the need to couple bio-molecular, microbiological and analytical chemistry techniques to unravel the accurate role of microorganisms in tin and mercury biogeochemistry. The study of the molecular determinism of the alkylation and dealkylation of mercury and tin by the microorganisms is now a necessity to better understand the functioning of the co-occurring mechanisms implied in the regulation of net TBT degradation and methylmercury production in aquatic ecosystems.

OC - 005

Bio-accessibility of arsenic species and of toxic and non toxic elements in seafood by combination of a simple continuous on-line leaching method and inductively coupled plasma mass spectrometry

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The bio-availability of an element, ie, its ability to be absorbed in the systemic circulation system, depends on its bio-accessibility, which is defined as its mobilization during digestion in the gastro-intestinal tract.

Several methods exist to evaluate bio-accessibility, but they are generally time-consuming. A quick and simple on-line leaching method was used to assess the maximum bio-accessibility of arsenic species and of several elements in seafood by pumping artificial digestive juice through a column fill with the solid food sample (maintained at 37°C in a thermostated water bath), which is connected to the nebulizer of an inductively coupled plasma mass spectrometry (ICPMS) instrument. This approach allows the continuous detection of the progressive elements as they are released from the food, in contrast to usual batch methods.

In order to check mass balance, the remaining residues from the columns were analyzed for their total content of the studied elements.

The maximum bio-accessibility of arsenic species and of total aluminium, arsenic, cadmium, barium, lead, and vanadium, manganese, copper, zinc, selenium, molybdenum was estimated from certified reference materials (CRMs) and real freeze-dried seafood samples i.e. fish (salmon, saithe and tuna), crustaceans (shrimp), and mollusks (mussel, scallop), the species most consumed by the French population.

The results obtained indicate very different behavior according the element and/or the matrix studied.

OC - 006

Characterization of Cu-, Mn-, Zn- and Fe-glycinates and development of an analytical methodology for their determination in premixtures

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The bioavailability of essential trace elements (Cu, Mn, Zn and Fe) depends on their chemical form. One of the most efficient sources are the complexes of trace elements with glycine (glycinates), specially in regards to sulfates forms. However the trace elements inclusion as feed additive is still based on recommendations related to inorganic forms. This is mainly due to the absence of analytical method allowing the specific determination of glycinates. The objective of this work was therefore to develop a method for the speciation of glycinates ($[M(Gly)_x(H_2O)_y(SO_4)_z]_n$, (with M = Zn, Cu, Mn or Fe)).

In a first step, the stability of the glycinates in solution was verified by electrospray TOF MS. Each glycinate in solution was a mixture of complexes with polymerization degrees ranging from $n = 1$ to $n = 4$ depending on the metal which were fully or partially dehydrated.

A method was then developed for their specific determination. Amongst the different methodologies investigated, the best results were obtained by the coupling of capillary electrophoresis (CE) with ICP MS detection. The metal-glycine complex moiety was found to be preserved during capillary electrophoresis. The detection limits, calculated as 3 times the standard deviation of the blank plus the blank, were between 0.05 – 0.2 $\mu g.mL^{-1}$ (as metal) and the calibration curves were linear over more than one order of magnitude. Repeatability for glycinate standards was below 12% and the analytical precision was typically within 15%.

The coupling CE – ICP MS was finally applied for the determination of glycinates in premixtures of different compositions. A good agreement between the target and measured concentration was obtained showing the suitability of this technique and raising its potential for further studies on the bioavailable form of glycinates.

2° - Direct and in-situ speciation analysis OC - 007

The ID21 beamline at the European Synchrotron Radiation Facility: an ideal tool for sub-micrometric 2D speciation analyses

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The ID21 ESRF is beamline dedicated to X-ray and FTIR micro-spectroscopy. Localization and speciation of trace elements is primarily done using micro-X-ray fluorescence (µXRF) and micro X-ray absorption spectroscopy (µ-XANES) in the tender X-ray domain (now extended to 2-9.2 keV). ID-21 has sensitivity in the low ppm range and allows localization with a sub-micron beam of various elements. The scanning X-ray microscope (SXM) is designed to cover a relatively wide range of elements of interest in environmental science.

The SXM offers a very high versatility in terms of focusing optics, detection and sample environment. The X-ray beam spot size can be tuned from macro (200 µm) to sub-micro (~500 nm), which then allows localization of trace elements at subcellular level. A large panel of complementary detectors is available and provides: high sensitivity, high throughput, or high spectral resolution, which enables the collection of µ-XRF and µ-XANES spectra on a large variety of environmentally relevant samples. The samples can be studied in various conditions (room temperature, cryo, wet cells).

The X-ray scanning microscope is therefore highly appropriate for *in-situ* studies of trace metals and metalloids such as Ti, Cr, Fe, Co, Ni, Cd, Ce, and Cu, and gives simultaneously access to mapping and speciation of lighter elements such as P, S, Ca which can be involved in fixation/elimination mechanisms. Additionaly, ID21 has a SR-based FTIR end-station that can provide complementary molecular mapping, with a ~5µm lateral resolution.

In summary, ID21 offers a multimodal set up of state-of-the-art techniques for micro-spectroscopies in environmental science.

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OC - 008

Titration, EXAFS and Molecular Dynamics Modeling Study of Cu(II) Ions Sorbed on the Model Biopolymer Xanthan

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Xanthan, a carboxylic acid containing non-gelling bacterial exopolysaccharide of known structure produced by *Xanthomonas campestris* strains was investigated with respect to its site density, acid-base reactivity, folding capacity, Cu bond strength and Cu sorption structures. This biopolyer was shown to bind Cu with an unusual bond strenght – pH relationship. Thus, between pH 3 and 5 Cu sorption on Xanthan decreases, which is unusual and contrary to convential observations. Molecular dynamics calculations (Cerius2 software, universal force field) indicate that this behavior relates to structural order, the metal ion bond strenght increases with increasing structural disorder of Xanthane. In the disordered state prevailing at low pH, more inter- and intrachain chelating configurations are formed leading to the thermodynamically observed increase of the Cu(II) bond strenght. Inversely at higher pH, the prevailing ordered states leads to rigid chain configurations and a consequently decreased number of Cu(II) chelating structures. The overall Cu bond strenght compares to that of small model chelates of intermediate bond strenght, and surpasses those of the Xanthan constituting monocarboxylic acids. In this respect, the bond strenght compares to those typically found in other organic compounds, such as bacterial substrates or reactive soil organic matter (humic acids). This work thus suggests that the bond strenght of bivalent cations (for instance copper) in disordered biopolymers (for instance Xanthan) increases compared to that of the constituting functional groups, as the biopolymer structure generates bond-strenght increasing stuctural configurations.

OC - 009

Direct Arsenic speciation in SPION Loaded Cellulose sponge by XAS

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Arsenic biogeochemistry has received public and scientific attention due to environmental and public health disasters around the world. Decontamination process is made in several ways being adsorption process most efficient. In this concern, nanoparticles have been proposed as an appropriate material to increase the arsenic adsorption from contaminated waters. The main objective of the present study is to characterize the different arsenic species after their adsorption on Superparamagnetic Iron Oxide Nanoparticles (SPION) from arsenic solutions containing low concentrations of arsenate, arsenite or related mixtures. This study was performed by XAS (X-Ray Adsorption Spectroscopy) technique using synchrotron radiation for the direct characterization of the arsenic adsorption process and to obtain information to better understanding the capacity of a SPION loaded cellulose sponge to adsorb Arsenic species. This may lead to design SPION potential applications to treat Arsenic contaminated waters. The parallel study of iron speciation in SPION revealed the behaviour of such material on the Arsenic adsorption-desorption process.

XANES analyses were performed at two synchrotron facilities: beamline BM25 (ESRF, Grenoble) for As and beamline A1 (HASYLAB, Hamburg) for Fe. The photon absorption of As was recorded at the edge energy for its K line at 11867eV. The photon absorption of Fe was recorded at the edge energy for its K line at 7112eV. Fluorescent line intensities were measured accordingly.

The effect of arsenic species in the adsorption process was evaluated to ascertain the quantitative contribution of each As species. Results show that arsenate species is predominant, being easily removed from the contaminated water with the SPION adsorbent system. On the other hand, adsorption differences were clearly observed when varying the As solution pH. The analysis of synthetic samples of Arsenic species mixtures has verified the prediction from individual standards.

Acknowledgements

Present study has been carried out with the support of the Spanish Ministerio de Ciencia e Innovación, project CTQ2009-07432 (subprograma PPQ)

OC - 010

In situ determination of free trace metals and labile complexes in Pyrenees rivers by using screen-printed electrodes

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Predicting the bioavailability of trace elements in natural environments, such as a freshwater, needs to consider the labile complexes (as a potentially bioavailable pool). As lability of a complex depends on the time and spatial scales of the sensor used in the measurement, comparison of lability measurements requires a detailed consideration of the processes involved in the different sensors used. When the internalization step is slow enough, the free ion concentration determines the uptake. An analytical challenge is the development of methodologies able to determine *in situ* the free metal ion concentration and the metal availability in natural waters at different time scales.

Two techniques have been implemented with a disposable sensor which can be deployed *in situ* and thus, avoid problems of contamination. The first one, called stripping chronopotentiometry (SCP) allows the determination of labile complexes [1] whereas the second one, called Absence of Gradient and Nernstian Equilibrium Stripping method (AGNES), is specific for the free metal ion concentration determination [2, 3].

First, the effects of environmental conditions like pH or ionic strength and the required parameters for *in situ* analyses have been studied in synthetic solutions of metals (Cd, Pb, Zn). Then, the speciation of well known complexes were studied and compared with Visual MINTEQ results. Finally, SCP and AGNES were carried out *in situ* in a freshwater sample (Spain).

Both methods have been successfully implemented in multicontaminated synthetic solutions without deaerating. The ionic strength appeared as an important parameter to take into account for *in situ* analyses. Investigations are in progress to propose an analytical procedure to consider this parameter in AGNES determinations.

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OC - 011

Metal speciation dynamics in soft ligand thin-films probed by dielectric relaxation spectroscopy: a theoretical analysis

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In natural systems, biotic and abiotic soft ligand particles, *e.g.* bacteria and humic acids, are known to impact on the binding, transport and fate of vital and toxic compounds like heavy metals. The reactivity of such particles with respect to metal ions is intrinsically governed by a coupling between kinetics of complexation within the charged soft ligand part of the particle together with extra- and intra-particular metal transport *e.g.* by diffusion,[1-2] conduction[3] or convection.[4] So far, theoretical and experimental studies have essentially analyse the dynamics of metal complexation in dispersions of soft ligand particles under steady-state conditions only (non-equilibrium chemical regime).[1-4] In this presentation, we argue that dielectric relaxation spectroscopy (DRS) may provide valuable information on metal speciation dynamic features in soft ligand systems over a frequency range that encompasses time windows pertaining to chemical equilibrium, transitory and steady-state regimes. The discussion is based on a theory for the evaluation of the dielectric response of a soft thin ligand film immersed in an electrolyte where metal ions can be complexed by ligand sites distributed within the film. In details, electric double layer polarization is determined from the local concentrations of indifferent ions, metal and complex species, all derived upon solving numerically the Poisson equation in conjunction with Nernst-Planck equations amended for a chemical source term. Variations of the real part of the dielectric permittivity with frequency are then discussed for various local rate constants of complex formation/dissociation within the film, these constants being in line with Eigen mechanism.[5] The magnitudes of these characteristic chemical reaction frequencies as compared to that for metal transport from bulk solution to ligand sites strongly determine the shape of the dielectric response of the ligand system. As such, the DRS provides a direct method for addressing the dynamic properties of metal complexes, *i.e.* apprehending -within a given time window- whether complexation process is mainly limited by chemical kinetics or by combined diffusion and conduction transports.

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3° - Speciation of metal species in colloidal and nano-materials OC - 012

Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by ICP-MS

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Nowadays, the lack of reliable methods to determine Engineered Nanoparticles (ENPs) identity, concentrations and characteristics in complex environmental samples at environmentally relevant concentrations, is one of the largest gaps in environmental nanosciences. Single particle detection using ICP-MS can be considered as one of the challenging analytical approaches necessary to assess the environmental impact of the release of ENPs into the environment.

In single particle detection, when one nanoparticle is introduced into the ICP, the atoms of the analyte produce a flash of gaseous ions in the plasma, which are measured as a single pulse by the detector. The number of counts of this single pulse is related to the quantity of analyte atoms in the nanoparticle, and the frequency of the pulses is proportional to the number concentration of nanoparticles. Adequate time resolutions are required to ensure that each pulse correspond to just one nanoparticle. On the other hand, analyte in dissolved forms will produce pulses of averaged constant intensity.

In the present work the different behaviors presented by both dissolved silver and silver nanoparticles under ICP-MS single particle detection conditions have been used to differentiate directly between both forms of silver. A methodological approach based on single particle detection using ICP-MS for identification, characterization and determination of mass and number concentration of silver nanoparticles in aqueous samples will be presented.

This work has been sponsored by the Project CTQ 2009-14237-CO2-01 of the Spanish Ministry of Science and Innovation.

OC - 013

Study of natural colloids as environmental nanovectors of toxic elements in contaminated soils by asymmetric flow field-flow fractionation (AsFlFFF) coupled to ICP-MS and x-ray absortion spectroscopy

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Colloidal matter present in natural acuatic systems consists of a heterogeneous mixture of polidisperse inorganic and organic components, with sizes between a few nanometers to 1 µm. Colloids mobility and their role as metal nanovectors in natural soil systems are recognized as important phenomena in the pollution processes of the environment. In spite of it, the soil physical and chemical conditions controlling colloid facilitated metal transport should receive further experimental and theoretical attention.

The present work is part of a project devoted to the investigation of the mechanisms that determine the transport, retention and distribution of toxic elements in contaminated soils. These research includes the use of thecniques such as asymmetric flow field-flow fractionation (AsFlFFF) coupled to ICP-MS to characterize the soil colloidal fraction and X-ray absorption spectroscopy for element speciation in colloidal surfaces.

The colloidal fraction is isolated by centrifugation, prior to the separation with AsFlFFF. Size characterization is carried out by calibration of the AsFlFFF with polystyrene and silica standards under the same experimental conditions. As elemental detector, a mass spectometer with ICP ionization source (ICP-MS) is used, which provides information about the compositional chemistry, as a function of particle size of the nanocolloids eluted by AsFlFFF. This system allows the characterization and quantification of the toxic elements under study associated with these colloidal species.

Soil samples were similarly processed and samples of colloidal particles of selected size range were collected onto ultrafiltration membranes for subsequent X-Ray absorption spectroscopy analyses of As in order to perform solid-phase speciation studies. Preliminary results for contaminated soils will be presented.

This work has been sponsored by the Project CTQ 2009-14237-CO2-01 of the Spanish Ministry of Science and Innovation and the Project CGL2010-17434 financed by the Spanish National Research Plan.

