

# **OPENING AND PLENARY LECTURES**

*Amphitéâtre du Muséum d'Histoire Naturelle*

**OPENING - Tuesday 9<sup>th</sup> July, 9:00**

*Chair: F. De Vleeschouwer*

***Green revolution and global cycling of metals  
in the environment***

by Jerome Nriagu

**PLENARY - Tuesday 9<sup>th</sup> July, 9:45**

*Chair: J. Sonke, L.-E. Heimbürger, L. Maurice, C. Dufour*

***Methylation of mercury in the ocean: Insights  
from measurements and models***

by Robert Mason

***PLENARY - Wednesday 10<sup>th</sup> July, 9:00***

*Chair: K. Francesconi*

***Arsenic removal from groundwater by household sand filters in Vietnam***

by Andreas Kappler

***PLENARY - Thursday 11<sup>th</sup> July, 9:00***

*Chair: C. Dumat*

***Developments in the estimation of human exposure to potentially harmful substances in soil using bioaccessibility measurements***

by Mark Cave

***ABSTRACT BOOK***  
***Sorted by Session and Schedule***

***Topic 1***  
***Biogeochemistry and Health***  
***(including cross topics 1-2 and 1-3)***  
***Oral Presentations***

# ***Green revolution and global cycling of metals in the environment***

Jerome Nriagu<sup>1,@</sup>

**1** : Department of Environmental Health Sciences, School of Public Health  
*University of Michigan Ann Arbor, MI 48109 - United States*

The first “Green Revolution” involved the development of high-yielding varieties of cereal grains, expansion of irrigation infrastructure, modernization of management techniques, distribution of hybridized seeds, synthetic fertilizers, and pesticides to farmers and has been credited with saving over a billion people from starvation. The presentation will focus on influence of Green Revolution on the environmental cycling of trace metals at the regional and global scales. It is argued that the Revolution has dramatically reduced many essential trace metals (especially zinc, copper, cobalt and iron) while increasing the toxic metals/metalloids (arsenic, mercury, vanadium and molybdenum and cadmium) in our food supply. The changes in dietary intake of trace metal are believed to be exerting a significance (deleterious) influence on the health of human populations in many parts of the world. I argue that the benefits of the First Green Revolution are over-emphasized and full accounting of the negative costs are necessary as the Second Green Revolution is being contemplated.

# New regional geochemical data from Ireland: investigating trace element distributions in topsoil and potential agricultural impacts

Katherine Knights<sup>1,@</sup>, Mairead Glennon, Ray Scanlon<sup>@</sup>

1 : Geological Survey of Ireland (GSI) - **Website**  
Beggars Bush, Haddington Road, Dublin 4 - Ireland

The Geological Survey of Ireland has recently completed regional-scale surveying of soils, stream sediments and stream waters geochemistry across the northern region of Ireland under the *Tellus Border* project. A survey of neighbouring Northern Ireland was completed in 2007 and multi-element analytical data are currently being integrated to provide seamless cross-border mapped datasets.

High density multi-element topsoil geochemical data have been systematically collected (at a density of 1 sample per 4 km<sup>2</sup>) in Ireland and are now made freely available via the web[1]. An objective of the geochemical surveys is to measure and map the distributions of trace elements in the surface environment, and to describe their sources and mobilities. A number of agricultural animal health and trace elements issues are known; such as excessive molybdenum (Mo) and associated inhibition of copper (Cu) in cattle and sheep; and zinc (Zn) and copper (Cu) deficiencies over acidic soils in upland areas including commonage land widely used for sheep grazing. The bedrock lithologies, parent materials and land use are under investigation in terms of attributing sources and controls on distribution of these elements. New data, for example for Mo, reveal much improved spatial representation of potentially excessive Mo across shales, limestones and greywackes in Ireland, an improvement upon previous lower-density soil geochemical surveys in the area[2]. Agriculture is critical to the economy of Ireland, and farmers, agricultural advisors and agencies are a key sector to whom the authors are aiming to maximise the use of geochemical data in land use management and planning decisions, especially in a region where land is generally marginal in terms of productivity and economic sustainability.

*Tellus Border* is funded under the Environment theme of the EU Regional Development Fund INTERREG IVA Programme (managed by SEUPB[3]), and co-funded by the Department of the Environment, Community and Local Government (RoI), and the Department of the Environment (NI).

[1] [www.tellusborder.eu](http://www.tellusborder.eu)

[2] Soil Geochemical Atlas of Ireland, Teagasc & EPA Ireland, 2007.

Fay, D. Kramers, G. Zhang, C. *Soil Geochemical Atlas of Ireland*. URL: <http://erc.epa.ie/safer/resource?id=4856ff8c-4b2b-102c-b381-901ddd016b14> Last Accessed 15/02/2013.

[3] Special EU Programmes Body (SEUPB) <http://www.seupb.eu>

# Geochemical mapping of soil in Athens, Greece

Ariadne Argyraki<sup>1,\*,@</sup>, Efstratios Kelepertzis<sup>1,@</sup>

1 : Faculty of Geology and Geoenvironment, University of Athens - Greece

\* : Corresponding author

Urban geochemical mapping studies are useful for establishing a baseline for the urban environment, satisfying the legislative-driven demand for geochemical information on the urban chemical environment, locating polluted areas, assessing the contribution of parent materials and anthropogenic activity to the geochemical baseline, assessing risks to other compartments of the urban environment (e.g. groundwater) and identifying sources of potentially harmful elements (PHEs).

This study presents the urban geochemical map of Athens, with population exceeding 3 million in 2011, based on multi-element analysis of surface soils (0-10 cm) with emphasis in the spatial distribution of PHEs. Soil sampling was based on a regular 1km x 1km grid, laid over the survey area covering more than 200 km<sup>2</sup>. Sampling locations within the grid cells were selected giving priority to playgrounds, schools and urban parks. The < 100 µm fraction of a total of 240 soil samples were analysed for Pb, Zn, Cu, Cr, Ni, Co, Mn as well as for major elements after a strong acid dissolution. Organic carbon and soil pH were also measured. Geochemical maps were plotted within GIS enabling recognition of spatial trends in elemental concentrations and potential sources of the elements. It was found that the studied PHEs form two groups, one reflecting anthropogenic activity and another representing the influence of local geology. A spatial correlation was identified between serpentine soils and ophiolitic rocks, outcropping at the margins of the Athens basin, and elevated concentrations of Cr, Ni and Co. The second group of elements included Pb, Zn and Cu and displayed maximum concentrations in the centre of the city of Athens and in Piraeus. Average concentrations of Pb (60 mg/kg), Zn (90 mg/kg) and Cu (40 mg/kg) were comparable and somehow lower than reported averages from other major cities around the world. Chromium, Ni and Co with averages of 74 mg/kg, 89 mg/kg and 16 mg/kg respectively showed relatively increased concentrations reflecting the influence of local geology on surface soil composition.

The research outcome will contribute to the evaluation of quality characteristics of urban soils in Athens and draw attention to areas of any environmental or health risks. Further work will focus in the city core area where the highest concentrations of anthropogenic elements were observed. Specific factors affecting this enrichment are possibly linked to population density, vehicular emissions and historical development of the city of Athens.

# Investigating the difference between anthropogenic and geogenic contamination – identifying domains and calculating Normal Background Concentrations in Northern Ireland

Rebekka Mcilwaine<sup>1,\*,@</sup>, Siobhan Cox<sup>1,@</sup>, Rory Doherty<sup>1,@</sup>

**1** : Queen's University Belfast (QUB), *School of Planning, Architecture and Civil Engineering, David Keir Building, Queen's University Belfast, Belfast, BT9 5AG - United Kingdom*

**\*** : Corresponding author

The Tellus survey of Northern Ireland has identified elevated levels of potentially toxic compounds (PTCs) in soils that are thought to be associated with both geogenic and anthropogenic sources of contamination. Anthropogenic contamination is often bound to mineral surfaces. This differs from geogenic contamination, which is often bound into the soil mineral matrix. This can result in anthropogenic contamination being more bioaccessible than geogenic contamination. Differentiating between geogenic and anthropogenic sources provides for a more robust understanding of whether elevated PTC concentrations pose a risk to human health at a site specific, local or regional level.

We will examine a number of PTCs that are of concern in Northern Ireland, and define anthropogenic and geogenic domains. Geogenic metals including nickel and vanadium will be considered, as well as elements that are also associated with anthropogenic sources (eg lead and arsenic). A variety of mapping and statistical techniques are used to identify domains. Normal Background Concentrations (NBCs) will be calculated for significant domains, using the recently published BGS methodology that was developed for use within the Contaminated Land regime in England and Wales.

The methodology is investigated and refined by considering aspects such as sample depth and differing analytical approaches. It is likely that anthropogenic impacts will affect shallow samples while geogenic influences will have more of an effect on the deeper samples. Depending on the source of the contamination, differing analytical methods may measure different proportions of total contamination present. This study provides key data on the levels of geogenic and anthropogenic contamination present in the soils of Northern Ireland and their respective sources.



# Urban Soil Dust for Assessing Environmental Pollution and Human Exposure

Xiangdong Li<sup>1,@</sup>, Xiangyang Bi<sup>1,@</sup>, Siyuan Liang<sup>1,@</sup>

1 : The Hong Kong Polytechnic University. Dept. of Civil & Environmental Engineering - Hong Kong SAR China

This study used a novel *in situ* sampling method to investigate the particle size distributions of trace metals and Pb isotope compositions of soil dust, bulk surface soil, and road dust samples from a representative urban area. The concentrations of trace metals in different particle fractions of soil dust and road dust generally increase as particle size decreases, while trace metals in bulk soil samples tend to uniformly distribute among various particle size fractions. About 40% of trace metals in soil dust and road dust samples were associated with particle size fractions of < 100  $\mu\text{m}$ , while the figure was only 20% for those in soil samples. A clear tendency for Pb isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) to decrease as particle size decreased was found in the soil dust samples. Soil dust and bulk soils had Pb isotope ratios between those of the known industrial emissions and natural sources. In addition, the Pb isotope compositions of soil dust were closer to those of industrial sources than to those of the corresponding soil samples. Road dust collected from a busy road had Pb isotope compositions clearly different from those of soil dust and soils, as well as from those of known industrial sources. The results of the present study suggest that *in situ* collected soil dust may be a more sensitive and effective indicator of anthropogenic metal contamination and risk to human health in urban areas than soil and road dust samples.

# Concentrations and Bioaccessibility of Trace Elements in Different Granulometric Fractions of Smelting and Mining Impacted Dusts: Influence on Exposure Assessment

Sylvaine Goix<sup>1,\*,@</sup>, Priscia Oliva<sup>3,@</sup>, Jean-Louis Duprey,  
Melissandre Carré<sup>3,@</sup>, Joël Bourderioux<sup>3,@</sup>, Sylvie Castet<sup>3,@</sup>,  
Jacques Gardon, David Point<sup>3,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Geosciences Environment Toulouse (GET), IRD, 14 avenue Edouard Belin, 31400, Toulouse - France

\* : Corresponding author

Incidental ingestion of soil are main routes of Potentially Harmful Elements (PHE) exposure (e.g., As, Cd, Pb, Sb), especially for children playing on contaminated ground. Exposure assessment consists in two major steps: knowing the amount of PHE that comes in contact with the body (i.e., external exposure), and the part of the PHE that reach the systemic circulation (i.e., internal exposure). The external exposure through soil ingestion is mainly controlled by particles size whereas the amount of PHE absorbed is dependent of its bioavailability.

Dusts from football fields were collected in mining and smelting urban area<sup>1</sup>. Particles were separated into 5 granulometric fractions: 2000-200 µm (coarse sand), 200-50 µm (fine sand), 50-20 µm (coarse loam), 20-2 µm (fine loam) and

Bulk samples were highly contaminated, especially in the smelting environment (>16000 µg/g Pb). Clay fraction was globally the most concentrated in PHE. Bioaccessibility in bulk sample varied according to the environment: Cd>Pb>Zn>As>Sb=Sn (from 84% to 1%) in smelting district and Cd>Zn>Pb=As>Sn=Sb (from 86% to 1%) in mining district. Highest difference was observed for Pb (62% bioaccessible in mining and 13% in smelting dust). PHE bioaccessibility was not strictly proportional to particles size, and some PHE were more bioaccessibles in loam or sand than in clay.

The choice of the granulometric fraction to consider for exposure calculation induced important differences in the health risk assessment.

# Empirical and IEUBK derived model simulations of blood Pb levels in children exposed to Pb-smelter contaminated soil/dust at Mitrovica, Kosovo

Ndokiari Boisa<sup>1,@</sup>, Graham Bird<sup>2,@</sup>, John Dean<sup>3,@</sup>, Jane Entwistle<sup>4,\*,@</sup>

**1** : Department of Geography, Faculty of Engineering and Environment, *Northumbria University, Newcastle upon Tyne, NE1 8ST - United Kingdom*

**2** : School of Environment, Natural Resources and Geography, *Bangor University, Bangor, Gwynedd, Wales, LL57 2UW - United Kingdom*

**3** : Department of Applied Sciences, Faculty of Health and Life Sciences, *Northumbria University, Newcastle upon Tyne NE1 8ST - United Kingdom*

**4** : Department of Geography, Faculty of Engineering and Environment - **Website** *Northumbria University, Newcastle upon Tyne, NE1 8ST - United Kingdom*

\* : Corresponding author

This study utilizes a physiologically-based *in-vitro* extraction method to assess the oral bioaccessibility of Pb in surface soils and metallurgical waste in Mitrovica, Kosovo and then models blood Pb concentrations in children (< 6 years) using the Integrated Exposure Uptake Biokinetic (IEUBK) model (USEPA, 2007). Data for Pb levels in scalp hair ( $\leq 120 \mu\text{g/g}$ ) and blood ( $\geq 650 \mu\text{g/dL}$ ); WHO, 2004) for children that have lived within the internally displaced peoples (IDP) camps in Mitrovica indicate significant Pb uptake has indeed taken place.

Using an adjustment for air Pb concentration (after Arditoglou and Samara, 2005) five model simulations were undertaken on the < 250  $\mu\text{m}$  fraction (unless otherwise stated): Run 1, on the total Pb concentration and the model default absolute bioavailability (ABA); Run 2, on the < 10  $\mu\text{m}$  fraction total Pb concentration and the model default ABA; Run 3, on the total Pb concentration and site-specific % gastric bioaccessibility; Run 4, on the total Pb concentration and site-specific ABA; Run 5, on the total Pb concentration and site-specific % gastrointestinal bioaccessibility.

Blood Pb concentrations predicted for children from all five simulations have indicated levels above the blood lead level of concern (10  $\mu\text{g/dL}$ ) for long-term health risk (CDC, 2005). Our IEUBK modelling predicted blood Pb concentrations for soils using % gastric bioaccessibility (Run 3) and % gastrointestinal bioaccessibility (Run 5) to be 4.5 – 43.8  $\mu\text{g/dL}$  and 1.1 – 41.8  $\mu\text{g/dL}$ , respectively, and the ranges are consistent with the adjusted empirical mean blood Pb data for children from the IDP camps (15.6 – 41.8  $\mu\text{g/dL}$ ) reported by Brown et al., (2010). Adjustment of the model default bioavailability coefficient (30 %) with site-specific ABA data (Run 4) indicated a blood Pb range of 1.8 - 29.1  $\mu\text{g/dL}$  which is an underestimation compared to the empirical data from the site.

## References

Arditsoglou, A., and Samara, C., (2005) Levels of suspended particulate matter and major trace elements in Kosovo: a source identification and apportionment study. *Chemosphere* **59**, 669-678

Brown, M.J., McWeeney, G., Kim, R., Tahirukaj, A., Bulat, P., Slya, S., Savic, Z., Amitai, J., Dignam, T., and Kaluski, D.N., (2010) Lead poisoning among internally displaced Roma, Ashkali and Egyptian children in the United Nations Administered province of Kosovo. *European Journal of Public Health* **20**, 288-292

CDC. (2005) Preventing Lead Poisoning in Young Children. Centre for Disease Control and Prevention, Atlanta: USA

United States Environmental Protection Agency (2007) User's guide for the Integrated Exposure Uptake Biokinetic model for lead in children. Office of Superfund Remediation and Technology Innovation: EPA 9285.7-42.

WHO, 2004. Preliminary Report on Blood Lead Levels in North Mitrovica and Zvecan. WHO, Pristina.

# Environmental and sanitary risk assessment and management in associative gardens: vegetable quality in relation with practices and context

Camille Dumat<sup>1,2,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France

**(1) Importance of the work and objectives:** A growing interest in gardening is observed at the global scale and produce quality plants is the main objective of the gardeners (Gojar & Weber, 1995). Soil bio-physicochemical properties can be strongly modified by the practices, but due to the complexity of the mechanisms involved in the transfer of substances (Dumat 2006), gardeners only have a partial view. However, many chemicals can potentially flow or accumulate in their soils, atmosphere, waters and finally vegetables (Bappet data base; Chenot et al., 2013).

**(2) Methodologies:** In associative gardens from Midi-Pyrénées Region (it means around 40 experimental gardens) complementary studies are performed: (1) measure of total or bioavailable metals concentrations in vegetables, soils, atmosphere and waters; (2) soil parameters (pH, organic matter...); (3) (Eco)toxicity: earthworms, plants biotests and bioaccessibility measures; (4) surveys are conducted with the gardeners on their practices.

**(3) Main results and conclusions:** In relation with the different cultural practices of gardeners, significant changes were identified for various soil physicochemical parameters: pH, organic matter content and exchangeable copper and CEC. Over-fertilization (N, P and K) has often been observed. In addition, analysis of water quality used for watering productions showed arsenic concentration above the regulatory value for one studied site. Sanitary risk assessment, including measures of As bioaccessibility in vegetables and quantification of productions to precise the exposure, is therefore actually performed. As gardens are complex ecosystems, their sustainable management involves the development of pluridisciplinary scientific projects as the program "JASSUR" for "Associative Urban Gardens and Sustainable Cities: practical functions and risks", 2013-2015.

# Is it possible to sustainably manage lead soil contamination at allotment and domestic gardens?

Roslyn McIntosh<sup>1,@</sup>, Andrew Hursthouse<sup>2,@</sup>

**1** : School of Engineering and Science - **Website**  
*Paisley, PA1 2BE - United Kingdom*

**2** : School of Science, University of the West of Scotland (UWS) - **Website**  
*PA1 2BE, Paisley - United Kingdom*

Adopting a decentralised approach, each local authority in the UK has developed a risk-based inspection strategy for the identification, assessment and remediation of contaminated land. These strategies are tailored to the priorities of the local authority, taking into consideration available resources and local environmental characteristics. The public has statutory rights to openness and transparency from authorities acting to protect their interests. However, low confidence in assumptions within the risk assessment and ambiguity within the decision making implied by these strategies can affect the transparency of the assessment and remediation process leading to a precautionary approach.

The contaminated land conceptual site model is complex and there is no 'all-inclusive' risk assessment or decision making tool available. This case-study of allotment and domestic garden scenarios examines the challenges in conducting a risk-base assessment by deconstructing the decision making processes carried out to determine whether lead contaminated soil is presenting unacceptable risk to human health.

Existing legislation and risk-based policy expects a proportionate response from the enforcing authorities and there is the scope to implement sustainable land contamination management strategies within the regime. However, this would require consideration of other social, economic and environmental factors beyond the decisive risk assessment calculations customarily applied in the regulatory decision making process.

# Spatial Assessment of the potential impact of Black & Grey Shales on human exposure to potentially toxic elements in S.E. Nigeria.

Therese Nganje<sup>1,2,\*,@</sup>, Andrew Hursthouse<sup>3,\*,@</sup>

**1** : Aniekan A Edet (Department of Geology, University of Calabar, P.M.B!5, Calabar,Nigeria),  
*Department of Geology, University of Calabar P.M.B. 1115 - Nigeria*

**2** : Christopher I Adamu (Department of Geology, University of Calabar, P.M.B 1115 Calabar, Nigeria),  
*Department of Geology University of Calabar P.M.B. 1115, Calabar - Nigeria*

**3** : School of Science, University of the West of Scotland (UWS) - **Website**  
*PA1 2BE, Paisley - United Kingdom*

\* : Corresponding author

The black and grey shales of SE Nigeria provide important example of natural geological materials containing potentially toxic elements (PTE). A total of 89 samples comprising 25 each of shales, soils , water and 14 samples of edible crop plants were collected across the shale region and were analyzed for a range of PTEs (including Cd, Cu, Hg, Mo, Se, Pb, Zn and U) using standard techniques. The results showed moderate to significant enrichment compared to world average shale values for a number of elements. The soils developed from these rocks and the streams draining the region reflect the parent material and are similarly enriched in PTEs. The soils were moderately acidic and many element concentrations exceeded the Nigerian Department of Petroleum Resources target values for non-polluted soils at numerous sites. The highest soil hazard index (SHI) of 15.78 was recorded at a site (Odukpani Formation) in the southeastern part of the study area, due to excessive Cu and Zn levels. The water samples were acidic to neutral (pH 2.95-7.49) with high concentrations of Al ( 0.64-42.89mg/L), Ni ( 0.03- 13mg/L), Pb (0.2- 12.14mg/L), SO<sub>4</sub> (0.35-275.9mg/L) and Fe ( 1.37- 27.85mg/L), and of low salinity ( EC< 1000 µs/cm). The water quality of the region failed to meet the WHO aesthetic and health significance standards particularly for SO<sub>4</sub>, conductivity and Pb. A Water Hazard Index value of 45.64 indicated extreme toxicity for water draining Asu River shale in the central part of the study area. The concentrations of PTEs such as As, Cd, Hg,Mo, Pb ,Se determined in some edible crop plants, exceed the range quoted for terrestrial plants by international regulatory agencies (FAO/WHO). The impact of this enrichment of the soil, water and edible crop plants by PTEs is of great concern due to the demands of subsistence agriculture in the region.