OC - 014

Size characterization and quantification of silver nanoparticles by asymmetric flow field-flow fractionation (AsFlFFF) coupled to ICP-MS

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Silver is one of the most used substance in the manufacture of nanomaterials and is involved in a big number of consumer products. The interest of silver nanoparticles lies on its biocide properties, being used in cleaning products, antimicrobial treatments of textile fibers and plastics, containers, air and water filters or materials for medical purpose.

Nowadays, a number of techniques are available for the characterization of these nanoparticles and related nanomaterials (e.g., microscopy or light scattering based techniques), although studies related to their potential toxic effects and their occurrence in the environment require more selective and sensitive analytical methods.

A method for size characterization and quantification of silver nanoparticles in aqueous suspensions by Asymmetric Flow Field-Flow Fractionation (AsFlFFF) coupled to ICP-MS has been developed. The coupling of AsFlFFF with ICP-MS ensures a multielement detection capability of inorganic nanoparticles in accordance to the trace concentrations expected.

Recovery values higher than 90 % were achieved for the silver nanoparticles standards studied. A limit of detection of 5,6 $\mu g \cdot L^{-1}$ of silver, which corresponds to a number concentration of $1 x 10^{12}$ L^{-1} for nanoparticles of 10 nm, was achieved for an injection volume of 20 µL.

The method developed has been applied to the size characterization and quantification of silver nanoparticles present in consumer products. Size characterization by AsFlFFF is compared with those obtain by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS). The results obtained in several consumer products will be presented.

This work has been sponsored by the Project CTQ 2009-14237-CO2-01 of the Spanish Ministry of Science and Innovation.

OC - 015

Metal association with the colloidal fraction in highway stormwater analyzed with Field-Flow Fractionation coupled to Inductively Coupled Plasma Mass Spectrometry (FFF-ICPMS)

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The stormwater runoff from highways contains high level of metal pollutants. The legislation regarding metals in stormwater is weak in many countries and does not consider speciation, partly because the suitable methods and protocols are missing. We have used Field-Flow Fractionation coupled to Inductively Coupled Plasma Mass Spectrometry (FFF-ICPMS) to study how the association of metals to different colloidal size fractions changed across and between two storm events and related the results to factors like vehicles per hour and length of preceding dry period. FFF has many advantages; it is a mild separation method and it continuously separates particles according to their diffusion coefficient without the pre-set discrete size limits used in many other analytical fractionation methods. The retention time can be directly converted to hydrodynamic radius through the FFF theory and the Einstein-Stokes equation. In combination with ICPMS the metal content of different size fractions can be determined. The ICPMS has the advantage of being a multi element detector with detection limits in the ppb rang, well below most regulatory limits. The samples were analyzed under different flow conditions resulting in two size windows of ~5 to 200 nm and ~1 to 40 nm. About 15 of the 23 measured elements gave size fraction peaks detectable over the background. The elements could be divided into four groups according to their particle size distribution and how the distribution varied over the storm event. Some of the elements were present in different groups in the two storm events, while others associated in both events. The general trends over the events were similar. For some elements the co-variations in size distribution are clear which indicates that the elemental signals come from the same particle composition. For example lead, Pb, seems to associates with iron, Fe, for the size.

4° - Metal speciation in the environment and legal aspects **OC - 016**

Geogenic Se speciation and distribution in French soils: influence of organic matter content and land use

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Selenium is an essential element of environmental interest owing to the narrow range between its nutritionally required and toxic concentrations. Its long-lived radioisotope 79Se is found in high level nuclear wastes for which a geological disposal in deep clay formations is considered to be a safe option. Generally, soil Se is considered as the primary Se source for plants. For safety assessment, the radiological and chemical risk associated to Se release into the biosphere must be assessed on a long-time scale. Therefore, native Se mobility, including its distribution and speciation, must be understood. Previously optimized methodology for soil Se speciation in parallel single extractions was applied to 29 soils characterized by an organic matter content ([OM]) gradient. A large [OM] gradient was studied considering culture, grassland and forest soils, with a gradient within each land use type. Statistical approach was used to evaluate the main soil parameters affecting Se speciation and mobility. At short-term (water-soluble and exchangeable Se), Se mobility is similar whatever the land use type is and, is mainly affected by adsorption onto minerals containing Fe and Mn. As expected, NaOH-extracted Se was correlated to soil [OM]. However, NaOH-extracted Se quantity was significantly lower for culture than for forest soils ($P<0.05$), even for equal soil [OM]. Moreover, correlations between organically bound Se and soil parameters indicate different behaviors of this Se fraction for culture and forest soils. For each land use type, water-soluble Se contained Se(IV) and/or Se(VI), whereas in phosphate and NaOH extracts, only Se(IV) was detected. These results reflect the greater tendency of Se(IV) to sorb onto soil components. However, significant amounts of unknown Se species were observed, in particular in water-soluble and organically bound Se fractions, and correlated to soil [OM], which could be indicative of organo-Se molecules and/or complexes.

OC - 017

Local coordination and speciation of arsenic in the root-soil interface of the desert plant *Prosopis juliflora*

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Plants modify the bioavailability of As in the rhizosphere. Biogeochemical processes differ between the bulk and the vegetated soil. Synchrotron X-ray fluorescence (µXRF) and X-ray Absorption µXAS are powerful *in-situ* techniques that allow to create a profile of As speciation and spatial relationships between As and other elements in the rhizosphere. This research investigated As speciation in the rhizosphere of mesquite (*Prosopis juliflora*) plants. The capacity of mesquite plants to accumulate As from soil (50 mg As kg^{-1} soil) has been demonstrated in a previous study [1]. The selected soil for this study was a sandy clay loam treated with As(III) (40 mg As kg^{-1}, introduced as As_2O_3). In the current conditions, arsenic did not inhibit the germination rate of the plants. Rhizosphere soil and freeze dried root tissues of one month old plants were analyzed by bulkXAS to obtain average speciation of As in the soil and roots. Arsenic was found as As(V) in the soil whereas in the roots it was found as As(III). µXAS and µXRF studies from resin embedded soil cores confirmed the presence of As(V) in the soil mainly in the form of iron arsenates. In the roots, results showed As is reduced to As(III) and coordinating to sulfur possibly from low molecular weight thiols. Additionally, 30µm thin root cross sections prepared using a cryotome were also analyzed and the results showed more than 60% of the As in roots is present as an As(III)-S species.

1. Lopez-Moreno et al. 2008. Environmental Chemistry 5:320–331.

OC - 018

Speciation and analysis of bioavailability of ^{90}Sr, ^{210}Pb, ^{210}Po and Ra isotopes in marine macroalgae from the Bulgarian Black Sea zone

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Many substances pollute the marine environment. Some of them represent double risk stressors as toxic and as a radioactivity element. In order to select an aquatic organism as an indicator of water pollution we focused on in five macroalgae species (red *Ceramium rubrum*, brown *Cystoseira crinita* and green *Ulva rigida, Cladophora vagabunda and Enteromorpha intestinalis*) and in mussels *Mytilus galloprovincialis.* The mussel was chosen as one of the most invasive.

Experiments in the field were conducted on collection of citied biota, collected from natural substrates along the Bulgarian Black Sea coastal line.

Levels of radionuclides ^{90}Sr, ^{210}Pb, ^{210}Po and Ra isotopes were determined using classical gamma spectrometry and fast reproducible radiochemical method. Advantage of the second one is the extremely small amount (0.25g) of sample material. Measurements were performed on tree different kind of radiometric equipments and show compatible results. The low grade of concentration and the specificity of studied isotopes make practically impossible the application of standard chromatographic methods.

Comparison of the mean values and range of specific activities / concentrations enable estimation of accumulation capacities of the different marine organism for the investigated species. The comparative results are discussed in connection with natural marine environment.

Radioecological status of aquatic ecosystem along the Bulgarian coastal line is evaluated for one of the macro-algae.

The proposed study is useful for identification of environmental stressors and gives reliable information for isotope migration in the marine environment. Investigations of nuclide concentrations in suitable organisms bio-indicators such marine macroalgae and mussels can be used to predict the potential hazard for the population.

OC - 019

Verification of the success of restrictions for tributyltin by retrospective monitoring of archived biological samples from North Sea and Baltic Sea by SID-GC/ICP-MS

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For several decades tributyltin (TBT) was used extensively as antifouling agent in coatings of ships. Although the high toxicity to aquatic organisms and endocrine effects e.g. on mussels were known since the 1980s, not until 2003 the use of TBT-based antifoulants within the European Union was completely banned. To verify the effectiveness of this measure a retrospective monitoring study was initiated. Appropriate archived samples were retrieved from the German Environmental Specimen Bank (ESB) including standardized homogenate samples of eelpout (*Zoarces viviparus*) and blue mussel (*Mytilus edulis*). Within the ESB representative organisms (bioindicators) are sampled in typical German ecosystems annually since 1985. Specimens are prepared in a standardized manner for cryogenic storage. Thus, a unique environmental archive was established allowing retrospective analysis in order to assess the efficiency of legislation and to monitor the status of our ecosystems. Since an effect- and assessment related biomonitoring based only on the determination of total element concentration can not be sufficient, the implementation of speciation analysis is necessary to supply compound specific information refining the accuracy of the ecotoxicological risk assessment. This is of interest especially for tributyltin (TBT) which can be degraded to dibutyltin (DBT) and monobutyltin (MBT) which are also of ecotoxicological relevance.

The digestion of organic tin compounds in biota is performed by alkaline digestion with tetramethylammoniumhydroxide (TMAH) and subsequently applied microwave radiation followed by derivatization with sodiumtetraethylborate and extraction in hexane. Thereafter separation of the different compounds via GC and detection by sector field ICP-mass spectrometry is performed. Species-specific isotope dilution with enriched isotope standards is applied for quantification. After the EU-wide ban a significant decrease of TBT contamination in mussel and fish could be observed. The results demonstrate the effectiveness of the legal measures undertaken to control TBT inputs into the aquatic environment. Nevertheless, TBT is still a relevant pollutant. TBT water concentrations calculated from the tissue concentrations by using appropriate bioconcentration factors are in the range of the Environmental Quality Standard derived in the context of the Water Framework Directive (0.2 ng/L). Thus adverse effects to marine organisms cannot completely be excluded.

OC - 020

Mercury species in Austrian fish samples

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To generate a basis for an assessment of the occurrence and partitioning of the "priority pollutant" mercury in Austrian biota and to investigate if Austrian fish is safe for human consumption two fish species, European chub and common carp were analysed for mercury and methyl-mercury.

In January 2009, the European directive establishing environmental quality standards (EQS) in the field of water policy (directive 2008/105/EC) entered into force and member states were obliged to adopt national legislation to comply with this directive by 13 July 2010. As mercury is known to bio-accumulate, member states are asked to apply an EQS for biota. For mercury and its compounds the EQS is 20 µg/kg (wet weight) in prey tissue.

With respect to food safety for human consumption, several international organisations have established recommendations or legal limits for mercury or methyl-mercury intakes which are estimated to be safe or without applicable risk to health. As regards mercury, the EFSA adopted on 24 February 2004 an opinion related to mercury and methyl-mercury in food and endorsed the provisional tolerable weekly intake of 1.6 µg/kg body weight. The European community allows 500 µg/kg (wet weight) mercury in fishery products and in muscle meat of fish with some exceptions.

OC - 021

Arsenic speciation in freshwater plankton

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Since the 1930s, gold mines have been operating across Canada (e.g. Yellowknife, NWT, and Seal Harbour, NS). The mining activities resulted in a high arsenic contamination in the aquatic systems surrounding the mines; lakes and rivers in Yellowknife and ocean coast in Seal Harbour. ESG (Environmental Sciences Group, Kingston ON, Canada) has been studying the cycling of arsenic in these contaminated environments for over 15 years (e.g. Bright *et al.*1996, Koch *et al.* 2000, Koch *et al.* 2007, Moriarty *et al.* 2009).

Arsenic is mainly found as a highly toxic inorganic compound in water, while animals contain methylated compounds, with the non-toxic arsenobetaine being the main compound found marine organisms. For health and safety reasons, such as the exposure of local populations, there is still a need to understand the cycling of arsenic through the food, and the pathways of formation of the non-toxic arsenobetaine compound.

The present work studies arsenic speciation at the base of the freshwater food chain, specifically, in plankton. Arsenic speciation in marine plankton showed the presence of arsenosugars in phytoplankton and arsenobetaine as main compound in zooplankton, while information on the freshwater environment is very scarce (Shibata *et al.* 1996, Shimoda *et al.* 2010, Muray *et al.* 2003). In this study, phytoplankton and zooplankton species were collected from contaminated lakes and background lakes of Yellowknife, NWT. Arsenic speciation was measured with HPLC-ICP-MS on water-extracts and X-ray Absorption Spectroscopy (XAS) on the whole solid sample and residues from extraction, in order to access speciation on the non-extractable arsenic.

The results show that unlike marine phytoplankton, freshwater phytoplankton seems to not methylate arsenic. Only inorganic arsenic was found on these samples. However freshwater zooplankton showed the formation of several methylated-compounds, with arsenosugars as the most abundant in all samples, and traces of MMA, DMA and even arsenobetaine in the non-contaminated lakes. The proportions of these compounds in zooplankton organisms varies according to the zooplankton species analysed and the arsenic concentration in the lake.

OC - 022

Cu and Zn speciation in the Zenne River, Belgium

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Speciation of trace metals such as Cu and Zn has been seasonally assessed using HR-ICP-MS and voltammetric techniques (differential pulse anodic and adsorptive cathodic stripping voltammetry) in the Zenne, a river which is strongly impacted by urbanization in the Brussels region (Belgium). Total dissolved concentrations ranged from 0.6nM to 1.3µM for Zn and from 0.49nM to 64nM for Cu between September 2009 and July 2010. The speciation in the dissolved phase was used to estimate trace metal lability while the partition between dissolved and particulate phase was used to estimate distribution coefficients (Kd). Results show that natural metal-complexing organic ligands dominate metal speciation in the Zenne River and regarding the distribution coefficient values, Cu and Zn display similar trends with 2 maxima localized around one of the wastewater treatment plants and in a tributary of the river. Analyzing historical data, a decreasing trend in metal concentration is observed but some maxima are still recorded.

OC - 023

Reaching European regulatory levels of priority PBDEs in water samples: Isotope Dilution GCMS using ^{81}Br-labelled standard

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Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in polymeric materials. As these compounds are incorporated as additives, they can easily release into the environment, being distributed worldwide and found in nearly all environmental compartments. Owing to the adverse effects linked to the exposure to these compounds the EU has issued a Directive (WFD) which includes six of the PBDEs in the list of priority substances that need to be measured in European fresh waters at very low concentration levels (0.5 $pg \cdot g^{-1}$). Therefore, the main objective of this work is the development of a fast, simple and reliable methodology for the determination of the six priority PBDEs in natural water samples in order to meet the requirements of the WFD in terms of sensitivity, precision and accuracy.