# **A tiered approach for the assessment of human health risks due to the consumption of vegetables from cadmium contaminated land**

**Frank Swartjes**<sup>1,@</sup>

**1** : National Institute for Public Health and the Environment (RIVM) - **Website**  
*P.O. Box 1, 3720 BA Bilthoven - Netherlands*

With a fast growing world population, there will be an increasing pressure on agricultural land for growing consumption crops. Moreover, consumption crops are often grown in urban areas for economical reasons (third world countries) and in the framework of sustainable urban development (urban farming in first world countries). One of the limitations, however, is soil contamination. The most critical contaminant is cadmium, since cadmium is easily taken up by vegetables. Cadmium has no known biological functions in humans and can result in kidney and liver dysfunction and, on the long-term, in osteoporosis. It is known that consumption of vegetables with cadmium concentrations lower than the phytoxicological concentrations in vegetables might result in adverse human health effects. Vegetable consumption can significantly contribute to overall cadmium exposure.

To be able to assess the human health risks of vegetable consumption from cadmium contaminated land in a scientifically-based and efficient way a tiered approach has been developed. Successively, in each tier the degree of conservatism decreases, while site-specificism and complexity increases. The underlying principle is: 'simple when possible and complex when necessary'. The tiered approach is structured as follows: Tier 0 concerns a quantitative evaluation of the possibilities for experiencing adverse human health effects due to vegetable consumption. In Tier 1 the actual cadmium concentrations in soil are compared with a toxicologically-based critical soil concentration. Tier 2 offers the possibility for a comparison of calculated site-specific exposure with the toxicologically-based Reference dose. Finally, in Tier 3, a standardized measurement protocol is followed, which allows for sampling of a significant number of representative crops in the field. Subsequently, the measured cadmium concentrations are tested in an exposure calculation.

# Geochemical tools to assess human methyl-mercury exposure crossing Hg speciation and stable isotope fractionation

Laure Laffont<sup>1,\*,@</sup>, Laurence Maurice<sup>1,\*,@</sup>, Jeroen Sonke<sup>1,@</sup>,  
Sylvain Bérail<sup>2,@</sup>, Régine Brachet<sup>3,@</sup>, David Amouroux<sup>2,@</sup>,  
Philippe Behra<sup>4,@</sup>

**1** : Géosciences Environnement Toulouse (GET) - **Website**

*Université Paul Sabatier - Toulouse III, Observatoire Midi-Pyrénées, CNRS : UMR5563, IRD : UR234  
14 avenue Edouard Belin 31400 Toulouse - France*

**2** : Laboratoire de Chimie Analytique, Bio-inorganique et Environnement (IPREM-LCABIE)

*CNRS : UMR5254, 2 Avenue P. Angot, Hélioparc Pau Pyrénées, 64053 Pau cedex 9 - France*

**3** : Environnements et Paléoenvironnements Océaniques (EPOC)

*Université Bordeaux 1 Avenue des Facultés - 33405 TALENCE CEDEX - France*

**4** : Laboratoire Chimie Agro-Industrielle (LCA), Université Paul Sabatier - Toulouse III, ENSIACET –  
4, allée Emile Monso – 31030 TOULOUSE Cedex 4 - France

\* : Corresponding author

Methylmercury (MMHg) is one of the most important chemical species due to its toxicity which can affect the neurological system. People are submitted to this toxic exposure through diet and mainly through fish consumption except in China where in some place, rice consumption can account for 95% of the daily intake of MMHg. Hair has been recognized as a good biomarker to evaluate MMHg contamination in the human body. There is a substantial interest in developing a tracer tool that may distinguish and quantify the different sources of Hg species exposure.

The use of Hg isotopes to trace processes and sources of Hg in the environment has emerged over the last decade. Our objective is to identify methylmercury sources in human hair of Southern populations from South America: i) indigenous people from French Guiana (Oyapock basin) living in a gold-mining area and in a pristine area and ii) gold-miners from Bolivia exposed to both inorganic and organic mercury.

In the case of MMHg exposure through fish diet the ensemble of mass dependent fractionation (MDF) and mass independent fractionation (MIF) isotope signatures is able to identify fresh water and marine fish MMHg exposure. Isotopic analysis is therefore a complementary tool to speciation analysis. While human metabolism shifts dietary MMHg MDF signatures by approximately +2‰, this feature appears to be robust across four different populations (from Europe, French Guiana and Bolivia). In gold-miners hair, isotopic signatures were found to reflect a binary mixing between inorganic Hg and methylmercury with two different sources of the latter highlighted by distinct D201Hg: one from marine fish and the other one from freshwater fish. This observation was correlated with Hg speciation in hair showing a d202Hg increasing with methylmercury percentage in hair ( $r^2=0.66$ ,  $n=23$ ).



# Mad, bad or sad? Mental health and the environment

Alex Stewart<sup>1,\*,@</sup>, Mike Bradley<sup>@</sup>

1 : Cheshire & Merseyside Health Protection Unit, Rail House Lord Nelson Street Liverpool L1 1JF, United Kingdom - **Website**

\* : Corresponding author

## Importance & Objectives

The environment is well recognised to affect mental health: lead alters behaviour; green spaces improve health. The general public calls our Public Health help-desk in Liverpool with many varied environmental concerns, contributing to the work-load without necessarily being easy to solve. We examined all such enquires over a 16-month period to improve both understanding of the concerns and our Public Health response.

## Methods

All enquiries are logged by administrators; clinical staff (nurse/doctor) contact the caller for further information or to give advice. We reviewed the notes for common mental health themes. Particular attention was given where the records indicated abnormal complaints or bizarre behaviours, or where follow-up by multi-agencies found no physical or rational cause for concern. Records were scrutinised for potential evidence of poor mental health affecting the individuals involved.

Where relevant topics were identified, focussed literature searches were performed, using interchangeable topical terms including “chemical”, “sensitivity”, “hypersensitivity”, “parasitosis”, “infestation”, “delusion”, “hallucination”, “paranoia”, “psychosis”, “mental health”, “paraphrenia”, “schizophrenia”, “psychiatric”, “depression”, “mood”, “complaint”, “concern”, “worry” and “public health”.

## Main Results & Conclusions

Several clear cases with potential psychiatric components were identified (recognising the diagnostic limitations), including emotional or psychosomatic problems arising from noise and tinnitus (persistent ringing in ears), persecutory delusions (from neighbours with chemicals), partition delusions (belief of being interfered with by a chemical invading their home), multiple chemical sensitivity and electromagnetic hypersensitivity (both: non-specific symptoms with exposure to doses below those known to cause harmful effects - includes petrol, perfumes, pesticides), related delusions about parasites and chemicals giving a monosymptomatic hypochondriacal psychosis characterised by a single paranoid delusion with no additional thought disorder.

Case studies were developed to aid staff learning and a structured approach to such enquiries was taken to reduce staff stress, improve patient compliance and identify appropriate multi-agency interventions.

***Topic 1***  
***Biogeochemistry and Health***  
***(including cross topics 1-2 and 1-3)***  
***Poster Presentations***

# Individual particle characterization to evaluate their potential human health impact

Sophie Sobanska<sup>\*</sup>, Vincent Dappe<sup>\*</sup>, Tian Tian Xiong<sup>1,2</sup>, Camille Dumat<sup>1,2,@</sup>, Eva Schreck, Nicolas Nuns, Philippe Recourt, Myriam Moreau<sup>@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France

**\*** : Corresponding author

Industrial activities such as ferrous and non-ferrous smelters including lead recycling facilities may emit numerous fine and ultra-fine metallic particulate matters (PM). These PM emissions increase in the atmosphere with the use of more effective filters in facilities [1]. The metal-rich industrial fallouts may represent a sanitary risk for the population through particle inhalation and contamination of surrounding environment (air, soil, vegetable) The characterization of individual particles, including metal speciation, size and heterogeneity within particles, is as important as metal levels measured in atmospheric samples. Actually, determining properties at an individual particle scale provides useful information to evaluate its solubility, its reactivity, its bioaccessibility and therefore, its sanitary impact [2,3].

This work presents a detailed characterization of individual particles emitted by a lead-battery recycling facility, using combined spectroscopic and imaging techniques. The particles were sampled in the courtyard of the plant by cascade impactor (PM10 Dekati) to separate particle sizes in two fractions (i.e. 10 to 1  $\mu\text{m}$  and < 1  $\mu\text{m}$ ). Morphology and elemental composition of size-segregated particles was determined by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray system (MEB-EDX). Molecular characterization of the same particles was carried out by Raman microspectrometry after a carefully relocation of the samples. The Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was performed to characterize the surface (few nanometers) composition of individual particles. We demonstrated that lead-rich particles were mainly in the finer size fraction. The lead speciation evolves with granulometric distribution. Combined species containing Pb/Fe or Pb/Na were found in the two granulometric classes. ToF-SIMS results showed that Pb-Na species are mainly found on the particle surface. These results were compared with the composition of primary particles and bioaccessibility results [4].

[1] Zhang et al., 2005, J. Aerosol Science 36, 211–233.

[2] Uzu et al., 2010, Environ. Sci. and Technol., 44, 1036-1042.

[3] Falgayrac et al., 2012, J. of Phys. Chem. A, 116, 7386-7396.

[4] Uzu et al., 2011, J. of Hazard. Mat., 186 (2-3), 1018-1027.

# Human exposure to fluoride from drinking water – a pilot study in the East Midlands region, UK

Aradhana Mehra<sup>1,\*,@</sup>, Paul Lynch<sup>1,@</sup>, Sohel Saikat<sup>2,@</sup>, Louise Samson<sup>1,@</sup>, Imuetinyan Aigbogun<sup>1,@</sup>, Oluwatobi Oluleye<sup>1,@</sup>

1 : University of Derby, Kedleston Road, Derby DE22 1GB - United Kingdom

2 : Health Protection Agency, HPA CRCE Second Floor, 151 Buckingham Palace Road London SW1W 9SZ - United Kingdom

\* : Corresponding author

Fluoride is an essential element in our diet which promotes healthy bone growth and prevents dental caries, however, when present in excess it can cause detrimental effects such as dental fluorosis, mottling of teeth and skeletal and crippling fluorosis. Drinking water has the largest contribution to our daily fluoride intake (WHO, 2012), and estimates suggest that 75% of our daily dietary fluoride is from water and water-based beverages (USDA, 2004). The present study aims to assess human exposure to fluoride from household drinking water using the East Midlands region of the UK as a case study. The water in this region is supplied by Severn Trent Water, and households vary in their drinking water consumption practices where some consume the water obtained from the tap, whereas others filter or boil the water before consumption. Samples of tap water (first water from tap in the morning, and first flush after 15 seconds) were collected from households and the fluoride content analysed by ion selective electrode. The effect of boiling and filtration was determined by analysing the waters for their fluoride content after boiling for ten minutes, and filtration using a 45um Millipore filter paper, respectively. The findings of this study showed that fluoride content of the first morning waters ranged between 0.22 – 1.69 mg/L, and although the concentrations were reduced in the first flush samples, the difference was not statistically significant. Concentrations of fluoride in the water for both the first morning and first flush were reduced on filtration, but the difference was not statistically significant, and the fluoride content of boiled waters did not show any regular trends. The findings are discussed in light of the WHO drinking water fluoride guideline values of 1.5 mg/L with a target between 0.8 – 1.2 mg/L to maximize benefits and minimize harmful effects.

# Adaptative strategy of *S. vulgaris* metallophyte plant to soils polluted by metals

Annabelle Austruy<sup>1,\*,@</sup>, Yann Foucault<sup>1,2,3,@</sup>, Tian Tian Xiong<sup>1,2,@</sup>, Thibaut Lévêque<sup>1,2,@</sup>, Cécile Moussard<sup>4,@</sup>, Adnane Hitmi<sup>5,@</sup>, Camille Dumat<sup>1,2,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Société de Traitements Chimiques des Métaux (STCM), 30-32 Avenue de Fondeyre 31200 Toulouse - France

**4** : Laboratoire Biologie IUT Aurillac, Université d'Auvergne - Clermont-Ferrand I, 100 rue de l'Egalité 15000 Aurillac - France

**5** : UMR A 547 Physique et Physiologie Intégratives de l'Arbre Frutier et Forestier (PIAF UMR A 547), Université Blaise Pascal - Clermont-Ferrand II : UMRA 547, 100 rue de l'Egalité 15000 Aurillac - France

\* : Corresponding author

The study of the vegetation growing on strongly polluted soils carries important data for improving remediation techniques. The metallophyte vegetation was evidenced as an adaptation to disrupted ecosystem by anthropological activities. Three different strategies can be used for the tolerant plant species, i) the accumulators for which metals are concentrated preferentially in the aerial biomass, ii) the "excluders" which present a low foliar concentration and iii) the indicators which present no control of the translocation, consequently, the root and foliar concentrations are proportional to the soil contents.

This study focused on the physiological mechanisms description of the metal tolerance in a pseudometallophyte species, *Silene vulgaris*. This plant species was found on two different industrial sites, i) the former industrial site of Auzon in Haute-Loire (Auvergne, France) presenting a strong As, Sb, Cd, Cu and Pb soil pollution and (ii) an industrial site near Orleans (France) presenting a strong Pb soil contamination due to atmospheric particles fallout. Metal contents in roots and leaves of *S. vulgaris* sampled in both sites were determined after a soil pollution characterization (total and bioavailable content of pollutants and physico-chemical characteristics of the soil).

The results showed that *S. vulgaris*, as of lot metallophytes, favored the exclusion of pollutants by limiting their root absorption, while a significant foliar uptake of lead was observed due to particles-leaves interaction. The study of this resistant plant, by its capacities of detoxification, immobilization or absorption of metals, could be useful to estimate the potential risk of metal transfer within the ecosystem, and could also be applied to soil phytoremediation.

## **“Environment Health and Society” a cross-disciplinary approach at the Midi-Pyrénées Observatory (Toulouse, France)**

Sylvia Becerra<sup>1,\*,@</sup>, Camille Dumat<sup>2,3,\*,@</sup>, Laurence Maurice<sup>1,@</sup>,  
Cathy Liousse<sup>4,\*,@</sup>

**1** : Géosciences Environnement Toulouse (GET) - **Website**

*Université Paul Sabatier - Toulouse III, Observatoire Midi-Pyrénées, CNRS: UMR5563, IRD : UR234  
14 avenue Edouard Belin 31400 Toulouse - France*

**2** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**3** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France

**4** : Laboratoire d'aérogologie (LA), CNRS : UMR5560, OMP 14, Avenue E. Belin 31400 Toulouse - France

\* : Corresponding author

The human activities, urban, rural or industrial, have a significant impact on the environment at the global scale and become today a major concern for societal issues. The French Government is initiating an “energetic transition” in 2013 on major environmental issues, including health and environment risks. The aim of the “Environment, Health and Society” research axis initiated in 2007 at the Midi-Pyrénées Observatory consists in linking academic disciplines around a same global question related to local and global environmental changes. Its expertise concerns: : i) the contaminants, organic, metallic, and emerging molecules, ii) their measurements in natural or impacted environments, iii) their biogeochemical cycles, iv) the exposure trends and the associated risks for human health and v) the vulnerability and adaptability of people and the response of public policies. Interactions with institutional partners are developed at local, national and international scale, particularly in Southern countries, in Asia, South America and Africa, where mining and oil exploration activities have direct impacts on the environment, biodiversity and human health.

Research projects are classed in three large topics:

1) “Environment and Health” regarding the impact of pollutants and pathogens on the environment, their transformation and transfer in the trophic chain and the risks for human health. Multidisciplinary and coupled (modeling/in situ measurements/batch experiments) approaches are developed. Our recent results concern: (i) the water quality with a recent focus on drug residues; (ii) population exposures to toxic heavy metals by inhalation, ingestion and dietary habits; (iii) biological impact of combustion aerosols (iv) use of living organisms as biotests or cytotoxicity approaches, to rehabilitate polluted media and for environmental survey, infectious diseases, ...

2) “Environmental hazards, vulnerability and resilience factors”: the objective is to understand and evaluate the health vulnerability of local populations exposed to environmental risks due to human activities.

3) “Integrated modeling”: the use of spatial tools like GIS permits a mapping of environmental and social risks, which combined to SMA models allows to integrate physical, chemical and biological data with human actors involved in the problematic.

# Relating global iodine distribution to IDD: questions for multi-professional research

Alex Stewart<sup>1,\*,@</sup>, Annie Worsley<sup>2,@</sup>

**1** : Cheshire & Merseyside Health Protection Unit (CMHPU) - **Website**  
*5th Floor, Rail House Lord Nelson Street Liverpool L1 1JF - United Kingdom*

**2** : Department of Geography and Environmental Management (UWE) - **Website**  
*Frenchay Campus Coldharbour Lane Bristol BS16 1QY - United Kingdom*

\* : Corresponding author

Despite the assertion in the Geochemical Atlas of Europe that soil developed in recently glaciated areas is usually iodine poor, because iodine has not yet been highly accumulated from atmospheric precipitation, the maps of topsoil and subsoil in the same Atlas belie that, showing a clear east-west gradient, suggesting maritime control.

Recent literature shows that photochemically active iodine compounds of marine origin are important in atmospheric chemistry; similar organic iodine compounds make up a significant proportion of orographically deposited iodine, with concentrations decreasing with altitude. The global atmospheric circulation plays an important role in the distribution of iodine across continents from focused intertidal, coastal and oceanic marine sources. Soil iodine is bound up with organic carbon and stream iodine may reflect mobility rather than leaching. Overall, the biophile nature of iodine is central to its global cycle, leading to unanswered questions concerning environmental iodine and the iodine deficiency disorders (IDD) (e.g. goitre, cretinism).

Our own work suggests that bio-geographical constraints control much of the spatial distribution of IDD, with global variation related to ecology rather than geochemistry. Questions remain that demand multi-professional approaches, largely lacking in iodine studies to date. Locally, variation in the spatial distribution of soil iodine sometimes parallels spatial variation in IDD: how constant is this at a continental or global scale? How does iodine bioavailability and mobility in soil relate to the distribution or aetiology of IDD? What is the role of soil fauna in retaining or mobilising (biophilic) iodine? What are the sources and pathways of iodine into animal diets? What proportion of marine-sourced iodine is biological (algal) and what chemical (photolytic / sublimation)?

The answers to these questions will aid understanding of the global distribution of IDD and contribute to improved control measures.

# Particle size analysis of metallurgical waste dump for pollutants transport characterization

Orianne Houecande<sup>1,@</sup>, Didier Graillet, Jacques Moutte<sup>@</sup>

1 : Ecole des Mines de Saint Etienne (EMSE) - **Website**

Ecole Nationale Supérieure des Mines de Saint-Etienne 158 cours Fauriel, 42100 Saint Etienne - France

## Importance of the work and objectives

High levels of trace elements in soils may increase contamination risks for animals and human health. Substantial researches are continuously achieved to assess risks on polluted soils but few include contamination from steelworks waste.

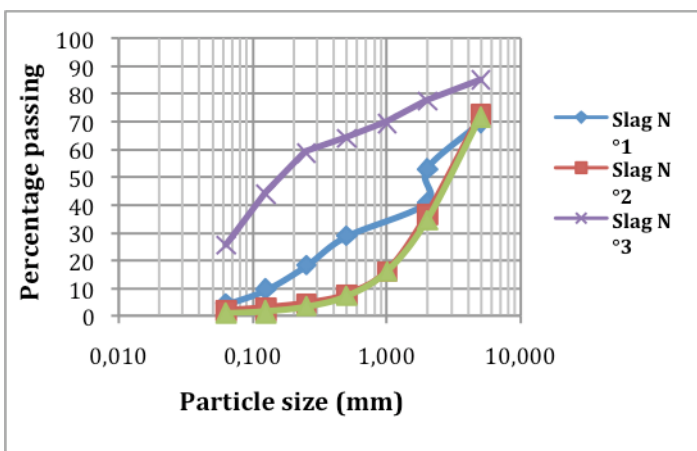
However particles size analysis may allow monitoring in highly contaminated soils depending on traces metals physicochemical and sorption properties. Slag heaps study is preliminary stage to investigated particles materials for pollutants transport characterization.

## Methodologies

Four slag heaps were sampled and sieved into eight class sizes from 5 mm to 63 µm. Laser particle size analyzer and scanning electron microscopy were used to observe sample distribution under 63 µm. The size analysis was achieved in liquid dispersion using Fraunhofer theory. Pump flow parameters and agitation rate were changed during the observation. Particle disaggregation was performed with internal ultrasounds during 4min and completed with an external ultrasound (power 140 W) soaked in 20 ml of suspension.

## Results and conclusion

The figure and table summarize respectively the results of sieved analysis and the laser size analyzer volume fractions (< 63µm) depending on diameters. For example, d(0.5) divides distribution in two equal parts. No significant difference was observed between slags in this table. Parameters variation or increasing ultrasound duration improves weakly particle disaggregation. Slags 2 and 4 have low percentage of small particles with an exponential slope while the two others have almost linear slope and a low slip towards size 2mm.



	d (0.1)	d(0.5)	d(0.9)	Mode
<b>Slag N°1</b>	4.7	25.6	59.5	35.9
<b>Slag N°2</b>	4.9	26.0	61.9	36.5
<b>Slag N°3</b>	7.9	25.0	50.2	28.6
<b>Slag N°4</b>	4.8	25.7	61.9	37.8



# Release of the mobile forms of hazardous elements from the glass-works fly ash into soils

Martin Udatný<sup>1,\*,@</sup>, Martin Mihaljevič<sup>1,@</sup>

**1** : Charles University, *Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 43 Prague - Czech Republic*

\* : Corresponding author

The release of hazardous elements from wastes from high temperature processes represents a risk for the environment. We focused on alteration of fly ash (FA) from glass-works, which produced glass with high amounts of PbO. Fly ash from electrostatic filter contains elevated concentrations of Pb, Zn, Ba and Sb. Historically small amount of FA may have been emitted from factory and can have settled in the surrounding environment (soil).

To assess possible risk for the environment we placed samples (0.5g) of the FA in small nylon bags into 11 individual horizons in soils with different vegetation cover (spruce, beech and unforested area). All sites are situated in locality, which was contaminated by sulphur oxides before 1990s and soils have low pH. Samples of the FA were exposed in soils for a period of one year and then were removed together with samples of soils, which immediately surrounded the bags with the FA.

Concentrations of studied elements in the FA and in the soil samples (initial and after exposure) were determined by ICP-MS. The speciation of elements was determined by BCR sequential extraction procedure (SEP). The amounts of Pb, Zn, Ba and Sb bound in individual fractions of SEP (exchangeable/acid-extractable, reducible, oxidizable, residual) were determined.

The SEP results indicate that Zn and Ba may pose a potential risk for the environment. Their concentrations in the first, most mobile and bioavailable fraction, in all monitored sites and horizons of exposed soils increased. Most significant increases were observed in top soil horizons (litter and A), where the concentrations increased by a factor 3.6 – 9.5 (Zn) and 2.3 – 12.4 (Ba). In these horizons were the achieved concentrations in the range 14.7 – 33.1 ppm (Zn) and 10.8 – 68 ppm (Ba).

# **An application of X-ray absorption spectroscopy for the transformation of trace metal speciation through open burning of electronic waste**

**Takaaki Itai<sup>1,@</sup>, Masanari Otsuka<sup>1,@</sup>, Asante Kwadwo<sup>1,@</sup>,  
Takahashi Shin<sup>1,@</sup>, Shinsuke Tanabe<sup>1,@</sup>**

**1** : Center for Marine Environmental Studies, Ehime University  
2-5, Bunkyo-cho, Matsuyama, Ehime 790-8577 - Japan

Rapidly developing countries face increasing amounts of electronic waste (e-waste), both, from domestic generation and illegal imports. Uncontrolled e-waste recycling can induce environmental pollution, since e-waste contains toxic substances such as lead, mercury, arsenic, cadmium, selenium, hexavalent chromium, and flame retardants that generate dioxins emissions upon burning. Although knowledge on the speciation of metals/metalloids in soil from e-waste recycling areas is important to assess their toxicity and mobility, such information is scarcely reported. While the primary chemical form of metals can be estimated, appraising changes in chemical forms during recycling processes is difficult. In this study, to assess changes in chemical forms of potentially toxic elements, e-waste recycling sites in Accra (Ghana) were chosen. Soil and ash mixtures were collected from open burning sites where some electric products were burnt to recover Cu. Speciation of Cl, Cu, Zn, As, Br, Pb in soil/ash mixtures was conducted using X-ray absorption fine structure spectroscopy. The results indicated that Cu and Zn occurred in soil/ash mixture as different salts and the predominant species were likely CuCl<sub>2</sub> and ZnS, respectively. Since Cu is originally in metallic form before burning, it could be converted to CuCl<sub>2</sub>, which can catalyze dioxin formation during open burning processes. Predominant As species in soil/ash mixture was arsenate which is less toxic than As<sub>2</sub>O<sub>3</sub>, the most common As compound in industrial by-product. This result also reflects possible conversion during open burning. Chloride and Br were mostly present in soil/ash mixture as inorganic salts despite the fact that the original forms were plausibly organic compounds such as flame retardants. Predominance of inorganic Br in soil/ash mixtures might be attributed to the conversion of organic Br by thermal decomposition. Considering all, formation of dioxin like compounds is probably high in these areas and hence further comprehensive monitoring is needed to assess the health risk for the e-waste recycling workers.

# Assessing the efficiency of fractionation protocols in evaluating the environmental impact of potentially toxic elements in steel production by-products

Kiri Rodgers<sup>1,@</sup>, Andrew Hursthouse<sup>\*</sup>, Simon Cuthbert<sup>\*,@</sup>

**1** : University of the West of Scotland (UWS) Faculty of Science and Technology, School of Science, High Street Paisley PA1 2BE Scotland, United Kingdom - **Website**

**\*** : Corresponding author

The potentially toxic elements (PTEs) that are present in the steel production by-products, such as copper, nickel, manganese and zinc, require robust management to minimise environmental contamination. This is a worldwide problem, and locally, in the UK is addressed by EU waste management protocols such as Waste Acceptance Criteria (WAC) testing that simulates worst case scenario leaching potential, and Toxicity Characteristic Leaching Procedure (TCLP) (e.g. USEPA 1311) which measures leaching potential by extraction reagents. These regulatory tests are designed to assess and dictate disposal approaches which are based on the presence of hazardous substances and their potential to impact on the environment, which is ultimately dependent on their chemical form or “speciation”.

Within the steel industry it is vital to be able to differentiate different chemical forms of elements as this can determine very different disposal routes e.g. disposal of hazardous waste is typically £64 per tonne and non-hazardous £2.50 per tonne (HMRC, 2012). Sequential extraction methodology can be used to operationally speciate the solid by-products to allow more precise classification. In the case of zinc; as ZnO, toxicity is low and waste can be disposed of as non-hazardous, but when present as ZnS, a higher toxic risk exists and it must be disposed of as a hazardous waste, with significant economic liability for the producer.

The 1979 Tessier sequential extraction protocol is commonly used to fractionate different metal species in solids and an adapted 7 step procedure has been used in order to distinguish between more species i.e. oxides and sulphides. This study reports on the application of sequential extraction methods, to provide better informed waste characterisation protocols and evaluate the impact of sample preparation and reproducibility on waste classification.

# Antibiotics in Livestock Wastewater and Its Control by Radiation

Tak Hyun Kim<sup>1,\*,@</sup>, Seungjoo Lim, Sang-Hun Lee, Sun-Kyoung Kim, Jun-Young Kim<sup>@</sup>

1 : Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeongeup, Jeonbuk, 580-185 - South Korea

\* : Corresponding author

Antibiotics are widely used to treat or feed additives on the livestock farms, and the excreted metabolites via urine or feces are usually directly distributed to the environment or stored before treating them in the livestock wastewater treatment plants. Occurring in the environment even in low concentrations, these compounds are a threat to human health and ecosystems, irrespective of their bioactivity. Generally, organic compounds in wastewater can be degraded by advanced oxidation processes (AOPs). Recently, radiation technology has been given more attention to treat these micropollutants and to enhance the biodegradability of wastewaters.

In this study, the occurrence of a total of eleven antibiotics in the livestock WWTP in Korea was investigated, and the controls of antibiotics in livestock wastewater were carried out. Antibiotics in livestock wastewater were analyzed using a liquid chromatography/electrospray-mass/mass (LC/ESI/MS/MS). The radiation experiments were carried out using an electron accelerator (1 MeV, 40 kW).

As results, among eleven antibiotics, high concentrations of sulfathiazole, sulfamethazine, sulfamonomethazine and tetracycline were detected in the influents. The frequencies of chlortetracycline, oxytetracycline, and disinfectants in the influents were high. High concentrations of Lincomycin, chlortetracycline, and formaldehyde were detected in the effluents. The frequencies of chlortetracycline and formaldehyde in the effluents were still high. Antibiotics in livestock wastewater were removed effectively by electron beam irradiation. The concentrations of sulfadimethoxine, sulfamethoxazole, sulfamonomethaxine, and erythromycin decreased more than 80% with a 10 kGy electron beam dose.

The refractory compounds such as antibiotics and disinfectant contained in the livestock wastewater were decomposed into easily biodegradable compounds through electron beam irradiation. In an advanced biological treatment process combined with electron beam pretreatment system, the removal efficiencies of the organics and nutrients (N, P) were enhanced due to the radiation pretreatment effect.

# Release of antimony and other heavy metals in antimony ores during acid leaching

Mengchang He<sup>1, \*, @</sup>, Xingyun Hu, Sisi Li<sup>@</sup>

**1** : State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, China - **Website**

\* : Corresponding author

China has the most abundant antimony (Sb) resources of any country in the world. Due to dissolution of Sb minerals large quantities of Sb have been released, resulting in serious Sb contamination of the local environment. In this paper, the issues of acid mine drainage and heavy metals contamination in the Sb mine district were explored by studying the static leaching process of four Sb ores from an important Sb mine of China. After pretreatment, grain sizes between 0.15 and 0.075 mm of the four samples were analysed for mineralogical identification, textures, and chemical compositions using X-ray powder diffraction, scanning electron microscopy, and inductively coupled plasma-atomic emission spectrometry, respectively. Samples were mixed with pH 2 ultrapure perchloric acid aqueous solution at a ratio of 0.5 g to 50 mL, and then shaken for 288 h at 25±1 °C. The mixtures were sampled at certain reaction time, filtered. pHs and concentrations of metal elements in the filtered solution were analysed. The corresponding leached minerals were dried for subsequent analysis.

Elemental analysis showed the Sb Wt% in leaching extracts of the four minerals is 40%~66%. Hazardous heavy metals, such as As, Pb, Cr, Cd, and other metals Fe, Mn, Zn, Cu, W, Sn and silica were also detected. XRD results illustrated that the four samples are mainly composed by Sb<sub>2</sub>S<sub>3</sub> with minor SiO<sub>2</sub>. Leaching data revealed that concentration of Sb, Fe, As, Cr, Mn, S increased with increasing leaching time (until 200 h) and then increased gently. However, pHs were almost invariably during the 288 h reaction. The SEM graphs displayed that the small grains, sharp edges in leached minerals were dissolved and smooth surfaces of original samples became rough after leaching.

The elevated concentrations of a broad range of potentially toxic 'heavy metals' by acid leaching of sulfide minerals and the predominance of their generally more harmful, cationic forms at low pH, present serious risks to all forms of life in receiving water bodies.

# GIS as a tool to identify potential associations between environmental and health data

Chaosheng Zhang<sup>1,@</sup>

1 : GIS Centre, Ryan Institute and School of Geography and Archaeology, National University of Ireland, Galway (NUI Galway), Ireland - **Website**

Geographical information system (GIS) is widely recognised as useful tools in environmental and health studies. With the large number of environmental and health databases constructed at regional, national and international scales, the analyses of such data and their associations become a challenging task. Spatial analysis functions in a GIS provide useful tools for interpretation of environment and health data which contain both attribute and spatial information. The topics discussed in this study included spatial outlier identification and spatial variation. Outliers in a dataset can cause biased statistical results if they are not properly identified and handled. Spatial outliers are identified based on a comparison with their neighbouring data, and they may imply a different process from the background such as pollution or disease hotspots. Spatial variation has been conventionally evaluated using visual interpretation based on maps, but the development of local statistics enables its quantification spatially. When the spatial outliers and/or spatial variation of environmental and health data show common or similar spatial patterns, they provide information of their potential associations. These issues are demonstrated using environmental geochemical data from Ireland, with the potential of inclusion of health data in the near future.

# Application of factor analysis and geostatistics to identify processes controlling the distribution and bioaccessibility of trace elements in Northern Ireland soils

Sherry Palmer<sup>1,@</sup>, Ulrich Ofterdinger<sup>1,@</sup>, Jennifer Mckinley<sup>2,@</sup>

**1** : Queen's University Belfast; School of Planning, Architecture and Civil Engineering (QUB SPACE), David Keir Building, Stranmillis Rd, Belfast, BT9 5AG - United Kingdom - **Website**

**2** : Queen's University Belfast; School of Geography, Archaeology and Palaeoecology (QUB GAP), Elmwood Ave, Belfast, BT7 1NN - United Kingdom - **Website**

Geologic and environmental factors acting over varying spatial scales can control trace element distribution and mobility in soils. In turn, the mobility of an element in soil will affect its oral bioaccessibility. Geostatistics, kriging and principal component analysis (PCA) were used to explore factors and spatial ranges of influence over a suite of 8 element oxides, soil organic carbon (SOC), pH, and the trace elements nickel (Ni), vanadium (V) and zinc (Zn). Bioaccessibility testing was carried out previously using the Unified BARGE Method on a sub-set of 91 soil samples from the Northern Ireland Tellus1 soil archive. Initial spatial mapping of total Ni, V and Zn concentrations shows their distributions are correlated spatially with local geologic formations, and prior correlation analyses showed that statistically significant controls were exerted over trace element bioaccessibility by the 8 oxides, SOC and pH. PCA applied to the geochemistry parameters of the bioaccessibility sample set yielded three principal components accounting for 77% of cumulative variance in the data set. Geostatistical analysis of oxide, trace element, SOC and pH distributions using 6862 sample locations also identified distinct spatial ranges of influence for these variables, concluded to arise from geologic forming processes, weathering processes, and localised soil chemistry factors. Kriging was used to conduct a spatial PCA of Ni, V and Zn distributions which identified two factors comprising the majority of distribution variance. This was spatially accounted for firstly by basalt rock types, with the second component associated with sandstone and limestone in the region. The results suggest trace element bioaccessibility and distribution is controlled by chemical and geologic processes which occur over variable spatial ranges of influence.

# Assessment of Heavy Metals Concentration (Cd, Cr, Cu, Fe, Mn, Pb and Zn) in water samples of Cahora Bassa Dam in Mozambique and the environmental effect

Noor Gulamussen<sup>1,@</sup>

1 : Eduardo Mondlane University (UEM) - Mozambique

Water quality has become a very big issue today, particularly because of the tremendous growth of the nation's population and urban expansion and development. Around the world, many researchers investigate the impact of the increasing concentrations of heavy metals in the environment. The sources can be the litogenic and/or antropic activities.

The Zambezi basin is being affected by pollution problems associated with industrial development, energy production, deforestation and pressure on the natural resources.

The direct sources can be identified by direct discharges of urban, industrial and mining activities, and the deficient residual water treatment. This pollution can be transferred to the dam though the discharges of the Kariba and the contributions of Manyame/panhame river basin, the most urbanized of Zimbabwe, also from industries (paper, chemical products and fertilizers) and mining extraction of coal, copper, niquel, gold and other metals. In Zambia, the transport of pollutants can result from the discharge of urban, mining and industrial effluents on Kafue basin in Copperbelt region.

Cahora-bassa dam is located along the Zambezi river in Mozambique, one of the major rivers in Africa that passes through Angola, Botswana, Malawi, Mozambique, Namibia, Tanzania, Zambia and Zimbabwe.

In the Zambezi River nearly Mozambique, the highest impact of this pollution is not well investigated and registered, it gives credit that the quality of vegetation, soils and water are negatively affected.

In this study, concentrations of Cd, Cr, Cu, Fe, Mn, Pb and Zn from Cahora Bassa dam were determined by AAS and compared with USEPA, DWAF and OMS limits.

The concentrations of the heavy metals was between 0.12-0.21 µg/L for Cd, 0.14-0.34 µg/L for Cr, 0.46-0.97 µg/L for Cu, 104-180 µg/L for Fe, 1.24-4.43 µg/L for Mn, 3.01-9.81 µg/L for Pb and 30-35 µg/L for Zn. There are above USEPA, DWAF and OMS limits for domestic, farming and industry use.

The results show that the levels Cd, Cu and Zn was higher than the DWAF limits for aquaculture (0-0.2 µg/L, nd and ≤ 0.03 µg/L respectively) and maintenance of aquatic systems (≤0.15 µg/L, ≤ 0.0003 µg/L and □0.002 µg/L respectively) meaning that there are not adequate for that use.



# Geochemical background and health status of inhabitants of the Slovak Republic

Stanislav Rapant<sup>1,@</sup>, Veronika Cveckova<sup>1,@</sup>, Katarina Fajcikova<sup>1,@</sup>, Maria Letkovicova<sup>2,@</sup>

1 : State Geological Institute of Dionyz Stur (SGIDS) - **Website**

*Mlynska dolina 1 81704 Bratislava - Slovakia*

2 : Environment a.s., *Dlhá 110 Nitra - Slovakia*

Geological environment of the Slovak Republic was divided to 8 main geological units for the evaluation of its potential negative impact on health status of inhabitants: Paleozoic, Crystalline, carbonatic Mesozoic and basal Paleogene, carbonatic-silicate Mesozoic and Paleogene, Paleogene flysch, Neogene volcanics and Neogene and Quaternary sediments. Further, datasets of environmental indicators (contents of chemical elements/compounds in groundwater, soils) and health indicators (indicators of health status and demographic growth) were divided according to these geological units. Based on these data, rock environment built up by Neogene volcanics was identified as the most unfavourable while as the most favourable rock environment documented Paleogene sediments (sandstones, shales, claystones) are documented. The most significant differences between these two geological environments were documented mainly for following health indicators: mortality due to diseases of digestive and respiratory system (more than 100%), mortality due to cardiovascular diseases, mortality due to diseases of endocrine system (nearly 50%) and also mortality due to oncological diseases (nearly 30%). These associations are supposed probably to relate to deficit contents of Ca and Mg in drinking groundwater of Neogene volcanics that are on about half levels in comparison to groundwater Ca and Mg contents of Paleogene sediments.

# The impact of geological environment on health status of residents of the Slovak Republic

Veronika Cveckova<sup>1,@</sup>, Zuzana Dietzova<sup>2,@</sup>, Katarina Fajcikova<sup>1,@</sup>, Maria Letkovicova<sup>3,@</sup>, Stanislav Rapant<sup>1,@</sup>, Darina Sedlakova<sup>4,@</sup>

**1** : State Geological Institute of Dionyz Stur (SGIDS) - **Website**  
*Mlynska dolina 1 81704 Bratislava - Slovakia*

**2** : Regional Office of Public Health, *Ipeľská 1 Košice - Slovakia*

**3** : Environment a.s., *Dlhá 110 Nitra - Slovakia*

**4** : Office of the WHO in the Slovak Republic, *Limbová 2 Bratislava - Slovakia*

The geological environment of Slovakia is particularly varied. Diverse geochemical conditions have positive or negative impacts on human health. This project will focus on assessing the negative impacts of both natural (geological) conditions and anthropogenic contamination on human health.

The project's main objective is to reduce the negative impact of geological conditions on the health of the population of the Slovak Republic. Specific objectives are:

- To compile data on environmental indicators for groundwater and soil from the whole territory of the Slovak Republic;
- To compile data on the health indicators for the Slovak Republic that are most influenced by geological conditions;
- To link the environmental- and health- indicator data and assess their interrelationship;
- To identify and characterize the areas whose residents suffer from health problems associated with an unfavorable geological environment;
- To carry out environmental-health analysis by regions, and to define maximum levels for chemical elements/compounds in soil and groundwater based on negative human health effects;
- To draw up a proposal to reduce the negative environmental impact of geological conditions on the health of the Slovak population; and
- To implement the proposed measures.

The main result of the project will be gradual and long-term improvement of the health status of Slovak resident population.

# Challenges in drinking water quality control in South Estonia – removal of naturally high iron at water treatment plants

Enn Karro<sup>1,\*,@</sup>, Mariina Hiiob<sup>1,@</sup>, Andres Marandi<sup>1,@</sup>, Marge Uppin<sup>1,@</sup>

1 : Department of Geology, University of Tartu, *Ravila 14a, 50411 Tartu - Estonia*

\* : Corresponding author

Groundwater abstracted from the terrigenous Middle Devonian (D2) aquifer system is the main source of drinking water in South Estonia. Naturally high iron and manganese concentrations are the greatest water quality problems in this region. The content of Fetot exceeds the limit value of 0.2 mg/L set to the drinking water in 70% of the wells. In places the Fetot concentrations up to 16 mg/L have been detected. High Fetot concentrations are mainly caused by high Fe<sup>2+</sup> contents in groundwater, referring to the domination of reducing conditions in aquifer system.

The aim of performed pilot study was to estimate the effectiveness of groundwater purification systems. Water treatment facilities convert the dissolved forms of iron and manganese into insoluble forms so that those could be filtered out. Eight different water treatment systems were used in 20 studied water treatment plants. Filter materials such as Manganese Greensand, Birm, Nevtraco, Hydrolit-Mn, Magno-Dol and quartz sand were combined with aeration.

The results of the study show that Fetot content in abstracted groundwater (0.46-4.46 mg/L) was reduced to the level of 0.03-2.13 mg/L during the purification. Still, of 20 water treatment plants only 13 achieved a reduction of iron concentration to the level corresponding to the drinking water requirements. The systems with pre-aeration remove iron effectively, then pre-aeration is not applied, Fetot content remains between 0.22-2.13 mg/L. Manganese content decreased below the maximum concentration limit in only 25% of the systems and when the filter material was Birm or quartz sand and pre-oxidation was applied.

While the oxygen-poor conditions prevail in the D2 aquifer system, pre-aeration is needed in order to increase the effectiveness of the purification process. Furthermore, to achieve the best results in water cleaning, the treatment facilities should be maintained regularly and according to the requirements of their deliverer and producer.

***Topic 2***  
***Biogeochemistry and Ecotoxicology***  
***(including cross topics 2-3)***  
***Oral Presentations***

# Assessment of three fluvial sediment sampling methods for understanding the evolution of heavy metals and their toxicity in Oka River catchment (Northern Spain)

Miren Martinez-Santos<sup>1,@</sup>, Luis Montoya-Armenta<sup>2,@</sup>, Borja Muñoz-Leoz<sup>2,@</sup>, Estilita Ruiz-Romera<sup>2,@</sup>

**1** : Department of Geodynamics, University of the Basque Country Sarriena auzoa z/g, Leioa, Basque Country, Spain 48940 - Spain

**2** : Department of Chemical and Environmental Engineering, University of the Basque Country, Alameda Urquijo z/g, Bilbao, Basque Country, Spain 48013 - Spain

Heavy metals are regarded as serious pollutants of aquatic ecosystems, due to their persistence, toxicity, and ability to be incorporated into food chain. Therefore, obtaining representative samples of fluvial sediment is of fundamental importance in studies concerned with quantifying geochemical fluxes and understanding water quality. Three methods have been used to collect sediments along time and different hydrodynamic situations: a discontinuous spot sampling method (surface bottom sediments, SBS) and two continuous methods (time-integrated sampling, TIS, and suspended sediment concentration, SSC, measured during five flood events). Heavy metals concentrations (Cu, Ni, Pb, Cr, Mn, Zn and Fe) of the sediments collected by these three methods do not show statistical differences (except Cu and Fe), thus any of them could be used to collect representative fluvial sediments. However, neither TIS nor SBS allow us to clarify the evolution of heavy metals concentration and their risk of toxicity in a highly detailed way during flood events. The pollution status of suspended sediments during five flood events was evaluated by employing effects quotient (ERMQ index) based on sediment quality guidelines. The rising and falling limbs sediment samples exhibited a higher pollution index (0.51–1.5) and can be considered of medium-high priority. Medium-low risk was never exceeded at flow peak, where, in contrast, high concentration of Cu (2.6 ug/L), Ni (3.44 ug/L), Zn (48.5 ug/L), Pb (0.36 ug/L) and Cr (0.27 ug/L) were recorded in dissolution. Remobilisation of sediment-associated contaminants during floods leads to metal release due to solubility processes, particularly during flow peak. Finally, the good potential relationship ( $r^2=0.80$ ) established between turbidity and ERMQ index can be used to infer the toxicity risk level in future floods. Knowledge of heavy metals behaviour could help the managers of the Urdaibai Biosphere Reserve (Oka River catchment) to take more effective measures for regulation and conservation.