River water samples were spiked with a mixture of ^{81}Br-labeled BDEs in methanol. Samples were liquid-liquid extracted with isooctane and organic extracts were preconcentrated under nitrogen. Finally, extracts were injected in a GC(NCI)MS system and concentrations were calculated for each priority congener by the inorganic isotope dilution equation. The GC(NCI)MS system was first evaluated in terms of precision and accuracy for isotope ratio measurements showing appropriate characteristics for its application to IDA. Then, the proposed methodology was validated using a standard reference material (Lake Michigan Fish Tissue SRM 1947). The proposed IDA methodology was finally applied to the determination of the six priority PBDEs in water samples from the River Nalón (Asturias). Obtained concentrations were always below the Environmental Quality Standards (EQS) established by the WFD. River water samples fortified at the EQS level showed good recoveries for all congeners. Limits of detection expressed as three times the standard deviation of ten individual blanks were below 0.09 $pg \cdot g^{-1}$ for the six priority PBDEs.

OC - 024

Physico-chemical and Metal Speciation analysis of vegetable field soils and its Correlation studies

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Chemical speciation has emerged as an important field of environmental science and as a significant tool for the interpretation of chemodynamics properties and toxicity of chemical substances. Speciation analysis measures the quantities of one or more individual chemical species in the substance and the forms in which they occur in natural systems.

The present study is designed with the objective to investigate the relative abundance of six trace elements and its speciation in three different vegetable field soils of two cities of Punjab, Pakistan.

Each soil sample was characterized for its physico-chemical parameters to probe the relationship with the chemical forms of elements. Thirty sub-soil samples of onion (*Allium cepa*), garlic (*Allium sativum*) and pea (*Pisum sativum*) fields were collected from each field from three different areas of Rahim-Yar-Khan and PindiGheb. Composites soil samples were analyzed for its physico-chemical parameters like pH, color, bulk density, electrical conductivity, moisture, organic matter content, available phosphorus, nitrates, sulfates and chlorides.

Total metal content and speciation of six elements i.e., Cd, Cr, Cu, Ni, Pb and Zn was determined experimentally following the sequential extraction into exchangeable, carbonate bound, Fe/Mn oxide and organic matter bound fractions with the help of flame atomic absorption spectrophotometer. The physico-chemical characterization of the vegetable soil samples of two cities of Punjab province, i.e., Rahim-Yar-Khan and PindiGheb showed significant differences in the values of bulk density, chlorides and moisture content.

Density was higher for PindiGheb soil whereas Rahim-Yar-Khan soil samples showed remarkably higher chloride content. It was interesting to note that electrical conductivity and nitrogen/nitrates depicted similar behavior for soil of both cities. Organic and moisture content determined in soil samples of two cities was very low owing to dry, hot climate of the region.

The role of type of vegetables grown can’t be neglected. It was found experimentally that a variation in the values of physico-chemical parameters exist in the soil samples of three vegetables. A significant variation was noted for electrical conductivity, nitrated and chlorides. However, calcium carbonate concentration is found to be consistent. The results indicated that chemical speciation of copper and zinc showed pair behavior for onion, garlic and pea fields of Rahim-Yar-Khan, whereas the same pair trend is observed for only onion fields of PindiGheb. Speciation analysis confirms the chromium as the most toxic element representing the relatively higher residual concentration in all samples. The correlation matrix illustrates the significant negative relation of Zn/Cr and Cd/Pb in PindiGheb and Rahim-Yar-Khan, respectively.

OC - 025

Application of kinetic catalytic method for the determination and speciation of selenium in environmental water

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A simple and sensitive catalytic kinetic method was optimised, validated and successfully applied for the determination and speciation of inorganic selenium at parts per billion levels in synthetic and real water samples. Experimental variables affecting the sensitivity of method were investigated and optimum conditions were established. Two techniques of data treatment, initial rate and fixed time method, were used and compared for their sensitivity. The limit of detection of the methods were found to be 1.3 µg L^{-1} and 14.7 µg L^{-1} for the Initial rate and Fixed time method, respectively. Standard reference materials consisting of selenium standards and real water sample were used to validate the method. The accuracy and precision was determined using recovery studies in the lower range of selenium concentration. The reproducibility of the method was investigated using quality control procedures. Different sample digestion techniques were studied for determining the concentrations of different inorganic selenium species in water. The existing standard digestion techniques, HCl method for the determination Se(IV) and American Public Health Association method for the determination of total Se were found to be suitable with minor modifications. Within and between day analysis of selenium standards showed very good reproducibility and precision of the method. The proposed method was applied to environmental water samples collected from Suva and Labasa areas in Fiji. Overall, it was found that the proposed method is reliable and accurate for environmental monitoring of inorganic Se in the aquatic system. In addition, water samples tested showed that Se levels were below detection limit of the method, hence within the limits set by the World Health Organisation.

5° - Speciation in industrial applications **OC - 026**

A closed cycle for removing and recovering selectively chromium, copper, nickel and zinc from real electroplating effluents

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Usually electroplating effluents contain multiple heavy metals. An important point related to the metals recycling is linked with the strategy to remove and recovery selectively metals from the solution. The selective recovery of several heavy metals, with high yield and purity, is an ambitious and difficult challenge.

In this communication, the development of a closed cycle for removing and recycling selectively, with high yield and purity, four heavy metals (Cr, Cu, Ni and Zn) coming from the treatment of a real electroplating effluent is reported. For this purpose, a hybrid technology, which combines chemical precipitation at pH 6.0 with a subsequent biotechnological-based process, was implemented. After the third batch, metal concentrations were lowered to values below the legal limits of discharge. Then, contaminated biomass was incinerated and ashes were totally acid digested under microwave conditions. From this solution, Cu was recovered (97.6%), as metallic Cu, by electrolysing the solution at a controlled potential. Subsequently, 87.9 % of Ni was recycled, as $Ni(OH)_2(s)$, by simultaneous alcalinization of the solution at pH 14 and oxidation of Cr(III) to Cr(VI); 82.7 % of the total amount of Zn was recovered, as $Zn(OH)_2(s)$, and 95.4% of Cr(VI) remained in solution, as chromate, after adjusting the pH of the remaining solution at pH 10.

This is the first time that a closed cycle was developed to recycle selectively Cr, Cu, Ni, and Zn with high yield and purity (99.8 and 85.2 % for Cu and Ni, respectively). The developed process can be easily implemented and constitutes a positive approach to the wastewater treatment since it combines the minimization of environmental liabilities with financial benefits (recovered metals can be re-sailed or re-used in the process).

OC - 027

Arsenic bioaccumulation and speciation in different plants species from two highly polluted mining areas

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The aim of this work is try to understand the behaviour of different terrestrial plants grown in arsenic polluted soils, specifically in two mercury mines in northern Spain.

On one hand, since arsenic toxicity depends on the species it presents, speciation studies were performed in the different parts of some plants species. A HPLC-ICP-MS system with an anion exchange column was used to separate the four more common species: As(III), As(V), MMA, DMA. A method to effectively extract arsenic species without altering its speciation was developed and optimised. The extraction was carried out with 0.2g of sample and 25ml of 0.3M orthophosphoric acid in open vessels using a graphite heating block at 90°C for 1 hour. Extraction yields ranged between 70 and 96%. There was no difference between the speciation in the different parts of the plants. Inorganic arsenic forms were predominant, mainly As (V), representing usually more than 75% of extracted As, although a non-negligible part was As(III). Little amounts of MMA and DMA were found in some samples.

On the other hand, we studied arsenic uptake and accumulation processes by the plants, likewise arsenic transfer from these polluted soils to plants. Plants in these sites presented high arsenic concentrations. Arsenic concentrations depended on the considered part of the plants. Usually the lowest arsenic concentrations were found in stalks (32-377 mg/Kg) and leaves (6-359 mg/Kg). Roots were the responsible of accumulating the most part of arsenic in the plants (45-1371 mg/Kg). Radicle roots accumulated much more quantity of arsenic than woody roots.

Arsenic transfer factors and bioaccumulation factors from soils to plants for every plant species were calculated. The high values obtained for two species were striking. The species were "Dryopteris filix-mas" and "Calluna vulgaris (L.) Hul", the last one defined as As-hyperaccumulating plant in literature.

OC - 028

Mercury characterization in contaminated soil and tailings using sequential extraction and thermal desorption

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The focus of this investigation is research of the mercury species in environmental samples and the assessment their toxicity with respect to their mobility and bioavailability. Mercury forms in contaminated environmental samples were studied by means of a sequential extraction and a thermal desorption from the solid phase. This study was realized on the samples of soil, tailings and sediments of Mongolia.

The used sequential extraction procedure involved these fractions: water soluble mercury, extractable mercury in an acidic medium, mercury bound to humic substances, elemental Hg and mercury bound to complexes, HgS and residual mercury. In addition to sequential extraction, the distribution of mercury species was studied with dependence on the size of soil particles – 1.25-1, 1-0.5, 0.5-0.125, 0.125-0.063 mm and < 0.063 mm.

The thermal desorption method is based on the thermal decomposition or desorption of Hg compounds at different temperatures. At the continuous determination of released volatile Hg, the result is expressed as Hg absorbance versus temperature plot, so-called Hg release curve. The thermal desorption of mercury from the solid phase was carried out using the special heating unit connected to the measuring cell placed inside atomic absorption spectrometer. The following four species were observed: Hg^0, $HgCl_2$, HgS and Hg(II) bound to humic substances. The Hg release curves of the prepared artificial soils and real samples were obtained and their applicability to the speciation analysis was considered.

This study process of environmental samples provides the following assessment of risks and is suitable for a speciation analysis of mercury in soils and similar materials.

Acknowledgements

This work was supported by the project MSM 0021622412 of the Ministry of Education, Youth and Sports of the Czech Republic, the project MUNI/A/0992/2009 and international development project of Ministry of Environment of the Czech Republic in Mongolia „Technical and technological support for removal of ecological loads resulting from illegal mining within the central part of Mongolia“.

OC - 029

Speciation of Gd-Based MRI Contrast Agents in Wastewater Treatment Plants

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Today, almost every second MRI procedure is enhanced by contrast agents, resulting in about 20,000,000 applications per year worldwide. The commonly used formulations are highly concentrated, thus leading to a very high input of anthropogenic Gd into the environment. Although this has already caused a strong anomaly for Gd concentrations in surface waters, only the total concentration of Gd is typically determined by ICP-MS. There is little knowledge about the concentration of various Gd species in wastewaters and their behaviour in wastewater treatment plants.

Our approach comprises the hyphenation of hydrophilic interaction chromatography (HILIC) with inductively coupled plasma mass spectrometry (ICP-MS). HILIC/ICP-MS exhibits high separation efficiency for the simultaneous separation of the MRI contrast agents and the required selectivity and sensitivity for trace determination in wastewater samples. ICP-MS provided additional quantification independent on the Gd species.

Influent- and effluent-wastewater of two sewage treatment plants was sampled as composite samples for 2 hours and 24 hours respectively. By knowing the quantities of water that entered the sewage treatment plant during the period of the sampling, the absolute quantity of Gd-complexes could be determined. Also, the Gd total concentrations were determined. HILIC/ICP-MS was used to determine the concentration of various Gd-complexes used as MRI contrast media in composite wastewater samples. With an LOD of 0.8 nmol/L and an LOQ of 2.5 nmol/L, respectively, the required selectivity and sensitivity for trace determination in wastewater samples could be reached. Results obtained from two sampling campaigns indicated that approximately one third of the complexes is removed during wastewater treatment.

OC - 030

Metal speciations in environmental and clinical applications

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In the subject of trace analysis, evolutionary instrumentation and material development are the current trends to re-invent the definitions of sensitivity and selectivity in the field of elemental speciations, which in fact has become an indispensible tool for environmental management and clinical monitoring. In the world's raising knowledge and demands for the quality of human health, the strategies of method development is conforming to the stringent requirements of analytical standards.

Chromium, arsenic and selenium are examples of environmental analytes that draw legislation controversies which otherwise be resolved when the actual species distribution is profiled. In the first part of our presented work, seven species of these elements, namely Cr(III), Cr(VI), As(III), As(V), monomethylated As, Se(IV) and Se(VI), were simultaneously determined by liquid chromatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS) with dynamic reaction cell (DRC) that offers optimized sensitivity at sub-ppb levels to the selected elements (1). The integration of DRC has drastically removed the polyatomic interference encountered. The high through-put of this method has fulfilled the hustle routine of environmental water analysis. And yet, some of these species, especially Se, with ultra-trace occurrence in natural water system is still an existing challenge to the instrument's sensitivity. This has intrigued the investigation in Se preconcentration.

In the second presented work, we have developed a new tetrabutylammonium hydroxide-immobilized activated carbon (AC-TBAH) material for selective Se(IV) and Se(VI) enrichment (2). The assigned anion-exchange functionality on the porous AC surface offered outstanding enrichment factors for ppt-level speciation with LC-ICP-DRC-MS. Speciation analysis in natural water samples further validated the robustness of the material which hence represents a low-cost substitute for anion exchange resins for routine applications.

Apart from vigorous development of material design for analyte extraction, trends in sample preparation is growing into micro-scale as known for sounding procedural convenience and minor sample consumption. The application of solid-phase microextraction has recently been extended beyond volatiles analysis by GC. Our third presented work demonstrates the original application of SPME-LC-ICP-MS in organomercury speciation in human urine which realized rapid screening and identification of mercury poisoning incidence (3). With growing maturity of speciation research, its critical role in the areas of environmental and biological monitoring confers a definite assurance to quality life.

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OC - 031

New analytical approach for silicon speciation in petroleum products

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Silicon and its chemical species are of considerable importance in the petroleum industry. Due to its unique properties, Polydimethylsiloxane (PDMS) is used as antifoaming in the oil and gas industry particularly during the crude production and refining process. Despite its initial thermal stability, the complexity of the industrial processes induces PDMS degradation. This induces a wide array of silicon species in petroleum products at very low concentration levels (µg/kg), that can act as severe catalyst poisons. In order to improve the overall refining process, it is therefore fundamental to achieve silicon speciation. Up to now, only a total determination of silicon by elementary analysis can be achieved in the different products. The complexity of petroleum matrices, the wide variety of compounds as well as possible contamination problems occurring during silicon analysis has hampered the development of analytical speciation developments in general.

The present study deals with an analytical approach which was developed to promote both identification and quantification of Si species. GC combined to mass spectrometry (MS) in single ion monitoring mode (SIM) was allowed to quantify for the first time the presence of several low molecular silicon compounds in the refining process. The overall budget in terms of Si content between hyphenated techniques and total Si analysis showed that there is a general underestimation. GC/MS in SIM mode detection cannot take into account all present species. Thus, new unidentified species could be present in products. For further identification, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) was used. The identification of new species was facilitated by a novel method based on the Kendrick diagram construction.

6° - New analytical strategies for metal speciation including isotopic information OC - 032

Species-specific isotope ratio of mercury in biological tissues

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During environmental/biological processes, isotopes of mercury are fractionated between different species, i.e. elemental Hg^0 species, ionic IHg^{2+} species or organic $MeHg^+$ and Me_2Hg species. Due to the toxicity of Hg, especially the organic forms, the study its isotopes is nowadays an important way to understand the complex biogeochemical cycle of mercury.