# Trace elements bioavailability in saline terrestrial environment

Lana Matijević<sup>1,\*,@</sup>, Davor Romić<sup>1,@</sup>, Marija Romić<sup>1,@</sup>

**1** : University of Zagreb Faculty of Agriculture - **Website**  
Svetosimunska 25, 10000 Zagreb - Croatia

\* : Corresponding author

Processes that control the mobility, transformation and toxicity of metals in soil are of special importance in the soil root developing zone. For this reason, there is a considerable interest in understanding trace elements behaviour in soil, with special emphasis on processes by which plants take them up. Increased root zone salinity due to saline irrigation can affect plant element uptake and trace elements accumulation in tissue. Long-term and extensive use of land for agriculture with frequent application of agri-chemicals is one of the major causes of trace metal, such as copper, nickel, zinc and cadmium, accumulation in soil. Accumulation of Cu in agricultural soil is a common consequence of using copper containing fungicides to control plant diseases. The soil property that most determines the sorption of TEs is organic matter (OM) content and Cu complexation by OM is an effective mechanism of Cu retention in soils, controlling thus its bioavailability. A greenhouse pot experiment was therefore conducted to study the effects of soil copper contamination in a saline environment on faba bean (*Vicia faba* L.) element uptake. Treatment with NaCl salinity was applied (control, 50 mM NaCl and 100 mM NaCl) on faba bean plants grown in a control and in a soil spiked with Cu (250 and 500 mg/kg). Low and high soil OM content trial variants were investigated. Cu accumulation occurred in faba bean leaf, pod and seed. Cu contamination affected plant element content in leaves (Na, Ca, Mg, Mn), pod (Mn) and seed (Mn, Mo, Zn). Root zone salinity also affected faba bean element content. Furthermore, Cu contamination – salinity and salinity – OM content interaction was significant for pod Cu content. Future research will be focused on the mechanisms of Cu translocation in plant and adaptation aspects of abiotic stress.

# Assessment of metal lability in freshwater sediments by passive sampling in response to bioturbation

Aymeric Dabrin<sup>1,@</sup>, Rodolphe Etienne<sup>1,@</sup>, Benoit J.D. Ferrari<sup>1,@</sup>,  
Marina Coquery<sup>1,@</sup>

**1** : Institut national de recherche en sciences et technologies pour l'environnement et l'agriculture (Irstea - UR MALY (Freshwater Systems, Ecology and Pollution Research Unit). Irstea, 5 rue de la Doua CS 70077, 69626 Villeurbanne Cedex - France

The bioavailability of trace metals in sediments depends upon many factors such as the target metal, its colloidal, dissolved and particulate partition, sediment physico-chemical characteristics and acid volatile sulphide (AVS) content. Moreover, organism's activity in sediments induces both a modification of redox conditions disturbing particulate and dissolved partition and an increase of metal diffusion at the sediment interface. It was shown that passive samplers such as Diffusive Gradient in Thin films (DGT) represent a powerful tool to assess metal availability in sediments (Dabrin et al., 2012). In order to assess the impact of bioturbation on metal availability at the sediment interface, we used DGT-probes to measure labile metals at the water-sediment interface with a sub-centimetric resolution on sediment enriched with different density of organisms.

Laboratory experiments were conducted using sediment placed in PVC tubes, allowing to use DGT probes and to simultaneously introduce organisms at environmental relevant density (6000 to 18000 ind. m<sup>-2</sup>, Goedkoop and Peterson, 2003). Two benthic species were tested: an insect larvae (*Chironomus riparius*), mainly living in the first top centimeter of the sediment; and oligochetes (*Tubifex tubifex*), living at greater depth in the sediment. Sediment columns also allowed millimetric measurements of oxygen, pH and redox potential, and for AVS measurements.

Results showed that oxygen penetration in the first millimeters of sediment increased with increasing chironomids density, inducing a strong decrease of AVS contents. The expected release of labile metals into pore waters induced by AVS oxidation was easily shown at highest density by DGT-probes for Mn and Ni. Labile concentrations in the first top centimeter of sediments increased by 180% (Mn) and 67% (Ni) between sediments without chironomids and sediments with the highest density of chironomids. As for oligochetes, since their distribution in sediment was deeper, benthic exchanges of water at the sediment–water interface were less important and no significant modification of redox conditions nor metal labile pore waters concentrations were shown.

## References:

- Dabrin, A., Durand, C.L., Garric, J., Geffard, O., Ferrari, BJD, Coquery, M., 2012. Coupling geochemical and biological approaches to assess the availability of cadmium in freshwater sediment. *Science of the Total Environment*, 424: 308-315.
- Goedkoop, W. and Peterson, M., 2003. The fate, distribution, and toxicity of lindane in tests with *Chironomus riparius*: Effects of bioturbation and sediment organic matter content. *Environmental Toxicology and Chemistry*, 22(1): 67-76.

# The influence of Mobile forms of PTEs on oak forest stands along an urban-rural gradient in Sofia region, Bulgaria.

Vanya Doichinova<sup>1,@</sup>, Miglena Zhiyanski<sup>1,@</sup>, Andrew Hursthouse<sup>2,\*,@</sup>

1 : Forest Research Institute-BAS, Sofia - Bulgaria

2 : School of Science, University of the West of Scotland (UWS) - **Website**

PA1 2BE, Paisley - United Kingdom

\* : Corresponding author

Forest parks in many urbanized areas are affected by the anthropogenic pollution as demonstrated by the poor health status of many trees. The concentrations of harmful agents like Potentially Toxic Elements (PTEs) can be very high in urban soils and their biological availability is an important issue for biota exposed in these environments. This study focuses on the mobile portion of PTEs (Cu, Zn, Pb, Cd) extracted by 1 M NH<sub>4</sub>COOCH<sub>3</sub> (NH<sub>4</sub>OAc) at pH = 7, to determine bioavailability for forest trees in oak ecosystems. The study sites were situated along an urban-rural gradient from the Sofia region of Bulgaria. The NH<sub>4</sub>OAc predominantly extracts the “biologically active” fraction of elements in soils (i.e. soluble, exchangeable and complexed components) and showed good positive correlation with PTE accumulation in trees.

Four experimental forest park sites planted on *Urbic Anthrosols* were selected along the urban gradient in the Sofia region (U1 – Borisova garden, U2 – Loven park, U3 – Western park and U4 – Northern park). The control sites located in rural zones and were natural soils ( R1 – German monastery (*Chromic Luvisols*), R2 – Tihia kat (*Eutric Cambisols*); R3 – Monastery meadows (*Mollic Cambisols*) and R4 – Beledie khan (*Chromic Luvisols*)). We obtained strong correlations between mobile forms of Cu, Zn, Pb, Cd in urban soils and a number of soil parameters (pH, CEC and texture). The mobility is related to soil pH with more acidic soils showing higher mobility. The element Cu was found to be less mobile through the soil profile and is localized in the top soil, where it is predominantly associated with soil organic matter. The range of total NH<sub>4</sub>OAc extractable Cu, Zn, Pb, Cd (mg/kg dry soil) at the different sites were: 0.74 – 2.61; 2.45 – 3.29; 1.34 – 3.28; 0.02 – 0.07 [URBAN], and 0.73 – 1.65; 1.20 – 5.29; 1.10 – 6.80; 0.02 – 0.18 [NATURAL]. The significance of the mobile proportion, was greatest for Cd in Urban soils samples where it reached 33.3% of the total content. The assessment of health status of oaks tree vegetation based on indices defoliation of crown and changes in color do not correlate significantly with the bioavailable concentration of PTEs in the soils.



## Caged gammarids for the characterization of contamination levels in continental waters

Jean-Philippe Besse<sup>1,@</sup>, Marina Coquery<sup>1,\*,@</sup>, Christelle Lopes<sup>2,@</sup>, Arnaud Chaumot<sup>1,@</sup>, Olivier Geffard<sup>1,@</sup>

**1** : Milieux aquatiques, écologie et pollutions (UR MALY) - **Website**

CEMAGREF, 5 rue de la Doua, CS70077, 69626 Villeurbanne Cedex - France

**2** : Laboratoire de Biométrie et Biologie Evolutive (LBBE) - **Website**

CNRS : UMR5558, Université Claude Bernard - Lyon I, INRIA, 43 Bld du 11 Novembre 1918 69622 VILLEURBANNE CEDEX - France

\* : Corresponding author

Monitoring trace metals and hydrophobic substances in water is challenging. Therefore, chemical biomonitoring (i.e., monitoring contamination in biota) is often proposed as a relevant approach to characterize the contamination of aquatic systems. Active chemical biomonitoring (i.e., using transplanted organisms from a reference site) allows controlling exposure time, age and size of organisms, therefore providing comparable results. As such active approaches are still an emerging issue for continental waters, we recently implemented an active biomonitoring approach based on the ecologically relevant amphipod *Gammarus fossarum*.

In a first study, Gammarids were translocated into cages to 27 sites in streams/river of the Rhône-Alpes basin. Study sites represented different physico-chemical characteristics and various anthropic pressures. To avoid the influence of biotic factors, only male with the same average body length were exposed and gammarids were fed during the experiment. After one week of exposure, concentrations of 11 metals/metalloids (Cd, Pb, Hg, Ni, Zn, Cr, Co, Cu, As, Se and Ag) and 38 hydrophobic organic substances (including PAHs, PCBs, PBDEs and organochlorine pesticides) were measured. All metals, except Ag, and 33 organic substances among 38 were quantified in *G. fossarum*, showing that this species is relevant for chemical biomonitoring. The control of biotic factors allowed a direct inter-site comparison of the bioavailable contamination levels. Overall, our results showed the interest and robustness of the proposed approach for assessing trends of bioavailable contamination in continental waters. Furthermore, we built threshold values of bioavailable contamination in gammarids, assuming that any concentration above such a threshold would be considered as representative of the bioavailable contamination at the sampling site. We will also present preliminary results on metals of a subsequent large-scale pilot study implemented in 2012 on more than 130 sites selected from across the French territory, to assess the validity at national scale of predetermined threshold values.

# Use of the "Comet" assay on higher plants and earthworms to assess the genotoxicity of anthropic contaminated soils.

Sébastien Lemière<sup>1,\*,@</sup>, Damien Cuny<sup>2,@</sup>, Fabien Bernard<sup>1,2,@</sup>,  
Sylvain Dumez<sup>2,@</sup>, Fabrice Nessler<sup>3,@</sup>, Anne Platel<sup>3,@</sup>, Franck  
Vandenbulcke<sup>1,@</sup>, Annabelle Deram<sup>2,\*,@</sup>

**1** : Univ Lille Nord de France. *Université des Sciences et Technologies de Lille - Lille I* : EA4515, LGCgE EA 4515, Lille 1, EcoNum-Ecotox, Cité scientifique, SN3, F-59655 Villeneuve d'Ascq, France

**2** : Univ Lille Nord de France. *Université du Droit et de la Santé - Lille II*: EA4483, LSVF, EA 4483, Univ Lille 2, Pharmacy Faculty, 3 rue du Professeur Laguesse BP83, F-59006 Lille Cedex, France

**3** : Univ Lille Nord de France. *Institut Pasteur de Lille, Toxicology Lab, Pasteur Institute of Lille*, 1 rue de Pr Calmette, BP245, F-59019 Lille Cedex, France

\* : Corresponding author

It is now well accepted that biological responses should be considered in risk assessments and management strategies for contaminated soils and wastelands. Among these biological responses, environmental genotoxicity has to be investigated. In order to study soil genotoxicity, we have to consider: 1) environmental and toxicological bioavailabilities of contaminants, influenced by soil factors and ageing phenomena, 2) their concomitant presences at low concentrations and 3) their potential toxic interactions.

Since methods of classical genetic toxicology, such as the *in vivo* rodent micronucleus assay after soil ingestion or the Ames test on soil extracts, did not seem fully satisfactory, we decided to use environmental genotoxicity markers. The "Comet" assay, a technique allowing the evaluation of DNA damage in a cellular population, was developed 1) on cells of two complementary plant species: *T. repens* (White clover, wild or cultivated mycorrhizal plant) and *B. oleracea* (Cabbage, cultivated species, non-mycorrhizal) and 2) on coelomocytes of the earthworm *E. fetida*.

In a first experiment, we conducted *in vivo* short to mid-term co-exposures (3, 10 and 56 days) using an urban-surrounding soil spiked with cadmium and/or lead at environmental concentrations. Later, we conducted *in vivo* short-term co-exposures using well-characterised soils originating from two different areas in Northern France, 1) from the vicinity of a former smelter and 2) from a suburban zone close to a battery plant. In both contexts, soils were sampled along a contamination gradient. The genotoxicity results, as well as metal bioaccumulation in the three species after each exposure, will be detailed and discussed.

Our results emphasized the complementarity of our three model species (trophic levels, exposure routes) and of their biological responses (precocity, intensity). The main conclusion of this work is that our battery of environmental genotoxicity markers is useful and relevant for environmental hazard assessment of anthropic contaminated soil.

# Linking chemical availability of trace elements with toxicological effects in earthworms exposed to moderately contaminated soils

Léa Beaumelle<sup>1,\*,@</sup>, Mickaël Hedde<sup>1,@</sup>, Jodie Thénard<sup>1,@</sup>, Jean-Pierre Pétraud<sup>1,@</sup>, Nathalie Cheviron<sup>1,@</sup>, Isabelle Lamy<sup>1,@</sup>

**1** : Physicochimie et écotoxicologie des Sols et d'Agrosystèmes Contaminés (PESSAC) - **Website**  
INRA-UR251, Batiment 6 RD 10 78026 Versailles Cedex - France

\* : Corresponding author

Assessing trace elements bioavailability in soils is still a challenge. The combined use of chemical and biological methods to study bioavailability has been recommended. Biomarkers of metal exposure or stress are supposed to represent metal toxicological bioavailability. However, few studies investigated the relationships between biomarkers and environmental availability of metals. Furthermore, biomarkers are mainly studied in heavily contaminated soils although several works have reported opposite patterns of biomarkers responses between low and high doses of metals.

The objective of this work is to study the relationships between environmental availability of trace elements in soils and the levels of biomarkers (energetic reserves) in earthworms used as model organisms.

Adult earthworms (*Aporrectodea caliginosa*) were exposed for 21 days to 31 agricultural soils uncontaminated or moderately contaminated *in situ* with Cd, Cu, Pb and Zn and covering a wide array of soil properties. Environmental availability was assessed both experimentally and theoretically after chemical extractions (CaCl<sub>2</sub>, EDTA) or modeling. Energetic reserves like lipid and protein contents were measured in earthworms at the end of the experiment.

Protein contents in earthworms increased with available metal concentrations, suggesting that earthworms reacted to metal exposure by synthesizing more proteins. This result is consistent with previous works that have shown a hormetic response of protein content to metal contamination. In addition, the response of lipid content to metal availability was found to be strongly affected by the soil texture.

The results stress the relevancy of earthworm energetic reserves in signaling exposure to moderate doses of trace elements, a conclusion that could not have been drawn using only total metal concentrations.

To our knowledge, this is the first work that reports relationships between earthworm lipid and protein contents, soil parameters and metal contamination.

# Metal species in water from metalliferous black shales and their implications for faunal uptake, N. Sweden

Gunnar Jacks<sup>1,@</sup>, Björn Sundblad<sup>2,@</sup>

1 : Åbo Akademi, FI-20500 Turku (abo.fi) - **Website**

*Domkyrkotorget 1, FI-20500 Turku - Finland*

2 : Ecolus Company, Blåklintsvägen, SE-61145 Nyköping - Sweden

Metal species have been studied in surface water from black metalliferous shales in northern Sweden. The shales are of Precambrian age in the Västerbotten county and of Cambrian age in Jämtland county.

The Precambrian shales contain about 1 % sulphides and the metals are mainly arsenic and zinc while the Cambrian shales contain elevated contents of uranium, molybdenum, nickel and vanadium. Metals were speciated by sampling water as unfiltered, filtered through 0.2 micrometer filters and treated by dialysis through 10 and 1 kDa dialysis membranes respectively. Unfiltered water could be considered to include all fractions including metal in suspended form while the filter would allow colloidal metals to pass. The dialysis would give species approximately of the molecular weights less than 10 000 respectively less than 1000.

In the Precambrian shale areas the transfer of arsenic from water to macroinvertebrate species and fish was studied. Elevated arsenic levels were seen in surface waters with elevated iron content and the arsenic was predominantly in suspended form. Benthic macroinvertebrates had elevated inorganic arsenic species (As(III) and As(V)) while fish did not show that. The inorganic arsenic is far more toxic than organic ones. The benthic macroinvertebrates are exposed to discharging reduced groundwater rich in As(III) while the benthic fauna only constitutes a fraction of the fish food. The rest, being mosquito larvae and other species in the water column, being exposed to far lesser bioavailable arsenic levels.

In the Cambrian shale areas molybdenum, nickel and uranium tended to be present in mostly dissolved forms. This indicates a higher bioavailability of the metals. While we have preliminary indications of that we have so far a limited amount of samples studied. Uranium may be taken up by fish directly from water e.g. through olfactory membranes. Fish has been shown to be a major portion of the food intake of uranium by humans.

# Marine sponges as indicators of PAH concentration and sources in coastal waters

Angela Wagener<sup>1,@</sup>, Karla Fontes<sup>1,@</sup>, Daniela Batista<sup>1,@</sup>,  
Adriana Nudi<sup>@</sup>

1 : Pontifical Catholic University of Rio de Janeiro (PUC-Rio) - **Website**  
Caixa Postal 38097 Rio de Janeiro, RJ, Brazil - Brazil

Marine sponges can be found at several water depths in the marine environment and due to its high filtering capacity may accumulate substances dispersed in seawater. The increasing in offshore oil exploration implies risk to marine life therefore it is desirable to identify suitable bioindicators for oil components and in special for PAH due to their toxicity. The goal of the present work was to validate the efficiency of *Hymeniacidon heliophila* as bioaccumulator of PAH and to characterize the PAH typology in comparison with the mussel *Perna perna*. For this 33 PAH (parental and alkylated homologs) were determined in seawater samples and in tissues of sponges and mussels sampled from several stations of different contamination levels in the coastal area of Rio de Janeiro, Brazil. PAH were evaluated in single individuals (11 from each observed station) as well as in pool of tissue from several sponges. The variability of Total PAH among individual sponges ranged from 16 to 47% and is independent of lipid content or sponge volume (size). In the sponges a preference to retain 5-6 ring PAH was observed. This is possibly due to the ability of sponges to retain particles which are smaller than 1  $\mu\text{m}$ , typically derived from fossil fuel combustion and therefore enriched in the high molecular mass PAH. In respect to the PAH typology in water and in sponges the later also show increment of pyrolytic compounds. In spite of this Total PAH concentration in the sponges is proportional to the contamination level in the sampled sites. The ubiquity of the species and the bioaccumulation pattern are typical of an organism suitable to successfully monitor the presence of PAH in seawater.

## Mollusks as sensitive indicators for monitoring heavy metal pollution in Khan Hoa coastal, Viet Nam

Tran Thi Mai Phuong<sup>1,2,\*,@</sup>, Nicolas Marmier<sup>2,\*,@</sup>, Charlotte Hurel<sup>2,@</sup>, Nguyen Ky Phung<sup>1,@</sup>

**1** : University of Science Ho Chi Minh City (Faculty of Environment) - **Website**  
227 Nguyen Van Cu street, District 5, Ho Chi Minh City - Vietnam

**2** : University of Nice Sophia Antipolis (EA 4228 ECOMERS, Faculty of Science) - **Website**  
Unice, Parc Valrose, 06108 Nice cedex 2, - France

\* : Corresponding author

For monitoring heavy metal pollutions of coastal area of Nha Trang bay, seven different marine benthic organisms (with special regard on natural populations), were collected from four coastal locations (Tan Dao, Ngoc Diem, Binh Tan, Cam Hai Tay) along the Nha Trang bay, Khanh Hoa province, Viet Nam, in dry and rainy seasons 2012. Some biologic parameters as organism length, width, height, dry weigh of soft tissues and heavy metals concentrations (Al, Fe, As, Cd, Cr, Cu, Ni, Pb, Zn) were measured. Metal concentrations of Al and Fe in the tissue of the four sites were similar and did not vary significantly and presented very lower compared to concentrations of these metals in the sediments. Concentrations of Al and Fe in the sediments were 20-100 times higher than the concentration in the mollusks. Then, bioaccumulated heavy metals in the different mollusks were compared and their correlation with the environmental compartment parameters (concentrations of heavy metal, pH, particles size, content of organic carbon in sediments) have been investigated.

Results indicated that different species showed different bioaccumulation of metals levels depending on the geographical location and physicochemical characteristic of sediments. The BSAF indicated a low potential bioaccumulation for Pb and Cr (BSAF<1) and a very high potential of accumulation for As, Cd, Cu and Zn. Two clams *Katelaysia hiatina* (Lamarck 1818) and *Glauconome virens* (Linnaeus, 1767) highly accumulate As, Cd and Zn, and then could be chosen as sensitive indicators for monitoring heavy metal pollutions in Khanh Hoa coastal, Viet Nam.