Isotopic composition in different elemental species is relatively new field in analytical chemistry. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) can measure not only isotope ratios with competitive precision and accuracy, but also it has all the advantages of an ICP ion source. Perhaps the most important of these advantages is the wide range of sample introduction devices that may be coupled to an ICP. In contrast to TIMS in which the sample introduction must be carried out “off-line”, MC-ICP-MS allows the continuous sample introduction into the ICP-source, providing more versatile and less time consuming isotope analyses. One illustrative example is the hyphenation of MC-ICP-MS with chromatographic techniques, such as gas chromatography (GC). This coupling is able to separate “on-line” the different species in which the element under study is present in the sample and measure “on-line” species-specific isotope ratios.

A simple and precise method to measure isotopic composition (δ-values) of different elemental species of Hg (Hg^0, Me_2Hg, MeHg and IHg^{2+}) in different biological tissues using GC-MC-ICP-MS is presented. The method can be also used for different concentrations of Hg species in the sample and the standard. The isotopic composition of several Hg species presented in the sample can be measured relative single species presented in the bracketing standard. The methodology allows studying isotopic composition of low abundant isotopes.

As an application of the new methodology for various biological samples, such as certified reference materials, fish muscle tissue, human hair, several organs of seal we have demonstrated the results of $\delta^{204}Hg$, $\delta^{202}Hg$, $\delta^{201}Hg$, $\delta^{200}Hg$, $\delta^{199}Hg$ and sometimes $\delta^{196}Hg$ in mercury species. Results demonstrate mass-dependent and mass-independent fractionation of Hg isotopes.

OC - 033

Lead speciation and isotopic composition as an indicator of anthropogenic contamination: comparison of buried and modern soils

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Investigation of Pb speciation and isotopic composition in paleosols and in their modern analogues may provide a new way of studying sources and levels of soil contamination. We investigated a chronological sequence of five paleosol buried below Bronze-Age, Iron-Age, and Medieval burial mounds (kurgans), covering about 4.5 millennia in Volgograd region, Russia. Modern reference soil profiles located near kurgans and samples of roadside soils were also investigated. The concentration as well as the isotopic composition of Pb were analyzed in each soil horizon using Q-ICPMS, after separation into total, carbonate-associated (1M ammonium acetate, pH 4.8), and acid-soluble (0.5 N HNO_3) fractions. "Mobile" Pb is considered to be a better indicator for anthropogenic Pb contamination than total Pb, since industrially contaminated soils are usually enriched in a less tightly bound Pb fraction. Our result demonstrated that the highest proportions of mobile Pb and the least "radiogenic" isotope ratios were detected in road-side soils, contaminated with gasoline Pb.

Upper horizons of modern reference soils were enriched with "mobile" Pb, in addition, the Pb isotopic composition the "mobile" lead fractions was slightly shifted towards "gasoline Pb" if compared to buried soils. On the other hand, we could not find any statistically significant difference between modern and buried soil in isotopic composition of total Pb.

Regression analysis showed that the soil carbonate content explained about 55% of the variation in mobile lead. Probably, carbonates act as a trap for percolating mobile lead, mostly of anthropogenic origin in modern soil. In all cases, the ratio between mobile lead and Ca (0.5N HNO_3) was much higher in the upper horizons of modern soils than in buried soils and may thus serve a sensitive indicator of anthropogenic Pb input.

OC - 034

A metrological approach for the assessment of selenium status in humans

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This study addresses a metrological approach for the assessment of Se status in humans in terms of serum selenomethionine (SeMet). The quantification of SeMet was carried out using a primary method of chemical analysis, namely species-specific isotope dilution in combination with (reverse phase) HPLC coupled to inductively coupled plasma-mass spectrometry. SeMet was released from the serum selenoalbumin by enzymatic hydrolysis. The total uncertainty budget and the main uncertainty sources were assessed for SeMet determination in three commercial serums, namely BCR-637 (certified for total Se) and two serum standards (Seronorm level 1 and 2, with indicative levels of total Se). The metrological approach reported here could be considered as a pilot study in terms of metrological determination of SeMet in human serum, hence being suitable for method validation and inter-laboratory comparison.

OC - 035

Detection and characterization of Se-binding proteins in wheat by gel electrophoresis and laser ablation-inductively coupled plasma-mass spectrometry

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Wheat contains 10 to 15 % protein including: (1) albumins and (2) globulins which are soluble in hypotonic or isotonic solutions, respectively, and (3) prolamins and (4) glutelins which are soluble in aqueous alcohols, dilute acids or bases, detergents, chaotropic and reducing agents. The prolamin (in wheat - gliadin) and glutelin (in wheat - glutenin) composes about 80 % of protein contained in wheat seeds and form the gluten components. Prolamins are storage proteins having high proline content. Glutenin is responsible for some of the refined baking properties in bread wheat, in which 20 % is high molecular weight (HMW) subunits relatively low in sulfur (S) and the other 80 % are low molecular weight (LMW) subunits high in sulfur. Since Se chemically resembles S, it is believed that Se is enriched in the LMW subunits of the glutelin. However, there is no information available on the distribution of Se-containing proteins in the different protein fractions of Se-enriched wheat.

The Se-containing albumins and globulins can easily be detected in water or isotonic extracts by SEC-ICP/MS, whereas this technique is not applicable for non-water soluble glutelins (prolamins does not contain Se). Therefore, gel electrophoresis is a method of choice extensively used for characterization and analysis of wheat proteins. The main problem is that the Se-containing proteins are minor and their identification fails in the presence of high non-selenized protein matrix, unless they are highly enriched and purified. Gel electrophoresis coupled to laser ablation with selenium-selective ICP/MS detection provides a promising approach for the identification of the Se- containing proteins in wheat. In the present study, results from ongoing experiments using LA-ICP/MS to detect and map the Se-containing protein size distribution of albumin/globulin and glutelins in Se-enriched wheat, will be presented.

OC - 036

Analysis of Selenoneine, Se-methylselenoneine and their sulfur analogs in human urine and blood samples by parallel coupling of bidimensional liquid chromatography with ICP-MS and ESI-LTQ Orbitrap MS detection

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Selenium is an essential trace element for which the margin between safe and toxic levels is narrow. Selenium is incorporated in antioxidant selenoenzymes such as glutathione peroxydase or thioredoxin reductase. The anticarcinogenic effects of Se have also been an increasing subject of research these last years. As the bioavailability, toxicity and chemopreventive effects of Se are species-dependant, the study of selenium metabolism in human is therefore of considerable interest. After absorption by the body, selenium is mainly excreted through urine and the study of the metabolites present in this matrix has provided valuable information to elucidate possible metabolic pathways.

Characterization of a novel selenium metabolite in urine, Se-methylselenoneine was achieved after sample purification SPE followed by the parallel coupling of bidimensional RP/HILIC chromatography with ICP-MS and ESI-LTQ Orbitrap MS detection.

This compound is a methylated form of Selenoneine which was recently discovered in tuna fish and turtle blood samples. Selenoneine is the selenium analog of ergothioneine, identified in rye ergot by Tanret in 1909. Regarded as a betaine, ergothioneine is an unusual amino acid recognized as the only naturally occurring thio-imidazole amino acid. It was demonstrated to play an important biological role as an antioxidant.

To confirm the biological significance of Se-methylselenoneine regards to Selenoneine and to discard the possibility of sample preparation artifacts, a new method was developed to monitor its actual presence, as well as the occurrence of its sulfur and/or non-methylated analogs, in non-preconcentrated urine but also blood samples of non-supplemented humans.

These experiments made possible the screening of the total content of ergothioneine as well as its selenized and/or methylated analogs in a single chromatographic run.

In all samples (urine and blood, derivatized or not), Se-methylselenoneine and its sulfur analog were observed. In derivatized samples, carboxamidomethylated selenoneine and its sulfur analog were present in blood but only the sulfur-containing compound was detected in urine. Moreover, different ratios “methylated/non-methylated” were observed between urine and blood samples, which seemed to indicate their active metabolization. The analytical tool developed here will be of a great importance to further study the occurrence and the potential metabolic role in mammalian organelles, cells and fluids of these very particular and promising redox metabolites.

6.3 Poster Contributions

1°- Speciation, lability, bioavailability and transformations PC - 001

Investigating the biosynthetic pathways involved in Se assimilation by cereal crops grown in a Se-rich environment by multidimensional HPLC ICP-MS and HPLC ESI-LTQ Orbitrap MS

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In the seleniferous areas of Indian Punjab, even crops that do not belong to the group of Se accumulators, such as cereal grains, have been found to tolerate and take up very high amounts of Se. This fact raised toxicological issues related to Se exposure of the local population and livestock. However, it is not clear how plants that are not Se accumulators are able to deal with such an high Se uptake and avoid the damaging effects on plant functions resulting from incorporation of protein selenoamino acids, especially SeMet, in plant proteins. Se-accumulators are able to prevent Se toxicity by biosynthesizing primarily nonprotein selenoamino acids, such as Se-methyl-selenocysteine (MeSeCys) and γ-glutamyl-Se-methyl-selenocysteine (γ-Glu-MeSeCys). However, previous investigation of Se speciation in local wheat showed that MeSeCys was present only and as a very minor compound (*J. Agric. Food Chem.* 2010, 58, 2295–2301). Understanding Se metabolism in Se-rich crops from these areas is important also because they may be promising raw material for naturally enriched products to be used to supplement human and animal diets in low Se areas.

In this study, we aimed to characterize the water soluble Se-compounds in samples of rice, maize and wheat from the above-named areas. Samples were extracted with Tris or ammonium acetate buffer, filtered and analyzed by SEC-ICP-MS using different columns. Orthogonal chromatography was carried out by gradient elution anion and cation exchange-ICP-MS. SeMet, Se-MeSeCys, SeIV and SeVI were detected in the extracts along with several unknown Se-species. Sample extracts were also preconcentrated and analyzed by coupling in parallel cation exchange chromatography to ICP-MS and ESI-LTQ Orbitrap MS. It allowed to confirm the identity of known Se-containing species and to identify novel metabolites.

The results give an insight into the biosynthetic pathways involved in Se assimilation by cereal crops grown in a Se-rich environment.

PC – 002

Metals speciation in fresh water by in situ analysis

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Human activities such as industrial and municipal wastewater release significant amounts of metals but their relative contribution to the overall toxicity of wastewater may be small and once released to receiving fresh waters, their toxicity remains unknown. It is now well known that the physicochemical conditions of waters influence metal speciation. Recent techniques of *in situ* dynamic sensor have been developed to assess bioavailable fraction of metal according to different relevant time scales of environmental processes. Diffusive gradient in thin films (DGT) are one of these speciation analyses. This technique allows to establish a permanent flux of labile metal through a gel and then to measure the labile concentration upon its deployment time. The device is made of two layers of hydrogel: a strong metal binding resin and a diffusive gel in contact with the bulk solution and covered by membranes. In order to investigate the contribution of the urban and industrial effluents on the total and labile metal species (Pb, Zn), DGT devices are deployed several days in 2 sites of the Meurthe river water (North-Eastern of France). These sites are located in the downstream and upstream of Nancy agglomeration. In parallel, characterization of the fresh water solution and suspension matter was performed in order to obtain the total and dissolved metal concentrations.

Preliminary results indicate similar physicochemical conditions (DOC, conductivities…) between the downstream and upstream of agglomeration. The total metal concentration are very weak (few ppb) and do not vary significantly between the 2 sampling sites. From DGT results, Zn metal species seem more labile than Pb. Moreover, for the same dissolved metal concentration on the 2 sites, concentrations of labile fraction vary from an element to another between the down- and upstream. We also observed that iron particles have a non-negligible impact in the analysis results and seems to diffuse within the gel. This study aims at understanding of the variation of Zn and Pb lability between the 2 sites as a function of environmental conditions and the influence of penetrating species on gels. This study is performed within the framework of the multidisciplinary research program on the Moselle River (Zone Atelier de la Moselle), the Meurthe river is one of its affluent.

PC – 003

Analytical selenoproteomics - identification and quantification aspects

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The biological essentiality of selenium and its putative cancer preventive properties spur interest in analytical methods able to provide data on the identity and quantity of the individual selenium-containing species present [1,2]. The biochemical processes lead to the incorporation of selenium into proteins as selenomethionine or selenocysteine. These processes are accompanied by the formation of a multitude of intermediate small-size (< 1 kDa) selenometabolites.

Selenium being incorporated in proteins covalently, selenoproteomics analysis can be carried out by any of the three canonical proteomics approaches (bottomup, topdown or shotgun). The Se-bearing protein or peptide can be recognized by its isotopic pattern, but in practice, the signal is suppressed by the more abundant, easier ionisable concomitant species. Therefore, it is essential to isolate or to purify the selenium-containing species in order to assure the optimum conditions for their electrospray MS analysis. The presentation discusses the advantages and limitations of the relevant protocols starting with sample preparation and selenoprotein purification. In particular, the advantages and disavantagies of two strategies based on (1) gel electrophoretic separation nad laser ablation - ICP MS and (2) chromatographic purification by SEC-ICP MS both followed by HPLC with the parallel ICP MS and ESI MS/MS detection will be discussed.

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PC – 004

Determination of organotin compounds in seawater at sub-nanogram per liter level by solid-phase extraction and GC-PFPD detection

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The most toxic among all organotin compounds is tributyl tin (TBT), mainly used as biocide in antifouling paints. It is on the list of priority pollutants in the European Water Frame Directive since it was established that TBT can cause chronic and acute poisoning of aquatic organisms already at a level of 1-2 ng L^{-1}. France was first to ban the use of TBT in antifouling paints in 1982, and since January 2008 its application is banned almost worldwide, including Croatia. According to Croatian regulation, the average TBT concentration in water must not be higher than 0.2 ng L^{-1}, while maximum allowed single concentration is 1.5 ng L^{-1}. Also, the OSPAR commission defined the Ecotoxicological Assessment Criteria (EAC) for TBT in seawater (based on possible adverse effects on mollusks populations) at 0.1 ng L^{-1} (lower value) and 1.5 ng L^{-1} (upper value).

According to existing regulative in European countries and Croatia, pollution of marine environment by TBT should be monitored by measuring concentration of butyl tin compounds in seawater. Analytical method used for this purpose should have detection limit (DL) as low as 0.2 ng L^{-1}. This very low DL can be reached, according to existing literature, only with sophisticated techniques such as GC-ICPMS, which is not readily available in routine laboratories. Therefore, it is essential to develop other methods for TBT determination in water with required DL, based on simpler and more economical techniques, such as GC-PFPD.

The aim of this work was to develop and optimize an adequate analytical method for speciation of OTC (BuT and PhT) in seawater using solid-phase extraction (SPE) as a preconcentration method, followed by detection with GC-PFPD. Performances of cartridges with different polar and non-polar stationary phases were investigated. For this purpose Oasis HLB polymer and HyperSep C_{18} have been used as sorbents, while derivatization with sodium tetraethylborate was performed either before or after solid extraction. Preconcentration conditions of OTC on SPE were investigated by using different solvents as eluents (hexane, methanol, ethyl acetate and acetonitrile) and eluent volume was optimized to obtain quantitative elution of retained OTC. Furthermore, other details as breakthrough volume, addition of complexing agents, in-flow and elution rate were studied as well.