# Effects of short-term exposure of *Xenopus laevis* tadpoles to multi walled carbon nanotubes on antioxidant enzymes activities and DNA damages

Rayenne Saria<sup>1,2,@</sup>, Florence Mouchet<sup>1,2</sup>, Annie Perrault<sup>1,2</sup>,  
Christophe Laplanche<sup>1,2</sup>, Emmanuel Flahaut<sup>3,@</sup>, Christian  
Gancet, Jean-Charles Boutonnet, Eric Pinelli<sup>1,2,@</sup>, Laury  
Gauthier<sup>1,2,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Institut carnot CIRIMAT (Centre inter-universitaire de Recherche et d'Ingénierie des Matériaux) (CIRIMAT) - **Website**

Université Paul Sabatier - Toulouse III, Institut National Polytechnique de Toulouse - INPT, CNRS : UMR5085

31062 Toulouse cedex 9 - France

Because of their growing annual world production capacities, carbon nanotubes are likely to be released in the environment, and would thus end in the aquatic compartment, well known as a main receptacle of pollutants. Nevertheless, until now, very few studies were realized on industrial multiwalled carbon nanotubes (MWNTs). Preliminary studies on *Xenopus laevis* larvae revealed an acute toxicity (mortality) at high concentrations (>50 mg/L) of MWNTs. In contrast, no chronic toxicity (growth inhibition) was measured after 12 days of exposure at lower concentrations (<10mg/L). In this study, we tested the effect of short time exposure (from 2 to 24 hours) of *Xenopus* larvae at low concentrations of MWCNTs (0.1 and 1mg.L<sup>-1</sup>) on oxidative stress and DNA damages. Amount of reactive oxygen species (hydrogen peroxide [H<sub>2</sub>O<sub>2</sub>]) and activities of antioxidant enzymes (Super Oxyde Dismutase [SOD], Glutathione Reductase [GR] and Catalase [CAT]) were measured. DNA damages were assessed according to the alkaline comet assay in red blood cells of *Xenopus*. For the concentration of 1 mg.L<sup>-1</sup>, the results obtained showed an evolution of the measured parameters over time with an increase in enzymatic activity of CAT and GR after only 4 hours of exposure to MWCNTs. Measurements of reactive oxygen species showed a strong H<sub>2</sub>O<sub>2</sub> production after only 2 hours. For the lowest concentration (0.1 mg.L<sup>-1</sup>) we observed a later induction of CAT and GR activities coupled with a strong H<sub>2</sub>O<sub>2</sub> production that occurred after 8 hours of exposure to MWCNTs. SOD activity did not change with time. The Comet assay results showed a significant enhancement of the comet parameters (tail DNA, tail length) at both concentrations (0.1 and 1 mg/L), fluctuating with exposure time. These results suggest that oxidative stress and DNA damages could be involved in the first stages of toxicity of these nanoparticles in the exposed *Xenopus* larvae in our test conditions.

## Carbon nanotubes and diatoms: a sticky story

Laurent Verneuil<sup>1,2,@</sup>, Jérôme Silvestre<sup>1,2,\*,@</sup>, Emmanuel Flahaut<sup>3,@</sup>, Florence Mouchet<sup>1,2,@</sup>, Laury Gauthier<sup>1,2,@</sup>, Eric Pinelli<sup>1,2,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France

**3** : Institut carnot CIRIMAT (Centre inter-universitaire de Recherche et d'Ingénierie des Matériaux). Université Paul Sabatier - Toulouse III, Institut National Polytechnique de Toulouse - INPT, CNRS : UMR5085, 31062 Toulouse cedex 9 - France

\* : Corresponding author

Manufactured carbon nanotubes (CNTs) are already widely produced and increasingly used. Because of their nanoscale and structure, CNTs have a high specific surface area approaching 1000m<sup>2</sup>/g in the case of double-walled carbon nanotubes. Several studies report on their effect on aquatic photosynthetic organisms. Among them, diatoms are ubiquitous and considered as a main primary producer in aquatic environments. They are characterized by the presence of an external siliceous structure called "frustule". Most diatoms are benthic and represent an important part of some photoautotrophic biofilms. They adhere and move on various substrates by producing extracellular polymeric substances (EPS). The great surface of CNTs and the adherence properties of benthic diatoms as well as the structure of their frustule allow strong interactions between them.

In this work, different techniques of microscopy were implemented to describe and characterize the interactions between a biofilm of freshwater diatoms and double-walled carbon nanotubes (DWCNTs). Light microscopy was used to visualize the structure of a biofilm exposed to DWCNTs. These observations were performed using various staining techniques and fluorescence observations. Results show the high affinity of DWCNTs for biofilm areas with high density of diatoms and EPS. They also show that diatoms strongly impact the dynamics of DWCNTs agglomeration. Scanning electron microscopy (SEM), used to visualize interactions of DWCNTs with the biofilm at cellular level, confirms that DWCNTs strongly adhere to EPS. However, it does not provide any evidence of their direct interaction with diatoms. Moreover, SEM highlights the efficient natural protection conferred by the diatom's frustule against penetration of CNTs into diatom cells.

This work contributes to improving the understanding of CNTs interactions with biofilms of freshwater diatoms. It also presents various microscopy approaches, suitable to assess and characterize interactions between nanoparticles and benthic microorganisms in freshwater environments.



# Ecotoxicology of systemic pesticides: detection and behavior in the environment for risk assessment

Jean-Marc Bonmatin<sup>1,@</sup>

1 : Centre de Biophysique Moléculaire (CBM) - **Website**  
CNRS : UPR4301, Rue Charles Sadron, 45071 Orléans cedex 02 - France

**Context and objectives:** There is an increasing concern in reducing pesticides and their impacts on the environment. New formulations were recently launched: systemic insecticides. They represent  $\frac{1}{4}$  of the world market. Imidacloprid and fipronil are the most representatives of the nicotinoid class and of the pyrazole class, respectively. Both act on the central nervous system for killing target insects. Only a few dozen of grams per hectare are necessary (for 100.000 maize plants for instance). However, these compounds can be very persistent in soils. Additionally, they can contaminate our food. After a chronic exposure, some deleterious effects can affect protected species such as bees.

**Methods:** In order measure the level of insecticide residues, several very sensitive analytical methods were developed (LC/GC-MS-MS). These methods were fully validated. They allow detecting compounds and their main metabolites at less than 1 ng/g (1 ppb) in soils and 1 ng/L in water (1 ppt). Field studies were performed and data were completed with random sampling over the whole French territory. Because other matrices appeared of a particular importance for risk assessment, other methods and studies were also developed for plants, milk and pollen.

**Results and conclusions:** Imidacloprid (nicotinoid) is poorly degraded in soils. Its half-life time  $t_{1/2}$  is 9 months. Thus it can accumulate by successive treatments of crops. Imidacloprid was also found in surface water, but not in groundwater. In harvested crops, its level is between 1 and 50 ng/g. The situation is identical for fipronil (pyrazole). Because corn is largely used to feed cattle, milk was analysed. Such milk contains 0.1 to 2 ng/L of fipronil. Imidacloprid and fipronil were also found at a few ng/g in pollen (maize, sunflower, canola...). This constitutes a major pathway of exposure of beehives and it can be correlated to the worldwide decline of pollinators.

# The Inhibition effect of heavy metals on COD removal in UASB reactor

Metlem Sarioglu Cebeci<sup>1,\*,@</sup>, Turgay Bisgin<sup>1,@</sup>

1 : Department of Environmental Engineering. *Cumhuriyet University, Faculty of Engineering, 58140-Sivas - Turkey*

\* : Corresponding author

Although heavy metal inhibition to the conventional anaerobic treatment processes has been reported, limited studies have been carried out for upflow anaerobic sludge blanket (UASB) reactor. In this study, the inhibition effects of copper (Cu) and zinc (Zn) heavy metals on Chemical Oxygen Demand (COD) removal efficiency were investigated in UASB reactor and heavy metal inhibition concentrations for hydraulic retention time (HRT) of 12 and 24 hour were determined. Influent COD concentration to the reactor was kept constant as  $3000 \pm 100$  mg/l by using glucose as primary carbon source. Studied heavy metal concentrations for both of them were 1, 5, 10, 15, 20 mg/l.

The influent Zn and Cu concentrations at which the COD removal efficiency decreased to 50% for HRT of 12 and 24 hour were found to be 13.37-13.71 mgZn/l and 12.67-13.01 mgCu/l, respectively.

***Topic 2***  
***Biogeochemistry and Ecotoxicology***  
***(including cross topics 2-3)***  
***Oral Presentations***

# Physico chemical characteristics of waters of the high valley of the Oued Bounamoussa (North East Algeria)

Lilia Zaoui<sup>1,@</sup>, Mohamed Besslama<sup>2,@</sup>

**1** : Biochemistry and Ecotoxicology. *Université Badji Mokhtar Annaba, B.P.12, Annaba, 23000 - Algeria*

**2** : Laboratoire des sols et développement durable. Département de biologie, Faculté des sciences. *Université Badji Mokhtar Annaba, B.P.12, Annaba, 23000 - Algeria*

Pollution is present in diverse places among which ground and water. The nature and the origin of these pollutions are very variable. They result from domestic, agricultural and industrial activities. These sources of chemical pollutions are very dangerous, as much for Man as for the environment. Because of continuous human activities, the continental surfaces such as soils receive and absorb waste which may contaminate groundwater.

The resources in surface and ground waters are one of the major wealth of Algeria. Water remains a limited and vulnerable resource which is indispensable to the life, to the development and to the environment. The water-ground relation is very complex and deserves a protection and a good management to insure the perenity of this resource.

Algeria as any country, is sensible to lead ground and water protection policies, which requires a perfect knowledge of this resource and the environment in the which these resources evolve.

With the aim to know the current state of water quality in the Algerian northeast, we achieved a study which concerns the quality of water and the grounds of the high valley of Bounamoussa (El Asfour, wilaya of El Tarf) in North East Algeria. The chemical results of the analysis of waters of the plain of Asfour showed that these waters are of an even strong average salinity, generally suiting for the irrigation of the salt-tolerant cultures on well-drained grounds which are very sensitive to the chemical variations due to the use of artificial fertilizers. The evolution of the salinity must be however controlled.

## Bioaccumulation of PAH in *Hymeniacidon heliophila*: field and bioassay study

Thais Massoni<sup>1,@</sup>, Karla Tellini<sup>2,@</sup>, Daniela Batista<sup>2,@</sup>, Adriana Nudi<sup>2,@</sup>, Angela Wagener<sup>2,@</sup>

1 : Pontificia Universidade catolica do Rio de Janeiro (PUC-Rio), *Rua Marques de São Vicente 225; 22453-900 Rio de Janeiro - Brazil*

2 : Pontifical Catholic University of Rio de Janeiro (PUC-Rio) - **Website**  
*1PUC-Rio – Pontificia Universidade Catolica do Rio de Janeiro Caixa Postal 38097 Rio de Janeiro, RJ, Brazil - Brazil*

Differently from mussels, marine sponges can be found at several water depths in the marine environment and due to its high filtering capacity may accumulate substances dispersed in seawater. The increasing in offshore oil exploration implies risk to marine life therefore it is desirable to identify suitable bioindicators for oil components and in special for PAH due to their toxicity. The goal of the present work was to determine the efficiency of *Hymeniacidon heliophila* as bioaccumulator of PAH, to characterize the PAH typology in comparison with the mussel *Perna perna*, and to measure accumulation and depuration rates of model PAH compounds in bioassays.

For this 33 PAH (parental and alkylated homologs) were determined in seawater samples and in tissues of sponges and mussels sampled from several stations of different contamination levels in the coastal area of Rio de Janeiro, Brazil. PAH were evaluated in single individuals (11 from each observed station) as well as in pool of tissue from several sponges. The bioassay included depuration and accumulation tests (duration of 96 hours) under controlled conditions, and PAH toxicity to the species was tested using the micronucleus assay. The variability of Total PAH among individual sponges ranged from 16 to 47% and is independent of lipid content or sponge volume. In comparison to mussels, sponges showed preference to retain 5-6 ring PAH. This is possibly due to the ability of sponges to retain particles which are smaller than 1  $\mu\text{m}$ , typically derived from fossil fuel combustion and therefore enriched in the high molecular mass PAH. In spite of this tendency Total PAH concentration in the sponges is proportional to the contamination level in the sampled sites. The ubiquity of the species and the bioaccumulation pattern are typical of an organism suitable to successfully monitor the presence of PAH in seawater.

# Toxicity of metal chlorides to *Xenopus* oocytes

Matthieu Marin<sup>1,\*,@</sup>, Sébastien Lemière<sup>2,\*,@</sup>, Guillaume Marchand<sup>1,2,@</sup>, Sylvain Demuynck<sup>2,@</sup>, Jean-François Bodart<sup>1,@</sup>

**1** : Université Lille1 Sciences et Technologies. *Université des Sciences et Technologies de Lille - Lille I : EA4479, Laboratoire de régulation des signaux de division, EA 4479, IFR 147, Cité Scientifique, F-59655 Villeneuve d'Ascq - France*

**2** : Université Lille Nord de France. *Université des Sciences et Technologies de Lille - Lille I : EA4515, LGCgE EA 4515, Lille 1, EcoNum-Ecotox, Cité scientifique, SN3, F-59655 Villeneuve d'Ascq - France*

\* : Corresponding author

All around the world, amphibians have declined dramatically over the last 30 years. This decline was first thought to be caused only by the destruction of aquatic habitats, but it was more recently also recognized as the result of anthropogenic contamination of surface still waters. Consequently, although all amphibian species benefit from the status of endangered species, intensive works have been performed to increase knowledge on both cellular events occurring during normal development and effects of contaminants on their life cycle. For instance, FETAX (Frog Embryo Teratogenesis Assay *Xenopus*) assay aimed at determining the impact of pollutants on the development using the model *Xenopus laevis*, a South African frog reared in laboratory conditions.

Nevertheless, few studies have been conducted using *Xenopus* germ cells as oocytes. Though these cells offer many advantages allowing both electrophysiological studies and morphological examination.

The aim of this work was to investigate the effects of metal contaminant (cadmium, lead, cobalt and zinc) exposures, at environmental concentrations, on *Xenopus* oocytes, using cell biology approaches. Two different goals were followed. First, cell survival was evaluated with both phenotypical and electrophysiological approaches, and secondly, the effect of metals on oocyte maturation was assessed with morphological observations (germinal vesicle breakdown) and electrophysiological recordings (calcium-activated chloride currents).

Our results show that metal chlorides did not affect cell morphology but strongly depolarized oocytes resting potential. In addition, cadmium chloride was able to inhibit progesterone-induced oocyte maturation in a dose-dependent manner. By contrast, alone, we demonstrated that cadmium as well as zinc, cobalt and lead, are able to enhance oocyte maturation. Finally, electrophysiological recordings revealed that metal chloride exposures could disturb calcium signalling in *Xenopus* oocyte by modifying calcium activated chloride currents.

Our results obtained with metal chlorides, demonstrated that *Xenopus laevis* oocyte could be an innovating lab model in ecotoxicology.

# Modelling of chromium sorption behaviour on episammic biofilms developed on streambed sediments

Diego Martiñá Prieto<sup>1,\*,@</sup>, Rosa Devesa-Rey<sup>2,@</sup>, Francisco Diaz-Fierros<sup>1,@</sup>, M<sup>a</sup> Teresa Barral Silva<sup>1,@</sup>

**1** : University of Santiago de Compostela (USC) - **Website**

*Dpt. Soil Science and Agricultural Chemistry. Fac. Farmacia. Campus Vida. 15782. Santiago de Compostela - Spain*

**2** : Defense University Center, Escuela Naval Militar. *Defense University Center, Escuela Naval Militar, Plaza de España 2, 36920 Marín - Spain*

\* : Corresponding author

Chromium concentrations with health hazard may be introduced into the environment as a result of different industrial activities. The main aim of this study was the assessment of Cr adsorption onto episammic biofilms as a potential bioremediation tool of situations with problematic Cr concentrations. A natural biofilm growth was carried out, in an indoor system, during 15 days with 8 g of riverbed sediment using 60 mL of natural river water as nutrient supplier. The samples were subjected to day-night cycles (12 h of light with 3,109 Lux of intensity) to reproduce the outdoor environmental conditions. In order to determine the adsorption isotherms, 60 mL of different initial Cr (C<sub>0</sub>) concentrations (0, 5, 25, 50, 100, 250 and 500 µg/L) prepared in 0.01 M CaCl<sub>2</sub> solutions, as background electrolyte, were added to the systems. To evaluate the adsorption capacity of the biofilm, sediment samples without biofilm followed the same treatment of the biofilm-sediment samples as control. Equilibrium Cr concentrations (C<sub>e</sub>) were analysed by ICP-MS. Adsorption isotherms were satisfactory adjusted by Freundlich and Langmuir models, with values of R<sup>2</sup> of 0.981 and 0.993 for sediment and 0.975 and 0.999 for biofilm-sediment system, respectively. Therefore, Langmuir isotherm is the most suitable model to adjust experimental data. The maximum adsorption capacity of the sediment and biofilm-sediment system given by Langmuir model was of 2.90 and 3.87 mg/kg, respectively. The percentage of C<sub>ads</sub> with respect to C<sub>0</sub> was of 78.38 ± 15.05 % for sediment and of 97.38 ± 3.41 % for biofilm, increasing the difference with increasing initial concentration (at the highest C<sub>0</sub> the difference was of 36.71 %). In conclusion, the presence of episammic biofilms contributes with a significant increase in Cr adsorption capacity of sediment and as a consequence it could play a great role in bioremediation of Cr contaminated waters.

## Available nutrients changes after electrokinetic-assisted phytoremediation in a mine contaminated soil

Nazaré Couto<sup>1,2,@</sup>, Paula Guedes<sup>1,2,@</sup>, Yujun Wang<sup>1,@</sup>,  
Alexandra Ribeiro<sup>2,@</sup>, Dong-Mei Zhou<sup>1,@</sup>

**1** : Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences. *Nanjing 210008 - China*

**2** : CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa. *Caparica - Portugal*

Different environmental repercussions arise from metalloids contamination in soil enforcing the need to find efficient remediation strategies and also understand how their application can affect soil characteristics.

Electrokinetic (EK) assisted phytoremediation was applied in soil contaminated with antimony and arsenic. Soil was sampled from a mine area located in southern Hunan Province (China). EK process, that aims the movement of contaminants towards the electrodes, was tested together with an hyperaccumulator (*Brassica juncea*) and a non-hyperaccumulator (*Lolium perenne*) plant species. Each pot was divided into three parts (cathode:central:anode) and planted in a proportion of 12:16:12 plant exemplars. Tests were also conducted with phosphate ammendment. The experiment was run for 15 days and direct current was applied 8 hours *per* day with a constant voltage (20 V).

The changes on available soil nutrientes (P, N and K), after EK-assisted phytoremediation experiments, were assessed in order to understand the changes occurred on soil nutritional status. In the treatments with P-ammendment, with and without EK, *B. juncea* presented *ca.* 23% higher P level than *L. perenne*. Without P-ammendment, EK treatment applied to *L. perenne* resulted in *ca.* 42% lower P concentration comparing with control (only plant). The content of soil ammonium, in general, was similar between treatments but the content of nitrate presented more expressive results in both species as the nutrient concentration decreased with EK treatment, namely in electrode compartments. Available potassium showed a tendency to migrate towards the cathode compartment in EK treatments.

This study showed that EK-assisted phytoremediation influenced soil nutritional status, independently of the used plant species.



# New insights on antimony biogeochemistry based on environmental archives, soil studies and toxicity assessments

Gael Le Roux<sup>1,2,\*,@</sup>, Eric Pinelli<sup>1,2,@</sup>, Mickaël Hedde<sup>3,@</sup>, Maritxu Guiresse<sup>1,2,@</sup>, François De Vleeschouwer<sup>1,2,@</sup>, Jérôme Silvestre<sup>1,2,@</sup>, Maxime Enrico<sup>4,@</sup>, Laure Gandois<sup>1,2,@</sup>, Fabrice Monna<sup>5,@</sup>, Charles Gers<sup>6,7,@</sup>, Anne Probst<sup>1,2,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Physico-chimie et Ecotoxicologie des Sols d'Agrosystèmes Contaminés (PESSAC)

*INRA : UR251, Batiment 6 RD 10 78026 Versailles Cedex - France*

**4** : Géosciences Environnement Toulouse (GET) - **Website**

*14 avenue Edouard Belin 31400 Toulouse - France*

**5** : Laboratoire ARTéTHIS, UMR6298 U. de Bourgogne-CNRS-Ministère de la Culture. *Université de Bourgogne, Bâtiment Sciences Gabriel 6 Boulevard Gabriel 21000 DIJON - France*

**6** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); 118 Route de Narbonne, 31062 Toulouse, France

**7** : CNRS ; EcoLab ; 31062 Toulouse, France

\* : Corresponding author

**BioGeoSTIB** is a project funded by ADEME (French Environmental Protection Agency). Its aim is to provide a better understanding of biogeochemical cycle disturbances of antimony by man. Specifically, it is focused on the atmosphere-soil-organism interfaces. Based on a multi-scale approach, the impact of antimony on organisms and organism communities and the factors of Sb dispersion in the environment aim to better characterized. This report gives the main results of 2 and ½ years of research.

Using peat bogs as environmental archives, we show that Sb contamination date back to the beginning of the metallurgy. Atmospheric deposition of Sb largely increased by 100 times during the Industrial Revolution compared to natural levels (~0,001-0,01 mg.m<sup>-2</sup>.an<sup>-1</sup>) estimated in the deepest peat layers. This disturbance in the antimony geochemical cycle modified its concentrations in soils. One main source of present Sb contamination is automotive traffic due to Sb in braking lines. This emerging contamination was characterized close to a roundabout. This additional source of Sb does not seem to impact soil fauna but Sb concentrations in soil solutions exceed 1 µg.L<sup>-1</sup>.

Genotoxicity tests have been performed on the model plant *Vicia faba* and show that antimony is genotoxic at its lowest concentrations and that there is a synergistic effect with lead.

It is a main issue to determine Sb critical loads in the environment but main identified lacks are thermodynamic data, which are not available yet, to model the behavior of Sb in soil solutions and the fact the antimony is always associated with other anthropogenic trace metals like lead.

Critical thresholds of Sb have been determined for the first time based on genotoxicity experiment. Simulations show that these thresholds can be exceeded in

the future, whereas present limits for invertebrates (US-EPA) are and will not be reached.

## **Biodiversity and adaptation of plants to environmental stress: response to cadmium in the model plant *Medicago truncatula***

Camille Dumat<sup>1,2,@</sup>, Ivana Todorovic, Godratollah Saeidi, Cécile Ben, Martina Rickauer, Laurent Gentzbittel<sup>\*,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

Cadmium, a metal widely present in polluted soils, is phytotoxic. Thanks to their ability to establish symbioses with nitrogen-fixing bacteria, legumes have an important role in sustainable development. *Medicago truncatula* has been established as the sequenced model legume: extensive data and genomic tools are available.

A collection of inbred lines from regions around the mediterranean sea with different soils and climates, represents the genetic diversity within the species. We use these tools (genomics and biodiversity) to study adaptation of *Medicago truncatula* to cadmium stress. 30 lines of *M. truncatula* were studied for their response to cadmium. Seedlings of *M. truncatula* were treated or not with 100µM Cd solutions and the effect on root development was studied. After acidic mineralization of plants, cadmium and other ions (K, Ca, P, Na, Mn...) were measured by ICP-AES or ICP-MS.