As a certified reference material for determination of OTC in seawater does not exist, verification of the method was performed by the comparative analyses of selected samples with GC-ICPMS. Detection limits, recovery rates, and the precision of the whole procedure have been determined. The method was applied to determination of organotin compounds in natural seawater samples from the Adriatic Sea.

PC – 005

Distribution of anionic arsenic species (As(III), As (V), MMAs, DMAs) by HPLC-HG-AFS in different tissues of brown algae *Lessonia trabeculata* (Laminariales; Phaeophyceae) exposed to different levels of contamination. Evaluation as a biomonitor of arsenic pollution

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Ecosystems have many different organisms and it is usually not feasible to evaluate the impacts of an environmental stressor for all of them. Instead, it is necessary to develop suitable pollution biomonitors to assess ecosystem health. In particular, macroalgae are one the most efficient and reliable biomonitors used to study metal pollution and have been used for several environmental assessments particularly due to their high capacity to bind to metals in aqueous solutions.

The morphological structure of a single individual of kelp or thallus can be separated into three main parts: blades, which concentrate most of the nutrient absorption and photosynthesis; stipes, which give structural support; and the holdfast, which attaches the kelp to the substrata.

When applying macroalgae in marine biomonitoring, some problems may arise due differences in arsenic accumulation by different thallus part. Most the papers dealing with kelp do not identify the part of the plant that was sampled, only few studies have examined intra-thallus variation of arsenic, but not arsenic speciation.

Considering that concentrations of arsenic species could vary throughout the kelp, it is important to determine which part accumulates the most and whether is a pattern. This information is important for posterior investigations, with the purpose of optimizing field work to obtain accurate results that trustfully represent environmental conditions.

The aim of this study is to evaluate the brown algae *Lessonia trabeculata* as a biomonitor for arsenic pollution. We determined the total and arsenic speciation in different tissue parts (blades, stipes and holdfasts) of *L. trabeculata* in an illegal sewage outfall zone and in a control zone, in central Chile. In the outfall and control zones three sites were sampled at 5, 30, and 60 m from the shore. Our results showed high concentrations of arsenic in holdfasts at the site closest to outfall, decreasing with distance and lower levels in the control sites. The main species of arsenic found in those examined in this study were As (III), As (V), and to a lesser extent DMAs, the sum that correspond to 30% of total arsenic.

On the other hand, found no statistically significant differences in the concentrations of each arsenic species in blades and stipe exposed to different levels of pollution. Therefore, to use *L. trabeculata* as a biomarker of arsenic contamination is advisable to use holdfasts.

The authors gratefully acknowledge the financial support of FONDECYT Project 11080235.

PC – 006

Roots of aquatic macrophytes: ecological niches for sulfate-reducing prokaryotes and impact on mercury methylation

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Sulfate reducing prokaryotes (SRP) are involved in the mercury biogeochemical cycle through mercury methylation and demethylation. Most of the activity of the SRP takes place in sediments where methylmercury is stored and may be a further source of contamination for food webs. Recent studies, conducted in tropical environments, showed that SRP also colonize aquatic plants roots biofilms in the water column. Moreover, high mercury methylation and demethylation potentials were observed in such water-roots interfaces. Inorganic and organic particulate material present on roots can accumulate metals by adsorption and promote the activity of SRP in such matrix, causing a possible source of contamination for food webs (suspension feeders or grazers). However, plant roots-SRP associations and their impact on mercury bioaccumulation are poorly documented in temperate ecosystems.

In south western France, invasive aquatic macrophytes like *Ludwigia peploides* colonize several lakes and rivers, causing damage to aquatic ecosystems and could interact with mercury biogeochemistry and bioaccumulation. Indeed, mercury concentrations close to the European toxicity norm (2.5 $mg.kg^{-1}$ dw) were reported in some fishes. In order to evaluate the possible contribution of these ecological niches on mercury speciation, SRP occurrence and diversity as well as mercury methylation and demethylation potentials are investigated in the sediments, the plants roots and the water compartments from three different freshwater ecosystems. Incubations realized with stable isotopes of mercury ($^{199}Hg^{2+}$, $CH_3{}^{201}Hg^{+}$) and analyzed by GC/ICP-MS, demonstrate mercury methylation and demethylation activities preferentially in plant roots. The use of a nested-PCR technique permitted the detection of SRP in all samples, including the water bodies and plant roots. These results tend to prove macrophytes roots can be an important place of methylmercury production and a potential pathway of mercury in food webs in such aquatic ecosystems.

PC – 007

The release of trace metals following the resuspension of seine estuarine sediments

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The Seine estuary sediments are impacted by high levels of trace metals, due to the industrial agricultural and urban waste discharge. As a result of all this, both the water and sediment quality of the seine river have been seriously affected.

The fate of contaminants in sediments is related to the nature and extent of biogeochemical transformations as well as their relative mobility and degradation under varying redox conditions. Sediments considered as not only sinks but also sources of potentially hazardous chemicals to the water. For example, the presence of important natural slumping events dredging operations, tides contribute to the sediment resuspension. Remobilization of a variety of contaminants to the dissolved phase can involve a potential threat for aquatic ecosystems.

To simulate these processes, fresh sediment collected from various sites in the upstream of Seine estuary were resuspended in river water at controlled temperature and in different conditions of solid/liquid ratio and rotation rate. The dissolved Cd, Pb, Ni, Cr and Zn concentrations measured during the resuspension experiments reflect the reactivity of the carrier phases and the competing release kinetics and removal mechanisms. Metals are released rapidly from sediment with a sharp peak at the beginning of the experiment, following, a decrease of trace metals concentration with time, that can be due to w coprecipitation and/ or adsorption processes. However, the decrease in solid/liquid ratio enhances greatly the percentage of remobilized metal from the studied sediment.

Finally, these preliminary results obtained in the framework of the national program SeineAval (ToxSeine Project) will be confronted to toxicity tests carried out on the same sediments to get new information on the metal mobility towards the biota.

PC – 008

Distribution of selenium, mercury and theirs species in fish muscle from fresh water lakes in Argentina

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Fish is an ideal component of a healthy and balanced diet because of its high nutritional value in terms of minerals (P, I, K), unsaturated lipids (oleic acid, linolenic acid and omega 3 series), phospholipids, vitamins (A, D) and proteins of high biological value. On the other hand fish can accumulate also heavy metals in their tissue; monomethylmercury (MeHg) is the organomercury compound most commonly found in fish which is recognized as a major environmental pollutant and health hazard for humans. One of the natural components that may protect against mercury (Hg) toxicity is selenium (Se). Se is an essential trace element for mammals with a very narrow concentration range between essentiality and toxicity [1]. The aim of this study was to determine total concentration and speciation of Se and Hg in fish samples from freshwater lakes in Argentina and what is more to distinguish between distribution of these two elements in soluble and insoluble part of the sample. To measure total concentration of Se, HG-AFS with the chemical and instrumental operating conditions according to Smrkolj and Stibilj was used [2]. After enzymatic hydrolysis of sample with Protease XIV, separation and detection of Se species were performed on HPLC using anionic or cationic exchange columns and coupled to ICP MS. In most chromatograms we obtained two peaks; the first peak was unidentified because it could not be attributed to any of the known Se species (Se(IV), Se(VI), Secys2 or SeMetSeCys while the second peak was identified as selenomethionine (SeMet). Total concentration of Hg and MeHg and their partitioning between soluble and insoluble part after enzymatic hydrolysis were also obtained.

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PC – 009

Arsenic contamination and its speciation in stream waters from three abandoned cinnabar mines

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Recovery of mercury from cinnabar ore containing high amounts of arsenic in the asturian mines (northern Spain) has left a legacy of arsenic contamination that poses risks for the surrounding environment. In this work levels and speciation of arsenic in stream waters affected by three abandoned cinnabar mines were examined.

Mine tailings constitute the major contamination source of arsenic in the studied areas releasing elevated amounts of arsenic to nearby sediments, where concentrations as high as 24800 mg/kg have been found. Surface waters from different points sited upstream and downstream the mine tailings were studied. Extremely high arsenic concentrations were found in downstream waters. In addition, a strong correlation between total arsenic in water and water extractable arsenic from the corresponding sediments was found, indicating a high mobility of arsenic.

Arsenic speciation studies were carried out by HPLC-HG-AFS. Arsenate (As(V)) was the dominant species in all samples due to the relatively high oxidic conditions found in all sampled points.

In La Soterraña mine site high arsenic concentrations were found. The pH values ranged 6.90-8.35 indicating that these points were not affected by acid mine drainage (AMD) and arsenic mobilisation is expected to be due to the solubilisation of certain arsenic minerals. Samples from La Peña showed the lowest arsenic total concentration as a consequence of the preventive measures taken in this mine site. However, arsenic concentrations remained higher than 1600 $\mu g.L^{-1}$ in downstream point. In Los Rueldos mining site the influence of AMD is evident. In this site the oxidation of sulphurs results in an important decrease in pH and the consequent solubilisation of heavy metals and arsenic.

PC – 010

Relation between lead speciation and microbial activity: long-term field experiment

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The most bioavailable and toxic forms of Pb in soils are dissolved metal and especially free metal ions in soil solution. However, the most ecotoxicological data are expressed as effect versus metal dose, and are based on the laboratory short-term experiments, which do not reflect situation in the field. Our aim was to combine the effect study with Pb speciation study and to derive critical endpoints for microbial community in terms of bioavailable metal forms in long-term field experiment.

Soil at the field plot was contaminated with Pb in soluble ($Pb(NO3)2$) and insoluble ($PbO2$) forms (0 - 1000 mg Pb /kg soil) in August 2001. Soil solution sampling (with Rhizon® samplers) and solid soil sampling and “mobile” metal content (1M $NH4NO3$ extraction) determination were carried our periodically during 2002-2010. Soil solution was analyzed for Pb, major cations (ICP-MS) and anions (IC), including dissolved organic carbon DOC (TC analyzer). Activities of Pb were calculated with a speciation program WHAM VI using data on soil solution chemistry, and directly determined using Donnan Membrane Technique (DMT).

Basal respiration rate (V basal), substrate-induced respiration rate (V SIR), soil microbial biomass (Cmic) were determined. Results were expressed as “dose”- response curves in terms of microbial biomass or basal respiration rate (% of control) as a function of “mobile” Pb content in soil, Pb concentration or Pb activity in soil solution. Results demonstrated that microbial response can be expressed as a function of bioavailable Pb form concentration (“mobile” Pb content/Pb soil solution concentration/Pb soil solution activity) independently on duration of the experiment and initial form of metal introduction in soil (soluble or insoluble). Data on V basal and C mic were fit to a log logistic dose response model and toxic endpoint concentration (EC10 values) were determined in terms of bioavailable Pb concentration.

PC – 011

Cytotoxicity and metallothionein induction in renal cell cultures after exposure to different cadmium species (soluble, micro- and nanoparticles)

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Cadmium (Cd) is an environmental pollutant affecting human health through occupational and environmental exposure. It is well described in the literature that exposure to soluble forms of Cd lead to end-stage renal diseases and that the conjugation of Cd with metallothionein (MT) is one detoxification mechanism leading to reduce Cd nephrotoxicity.

The aim of this study was to evaluate toxic effects and metallothioneins (MTs) induction following exposure to various Cd species, i.e. soluble ($CdCl_2$), particles at micro- (1 and 1.8 µm for CdO and CdS) and nano-scale (10 nm CdS) in renal cell lines (IP15 and LLC-PK_1). As Cd nanoparticles are very reactive, their toxicity and their biological responses can be strongly highlighted.

The cellular viability was evaluated by different assays (neutral red, MTT and WST-1) after Cd species cell exposures. Cd-MT complexation was investigated by means of Size Exclusion Chromatography coupled to ICP/MS after an appropriated sample preparation. The identity of metallothionein subisoforms was investigated by microbore HPLC with multimodal detection.

Results show that the cytotoxicity of $CdCl_2$ and CdO on renal cell lines was similar and significantly greater than that of CdS microparticles, probably due to their solubility. CdS nanoparticles induced, depending of cell type used, a decreased in cell viability. The analysis by SEC-ICP MS showed a significant induction of a Cd-containing compound matching the elution time of MT standards. Cd-peak matching the MT elution time was slightly induced for IP15 cells and poorly for LLC-PK_1 cells. Moreover, the cytotoxic effects of cadmium species were strongly correlated to the cellular Cd content. Metallothionein subisoforms study in cell cultures exposed to CdS nanoparticles confirmed the presence of known and the identification of new MT subisoforms.

This study was funded by ANSES (Agence Nationale de Sécurité Sanitaire de l'alimentation, de l'Environnement et du Travail (n°EST-2007-22)).

PC – 012

Gel-electrophoretic separation and LA-ICP MS mapping of iodine-containing proteins in edible seaweeds

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Seaweeds are generally considered as healthy food due to their low lipid content and a high amount of vitamins, proteins and minerals, including iodine. This element is essential for humans as it is involved in the synthesis of thyroid hormones; its deficiency causes, among others, goitre or cretinism. Seaweeds concentrate and metabolise iodine present in seawater and several low molecular weight iodine species have been already identified in these marine organisms. However, no data exist on the identity of iodine-containing proteins although their presence has been suggested by several research groups [1-3].

This work presents a systematic approach to specific extraction and characterization of I-containing proteins in 3 types of edible seaweed harvested in the Galician coast (North-Western Spain): Nori (*Porphyra umbilicalis*), Dulse (*Palmaria palmata*) and Sea Lettuce (*Ulva rigida*). The total iodine concentration in the samples varied from 55 ± 1 to 73 ± 1 $\mu g \cdot g^{-1}$ (on the dry weight). The inorganic species present had been removed by leaching with water and then several procedures were tested and optimized for protein extraction in view of their gel electrophoretic separation. Laser ablation coupled to ICP-MS was used for in-gel detection of iodine in protein bands and spots demonstrating directly, for the first time, the presence of I-containing proteins in algae extracts.

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PC – 013

Arsenic mobility in marine sediments: optimization of the determination of thioarsenical compounds in porewater

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The objective of ASEDMAR project is to develop a model combining geochemistry, bioavailability and ecotoxicity of arsenic in contaminated marine sediments. It was previously shown that arsenic in porewaters of marine sediment is mainly present as thioarsenicals and classical As forms (As(III), As(V) and methylated forms) remain generally low. Porewater playing an important role in the transfer of arsenic from sediment to the water column, its characterization in terms of As species is essential to understand and model the bacterial cycle of arsenic, which is not known in marine ecosystem.

Thioarsenicals determination was performed from solutions collected from sediment microcosms in anaerobic conditions that stimulate activity of sulfate-reducing bacteria with a transformation of sulfate to sulfide leading to a significant increase of dissolved arsenic. Speciation of As was performed by HPLC-ICP-MS according to the method of Wallschläger and Stadey (*Anal. Chem.* (2007), 79, 3873) allowing determination of As(III), As(V) as well as AsO_3S^{3-}, $AsO_2S_2^{3-}$, $AsOS_3^{3-}$ and AsS_4^{3-}. After sample conditioning under nitrogen, their stability was studied at different temperature (-20°C, immediate freezing with liquid nitrogen and a storage at -20°C, +4°C and room temperature) and at different periods of time (24 hours, 1 week and 2 months) to optimize their analysis in routine conditions. Whatever the temperature, it appears that the time of storage particularly influences the As(III) concentration that decreases with time. The As(V) content remaining stable and the sulfide concentration high, a combination of As(III) with sulfides can be considered because $AsO_2S_2^{3-}$ and AsS_4^{3-} increase with time. However, it was shown that the most important factor influencing stability is the absence of oxygen and a sample conditioning under nitrogen allows a good preservation of the samples for a few days.

This study was part of ASEDMAR project, supported by the French National Research Agency under reference “2008 CESA-003”.

PC – 014

Mercury speciation in dolphin liver by GC/LC-ICP-MS and LC-ESI-MS/MS combined with the use of isotopic tracers

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In this work Hg stable isotopically labeled species were used to assist the investigation of Hg species (i.e. IHg and MeHg) binding biomolecules in the aqueous soluble fraction of white-sided dolphin (*Lagenorhynchus acutus*) liver homogenate (QC04LH4). It has been suggested that Hg can bind thiol containing proteins/biomolecules. However most of the speciation studies are restricted to the discrimination between IHg and MeHg and carried out in the fish muscle due to its human consumption.

The aim of this study was to develop an analytical method to determine Hg species (i.e. IHg and MeHg) binding biomolecules in the liver sample. The partition of mercury species into the different tissue fractions revealed that MeHg is mainly found in the cytoplasm, and 80% of IHg is present in the solid residue.

The screening by size exclusion chromatography-ICP-MS analysis of the water-soluble fraction revealed the association of Hg with biomolecules in a wide molecular weight range. The analysis by GC-ICP-MS of the different size exclusion chromatography fractions has shown different ratios of IHg and MeHg. The cytosol was incubated with Hg isotopically labelled species isotopes, demonstrating an unambiguous specific affinity of the different biomolecules by IHg and MeHg.

The interaction of MeHg with proteins contained in the mentioned SEC fraction was investigated after tryptic digestion by µRP LC and parallel detection by ICP-MS and ESI-MS/MS. Molecular MS experiments were carried out by using high resolution instrument (Orbitrap) to ensure accurate determination of MeHg binding sites. The obtained results evidence the binding of MeHg to cysteine residue on the hemoglobin beta chain. Further potential MeHg binding proteins through Cys residues in the dolphin liver sample were also observed. These results suggest that hemoglobin is a major specific binding protein and certainly the main carrier of MeHg within the blood – liver system of such marine mammals.

2° - Direct and in-situ speciation analysis PC – 015

Semicontinuous monitoring of cadmium in waters using an electroanalytical device

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Among the multitude of highly toxic pollutants, heavy metals are closely monitored especially in waters because of their dangerousness even at the low µg L^{-1} level concentration.[1] Regarding the European legislation on the quality of water intended to human consumption, cadmium is one of the most dangerous heavy metals.[2]

Because of its small and light apparatus, stripping voltammetry gives the ability to perform rapid and low cost in situ and field measurements. Moreover, whereas other analytical techniques such as mass-spectrometry need some sample treatment before measurements, it has been shown that voltammetric measurements can be performed on untreated samples. The electrochemically accessible fraction of heavy metals species being usually correlated to the potentially bioavailable fraction, speciation information can also be directly deducted from untreated samples field analyses.

It is well known that the quality of analyses (repeatability, reproductibility …) is closely linked to the operator technical know-how. In order to circumvent this drawback and to perform autonomous monitoring, most of analytical techniques have acquired automation modules such as sample carrier. Electroanalytical chemistry suffers of the lack of automation devices.

In this way, in order to obtain automated, competitive and representative cadmium speciation information, a full-automated electroanalytical device has been developed. It is composed of an electrochemically adapted automation module and a competitive screen-printed sensor modified ex situ by a very low quantity of mercury. At first, the development of the reliable sensor will be discussed. Then the contribution of the automated apparatus to analyses will be presented. Coupled with an UV-photolysis unit, it has permitted the detection of both total and electrochemically accessible cadmium down to the sub µg L^{-1} level (0.2 µg L^{-1}) for only 60 s of deposition time in solutions containing 10 mg L^{-1} of humic substances.[4, 5]

Semicontinuous monitoring of a tap water doped with 5.3 mg L^{-1} of cadmium, in presence of traces of lead and copper, has been successfully achieved for 7 days. Moreover, potentialities of such device will be discussed.

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PC – 016

Cd speciation and localization in the hyperaccumulator *Arabidopsis halleri*

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Arabidopsis halleri is a model plant investigated for Zn and Cd hyperaccumulation. In this work *A. halleri* plants from metallicolous origin exposed to Cd and Zn were studied using an original combination of chemical and physical techniques to obtain insights on Cd hyperaccumulation mechanisms. Zn and Cd accumulation in leaves increased with time and with their respective concentrations in hydroponics. At the rosette scale, various Cd distribution patterns were found by ^{109}Cd autoradiography, regardless of the conditions: heterogeneous distributions with highest Cd intensities found in some young and mature leaves, or relatively homogeneous distributions. At the leaf scale, an enrichment of the petiole, central vein and trichomes was observed after 3 weeks. After 9 weeks, leaf edges were the most Cd enriched tissues, and regions along leaf vascular bundles appeared less concentrated. These distributions might suggest Cd re-allocation processes within the rosette. Bulk Cd K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy showed that Cd was predominantly bound to COOH/OH groups belonging to organic acids and/or cell wall components. Cd bound to thiol groups was found as a secondary species, whose proportion varied from 0 to 20%. Thiols ligands might correspond, at least partly, to glutathione found in significant amount in aerial parts, but not to phytochelatins. These results show that the mechanisms of Cd storage and detoxification in *A. halleri* differ from what was previously found for Zn.

3° - Speciation of metal species in colloidal and nano-materials PC – 017

Separation cadmium, copper, lead and nickel using modified multiwalled carbon nanotubes sorbent prior to determination the greenhouse soil in Jiroft area (Iran)

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This study determines total levels of cadmium, copper, lead and nickel trace elements in Jiroft area (Iran) greenhouse surface soil using ultrasound assisted digestion and preconcentration with modified multiwalled carbon nanotubes sorbent. Soil samples were digested in ultrasonic bath with perchloric and hydrofluoric acid. Then, the cadmium, copper, lead and nickel ions were separated and preconcentrated using modified carbon nanotubes sorbent. Multiwalled carbon nanotubes were oxidized with concentrated HNO_3 and then the oxidized multi walled carbon nanotubes were modified with 1-(2-pyridylazo)-2-naphtol. The sorption is quantitative in the pH range of 4.5-6.5, whereas quantitative desorption occurs instantaneously with 6.0 mL of 2 mol L^{-1} HNO_3. The concentration of cadmium, copper, lead and nickel in eluent was determined with flame atomic absorption spectrometry. The results showed that the soil concentration of these metals in greenhouse were higher than geochemical baseline concentration.

PC – 018

Exploring the potential of ICP-MS as analytical tool for detecting silica nanomaterials employed in the food sector

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Engineered inorganic nanomaterials (iENMs) are being manufactured in ever increasing quantities and finding a wide range of food-related applications, including food ingredients, additives, supplements and contact materials. Assessing the potential risk of iENMs requires methods of analysis that can be successfully employed in experimental studies addressing their interaction with biological systems. Characteristics of iENMs that affect their behaviour and toxicity include size, shape, surface properties, aggregation state, solubility, mass concentration and elemental composition.

Among the analytical tools used to determine relevant properties in nanotoxicological studies, ICP-MS plays a major role. It can be used as a detector of unparalleled sensitivity for the measurement of the mass concentration of iENMs in biodistribution studies, whereas hyphenated ICP-MS based techniques have a tremendous potential as characterisation tools. So far, ICP-MS has been used primarily for the detection and characterisation of iENMs based on such elements as selenium and noble metals. Application to oxide nanomaterials, such as SiO_2, has been hampered by analytical challenges, i.e., high background and substantial spectral interferences. Solutions to overcome these issues will be described along with relevant applications, focusing on studies on the potential health risk of silica ENMs employed in the food sector.

PC – 019

Flow field-flow fractionation / capillary electrophoresis – multidetection for uranium colloidal transport in soil

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Colloids have an important role in the environment because of their mobility, reactivity and transfer in geochemical systems. Colloid size and shape are key parameters that control their interaction with other environmental chemical species [1] and their role in the transport of trace element like heavy metals [2], pesticides [3] or actinides [4]. However, because of their diversity, small size and low concentration, the characterization of colloids needs convenient analytical tools. Hyphenated methods allow, with a few number of analytical steps, to obtain complementary information relevant for environmental studies with complexes matrices.

This study is focused on characterization strategy of colloidal phase of agricultural soils. This strategy involves capillary electrophoresis (CE) and flow field-flow fractionation (Fl-FFF) coupled to multi-detection techniques such as ultraviolet (UV), multi-angle laser light scattering (MALLS) and atomic mass spectrometry (ICP-MS). Shape distribution, mobility and chemical composition are estimated. Colloidal distribution of uranium is studied too. The main difficulty with CE is due to the impossibility to on line characterize the colloidal fraction. Thereby, to overcome this limitation a specific analytical strategy combining ultrafiltration Fl-FFF and CE was used. According to the sol nature, one or two colloidal fractions are identified between 1 and 450 nm. Uranium is mainly associated with the Al-rich colloidal fraction < 50nm. Fl-FFF-UV-MALLS and EC-ICP-MS couplings, allow the characterization of colloidal phases and the study of uranium-colloid association. This analytical strategy based on hyphenated method is a helpful key in the study of the role of colloid in the transport of trace element.

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4° - Metal speciation in the environment and legal aspects PC – 020

Survey of total Arsenic and Arsenic species in Italian rice

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Arsenic toxicity depends on the chemical form. Inorganic arsenic is more toxic than organic arsenic and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic. Generally rice, unlike food products of terrestrial origin, contains significant amounts of inorganic arsenic. Recently some Government Organizations (e.g. EFSA) debated the possibility to set an upper limit for total and inorganic arsenic in rice.

Arsenic speciation was realized in 70 Italian rice samples from different representative cultivation conditions. The adopted method was effective in preserving the arsenic species and suitable for routine analysis of large numbers of samples. Pulverized rice grains (approx. 1.5 g) were mineralized using HNO_3 0,28 M at 95°C for 90 min in a heating block system. The digested samples were filtered under vacuum-assisted sample filtration in order to obtain a faster and more complete filtration, with lower sample preparation time and sample manipulation. The HPLC-ICP-MS technique was used to measure the different arsenic species [arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)], which were separated using an anion-exchange column. It was possible to separate and analyze the four arsenic species in only 9 minutes. The sum of As(III) and As(V) is known as inorganic arsenic. Total As concentration in samples was determined directly by ICP–MS.

Certified reference material, NIST 1568a rice flour and IMEP 107, for total and inorganic As in rice, were included for quality assurance. Moreover, the sum of As(III), As(V), MMA, and DMA was compared with total arsenic and resulted similar.

The most abundant species in rice were As(III) and DMA. Total arsenic levels in the 70 Italian rice samples averaged 0.16 $\mu g\ g^{-1}$ (range 0.06-0.60 $\mu g\ g^{-1}$); inorganic arsenic averaged 0.10 $\mu g\ g^{-1}$ (range 0.04-0.16 $\mu g\ g^{-1}$). The percentage of inorganic arsenic tended to decrease with increasing the total arsenic.

PC – 021

Speciation of arsenic and selenium in surface water by anion-exchange chromatography SF-ICP-MS

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Within the framework of various international River basin programs arsenic pollution is monitored in Dutch surface waters among other matrices. Selenium is monitored on a national basis. To determine the impact on the aqueous environment of the amounts present (national) environmental quality standards are used. Current research into the speciation of both elements should lead to a better understanding of the extent of pollution, because toxicity of the various species differs extensively. This approach is expected to be incorporated into future legislation frameworks.

In relation to this a method for simultaneous determination of seven arsenic and selenium species in filtered surface water has been developed. Separation of arsenobetaine (AsBet), arsenite (As(III)), arsenate (As(V)), dimethylarsenic acid (DMAA), monomethylarsonic acid (MMAA), selenite (Se(IV)) and selenate (Se(VI)) was performed using anion-exchange chromatography coupled to SF-ICP-MS. A PRP-X100 column was used to separate the seven species within 15 minutes with ammonium carbonate as mobile phase. The arsenic and selenium species were quantified at m/z 75 and 82 respectively in low resolution mode ($M/\Delta M = 300$). Interferences of chloride ($^{40}Ar^{35}Cl$) on m/z 75 and bromide ($^{81}Br^{1}H$) on m/z 82 were chromatographically separated from the arsenic and selenium species. Samples with high chloride content have to be diluted prior to analysis to prevent a shift in retention times of the early eluting species and peak overlap with MMAA. Limits of detection were determined under reproducibility conditions in real surface water samples. For As(V) a LOD of 20 ppt was achieved, for all other species the LOD amounted to 5 ppt.

Surface water samples from different locations in The Netherlands were analysed. Spatial and seasonal variations in amounts as well as ratios (*i.e.* Se(IV)/Se(VI)) were observed. Future research will focus on assessment of the consequences for the aqueous environment.

PC – 022

Mercury speciation analysis in seafood by species-specific isotope dilution: method validation and occurrence data

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Human exposition to MeHg via fish consumption is a subject of great concern as this species is the predominant form of Hg in seafood and is particularly toxic. In this study, determination of mercury speciation in seafood was performed using multiple isotope dilution analysis (M-IDA), i.e. a technique of quantification that permits to detect and correct the final results from species losses and non-quantitative extraction, and gas chromatography coupled with inductively coupled plasma mass spectrometry (GC-ICP-MS). The goal of this project was to develop and validate an accurate method, based on isotopic dilution, which can be used as a reference analytical technique by government agencies to determine the speciation of Hg in seafood and seafood products.

In this work, the influence of three steps of the method of sample preparation (spiking procedure, extraction and derivatization) has been studied on certified reference materials (TORT-2 Lobster Hepatopancreas, DOLT-4 dogfish liver and BCR-464 tuna fish). The results have shown that the most efficient method was to spike the sample with isotopic labeled species before extraction by tetramethylammonium hydroxyl (TMAH) with a *digi*PREP device and derive them by propylation with a rotative agitation. The optimal method has then been validated using the same MRCs regarding limit of detection, fidelity and accuracy profile according to the recent French standard NF V03-110. The validated method has been applied on real samples of the second French Total Diet Study (TDS) to demonstrate its applicability on real samples and to estimate occurrence data.