Cadmium inhibited root growth, root fresh weight and dry weight of *M. truncatula* seedlings. Analysis of variance showed significant effect of genotype on all the parameters. Accessions responded differently to Cd stress as shown by the significant interaction between genotype and Cd treatment observed for root growth. Six lines were studied in detail. The ratio of root growth (Cd-treated/control) was used to identify tolerant and susceptible lines. Cd was accumulated preferentially in the roots, but part was transferred to the shoots. Although some difference between plant accessions was observed for this response, this was not statistically significant. The distribution of other cations from the seed reserve was affected by Cd-treatment in a genotype-dependent manner. These results provide first indications of mechanisms that allow the plant to tolerate Cd pollution. The differences and genetic bases of plant behaviour after Cd exposure could be exploited to use *Medicago truncatula* as a tool for ecotoxicological studies or for polluted soil bioremediation, while improving nitrogen status.

# Ecodynamics of perfluorinated acids in the Gironde estuary

Gabriel Munoz<sup>1,@</sup>, Pierre Labadie<sup>1,\*,@</sup>, Lobry Jérémy<sup>2,@</sup>,  
Jonathan Selleslagh<sup>2,@</sup>, Hélène Budzinski<sup>1,@</sup>, Virginie  
Bocquet<sup>1,@</sup>

**1** : UMR 5805 EPOC, LPTC research group. *Université Bordeaux 1, 351 Crs de la Libération, 33405 Talence - France*

**2** : UR EPBX Irstea. *Irstea, 50 Avenue de Verdun, 33610 Cestas - France*

\* : Corresponding author

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been used as additives in a wide array of applications, including water-resistant coatings and firefighting foams. PFASs are both extremely persistent in the environment and bioaccumulative, which explains the growing interest in the analysis of these compounds in water, sediments and wildlife. However, little is known about their ecodynamics, especially in estuarine ecosystems. Therefore, the main objective of the present work is to foster our understanding of the ecodynamics of PFASs. The Gironde estuary has been selected as the study site because of its ecological value: it is home to the largest assemblage of migratory amphihaline fish in Western Europe.

Water, sediment and biota samples have been collected in 2012 and are being processed. The contamination of biota is currently assessed for different organisms at the bottom of the food web, including benthic invertebrates (annelid worms, clams) and zooplankton (copepods, mysids and shrimps), for which there is virtually no data about PFAS bioaccumulation. The contamination of several fish species –grey mullet, meager, sea bass and sole – will also be presented. Finally, carbon and nitrogen stable isotope analyses will help characterize the trophic web structure.

Preliminary results indicate that PFASs are ubiquitous in both abiotic and biotic compartments. Levels in the water column were in the ng/L range and PFAS profile was dominated by perfluorooctane sulfonate and shorter chain carboxylic acids. Sediment levels were in the sub-ng/g range, as observed in ecosystems loosely impacted by anthropogenic activities. Preliminary results for biota showed that 14 PFASs could be quantified in European eel muscle.

Calculation of bioaccumulation factors (BAF), biota to sediment accumulation factors (BSAF) and trophic magnification factors (TMF) will follow up. In addition, a statistical modeling approach will also be implemented to evaluate the influence of trophic position and biometric characteristic on PFAS bioaccumulation in fish.

# **Microcystis spp. stational variation and its relation with water quality in an ecoturistic sinkhole from the Yucatan Peninsula.**

Viridiana Nava<sup>1,@</sup>, Daniela Ortega<sup>2,@</sup>, Laura Hernández-Terrones<sup>3,\*,@</sup>, Sergio Escobar<sup>1,@</sup>

**1** : Centro de Investigación Científica de Yucatán (CICY). Calle 8, No. 39, L 1, Mz. 29, SM 64, C.P. 77500, Cancún, Quintana Roo. México - Mexico

**2** : Centro de Investigación Científica de Yucatán (CICY). Calle 8, No. 29, Mz. 29. SM 64 C.P.77500 Cancún Q. Roo - Mexico

**3** : Centro de Investigación Científica de Yucatán. Calle 8, No.39, Mz. 29,, Lt 1, SM64 CP 77500 Cancún, Q. Roo. - Mexico

\* : Corresponding author

In continental water, the algae blooms are mainly related to cyanobacterias in which the most notable is the *Microcystis* genus, which are indicators of the eutrophication process that leads into water quality deterioration. In the central portion of Mexico this issue has received particular attention. Nevertheless, the related research about algae blooms in water bodies in the Yucatan Peninsula has been poorly evaluated although this natural water bodies are the main water supply for the population.

The main objective of this research is to evaluate the water quality (in terms of cyanobacteria abundance and its relation with environmental parameters) from a sinkhole located into the coastal strip of the Yucatan Peninsula. This sinkhole is actually being submitted to an intensive use and modification of its natural conditions for ecoturistic purposes. This study was carried out from July 2012 to January 2013; environmental parameters were measured (major nutrients and physical-chemical parameters). For the taxonomic analysis, phytoplankton superficial water samples were taken in the central part of the sinkhole. The higher algae densities were registered during November 2012, where Cyanoprokaryota division was the most abundant, with de *Microcystis* spp. domain. Although the predominance of this species suggests an advanced process of eutrophication, the results are not yet conclusive.

# Toxicity assessment of thallium using plant bioassays

Laura Crippa<sup>1,\*,@</sup>, Patrizia Zaccheo<sup>1,@</sup>

**1** : Dipartimento di Scienze Agrarie e Ambientali - Produzione, Territorio, Agroenergia - Università degli Studi di Milano (DiSAA), Via Celoria 2 - 20133 Milano - Italy

\* : Corresponding author

Thallium (Tl) is a potentially harmful element that has not been studied extensively, despite few studies have shown its high toxicity for human, plants and animals. Environmental accumulation of Tl is the result of both geogenic and anthropogenic inputs (farming, mining, manufacturing process, combustion of coal, and cement production).

The aim of our work was to evaluate thallium toxicity to plants by using three bioassays (root elongation test with *Hordeum vulgare L.*, germination test with *Lepidium sativum L.*, growth test with *Lactuca sativa L.*). Cress germination was shown to be affected by thallium (as TlCl) at concentrations up to 5  $\mu\text{mol L}^{-1}$ . Barley root elongation and lettuce growth at thallium concentrations up to 150  $\mu\text{mol L}^{-1}$ . Uptake and translocation of thallium into aerial parts of lettuce increased linearly with doses, with biological absorption coefficient (BAC) ranging from 0.02 to 0.03. In a sample from a mine degraded soil from a dumping site highly contaminated by thallium we performed the chemical fractionation of thallium, in order to study its distribution among soil components; more than half of total thallium was recovered in the residual fraction and 30% associated with soil organic matter. The tested bioassays revealed a high toxicity of the soil.

# Is a symbiotic bivalve a suitable organism to assess metal toxicity in aquatic environments ?

Audrey Caro<sup>1,@</sup>, Gaetan Chereau, Cecile Roques, Nicolas Briant, Remi Freydier, Francoise Elbaz-Poulichet<sup>@</sup>

1 : Laboratoire ECOSYM UMR 5119, CNRS, Université Montpellier II, IRD, IFREMER, Place Eugène Bataillon, CC 093, 34095 Montpellier cedex 5, France.

Bivalves are regularly used as biomonitors to assess the metal availability and toxicity in the water column of coastal or estuarine areas. The more frequently selected organisms remain oysters and mussels, as filter-feeding organisms. Generally, they bioaccumulate metals especially copper in direct proportion to their environmental levels. But this parameter is not a functional parameter. In this study, we proposed to assess the toxic effect of water in a highly contaminated harbor (Port-Camargue, south of France) based on the physiological response of bivalves. We selected 2 different bivalve species characterized by different ways of nutrition. *Ruditapes decussatus* is deposit feeder and filter-feeding organism whereas *Loripes lacteus* is a symbiotic bivalve that relies on its intra-cellular bacteria for their nutrition. The aim of the study was to compare the sensitivity of a symbiotic versus a filter-feeding bivalve, deployed in the harbor at 2 different sites (port entrance: 1 to 6µg/L labile Cu; technical zone: 12µg/L labile Cu). The physiological parameters investigated were : the specific clearance rate (SCR) for *Ruditapes* and the relative cell size of symbiotic bacteria and their genomic content for *Loripes*. Bioaccumulation was also measured for both species. A short exposure time (2 days) in the technical zone lead to a total loss of filtration activity (SCR) for *Ruditapes*; for *Loripes*, a light decrease in the relative cell size of symbionts was observed whereas their genomic content was not damaged. A longer exposure time (8j) was needed to get a clear decrease of the relative size of *Loripes*'symbionts but still no alteration of the genomic content. Thus, a clear difference in the sensitivity of both bivalve species results from this study, probably related with the nutrition way. The symbiotic bivalve *Loripes* could be a more reliable species than *Ruditapes* to evaluate the toxicity level of a metal contaminated aquatic environment.

## Assessment of cerium dioxide nanoparticles toxicity on four aquatic species at different trophic levels

Agathe Bour<sup>1,2,@</sup>, Florence Mouchet<sup>1,2,@</sup>, Laurent Verneuil<sup>1,2,@</sup>,  
Lauris Evariste<sup>1,2,@</sup>, Annie Perrault<sup>1,2,@</sup>, Jérôme Silvestre<sup>1,2,@</sup>,  
Eric Pinelli<sup>1,2,@</sup>, Laury Gauthier<sup>1,2,\*,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

Cerium dioxide nanoparticles (CeO<sub>2</sub> NPs) are being more and more used in the industry due to their unique properties, especially as diesel fuel additive or constituent of catalytic converters. This increasing use is expected to result in environmental release, and consequently there is an important need for their toxicity assessment. Our study aims at evaluating the potential harmful effects of raw CeO<sub>2</sub> NPs and citrate-coated CeO<sub>2</sub> NPs (Nanobyk®) on four aquatic species at different trophic levels. For this purpose we used diatoms (*Nitzschia palea*) as primary producers, chironomid (*Chironomus riparius*) and amphibian larvae as primary consumers (*Xenopus laevis*) and as secondary consumer (*Pleurodeles waltl.*). The evaluation of CeO<sub>2</sub> NPs acute toxicity (mortality at 48 or 96h, depending on the species) was realized on all species, from 0.1 up to 100 mg/L of NPs. Growth, development, time and rate of emergence, sex ratio and reproduction were also assessed as chronic endpoints for chironomids exposed between 0.01 and 1 mg/L of NPs. Genotoxic effects on amphibian larvae were evaluated at concentrations ranging from 0.1 to 10mg/L. The results reveal that no toxicity occurs on any of the four species during short time exposure, while adverse effects were observed on amphibian larvae from 1mg/L after 12 days of exposure. This approach constitutes a first step in the design of a new trophic chain for the investigation of nanoparticles impact in the environment.

# The karstic systems and the sustainable eco-turism in the Mayan Riviera.

Daniela Ortega<sup>1,@</sup>, Viridiana Nava-Ruiz<sup>1,\*,@</sup>, Laura Hernández-Terrones<sup>1,\*,@</sup>

1 : Centro de Investigación Científica de Yucatán (CICY). Calle 8, No. 29, Mz. 29. SM 64 C.P.77500 Cancún Q. Roo - Mexico

\* : Corresponding author

Río Secreto is an underground semi-flooded karstic formation with 14Km in length, with 15 natural outlets. Formerly known as Pool Tunich. It was discovered in 2006 and is located 5Km southwest of the urban area of Playa del Carmen, Quintana Roo, México. It is an invaluable example of the Yucatan Peninsula hydrogeology because it is an underground river encased in limestone.

This natural reserve was opened to the public in 2008 by the Mexican sustainable company named Río Secreto. An extensive monitoring has been carried out in the reserve to maintain the water quality, generate knowledge and in a short term, to decree a hydrogeology reserve in the region. This study focuses on the main biomonitoring results of four years at five sites in the reserve.

The parameters that have been monitored are water quality indicators such as the chemical (nitrates, nitrites, ammonia, phosphates and biochemical oxygen demand), bacteriological (total coliforms and *E. coli*) and physico-chemical (pH, T, EC, TDS).

Increasing concentrations of some parameters were seasonal (ammonia and biochemical oxygen demand). This trend is related to the number of tourists visiting the reserve in the season. Bacteriological analyzes are mostly below the maximum allowed by international regulations for recreational use.

The overall analysis indicates a high system stability so it is concluded that there has been no significant anthropogenic impact in this karstic area, proving a success story of sustainable ecotourism. In the medium term, with a continuous monitoring, this system may become a reserve hydrogeological within an urban area.



# Toxic metals profile of commercially sea foods from Turkey: contamination levels and dietary exposure assessment

Nuray Erkan<sup>1,@</sup>

1 : Istanbul University, Faculty of Fisheries, Department of Seafood Processing and Quality Control. Ordu cad. No. 200 Laleli, 34134 Fatih- Istanbul - Turkey

Some species of seafood may contain significant levels of mercury, cadmium, lead and arsenic. These substances are present at low levels in fresh waters and oceans, and they bio concentrate in the aquatic food chain at levels that are generally higher in older, larger, predatory fish and shellfish. Trace metals may have negative or positive effects on human health. These metals have long half-lives in the body and can accumulate in individuals consuming contaminated fish on a frequent basis. The FDA recommends that nursing or pregnant women and young children completely eliminate shark, swordfish, king mackerel and tilefish from their diets and limit the consumption of other fish to 340 g per week (3 to 4 servings/week) to minimize exposure to toxic metal.

In this study we measured the concentrations of Mercury (Hg), Cadmium (Cd), Lead (Pb), Arsenic (As) in 21 economically important seafood species with a Thermo electron X7 ICP-MS by EPA method (1994). Twenty-one seafood species (8 seawater fish, 1 freshwater fish, 6 crustacean and 6 mollusks species) of commercial importance were purchased at the Istanbul fish market, Turkey.

The levels of Hg (in 10 species) and that of Cd and Pb (in 2 species) were found to be higher than the maximum levels proposed by European legislation. The maximum As level permitted for fishes is 2.0 mg/kg according to Australia standard. Arsenic levels in the analysed fish samples were found to be lower than legal limits. Maximum tolerable weekly intakes were suggested for Hg (1.6 µg/week/kg bw), for Cd (7 µg/week/kg bw), for Pb (25 µg/week/kg bw), for arsenic (15 µg/week/kg bw). The average daily fish consumption in Turkey is 20 g per person, or 140 g weekly. The EWI (estimated weekly intake) Hg values for economically important seafood (three fish, one mollusk and two crustacean species) examined was higher than the recommended values. Monitoring of Hg content in fishery products is crucial for consumer health protection, especially in certain species that for physiological reasons concentrate Hg more easily than others.

# Health risks of toxic metals in the commercial fishes from Turkey

Özkan Özden<sup>1,@</sup>

1 : Istanbul University, Faculty of Fisheries, Department of Seafood Processing Technology and Quality Control. Ordu Cad. No: 200 Laleli 34134 Fatih, Istanbul - Turkey

Environmental pollution is a worldwide problem and heavy metals are considered the most hazardous pollutants. Therefore, the monitoring of toxic and essential metals is a major concern for food, medical and environmental scientists. Mercury (Hg), cadmium (Cd), and lead (Pb) are frequently found as environmental contaminants in seafood and are known by their toxic, mutagenic and carcinogenic effects. Food products of marine origin, mainly seafood, has the highest concentration of zinc, iodine and selenium, followed by red meat, dairy products and eggs and cereals.

The aim of the study was two-fold: first, to determine Hg, Cd, and Pb levels in fish muscle of fishes available in Istanbul markets, Turkey, and to compare the results with international maximum safe levels; second, to estimate the dietary intake of Hg, Cd, and Pb derived from fish consumption.

Determination of total Hg, Cd, Pb in fishes was performed by EPA 1994 method with a Thermo electron X7 ICP-MS. The analytical accuracy was monitored by analysing certified reference materials (LGC Promochem, mussel tissue (Cat No: ERMI-CE278).

This study investigated Hg, Pb, and Cd concentrations of four commercial fish species over one year. The reasons for variability in metal content from one month to another may have been due to different fish stocks in the catches, catches from different geographic regions, or physiological changes with season. The results suggest that consumption of these species from the Istanbul fish market may pose a problem for human health, as the mercury concentration of the four species exceeded the permissible limits for both the tissue and PTWI (limit is 1.6 µg/kg body weight) during at least one month. Although the tissue concentrations for Cd (limit is 7 µg/kg body weight) and Pb (limit is 25 µg/kg body weight) exceeded their respective permissible limits for some months, the PTWI values did not exceed the limits for these metals.

# Effects and accumulation of trace metals on the microarthropods community in contaminated soil

Annabelle Austruy<sup>1,2,@</sup>, Charles Gers<sup>3,4,@</sup>, Thibault Leveque<sup>1,2,@</sup>, Eva Schreck<sup>5,@</sup>, Yann Foucault<sup>1,2,6,@</sup>, Camille Dumat<sup>1,2,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); 118 Route de Narbonne, 31062 Toulouse, France

**4** : CNRS ; EcoLab ; 31062 Toulouse, France

**5** : Laboratoire Geoscience Environnement Toulouse (GET), 14 avenue Edouard Belin 31400 Toulouse, France

**6** : Société de Traitements Chimiques des Métaux (STCM), 30-32 Avenue de Fondeyre 31200 Toulouse - France

**Context and objectives:** At the global scale, soil pollution by inorganic strongly persistent pollutants induces environmental and sanitary risks. While the harmful effects of metals and metalloids on vegetation and macrofauna were widely studied, their impact on microarthropods (millimetric compartment) was only little studied. However, they significantly contribute to organic matter dynamic and have therefore a vital role in the soil life. Springtails were already used as ecotoxicological model due to their high sensitivity to various physical and chemical parameters of the environment. They could therefore allow to identify and quantify any anthropogenic disturbances.

**Methodologies:** Soil samples were collected from a contaminated historical site which presents a gradient of Pb contamination. The extraction of microarthropods was performed by the Berlese method. Our attention was first focused on the metal pollution effects on the structure of microarthropod communities (diversity and abundance). Then, an analysis of the pollutants contents in the springtails and corresponding soil samples was realized by ICP-MS and ICP-OES after acidic mineralization.

**Previous results:** Field experiments showed that even at strong pollution (above 4000 ppm of Pb), the microarthropods are present. In addition, previous results suggest that microarthropods can accumulate metals (Pb but also Cd, Zn). This study will allow to highlight the impact of trace metals on the microarthropod communities and in particular on springtails. Thus, the use of these living organisms as bioindicators to assess soil pollution will be tested.

# Thallium accumulation in soils and plants from sites of historical mining of Zn-Pb ores

Anna Stefanowicz<sup>1,\*,@</sup>, Marcin Woch<sup>2,@</sup>, Paweł Kapusta<sup>1,@</sup>

**1** : Department of Ecology, Institute of Botany, Polish Academy of Sciences - **Website**  
Lubicz 46, 31-512 Kraków - Poland

**2** : Department of Botany, Institute of Biology, Pedagogical University of Kraków. Podchorążych 2, 31-054 Kraków - Poland

\* : Corresponding author

Relics of historical Zn-Pb mining that can be found over a wide area of western Małopolska (S Poland) are small and inconspicuous heaps built of waste rock (dolomite). Although they are highly contaminated with metals and may threaten local environment, they have not been studied until recently. Thallium often accompanies Zn-Pb ores. Despite high Tl toxicity, it has been studied to a lesser degree than other toxic elements. Thus, the aim of our study was to assess Tl concentrations in soils and plants taken from old heaps. Ten species were chosen: *Achillea panonica*, *Carex hirta*, *Euphorbia cyparissias*, *Fragaria vesca*, *Hieracium pilosella*, *Leontodon hispidus*, *Potentilla arenaria*, *Plantago lanceolata*, *Scabiosa ochroleuca* and *Rumex cf. acetosa*. Soils and plants (divided into roots and shoots) were digested in HClO<sub>4</sub> and HClO<sub>4</sub>+HNO<sub>3</sub>, respectively. Additional soil samples were treated with EDTA. Thallium concentration was analyzed with AAS.

Total thallium concentration in soils ranged from 15.2 to 38.8 mg kg<sup>-1</sup>, exceeding values recorded for unpolluted areas. Thallium accumulation in plants was dependent on plant species (N = 8, p < 0.0001), plant part (p < 0.01) and species × plant part interaction (p < 0.001). The highest average Tl concentrations were in roots of *Plantago lanceolata* (22.6 mg kg<sup>-1</sup>) and *Scabiosa ochroleuca* (10.7 mg kg<sup>-1</sup>) and in shoots of *Euphorbia cyparissias* (10.4 mg kg<sup>-1</sup>). Most species accumulated Tl mainly in roots. Only *E. cyparissias* had more Tl in shoots than in roots. No significant correlation was found between total Tl in soil and its concentration in roots of the most accumulating species – *P. lanceolata* (p = 0.92). Correlation between EDTA-extractable Tl and Tl in *P. lanceolata* roots was only slightly significant (N = 14, r = 0.49, p < 0.08).

## In situ Evaluation of the impact of pesticides on Groundwater Associated ecosystems of the Ariège alluvial plain (France), ELISE project

Florence Mouchet<sup>1,2,@</sup>, Cécile Duchayne, Stéphanie Cadarsy, Laura Théolier, Alexandre Riberon, Nicole Baran, Laury Gauthier<sup>1,2,@</sup>

1 : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

2 : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

This project focuses on the assessment of contamination by pesticides, of water surfaces associated with the alluvial aquifer of the Ariège River (France). The studied area corresponds to an intensive agriculture dedicated notably to corn cultivation.

In this context, the major aim of this work is to characterize the impact of pesticides on aquatic organisms thanks to lab *and in situ* experiments. Water monitoring demonstrated that the herbicide metolachlor and its two main degradation products (ethane sulfonic metolachlor and metolachlor oxanilic acid) are frequently detected at significant concentrations. Toxicity assessment was carried out in lab conditions on amphibian's models (*Xenopus laevis*) exposed to (i) metolachlor and its metabolites as pure substances and (ii) to natural waters corresponding to a mixture of substances, to evaluate acute, chronic and genetic toxicities. Moreover, amphibian populations were studied on selected sites to establish the ecological parameters.