PC – 023

Copper concentration in soils of the wine-producing Aquitaine region, France

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In 1878, a parasite (*Plasmopara viticola*), called downy mildew, was introduced into the southwest of France and colonized all European vineyards. To fight against this fungus, copper (Cu) based fungicides have been applied extensively in wine-growing areas. Bordeaux mixture is the most commonly used product on vine**.** It results from the mixture of copper sulphate ($CuSO_4$, $5H_2O$) and lime ($Ca(OH)_2$). A long term application of copper-based fungicides to fight against downy mildew has lead to a soil contamination by this element. This work has for objective to understand at different scales copper behavior:

3. At regional scale (Aquitaine): to show that copper contamination is closely related to the presence of wine-growing. For this purpose, two national databases have been crossed: the French test soil database (BDAT*) and the national census of agriculture (RGA**). A statistical approach was used in order to determine the relationship between copper extracted by EDTA in cultivated topsoils of Aquitaine region and vineyard area in relation with used agricultural area.

4. At local scale i.e. wine-growing area: to evaluate soil contamination by copper, different methods are used: total copper, copper extracted by EDTA (assimilated to bioavailable copper), and copper extracted by $CaCl_2$ (assimilated to exchangeable copper) , . Then, soils profiles relative to copper concentration were determined. Complementary, the main physico-chemical parameters were considered in a statistical approach in order to evaluate their relative influence on copper contamination.

**Base de Données des Analyses de Terre*

***Recensement Général Agricole*

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PC – 024

Assessement of the heavy metals contens in soil and vegetables in some ecological system, 2010

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The authors present the research results obtained in 2010 in SIECOLEG Project (stage 3) regarding the assessment of some heavy metals (lead, cadmium, cooper) of 80 samples soils and 25 samples vegetables from some ecological system. The concentrations of heavy metals (Pb, Cd, Cu, Mn) in some matrix (soil, vegetable) were measured by using Schimadzu 6300 Atomic Absorption spectrometer (AAS) with graphite furnace atomizer and autosamples.

The concentrations of heavy metals in samples analysed (soil, vegetables) were in admissible limits.

PC – 025

Arsenic speciation at the molecular level in the indoor and outdoor materials of an abandoned Pb-Zn mine (Lanestosa, Biscay, north of Spain). Implications for natural environmental impacts

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The abandoned mine under study is located in a hill at 650 mts. above sea level, near the Lanestosa village (Biscay, north of Spain). This was a Pb-Zn (sulphide minerals around a calcite-dolomite environment) mine and was in operation till 1950. Since that time, some efflorescences and new mineral phases have been formed in the abandoned galleries. We have sampled those materials and compared them with the materials found at open air, in the mountain, but in a vertical position with regard to the abandoned galleries. The differences observed in the composition of both indoor and outdoor materials can be attributed to the formation of new mineral phases (re-precipitation of new solids from the dissolved cations and anions that percolate from the top of the mountain through the abandoned galleries). Chemical modeling can be used to identify possible reactions that explain the transformation from the original materials found outside to the new mineral phases found in the galleries. In particular, we have measured the acidity of the snow in the winter campaigns and found the pH to be 4.0±0.2.

Among the different metals, Arsenic shows a wide variety of species for both As(III) and As(V) oxidation states. The molecular speciation was performed by Raman spectroscopy (In-Via Renishaw microspectrometer, fitted with a 514 nm excitation laser).

The predominant Arsenic species found outside were those of As(III), namely arsenopyrite (FeAsS), claudetite (As_2O_3), getchellite ($AsSbS_3$), leiteite ($ZnAs_2O_4$) and orpiment (As_2S_3), while inside the abandoned galleries As(V) species were mainly detected, like erythrite ($Co(AsO_4)_2.8H_2O$) and olivenite ($Cu_2AsO_4(OH)$). Chemical simulations were performed to explain the conditions required to dissolve arsenic species outside and then re-precipitate new arsenic species inside. The standard oxygen concentration in the atmosphere and the high CO_2 content are enough to explain oxidation of As(III) species in the surface of the outside materials and further dissolution at pH lower than 8 (neutralization of carbonate phases with carbonic acid).

PC – 026

Copper speciation by Raman Spectroscopy of green-blue stalactites in Lantz cave (Navarra, north of Spain)

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Speleothems (stalactites, stalagmites and columns) are typically associated with mineral precipitation in the dark, enclosed environments of caves, and their growth is controlled by climatic factors and vegetation cover.

Lantz Cave is located between a large number of relatively small caves used by Romans with mining purposes, 2.5 Km far away from the village of Lantz (Navarra, north of Spain). The speleothems of the cave vary widely in their morphology and mineralogy causing different shapes. This study was focused on green coloration of stalactites. Water samples were sampled and measured by ICP-MS for the quantification of trace elements (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Ba and Pb). Furthermore, concentration ratios between the speleothem waters and freshwater in the cave were calculated. According to the results, trace element concentrations vary between dripping waters of the green stalactites and waters from other parts of the cave, being copper the element having a completely different behavior in comparison with the rest of the analysed, maybe due to the possible accumulation of this metal in the speleothems.

Thus, molecular copper speciation in speleothems was investigated by Raman spectroscopy measurements performed directly on the surfaces, using an InnoRam® handheld spectrometer (B&WTEKINC, Newark, USA) provided with a 785 nm excitation laser (nominal power of 225 mW) and a CCD detector.

In addition to the predominant aragonite (small and large crystals), calcite (columnar, fiber, and grain coating mats) and dolomite, some copper minerals were identified. These minerals were of Cu(I) and Cu(II) species (see Figure), like cuprite (copper(I) oxide, Cu_2O), tenorite (copper(II) oxide, CuO) and azurite (basic copper carbonate, $2CuCO_3(OH)_2$). Hollandite ($BaMn_8O_{16}$), quartz and carbon particles were also found in the samples. Moreover, the presence of the elements involved in the mentioned compounds was ascertained by means of X-ray Micro-Fluorescence measurements (μ-EDXRF, Rontec nowadays Brucker AXS; Berlin, Germany).

Finally, a chemical modeling was performed using the concentrations found in waters (dripping and fresh water) and the solid phases detected in the speleothems. The thermodynamic speciation studies confirmed the chemical stability of the copper species (molecular speciation) detected by Raman spectroscopy.

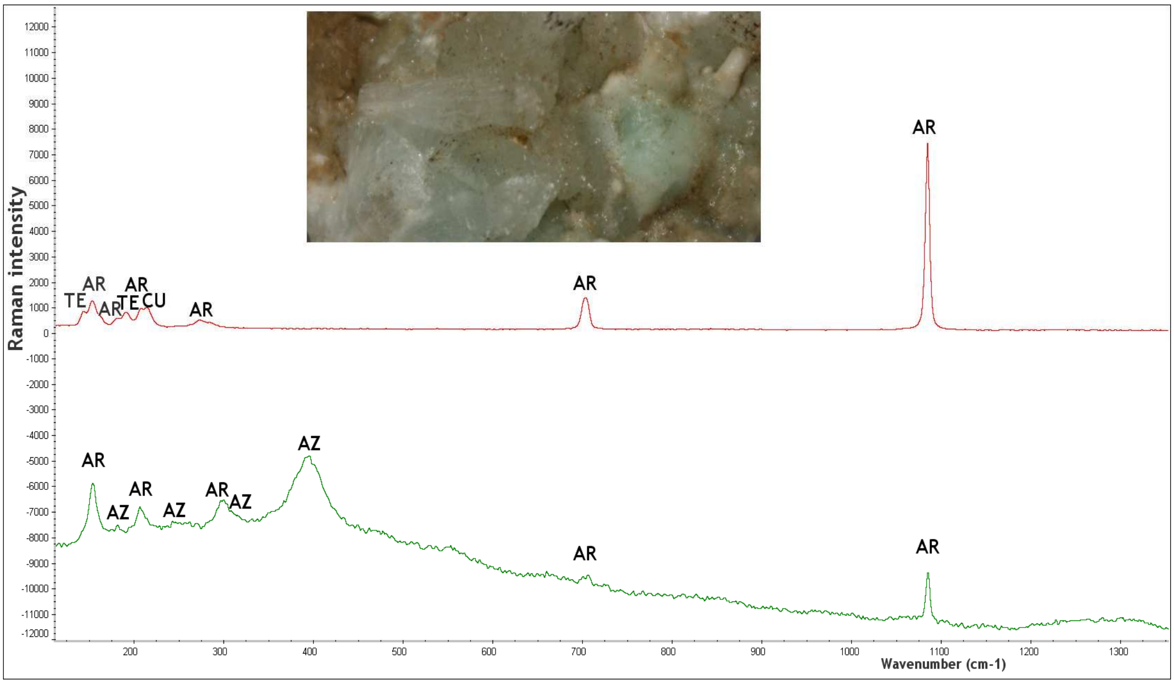

Figure.- Raman spectra of samples of green-blue stalactite from cave of Lantz; AR: aragonite, $CaCO_3$; TE: tenorite, CuO; CU: cuprite, Cu_2O and AZ: azurite, $2CuCO_3Cu(OH)_2$.

Acknowledgements

This work has been financially supported by the Basque Government through the Environmental Analytical Chemistry Project 2007–2012 (Ref. IT-245-07). Authors thank Esteban Faci and Gobierno de Navarra (Departamento de obras Públicas, Transportes y Comunicaciones) for the support.

PC – 027

Chromium speciation by Raman Spectroscopy of black slags wastes deposited in forest tracks since 20 years ago

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Black slags are by-products coming from the steel production by fusion process by means of electric arc furnace (EAF). Due to the high quantity that are produced, approximately 16 mT/year of steel slags in Europe[1], producers have used those "inert wastes" in several applications such as aggregate in bituminous mixes, concrete aggregate[2,3], agricultural uses, forest track[4]… Some uses mixed the slag with other materials in close containers (roads, concrete,..) but others left the slag to the open air for years. Consequently, the release of trace metals from those slags left to the open air can be a potential problem for our surrounding environment.

In this work black slags sampled in a forest track (Basque Country, Spain) have been analysed. Before use, the slags suffered a treatment at the steelworks consisted of outdoor cooling by water, crushing and sifting; any magnetic separation of ironed materials was done thus, slag samples having a visible amount of oxidised iron are common in the forest track analysed. The molecular characterization (speciation) of these samples was performed by Raman Spectroscopy using both: (a) an InnoRaman handheld B&WTEK$_{INC}$ spectrometer and (b) a Renishaw InVia micro-Raman unit.

The samples are highly carbonated (calcite) thus, a basic environment (pH>11) covers all the trace metals. Among them, some species of chromium(III) and (VI) were identified, like chromite ($FeCr_2O_4$) and hashemite ($BaCrO_4$) (see Figure).

Other species of iron(II) and/or (III) were clearly distinguished like magnetite, lepidocrocite, hematite and goethite indicating that samples are highly oxidised. As a conclusion, the high stability of the most risky species ($BaCrO_4$) can be ascertained as far as the calcium carbonate guarantees its insolubility. But if the basic calcite is neutralised (by atmospheric CO_2 or other acid), both Cr(III) and Cr(VI) species will be released by rainfalls to soils and waters around the forest track.

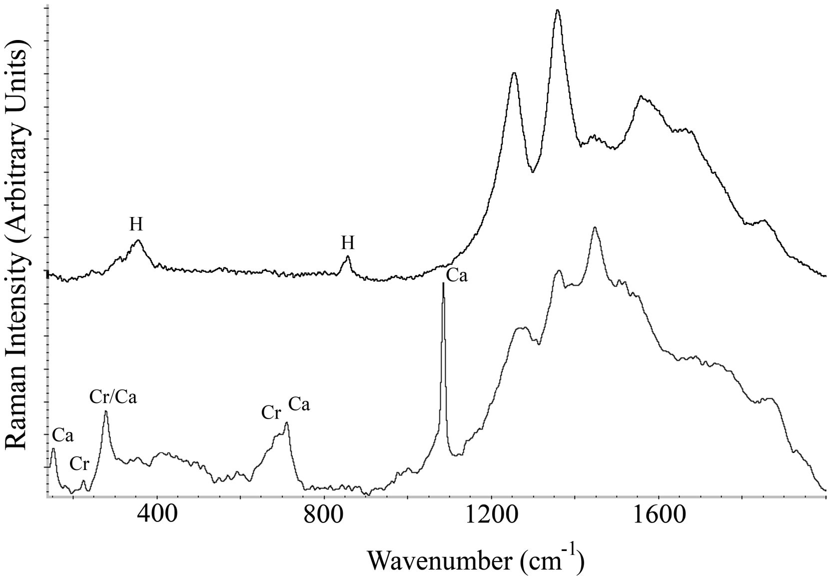

Figure. Raman spectra of black slags from the forest track; Cr: chromite ($FeCr_2O_4$), Ca: calcite ($CaCO_3$) and H: hashemite ($BaCrO_4$).

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Acknowledgements

This work has been realized thanks to the financing for Basque Government through ETORTEK BERRILUR 3 project (ref. IE10-273). L. Gomez -Nubla and J. Aramendia are grateful to the University of the Basque Country (UPV/EHU) and Basque Government respectively, for their pre-doctoral fellowships. Technical and human support provided by the Raman-LASPEA Laboratory of the SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged.

PC – 028

Analysis and speciation of Metals in Seawater using a portable voltammetric system

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As a result of the OSPAR convention (1998) and The Water Framework Directive of the European Parliament (2000/60/EC), the concentrations of metals and their inputs into seawater must be monitored by each country of the European Union. While some metals act as micronutrients for marine species, most metals are toxic at high concentrations. Metal speciation is also crucial: both bioavailability and toxicity are highly dependent on speciation. The use of anodic and cathodic stripping voltammetry can permit the determination of both the total concentration of a given metal and the concentration of uncomplexed metals. This project is using existing voltammetric methods to develop a portable and semi-autonomous voltammetry system capable of making measurements of multiple metals simultaneously in marine waters over a tidal cycle using ASV, and of carrying out speciation analysis using CSV. The instrument was deployed in semi-automatic mode at an aquaculture research station in the west of Ireland (MRI Carna) to study on site the evolution of concentrations of metals during a tidal cycle. Concentrations of the four metals and the variation of these throughout growth cycles of microalgae produced as food for zooplankton and fish raised in this facility were also studied. This work has been funded by Science Foundation Ireland (SFI).

PC – 029

Speciation and reactivity of mercury in natural waters (Adour estuary-Bay of Biscay) by using species-specific isotopic traces and GC-ICP-MS

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The chemical speciation of Hg in natural waters governs its biogeochemical behaviour and bioavailability. Along estuarine – coastal continuum, mercury may undergo significant changes in speciation due to changes in salinity regime, properties of the dissolved organic matter and photochemical reactivity. These important changes within a river discharge coastal plume will drastically control the net amount and bioavailability of monomethyl Hg (MeHg) transferred to the coastal zone via both biotic and abiotic methylation, demethylation and redox processes.

The objective of this work is to investigate the distribution of Hg species in coastal water samples and to characterize the role of coastal mixing zone in the reactivity of Hg. We are reporting results from two campaigns focused on the behaviour of ($MeHg^+$, Hg^{2+}) in the Adour estuary (South Bay of Biscay). The concentration of Hg species, filtered, unfiltered and particulate ($MeHg^+$, Hg^{2+}) were measured by using species-specific isotope dilution GC-ICP-MS and gaseous Hg species (Hg° and Me_2Hg) were performed by cryogenic trapping hyphenated to ICP-MS. Concentrations of filtered $MeHg^+$ and Hg^{2+} and unfiltered $MeHg^+$ measured in April 2007 are consistent with thous measured in May 2010.

The concentration of Hg species in water is related to the processes of chemical transformations (methylation, demethylation and reduction mechanisms). Thus, specific water incubation experiments (24h), using two isotopes ($^{199}Hg^{2+}$ and $Me^{201}Hg$) were exposed to sunlight or dark to investigate the photochemically induced transformation analysis processes. Additionally, filtered or unfilterd water samples are applied to discriminate abiotic processes that mediated by the plankton biomass. Methylation remains low within the estuarine plume (yield range: 0-0.4 %/day) while, MeHg is efficiently demethylated via biotic and abiotic pathways (6-50 %/day).

5° - Speciation in industrial applications PC – 030

Speciation of phosphorus decomposition products in a lithium ion battery electrolyte system

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For most commercial available batteries lithium, hexafluorophosphate ($LiPF_6$) is established as the conducting salt. Based on the high hygroscopicity of $LiPF_6$, such systems are always contaminated with a certain amount of water that accelerates decomposition of the conducting salt to LiF and PF_5, which subsequently may release hydrofluoric acid (HF). These first decomposition products, especially HF and PF_5, have a negative influence on the performance of the lithium ion batteries[1] and can further act as catalysts for the decomposition of the electrolyte.[2, 3]

This work focuses on the decomposition of the conducting salt and its reaction with the organic carbonates in the electrolyte system. For this purpose, samples were stored at 60°C and 95°C for several weeks and were continuously analyzed during this time. The characterization of the decomposition products was carried out by ion chromatography coupled to inductively coupled plasma optical emission spectrometry (IC/ICP-OES) and verified by ion chromatography coupled to electrospray ionisation mass spectrometry (IC/ESI-MS).

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6° - New analytical strategies for metal speciation including isotopic information PC – 031

A spatial analysis of mercury concentration and isotopic ratio in lichens from South Western France (Pyrénées-Atlantiques) (Session G2)

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A recent study demonstrated that analysis of the dispersion of mercury isotopes in epiphytic lichens can distinguish local anthropogenic sources of contamination and background atmospheric inputs (variable deficit in odd isotopes). The project proposes to study the variability of mercury atmospheric contamination in lichens of the Pyrénées-Atlantiques (South-West of France), a mesoscale area exhibiting urban, rural, mountain range and coastal land type. To this end, a purposive sampling was conducted in the area including geographic information system data output to take into account the different characteristics of such as population density, water balance and distance to the ocean. Different geographical areas were identified as urban, industrial, agricultural and forest where various species of lichens were collected such as *Usnea sp., Evernia Prunastri, Parmelia Sulcata et Lobaria pulmonaria,* and mixed in order to be representative of the biological diversity of each sampling site. Selected sample collection was also carried out during two different seasons (spring and fall). Comparison of mercury concentrations in lichens indicates relatively low levels over the Pyrénées-Atlantiques indicating no significant sources of contamination (from 0.038 to 0.160µg/g). Nevertheless, the isotopic composition of lichens determined by MC-ICP-MS may reveal a contribution of local sources for lichens collected in urban and industrial zones. Instead lichens taken away from these sources (agricultural and forestry areas) exhibit a background pollution linked to global atmospheric mercury inputs.

This study demonstrates that mercury isotopic composition, in opposition to mercury concentration, measured in lichens from less polluted area may provide a better discrimination of mercury atmospheric contamination pathways. The possibility of identifying sources of contamination despite similar concentrations of mercury in the investigated area will be discussed taking into account various geographical parameters available from each sampling sites.

PC – 032

Gel electrophoresis coupled to laser ablation - ICP MS in selenoprotein determination – a comparison study

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The use of laser ablation (LA) coupled with plasma mass spectrometry (ICP MS) for sensitive detection of heteroatoms in proteins separated by gel electrophoresis (GE) have been rapidly becoming a method of choice in metalloproteomics [1]. This method is especially attractive in studies of proteins containing covalently bound heteroatoms, such as selenoproteins, since conventional sample preparation procedures and GE separations can be used to the efficient extraction and separation of these proteins [2].

Despite its growing popularity, LA - ICP MS still suffers from some problems mainly due to the small amount of protein effectively trasfered to the plasma. Several instrumental approaches have been described in the literature for sensitive probing of selenoproteins in real life samples including bacteria [3], catfish fillets [4] and human plasma [5].

The presentation shows results of the comparison study of three different instrumental setups for quantitative analysis of selenoproteins in electrophoretic gels and blots. The performance parameters including detection and quantification limits, linearity and influence of the experimental conditions on the signal are reported and compared.

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PC – 033

Metal speciation in *Pisum sativum* (green pea) through the association of LC ICP-MS and LC ESI-LTQ Orbitrap MS couplings

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Metals play vital roles in life cycle of plants. They are usually complexed to organic molecules and are essential for metabolism of plants, especially for maintaining homeostasis or enzymatic activity. However, both excess and deficiency of metal may lead to severe toxicity because of metal substitutions in enzymes, inhibition growth or oxidative damage. For these reasons, plants developed several mechanisms to increase or decrease metal intake and accumulation. Producing metal complexing metabolites as well as membrane proteins involved in metal transport and compartment for storage allows them maintaining fragile balance between essentiality and toxicity of metals.

To date, little is known on molecular forms of metabolites involved in transport and storage of essential metals in plants because the identification of element species in plant fluids encounters a few obstacles. The two major are the low concentration of metal complexes and their various labilities during sample preparations and chromatographic separations. However, the combination of hyphenated techniques is an efficient tool for the investigation of metal speciation in plant fluids. Due to high sensitivity and spectral selectivity for element isotopes and for isotopic profile of molecules containing the elements of interest, LC-MS coupling either with an ESI-LTQ Orbitrap MS or with collision cell ICP MS were chosen (for high resolution molecular mass spectrometry and elemental mass spectrometry, respectively). Using an Orbitrap instrument allowed to obtain high resolution spectra, which were searched for metal specific isotopic pattern, for mass defects, for mass differences with chemical analogs or demetalated ligands (with or without postcolumn acidification) and, moreover, for inter-isotopic mass defects/ratio - a new tool to distinguish the presence of compounds containing multi-isotopic elements in complex mass spectra.

Speciation of various elements present in samples of post-phloem and xylem of *Pisum sativum* (green pea) were achieved by online coupling of size exclusion column (SEC) and hydrophilic interaction column (HILIC) to MS instruments. Several novel metal complexes with low concentrated elements (Fe, Zn, etc.) and trace elements (Cu, Mo, W, etc.) could then be identified.

PC – 034

Application of a ^{13}C-labeled calibration standard for the analysis of arsenobetaine in fish using HPLC-ESI-MS/MS

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There is an immense interest on the analysis of organic forms of arsenic due to the variety of species and their differences in toxicity and mobility. The high toxicological potential of inorganic arsenic species is known to cause adverse health effects. Methylated organic arsenic species like monomethylarsonic acid and dimethylarsinic acid possess lower toxic effects but are carcinogenic. Arsenobetaine and arsenocholine are the major arsenicals in seafood and were supposed to be nontoxic, but new studies indicate that they are transformed or metabolized *in vivo* to more toxicologic relevant species.

HPLC-ICP-MS has been established as a reference method for the analysis of arsenic species. However, the increasing numbers of publications on real samples show the shortfall and limitations of this technique. Namely the risk of co-eluting species combined with retention time irreproducibility poses a risk of misidentification. In the presence of unidentified species it is impossible to classify them if reference substances are not available. Additionally, the ICP-MS is not as prevalent as other detection techniques because of its higher-than-average expenses for purchase and operation. Moreover, monoisotopic arsenic is not applicable for isotopic dilution mass spectrometry (IDMS) with ICP-MS.

Using LC-ESI-MS deuterated or ^{13}C-labeled species can be used as internal standards. Hydrogen labels like ^{2}H or ^{3}H are known to induce isotope effects like deuterium-hydrogene exchange. Therefore stable isotope tracers of choice are ^{13}C-labeled species.

Our aim was to develop, characterize and evaluate a new approach based on a ^{13}C-labeled arsenobetaine ((trimethylarsonio)-1, 2-^{13}C-acetate, figure 1) calibration standard. For the first time the synthesized standard was used in real samples during an international interlaboratory comparison and helped to establish an HPLC-ESI-MS method as an economic alternative for the species analysis of arsenic compounds. We can clearly demonstrate that this standard is a powerful tool to assist the determination, quantification and monitoring of arsenic species in complex seafood matrices like mackerel, tuna fish or herring. Finally ESI-MS/MS is a reliable technique to quantify arsenic species by using a defined multiple reaction monitoring (MRM), a standard application for quantitative LC/MS/MS measurements.

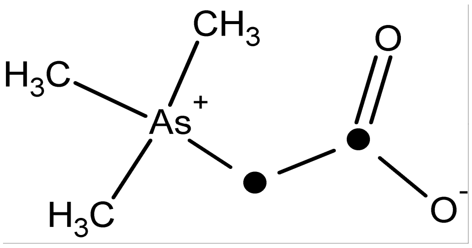

Figure 1: Structure of (trimethylarsonio)-1,2-^{13}C-acetate, the black dots symbolize the ^{13}C-positions.

PC – 035

Elemental (Sr:Ca, Ba:Ca) and $^{87}Sr:^{86}Sr$ isotopic signatures in otoliths by LA-MC-ICP-MS record natal origins of Atlantic salmon from the Adour basin

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Geochemical signatures recorded in calcified tissues of fishes have the potential to resolve outstanding questions about dispersal, rates of natal homing and migration dynamics of a wide variety of anadromous and catadromous species. Because otoliths are metabolically inert, accrete discrete layers incrementally, and incorporate some isotopes and elements in proportion to their ambient abundance, they can serve as useful natural tags that reflect the environmental history of a fish. In order to reconstruct early life-histories of Atlantic Salmon (*Salmo salar*) such as rates of natal homing or contribution of hatchery breed fish on the native wild stocks within the large Adour basin system, a spatial baseline of isotopic and elemental signatures was developed by targeting $^{87}Sr:^{86}Sr$ and concentrations of Sr, Ba and Ca within otoliths of juveniles accreted in natal streams (catchment basin of Oloron and Pau rivers) and hatcheries using LA-ICP-MS and LA-MC-ICP-MS. The combination of three elemental and isotopic signatures in otoliths yielded highly distinct river-specific signatures and was used successfully as natural tags to identify, first adult fish from hatchery or naturally spawned sources, second rivers of growth during juvenile stage. The addition of strontium isotope ratios has increased estimates of classification accuracy and rates of natal homing beyond that generally achievable based only on elemental ratios.

PC – 036

Using the potential of multiple isotopic tracers spiking methods to study mercury species bioaccumulation in earthworms

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Earthworms have a demonstrated ability to efficiently accumulate heavy metals from soils and, as a result, they are suggested to be an appropriate tool to predict bioaccumulation of trace metals, such as mercury (Hg), in the terrestrial food chain. However, metallic and inorganic mercury (IHg) do not bioaccumulate in terrestrial organism to the degree that monomethylmercury (MeHg) does. Therefore, studies aimed at understanding the bioaccumulation of Hg species in earthworms require precise and accurate determination of both MeHg and IHg avoiding the interconversion and/or degradation processes between Hg species. In this sense, the use of isotopically enriched species in combination with highly sensitive measurement methods, such as gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS), becomes a good alternative for the study of Hg speciation and reactivity in terrestrial invertebrates.

In this study, the potential of multiple isotopic tracers spiking methods has been used in combination with GC-ICP-MS analysis for two main purposes. Thus, the uptake and bioaccumulation of Hg species for earthworms exposed to naturally Hg contaminated soils has been studied using species-specific isotope dilution which has allowed correcting the transformation reactions that Hg species may undergo during the chemical analysis. On the other hand, exogenous labeled IHg was used as tracer to evaluate the extent of the reactions occurring during the exposition of the earthworms to naturally Hg contaminated soils spiked with isotopically enriched IHg. Furthermore, it has been possible to follow the evolution of both naturally occurring (endogenous MeHg and IHg) and isotopically enriched added (exogenous ^{199}IHg) species during uptake and depuration periods. In addition, differences on the Hg methylation and demethylation pathways for earthworms exposed to different Hg contaminated soils are discussed.

PC – 037

Validation of the analytical procedure for preparation of stable Cr(VI) and Cr(III) isotopic standard solutions from ^{50}Cr and ^{53}Cr enriched oxides

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Precise isotope ratio measurement by ICP-MS enables quantification of trace elements in environmental and biological samples. In combination with chromatographic procedures, species transformation may be followed in different environmental compartments and also during the analytical procedures.

Cr and its compounds are widely used in different industrial applications, so it is frequently present as a pollutant in the environment. The most stable Cr forms in the environment are Cr(III) and Cr(VI) oxidation states. The use of enriched stable isotopes as tracers in speciation procedures by ion-exchange chromatography coupled to ICP-MS provides opportunity to follow the oxidation – reduction processes of Cr(III) and Cr(VI) and to investigate the fate of Cr in the environment and biota.

The most commonly available Cr stable isotopes are ^{50}Cr and ^{53}Cr enriched oxides. For application of Cr enriched stable isotopes, adequate preparation of isotopic spike solutions is necessary. To fulfil that Cr speciation in the sample investigated is not disturbed, no excess of the reducing neither oxidising agents should remain in the isotopic spike solutions. Cr(VI) isotopic solutions are in general prepared by dissolving the Cr(III) oxide in $HClO_4$, followed by the addition of ammonia and H_2O_2 to quantitatively oxidise Cr, while the excess of H_2O_2 is removed by boiling. The procedure is time consuming and the risk exists that in the isotopic spike solution the excess of H_2O_2 still remains. Such isotopic spike solution may possibly influence the Cr speciation in the sample investigated.

In the present work procedure based on melting of Cr(III) oxide for quantitative preparation of ^{50}Cr(VI) and ^{53}Cr(VI) enriched spiking solutions is reported. The procedure for digestion of Cr(III) oxide to quantitatively prepare ^{50}Cr(III) and ^{53}Cr(III) enriched spiking solutions is also presented. The validation of the procedures for quantitative preparation of pure Cr(III) and Cr(VI) enriched stable isotope spiking solutions was verified by the speciation analysis. For this purpose anion-exchange FPLC was hyphenated with ICP-MS to simultaneously detect the separated ^{50}Cr and ^{53}Cr enriched stable isotopes of Cr(VI) and Cr(III). Speciation analysis demonstrated the suitability of the proposed procedures for the preparation of Cr isotopic spiking solutions. In addition, the artefacts in Cr speciation, which may be initiated by the traces of oxidising and/or reducing agents present in Cr enriched spiking solutions, are also shown. The outcomes of our investigation highlighted the importance of the adequate preparation of spiking solutions of Cr stable isotopes that may be used as reliable tracers in the investigations of the oxidation-reduction processes of Cr in wide range of environmentally relevant pH values.

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