The ecotoxicological assessment in *Xenopus* to S-metolachlor and metabolites under controlled conditions and to natural waters showed an absence of significant mortality and genotoxicity regardless of the concentration of S-metolachlor and the contamination level. In contrast, there was a significant growth inhibition in larvae exposed to S-metolachlor at 100 µg/L, a high concentration compared to a few ng-µg/L measured in water (around 0.005 µg/L). Moreover, growth inhibition was also observed in larvae exposed to natural waters depending on the gradient of contamination of sites. *In-situ* evaluation in amphibian populations present at these different sites suggests that the quality of surface waters affects amphibian species richness and body size in palmate newt (*Lissotriton helveticus*) in accordance with results obtained in laboratory conditions.

This study is one of the few that focuses on the effects of mixtures of pesticides, both *in situ* and in lab condition, especially in amphibians which appeared to be once again good indicators in biomonitoring studies of additional laboratory bioassays.

# Review of diffusive gradients in thin films (DGT): A novel technology for measurement of labile forms of chemicals in the environment

Chaosheng Zhang<sup>1,\*,@</sup>, Shiming Ding<sup>2,@</sup>, Di Xu<sup>2,@</sup>, Ya Tang<sup>3,@</sup>,  
Ming Wong<sup>4,@</sup>

**1** : GIS Centre, Ryan Institute and School of Geography and Archaeology, National University of Ireland, Galway (NUI Galway) - **Website**

*University Road, Galway - Ireland*

**2** : State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences (NIGLAS), *Nanjing 210008 - China*

**3** : Department of Environment, College of Architecture and Environment, Sichuan University (SCU), *Chengdu, Sichuan 610065 - China*

**4** : Department of Biology, Hong Kong Baptist University (HKBU), *Hong Kong - China*

\* : Corresponding author

The diffusive gradients in thin films (DGT) technology has been receiving increasing attention as it provides a novel approach for the *in situ* measurement of the labile forms of chemical elements (such as phosphorus, sulphur, arsenic and metals) in waters, sediments and soils. Based on the simple concepts of diffusion and absorption, the DGT equipment contains a binding gel layer which is able to absorb the labile elements via diffusion through a diffusive layer in a quantitative way. This paper reviews the principle and latest development of the technology and its applications in environmental studies. Compared with conventional methods, the DGT technology has significant advantages: “*in situ*” measurement, time averaged concentrations and high spatial resolution. The “*in situ*” feature avoids the artificial influences of sample collection and treatment which may change the forms of chemicals, thus providing “true” information of the bioavailable or labile forms in the environment. Due to the strong temporal variations of the dissolved forms of chemicals in waters, the time-averaged (normally in 24 hours) concentrations provide reliable and robust results. As the labile chemicals are absorbed on the binding gel, the spatial distribution of their concentrations in the environment can be obtained at a resolution of sub-millimetres and at the two-dimensional level in combination with the analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), computer-imaging densitometry techniques (CID) or a routine procedure consisting of 2D slicing, elution, and microcolorimetric determination. The feature of high-resolution measurement with the DGT provides novel information for the understanding of the micro-scale environmental processes. The DGT technology provides great potential for novel applications in agriculture, environmental monitoring and mining industry for the measurement of bioavailable forms of P, S, As and metals.

# Study of bioavailability and ecotoxicity of metals and metalloids in polluted soils to assess the efficiency of phytoremediation techniques

Yann Foucault<sup>1,2,3,\*,@</sup>, Camille Dumat<sup>1,2,@</sup>, Thibaut Lévêque<sup>1,2,@</sup>,  
Marina Couveigne<sup>1,2,@</sup>, Sylvaine Goix<sup>1,2,@</sup>, Muhammad  
Shahid<sup>4,@</sup>

**1** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

**3** : Société de Traitements Chimiques des Métaux (STCM)

STCM, 30-32 Avenue de Fondeyre 31200 Toulouse - France

**4** : COMSATS Institute of Information Technology, Vehari - Pakistan

\* : Corresponding author

In a context of sustainable development of cities around the world, the rehabilitation of brownfields has important implications for human health and ecosystems (Foucault et al., 2013). The development of remediation techniques effective in reducing risks to the environment and health is therefore required, particularly for soils polluted by metals and metalloids. Nowadays, the criteria for assess the dangerousness of polluted soils are currently based on total concentrations, however it's well known that bioavailability strongly influences the impact on living organisms.

A new phytoremediation technique using green manures crops (*Borago officinalis*, *Sinapis alba* L. and *Phacelia stala*) was tested on various soils polluted by metals and metalloids (Pb, Cd, Sb, Cu and Zn) sampled in one urban recycling lead-acid batteries plant. The 3 plants were cultivated 10 weeks in different exposure conditions: various pollutants concentrations (400 and 825 mgPb.kg<sup>-1</sup>) and physicochemical soil characteristics. The global influence on soil quality of phytoremediation was investigated by the measure before and after treatment of complementary parameters: (i) total and phytoavailable (CaCl<sub>2</sub>) concentrations and bioaccessibility; (ii) ecotoxicity of soil samples using modified *E. coli* strains, normalized *Daphnia magna* and *Alivibrio fischeri* bioassays on leachates; (iii) in addition soil refunctionalization was studied: soil respiration (Licor 6400), organic matter concentrations, pH and carbonates were measured.

Borage and mustard were able to grow on various polluted soils, reducing total inorganic pollutants concentrations in soils (maximum 60% for lead and 80% for Sb) and increasing soil respiration (maximum 40%). The phytoremediation efficiency depends on soil characteristics. In addition, ecotoxicity of soil samples was reduced by the treatment (maximum variation of 30%). But, the percentage of lead bioaccessibility increased after treatment (maximum variation of 20%). The efficiency of phytoremediation must therefore be evaluated comprehensively, classifying the objectives of the treatment.

Foucault et al. 2013, Journal of Hazardous Materials 246–247, 291–299.

# Availability of metals in bottom sediments and freshwater bivalve (*Corbicula fluminea* and *Anodontites tenebricosus*) - Ribeira de Iguape River – Brazil

Valéria Rodrigues<sup>1,\*,@</sup>, Joel Sígolo<sup>2,@</sup>, Estella Guimarães<sup>1,@</sup>

**1** : Departamento de Geotecnia, Escola de Engenharia de São Carlos, Universidade de São Paulo Av. Trabalhador São-carlense, 400, 13566-590 São Carlos - SP - Brazil

**2** : Departamento de Geologia Sedimentar e Ambiental, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 04280-000 São Paulo - SP - Brazil

\* : Corresponding author

The Ribeira de Iguape River, one of the most important rivers in the Brazilian southeastern state of São Paulo, has its source in the Paraná state, drains from Northwest to Southeast between São Paulo and Paraná states through the Ribeira Valley and reaches the Atlantic Ocean at Iguape, in the Southern coast of São Paulo. During almost the entire 20th century, the Ribeira Valley experienced an intense activity related to mining (gold and lead-silver mining). As consequence, it is estimated that the Ribeira de Iguape River received the discharges of residues rich in As, Cd Pb, Cu and Zn, for approximately 40 years. In order to verify the contribution of these mining wastes in the river contamination the compartments of sediments (bottom sediments) and biomonitor (*Corbicula fluminea* and *Anodontites tenebricosus* - freshwater bivalve) were evaluated. In order to assess the extent of impact of metals on the Ribeira de Iguape River catchment, it is necessary to establish pre-anthropogenic (*background*) concentrations in the sediment (analysing sediment from pristine regions of the catchment). Metals concentrations in bottom sediments were measured by ICP/AES. Metals concentrations in tissue samples (*Corbicula fluminea* and *Anodontites tenebricosus*) were measured by HR-ICPMS. In the bottom sediments were detected average levels of 21.45 mg/kg of Cu; 262.25 mg/kg of Zn; 8.20 mg/kg of Cd; 13.90 mg/kg of Cr and 106.18 mg/kg of Pb (*background* concentrations in sediments - Cu: 10.30 mg/kg; Zn: 37.40 mg/kg; Cd: 4.20 mg/kg; Cr: 21.13 mg/kg and Pb: 20.00 mg/kg). The highest mean metal enrichments (mean concentrations/background) are for Zn, Pb and Cd (7x, 5x and 3x, respectively). Based on these calculated backgrounds, pollution status was determined for the Ribeira de Iguape River and the spatial extent of pollution was examined. In the tissues of the *Corbicula fluminea* were detected average levels of 62.89 µg/g of Cu; 148.39 µg/g of Zn; 0.74 µg/g of Cd; 6.26 µg/g of Cr and 3.29 µg/g of Pb. In the tissues of the *Anodontites tenebricosus* were detected average levels of 1.00 µg/g of Cd; 152.89 µg/g of Zn; 14.79 µg/g of Cr and 4.40 µg/g of Pb. Lead concentrations in bottom sediments and biomonitor (*Corbicula fluminea* and *Anodontites tenebricosus*) were comparable to those reported for moderately contaminated sites. The results showed that Pb is bioavailable to the bivalves, exhibiting high concentrations that exceed the reference values for human consumption (2.00 µg/g). This indicates that the mining wastes discharged into the Ribeira de Iguape River are being transported and incorporated into the sediments, which may increase the availability of the metals for the biota.



## **Metal levels in sediments and aquatic plants (*Avecinnia marina*), Iran**

Alireza Pourkhabbaz<sup>1,2,@</sup>, Hamidreza Pourkhabbaz<sup>3,@</sup>, Iman Zarei<sup>1,@</sup>, Gholamreza Mortazavi<sup>3,@</sup>

**1** : Department of Environmental Sciences, Faculty of Environment, Birjand University. *Birjand - Iran*

**2** : Higher Education Institute of Birjand Hormozan. *No; 24, Toheed street 16, Birjand - Iran*

**3** : Department of Environmental sciences, Technology University of Behbahan. *Behbahan university, Behbahan - Iran*

Heavy metals caused many environmental problems in aquatic ecosystems. They accumulate in sediments and in aquatic organisms via the food chain. As being one of the main trophic levels in the food chain, aquatic plants can be used as indicator to measure metals in water or sediments.

In this study, the concentrations of heavy metals in organs (root, stem and leaf) of Mangrove plant (*Avecinnia marina*) and sediments were investigated from the Hara biosphere. Sampling was done in four stations from September to November 2011. Measurement in sediment samples were performed by total concentration method. The heavy metals were measured in sediment and plants samples by acid digestion method. Digests were made up to 25 ml in acid washed standard flask. The collected extracts were analyzed using GF-AAS to determine the concentration of Cu, Zn and Cr.

The results showed that chromium level in sediment samples were higher compared to global sediments, whereas this was not true for Cu and Zn. The elemental Geochemical Accumulation Index (I<sub>geo</sub>) showed that the sediment samples were at low level of contamination. The metal concentrations in the root tissues were higher than in the stems and leaves. There was a significant correlation with sediment pollution in this investigation. In final, *Avecinnia marina* can be used as bio-indicator for some metals in the Hara biosphere.

## Evaluation of bioavailable Cu by DGT technique in a contaminated marina and impact on living organisms (*Ruditapes decussatus*)

Nicolas Briant<sup>1,\*,@</sup>, Audrey Caro<sup>2,@</sup>, Remi Freydier<sup>1,@</sup>, Françoise Elbaz-Poulichet<sup>1,@</sup>, Gaetan Chereau<sup>2,@</sup>

**1** : HydroSciences Montpellier (HSM), CNRS : UMR5569, Université Montpellier II - Place Eugène Bataillon, CC MSE, 34095 Montpellier cedex 5 - France

**2** : Ecologie des systèmes marins côtiers (ECOSYM), CNRS : UMR5119, Université Montpellier II - Place Eugène Bataillon, CC 093, 34095 Montpellier cedex 5 - France

\* : Corresponding author

Port-Camargue on the French Mediterranean coast is the largest European marina with a capacity of five thousand moorings. Therefore, the water of the marina is highly contaminated as a result of anthropogenic activities and antifouling paint release. The goal of this study was to investigate the potential impact of water toxicity on biological organisms.

Clams (*Ruditapes decussatus*) were exposed in the water column of Port-Camargue during two days. Their filter-feeding way of nutrition was used as biological parameter (specific clearance rate SCR) to evaluate the impact of metal toxicity. The SCR were compared before and after exposure in the port. Metal pollution in the water column (especially copper concentration) was evaluated during clam exposure by the diffusive gradient in thin-film technique (DGT). The DGT were exposed for two days at 30 cm from the sediment surface and at the top of the water column. By DGT sampling, a gradient of labile Cu concentration was observed from the entrance of the harbor to the technical area, both at the bottom (from 1.05 $\mu\text{g.L}^{-1}$  to 12.55 $\mu\text{g.L}^{-1}$ ) and at the top of the water column (from 15.1 $\mu\text{g.L}^{-1}$  to 18.7 $\mu\text{g.L}^{-1}$ ). Bioaccumulation of copper in clams was also measured. The SCR of clams decrease significantly from the entrance (0.49L.h<sup>-1</sup>.gr<sup>-1</sup> dry weight) to the technical zone (no more detectable filtration activity) in comparison with unexposed controls (1.41L.h<sup>-1</sup>.gr<sup>-1</sup> dry weight). It represents, after 2 days of exposure, a loss in the filtration rate of respectively 65.3% in the entrance of the port and 100% in the technical zone. However no mortality was observed during clam exposure in the port. The study demonstrated the capacity of the DGT technique, coupled with biological tests, to measure the available fraction of metal pollution responsible for the toxicity of the water port on biological organisms.

***Topic 3***

***Spatial and Temporal Geochemical records of  
Pollution Including Catchment Studies***

***Oral Presentations***

# Isotopic Zn and Cd multitracing study of metal transfer processes in soils and lichens from an old mining area (São Domingos Mine, Portugal)

Nadine Mattielli<sup>1,\*,@</sup>, Fatima Africano<sup>2,@</sup>, Christina Branquinho<sup>3,@</sup>, Arno Delahaye, Réjane Vogel-Mota, Eléonore Couder, Joao X. Matos<sup>4,@</sup>

1 : G-Time, Département des Sciences de la Terre et de l'Environnement, Université Libre de Bruxelles (ULB), CP 160/02, 50 Av. FD Roosevelt, 1050 Brussels - Belgium

2 : Centro de Geologia, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016 Lisbon - Portugal

3 : Centro de Biologia Ambiental, Faculdade de Ciências, Universidade de Lisboa, Campo Grande 1749-016 Lisbon - Portugal

4 : Portuguese Geological Survey (LNEG), R. Frei Amador, 39 rc. Ap. 104, 7801-902 Beja - Portugal

\* : Corresponding author

Isotopic multitracing approach has been conducted in an old mining area for a better understanding of the metal transfer processes in a semi-arid environment.

Belonging to the Iberian Pyrite Belt (Alentejo, Portugal), the São Domingos Mine (SDM) accounted for one of the most important copper-pyrite mining and refinery area of the Iberian Peninsula until its closure in 1966. In the neighbourhood of the São Domingos village, about 5x10<sup>6</sup> metric ton of waste deposits and an acid mine drainage system (AMD) are observed.

Elemental and multi-isotope Zn-Cd analyses were performed on lichen samples, topsoils, unprocessed and processed ores and AMD salts collected within a 16 km<sup>2</sup> surface area.

As, Cd, Pb, Zn, Cu and Mn are identified as main atmospheric metal pollutants in soils and lichens, with maximum values recorded inside the village (As from 78 to 1500mg/kg). Lichens display higher enrichments over a wider area relative to soils.

Elemental and Zn isotopic compositions of the soils samples clearly distinguish highly contaminated soils ( $d^{66}\text{Zn} = -0.69 \pm 0.03$  to  $+0.07 \pm 0.05\text{‰}$  (2SD); Zn from 300 to 1054mg/kg; Pb from 1500 to 3745mg/kg) from geogenic soils ( $d^{66}\text{Zn} = +0.10 \pm 0.05$  to  $+0.22 \pm 0.04\text{‰}$ ; Zn from 23 to 150mg/kg; Pb from 29 to 100mg/kg). The lowest  $d^{66}\text{Zn}$  values are observed in the village.

$d^{66}\text{Zn}$  values of the lichens are only consistent with the soil isotopic signatures at the geogenic soil sites. At the highly contaminated spots, lichens significantly differ from the soils because either (1) in the village, lichen  $d^{66}\text{Zn}$  values ( $+0.05 \pm 0.01$  to  $+0.11 \pm 0.02\text{‰}$ ) reflect re-suspension of unprocessed Cu-pyrite tailings, or (2) in the valley, the lichen  $d^{66}\text{Zn}$  values ( $-0.07 \pm 0.03$  to  $-0.05 \pm 0.04\text{‰}$ ) reflect Zn fractionation by interaction with AMD salts (jarosite).

Preliminary  $d^{114}\text{Cd}$  data in soils show enrichment in light Cd isotopes, which suggests a strong effect of Cd adsorption on Fe-Mn oxi-hydroxides in regosols.

Zn-Cd isotopic multitracers applied to soils and lichens constitute a sensitive approach to discriminate processes that might simultaneously occur in complex metal polluted environments.

# An historical investigation of atmospheric pollution in France using lichens herbaria

Yannick Agnan<sup>1,2,@</sup>, Nathalie Sejalon-Delmas<sup>1,2,@</sup>, Anne Probst<sup>1,2,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

Transboundary and local air pollutions are main environmental problems since they are known to significantly affect the ecosystems. Acidic, nitrogenous and metallic contaminants are transported into the atmosphere and deposited as transboundary pollutants to the continents. Unfortunately, atmospheric deposition remains always difficult to evaluate, in particular in the past prior to network monitoring establishment. Lichens are known to be good indicators of air pollution because of (i) the lack of protective cuticle and root system, and (ii) their permanent biological activity throughout the year. They are thus powerful accumulators of atmospheric deposition of contaminants.

In this study, trace metals (e.g. Cd, Cu, Pb, Sn, Zn...) as well as metalloids (As or Sb) were measured by ICP-MS in several species of lichens and mosses collected in various sites located in background environment all over France. A temporal comparison was allowed by analyzing current and historical specimens of the same species from the same sites. The historical samples were collected from 1870 to 1996 and carefully kept throughout the years in the herbarium of the University of Toulouse.

Despite the registration of the geochemical background from weathering-derived aeolian dusts (Cr, Ni, Ti, or V) by lichens and mosses, the results of bioaccumulation indicated that atmospheric contamination had changed over time. In the late 19th century and early 20th century the combustion of fossil fuel led to significant emissions of Pb, Cd, and As recorded as increased concentrations in lichens, together with other elements from geochemical background. In contrast, Sb, Sn, or Cu concentrations were more significantly enhanced in current samples characterizing a more recent and local pollution, so-called "emerging contamination".

# Biomonitoring of trace metal atmospheric deposition in forest ecosystems by mosses and lichens. Relative influence of local environment

Laure Gandois<sup>1,2,@</sup>, Yannick Agnan<sup>1,2,@</sup>, Sébastien Leblond<sup>3,@</sup>,  
Nathalie Sejalon-Delmas<sup>1,2,@</sup>, Anne Probst<sup>1,2,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

**3** : MNHN

*Museum National d'Histoire Naturelle, Rue Buffon, 75005 Paris - France*

Lichens are widely spread in forest ecosystems and as mosses, they have no root system neither developed cuticles. For these reasons, both accumulate trace metals (TM) atmospheric deposition and have been used as biomonitors. Their metallic content can be influenced by local and long-range transport, soil or tree bark composition and leaching by precipitation. This study aimed at assessing the influence of local factors on metallic content of lichens and mosses and therefore the ability of these biomonitors to record long-range TM transport of pollutants.

The TM (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Ti, V, Zn) and rare earth element (REE) content of mosses and lichens were determined on samples collected in three forest plots (Ardennes, Massif Central and Pyrenees), belonging to the ICP (International Co-operative Program) network. In order to distinguish local (soil, leaching) influence from distant sources, TM content in three terricolous moss species and five corticolous lichen species have been related to soil, bedrock, open field precipitation (OFP) and throughfall (TF) composition.

Trace metal ratios show similar trends in lichens and mosses. Enrichment factors (EF) are consistently higher in mosses compared to lichens. For Pb, EFs calculated using UCC (Upper continental crust) range from 4 to 22 in lichens and from 9 to 192 in mosses, the highest values being measured in the north of France. Biomonitor composition reflects a mixture of the bedrock and local soil and atmospheric end-members, especially for Cu, Pb, Zn, Cd, Sb and Sn. The influence of local lithology through the weathering-derived aeolian dust is evidenced by the similar REE anomalies (Eu and Gd) measured in both lichens and mosses. The relative influence of local origin and processes in comparison to long-range atmospheric deposition depends on the considered element: biological role, lithogenic versus anthropogenic influence.

# Identifying controls on Normal Background Concentration variations of contaminants in English soil

L. Ander<sup>1,@</sup>, Mark Cave<sup>1,@</sup>, C. Johnson<sup>1,@</sup>

**1** : British Geological Survey (BGS) - **Website**  
*Keyworth Nottingham NG12 5GG - United Kingdom*

Normal Background Concentrations (NBCs) have been developed for England in support of the new Statutory Guidance for contaminated land. The NBCs for 5 inorganic contaminants (As, Cd, Cu, Ni and Pb) have been developed using systematically collected national datasets of soil chemistry. Exploratory data analysis defines domains of higher contaminant concentrations. These demonstrate three main types of control on variations in typical and widespread concentrations: (1) geological parent material (As, Cd and Ni); (2) urbanisation – encompassing urban and industrial activities (Cd, Cu and Pb); and (3) non-ferrous metalliferous mineralisation and mining (As, Cd, Cu and Pb). The latter represents (1) and (2) combined, where naturally occurring higher parent material concentrations over ore veins have been enhanced by historical extraction and refining processes leading to much wider dispersion of these elements across the surface environment of the orefields.

The data for each domain has been analysed by a robust statistical method, specified by a decision tree depending on the data distribution properties. This has then allowed computation of the 95th percentile of the upper confidence limit as the upper limit at, or below, which contaminant levels can be considered normal for the defined domain.

The NBC domains with higher concentrations of Pb and Cd are explored further for their most interesting features. Lead is of particular interest due to the high concentration of the urban NBC (820 mg/kg) compared to that of 180 mg/kg in the 'principal' typical domain of much of the surface area of England. The Cd domain, defined by the southern England (including part of London) Cretaceous Chalk parent material (NBC = 2.5 mg/kg), due to an as yet unexplained control, has an NBC greater than urban areas (2.1 mg/kg), but this domain is not associated with the Chalk further north in England.

## Anthropogenic lead records in buried and modern soils

Tatiana Pampura<sup>1,\*,@</sup>, Vitaliy Demkin<sup>1,@</sup>, Markus Meili<sup>2,@</sup>, Malin Kylander<sup>3,@</sup>, Anne Probst<sup>4,5,@</sup>

**1** : Institute of Physicochemical and Biological Problems in Soil Science RAS (IPBPSS RAS) - **Website**

*ul. Institutskaya, 2, Pushchino, Moscow region 142 290 - Russia*

**2** : Stockholm University, Department of Applied Environmental Science (ITM) - **Website**

*Svante Arrhenius väg 8 106 91 Stockholm - Sweden*

**3** : Stockholm University, Department of Geological Sciences (GEO) - **Website**

*Svante Arrhenius väg 8 106 91 Stockholm - Sweden*

**4** : Université de Toulouse ; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**5** : CNRS ; EcoLab ; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

Modern (uncontaminated and roadside) soils and paleosoils buried beneath two burial mounds (kurgans) in the Volgograd region of Russia were compared in terms of soil characteristics, mobile and total Pb concentrations, and isotopic composition, in order to study the effect of anthropogenic and climatic factors on Pb accumulation in soils. The potential of a kurgan to protect the underlying soil from lead deposition during the time since construction was assessed by profile analyses of unsupported <sup>210</sup>Pb. The activities of unsupported <sup>210</sup>Pb measured in the upper (0-10cm) layer of buried soils were found to be below the limit of detection. It was shown that concentrations of total and mobile Pb (acid-soluble and carbonate-bound), the fraction of mobile Pb in the total pool, and the enrichment of Pb relative to Ti and Sc were much higher in the roadside soils than in all others. The isotopic composition of Pb in all forms was enriched by the less radiogenic component and agreed with composition of Pb in Russian gasoline, Pb-ores, and modern aerosols.

Modern soils remote from roads differed from the buried soils much less than roadside soils. However, concentrations and fractions of mobile Pb were significantly higher in these modern soils than in paleosoils. This may be treated as evidence of an anthropogenic lead input, on the other hand, this may as well be explained by natural processes such as OM loss and lower degree of weathering in buried soils. The isotopic composition of mobile lead in the modern soils was slightly shifted towards "anthropogenic"-Pb. Signs of possible anthropogenic influence (less radiogenic Pb composition and increased concentration) in the mobile fraction of Pb from modern remote soils are practically invisible in terms of the total Pb. Contamination of soils with Pb in the study area is limited and localized along the motorways.



# Geochemical investigation of heavy metals distribution in the Musina area, Limpopo Province, South Africa

Jason Ogola<sup>1,@</sup>, Rejune Mundalamo<sup>@</sup>

1 : University of Venda (UNIVEN) - **Website**  
*Private Bag X5050, Thohoyandou 0950 - South Africa*

Copper deposits in the Musina area were discovered centuries ago by ancient indigenous Africans who exploited the resource on small-scale. Large scale mining, however, was not started until 1914 and since then, about 10,000 tons of copper had been recovered. Large-scale mining had raised concerns about the dispersion of heavy metals in the area, but no work had been undertaken to ascertain the extent and level of pollution in the area. The current study therefore focused on the distribution of heavy metals in soils as a result of copper mining at Campbell, Harper, Messina, Spence and Artonvilla in the Musina area. The work involved soil sampling (102 samples) and determination of Pb, Zn, Cu, As, Co, Ni, Cd, Mn and Cr by atomic absorption spectrometry (AAS). The highest concentration levels were: Pb-14.5  $\mu\text{g g}^{-1}$ , Zn- 141  $\mu\text{g g}^{-1}$ , Cu-1580  $\mu\text{g g}^{-1}$ , As-20  $\mu\text{g g}^{-1}$ , Co-17  $\mu\text{g g}^{-1}$ , Ni-63.4  $\mu\text{g g}^{-1}$ , Mn-352  $\mu\text{g g}^{-1}$  and Cr-110  $\mu\text{g g}^{-1}$ . Cadmium had concentration level of less than 4  $\mu\text{g.g}^{-1}$  throughout the study area. Five anomalous targets were identified four of them occurring over the Messina, Harper, Campbell and Molly Too mines respectively. This confirmed that the distribution of heavy metals in soil was due to mining activities.

The single factor method was used to determine the pollution levels of heavy metals in soil. Copper was found to be the main pollutant with the environmental quality index (Pi) of 4.5 around Messina mine, denoting high degree of pollution (Pi >3). At the Campbell mine site, the environmental quality index was 2.9 indicating moderate pollution. The anomaly maps indicated that the Messina mine site is the most polluted one with all heavy metals analysed having anomalous values, except Cd. The study recommends rehabilitation of the Messina tailings dams as they pose potential danger to human health.

# Long-term Dynamics of Urban Soil Pollution with Heavy Metals (Moscow)

Natalia Kosheleva<sup>1,@</sup>, Elena Nikiforova<sup>1,@</sup>

1 : 119991 Moscow Leninskie gory, 1 MSU, faculty of geography - Russia - **Website**

The growing urbanization aggravates the problem of environment pollution by various harmful substances, and heavy metals (HM) are of special concern. The purpose of this research is to study the accumulation of HMs in urban soils during a long time span as influenced by recession and growth periods in urban activities. The most strongly polluted the Eastern district of Moscow has been chosen as a study object. Results of 21-year-long (1989-2010) observations of the concentration levels and the spatial patterns of nine HMs in urban topsoils are presented. The quantitative parameters of soil pollution include the rates of annual increase of HM concentrations in several functional zones. The measurements of HM contents in the snow allowed to evaluate the contribution of atmospheric fallout to the environment contamination. The maps of geochemical anomalies were compiled using the data collected in 1989, 2005, and 2010.

The prominent transformation of morphological, physical and chemical properties of urban soils resulted in appearance of biogeochemical, sorption, and alkaline geochemical barriers in their topsoils. Some HMs are gradually accumulating on these barriers increasing the size of the technogenic anomalies. The growth of the total volume of industrial and vehicles' emissions between 1989 and 2005 caused significant deposition of Pb, Zn, Cu, and Cd. The intensive input of Cd to the soils is attributed to the application of sewage sludges as fertilizers. The relative increment of concentrations was the highest for Pb, Co, Cu, Ni, and Cr. In 2005-2010, the relative annual increment rate was the highest for Cr, Cd, Co, and Ni, and it grew by an order of magnitude as compared to the previous period. By contrast, Pb and Cu content was decreased due to exclusion of leaded gasoline as fuel for vehicles and closing of some harmful enterprises producing instruments and electronic equipment.

# Anthropogenic enrichment of trace metals in a peat profile from southern Greenland

Tim Mighall<sup>1, @</sup>, Antonio Martinez Cortizas, Malin Kylander, J. Edward Schofield, Kevin Edwards, Noemí Silva Sánchez<sup>@</sup>

**1** : University of Aberdeen. *Department of Geography & Environment, School of Geosciences, University of Aberdeen, Elphinstone Road, Aberdeen, AB24 3UF - United Kingdom*

Very few studies have considered the deposition of metals from atmospheric sources in Arctic peat bogs. Some success has been achieved by investigating lake sediment records, although knowledge of the temporal changes in long-distance atmospheric lead pollution over the last millennium are still not well established.

Ruins on the coast at Sandhavn in southern Greenland (59°59' N, 44°46' W), represent the remains of a settlement formerly occupied by both the medieval Norse and Inuit. Here, ombrotrophic peat deposits provided an opportunity to investigate the character of past interaction between these two cultures and to reconstruct a regional record of past atmospheric pollution. A peat monolith was collected from beside the ruins. Radiocarbon dating suggests that the peat began to accumulate *ca.* AD 1250. Analyses included determination of lithogenic and metal elements, and stable lead isotopes. <sup>210</sup>Pb dating was used to provide a high-resolution chronology at the top of the profile. Lead concentrations show a distinctive peak (*c.* 20 ppm) in the last 100 years. Ordination suggests that this increase can be attributed to atmospheric Pb pollution. Shifts in <sup>206</sup>Pb/<sup>207</sup>Pb ratios occur in 4 stages over the last 500 years: (S1) Between 1.14 and 1.43 at the base of the core. (S2) A rise to 1.363. (S3) Ratios decrease from 1.308 to 1.264. (S4) Samples become less radiogenic over the last century: 1.19 to 1.178. The GRIP ice core has natural background of 1.20/1.19 so ratios approaching 1.34 might be a specific local signal. A surface gasoline peak is also not recorded. Long distance transport could be homogenizing the signal. Recent isotopic ratios at Sandhavn are also higher than those recorded from western Greenland but fall within the isotopic range for European and Canadian sources. The Sandhavn record most likely represents a mixed pollution signal from Eurasian and North American sources (~1.16-1.19).

# Atmospheric metal pollution due to early mining and metallurgy in N Spain

Antonio Martinez Cortizas<sup>1,\*,@</sup>, Lourdes López-Merino<sup>2,@</sup>,  
Richard Bindler<sup>3,@</sup>, Tim Mighall<sup>4,@</sup>, Malin Kylander<sup>5,@</sup>

**1** : Universidad de Santiago de Compostela (USC), *Departamento de Edafología e Química Agrícola, Facultade de Bioloxía, Campus Sur s/n, Santiago de Compostela, Spain - Spain*

**2** : Brunel University, *Institute for the Environment, Brunel University, Uxbridge, London, Middlesex UB8 3PH - United Kingdom*

**3** : Umea University (UmU), *Department of Ecology and Environmental Science, Umeå University, Umeå, Sweden - Sweden*

**4** : University of Aberdeen, *Department of Geography & Environment, School of Geosciences, University of Aberdeen, Elphinstone Road, Aberdeen, AB24 3UF - United Kingdom*

**5** : Stockholm University, *Department of Geological Sciences, Stockholm University, SE-10691, Stockholm - Sweden*

\* : Corresponding author

The start of atmospheric metal pollution in N Spain has been dated back to 3200-3400 cal BP, although mining/metallurgy has taken place since the beginning of the Bronze Age (3th millenium BC). The lack of early evidence suggests: i) non-extensive, low intensity mining/metallurgy; or ii) that appropriate palaeoenvironmental archives have not been studied. Aiming to shed some light on this issue, we sampled a core from a mire, La Molina, located in an extensively mined area during Roman times and probably earlier. Geochemical analyses included the determination of biophyllic (C, O, N, H, S; elemental analyzers), lithogenic and metal (Si, Al, Fe, Ti, Ga, Rb, Sr, Y, Zr, Th, Cr, Cu, Zn, Pb; EMMA-XRF) elements, and stable Pb isotopes (Quadrupole ICP-MS).

PCA showed that peat elemental composition depends on organic/mineral content and changes in mineralogy. Average  $^{206}\text{Pb}/^{207}\text{Pb}$  background ratio (>8000 cal BP) is  $1.204 \pm 0.002$ , while lower ratios were found from 5010 to 2460 cal BP (Bronze-early Iron ages). During this period, the isotopic record is characterised by four phases: I) 5010-3945 cal BP, decreasing ratios (to 1.175); II) 3945-3520 cal BP, increasing ratios (to 1.192); III) 3520-2800 cal BP, decreasing ratios (to 1.169); IV) 2800-2460 cal BP, increasing ratios (to 1.186). Three isotope plots point to the use of local ores.

$\text{Pb}/\text{Al}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios are significantly correlated ( $R = 0.92$ ) and, once detrended from the main principal components, metals showed enrichments in agreement with the identified pollution phases. Copper, Cr and Pb were enriched in phases I to III and decreased sharply in IV; while Zn enrichments increased from phase III to mid IV and decreased abruptly by the end of phase IV (in agreement with previous findings). The results indicate that atmospheric metal pollution can be detected during the earliest phases of mining/metallurgy in N Spain, and record changes in the exploitation/use of the metals.

## Improvement in the understanding of mining legacy in the Pyrenees mountains using environmental archives

Adrien Claustres<sup>1,2,\*,@</sup>, Anne Probst<sup>1,2,@</sup>, François De Vleeschouwer<sup>1,2,@</sup>, Jeroen Sonke<sup>3,@</sup>, Florence Mazier<sup>4,@</sup>, Didier Galop<sup>4,@</sup>, Sandrine Baron<sup>5,@</sup>, Damien Rius<sup>4,@</sup>, Maxime Enrico<sup>3,@</sup>, Lars Heimbürger<sup>3,@</sup>, Gaël Le Roux<sup>1,2,\*,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

**3** : Géosciences Environnement Toulouse (GET) - **Website**

*CNRS : UMR5563, Observatoire Midi-Pyrénées, Université Paul Sabatier - Toulouse III, 14 avenue Edouard Belin 31400 Toulouse - France*

**4** : Géographie de l'environnement (GEODE) - **Website**

*CNRS : UMR5602, Université Toulouse le Mirail - Toulouse II, 5 Allée Antonio Machado 31058 TOULOUSE CEDEX 1 - France*

**5** : Travaux et Recherches Archéologiques sur les Cultures, les Espaces et les Sociétés (TRACES), *CNRS : UMR5608, Université Toulouse le Mirail - Toulouse II, MAISON DE LA RECHERCHE 5 Allée Antonio Machado 31058 TOULOUSE CEDEX 9 - France*

\* : Corresponding author

Pyrenees mountains have a long history of mining and metallurgical activities that could have impacted the natural biogeochemical cycles of trace metals (i.e. Pb, Hg, Ag...). Our aim is to investigate the impact of past and present human activities on metal soil contamination in the French Pyrenees. We want to decipher when, where and how the soils were contaminated by metals. We also focus our study on how the metals can accumulate specifically in mountainous ecosystems and how metal contamination can be related to other human-induced environmental changes in the past (i.e. deforestation, hydrological changes...).

For this purpose, environmental archives (peat, lakes...) have been sampled, freeze-dried, sliced and digested completely with a mixture of HNO<sub>3</sub> and HF acids. Then total trace metal content was analysed by ICP-MS. Core age-dating to reconstruct age-depth model was done with <sup>14</sup>C and <sup>210</sup>Pb. Statistical analysis, elements and elements ratios profiles were done to understand the origin of elements.

Our first results based on lake and peat records and focused on Pb contamination show a quite similar chronology during the last 5000 years along the entire Pyrenees range. Late Medieval mining activities seem to have largely contaminated Pyrenean soils (1 to 3 g m<sup>-2</sup> of Pb) and can in some area be larger than Pb contamination from the Industrial Revolution or the "leaded gasoline" era. A focus based on numerous environmental archives and proxies in a high-mountain catchment, close to Andorra, shows that chronological accumulation of metals in soils, peat and lakes are clearly related to other human impacts fingerprinted by paleoenvironmental data (pollen, charcoal). Our preliminary results show that an inventory of metals stored in mountainous soils since the beginning of metallurgy is necessary to understand possible release of these metals within the context of future environmental changes.

## Acidic peat chemistry and interactions with radionuclides ( $^{238}\text{U}$ and $^{226}\text{Ra}$ ) in a former mining area

Gabrielle Bordelet<sup>1,@</sup>, Catherine Beaucaire<sup>1,@</sup>, Vannapha Phrommavanh<sup>2,@</sup>, Michaël Descostes<sup>2,@</sup>

1 : Laboratoire de Mesures et Modélisation de la Migration des Radionucléides (L3MR), CEA Saclay DEN/DANS/DPC/SECR Bât. 450, BP 11, 91191 Gif-sur-Yvette Cedex - France

2 : AREVA - BG Mines, Groupe AREVA, 1, Place Jean Millier – F-92084 Paris La Défense - France

The environmental footprint of former uranium mining activities is a priority for AREVA. In order to guarantee a minimal radiological impact on the biosphere, it is important to understand the fate of uranium (U) and its decay products, in particular radium ( $^{226}\text{Ra}$ ).

In the environment, among solid phases which can retain U and  $^{226}\text{Ra}$ , organic matter is known to have a relevant affinity for U. Studies on metal sorption on organic matter are usually carried out on humic substances in presence or not of mineral phases. Peat is a complex material which combines many components such as organic matter (mostly composed of animal and plant remains with different degree of degradation) and mineral phases, each having their own specific influence on U and  $^{226}\text{Ra}$  retention.

This study is focused on peat samples collected from an acidic peatland (pH 6), close to a former mining site. We sampled three peat cores (two of them from localised areas where the radioactivity is significantly higher than the background) and analyzed them for carbonate content, total C, H, S, and N, mineral phases, cationic exchange capacity, U and its daughters' activities to characterise the solid phase. After an acid, a base and water washing treatment, the latter was used to perform adsorption/desorption batch experiments of  $^{238}\text{U(VI)}$  and  $^{226}\text{Ra}$  on peat material with varying detrital contents.

In the studied peatland, it seems that mining activity has contributed to increase the detrital load of the peat by 10% to 90%. In the localised areas with higher radioactivity, radionuclides are concentrated in the upper 40 cm of the cores. The results of batch experiments show that more than 90% of total U and 40% of Ra were retained by the peat. Those results will be discussed according to the depth and mineral matter content.

# Characterization of dissolved organic matter released from a Pyrenean peatland.

Théo Le Dantec<sup>1,2,@</sup>, Laure Gandois<sup>1,2,\*,@</sup>, Roman Teisserenc<sup>1,2,\*,@</sup>, Gaël Le Roux<sup>1,2,\*,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

In stream ecosystems DOM plays a key ecological role. It is a source of carbon and energy and contributes to greenhouse gases emissions and numerous chemical processes including complexation and mobilization of metals. Peatlands store huge amount of organic carbon and are important sources of DOM to surface water. These systems undergo local and global anthropogenic pressure which might impact their functioning. In this context an increase of DOM export from peatlands has recently been evidenced in Europe and North America, but the reasons remain unclear. This phenomenon is not yet documented in the climate specific mountainous ecosystems. Objectives of this study are to decipher the relative contribution of peatland to the riverine DOM and identify a specific peat signature from isotopic or molecular biomarkers (possibly a combination). It also aims to estimate the DOM influence on the dynamic of other elements especially trace metals. These investigations will provide tools to understand the DOM fate: origin, transformation in the peatland and exportation to stream.

Water have been regularly sampled upstream, into and downstream a minerotrophic Pyrenean peatland (Haut Vicdessos, Ariège, France). Water (major and trace element, DOC concentration, Specific UV Absorbance (SUVA)) and suspended matter (elemental (CHN) and isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ )) composition has been determined. Reverse osmosis and TFF have been used to concentrate DOC and POC for molecular analysis.

The results show that peatland area is an important source of a specific DOM to the stream. An increase of DOC concentration, aromaticity of DOM, as well as some trace elements (Fe, Al, Ni) concentrations is observed downstream of the peatland. Speciation calculations (WHAM-VI) show that these elements are complexed by DOM.

# **Mercury contamination and mitigation during the Permian-Triassic Extinction. Present and future lessons**

Hamed Sanei<sup>1,@</sup>, Stephen Grasby, Benoit Beauchamp, Peter Outridge, Gary Stern<sup>@</sup>

1 : University of Manitoba, c/o 3303-33rd St NW, Calgary, AB, T2L2A7 - Canada

A sedimentary record from the Canadian High Arctic shows significant mercury contamination occurred in association with volcanism and associated thermal metamorphism of carbonaceous deposits at the Latest Permian Extinction event, contributing to severe environmental stress at that time. Siberian Trap volcanism was coincident with timing of the latest Permian Extinction (LPE) 252 mya. Our study focuses on a sedimentary basin down wind of the Siberian Traps that would likely be highly affected by Hg release associated with the eruptions. A 130-m continuous sedimentary record from the Buchanan Lake section, Canadian High Arctic, shows unprecedented levels of Hg loading leading to the extinction. Mercury loading is attributed to combined effects of volcanic emissions in association with combustion of significant coal and carbonaceous deposits. Key to our results is the observation that there is a breakdown of the positive correlation between Hg and TOC at the extinction level. Mercury influx exceeded the scavenging capacity of organic matter (OM) in the Late Permian ocean, leading to major disruption of Hg drawdown processes mediated by organic carbon. This resulted in build up of dissolved Hg to maximum toxic levels at the LPE boundary. It is unlikely however that Hg loading is the sole cause of the LPE extinction, as the global ecosystem was already under stress by the time the Hg contamination event occurred at the LPE level, making this one of the series of inter-related events that led to the greatest extinction in Earth history. The post-extinction period is marked by progressive Hg mitigation, where the marine system lowered concentrations and re-established the internal Hg-OM drawdown process, allowing self-recovery from toxic Hg conditions.



# Evaluation of the forest ecosystems influence on the drinking water quality from surface sources in representative watersheds of the Struma river basin (Bulgaria) through statistical and GIS tools

Emiliya Velizarova<sup>1,@</sup>, Ivan Marinov<sup>1,@</sup>, Andrew Hursthouse<sup>2,@</sup>,  
Irena Ilcheva<sup>3,@</sup>, Ivan Nikolov<sup>@</sup>

**1** : Forest Research Institute - Bulgarian Academy of Sciences (FRI - BAS) - **Website**  
*St. Kliment Ohridski Blvd., 1756 Sofia - Bulgaria*

**2** : School of Science, University of the West of Scotland (UWS) - **Website**  
*PA1 2BE, Paisley - United Kingdom*

**4** : National Institute of Meteorology and Hydrology - Bulgarian Academy of Sciences (NIMH - BAS) - **Website**  
*66 Tsarigradsko shose Blvd., 1784 Sofia - Bulgaria*

We have evaluated temporal trends related to the quality of surface drinking water sources in representative small watersheds in highland mountain regions, in the *Struma* river basin (Bulgaria) where prevailing part of the population of the biggest cities of the region rely on that water supply. Using GIS-based tools the local watershed characteristics, influencing relevant (bio)chemical processes have been studied. Maps in scale 1: 10000 of the territory according to the type of land use, soil type differences and soil depth have been designed for the investigated watersheds. Multivariate statistical techniques were applied in order to establish relationships between key indexes for drinking water quality according to the EU Water Framework Directive (WFD) and environmental features of the watersheds (altitude, slope exposure, parent material, soil differences and forest type). The results of the statistical analyses revealed that the water temperature and the nitrogen concentrations, in the form of NO<sub>3</sub>-N, have increased over 10 years due to anthropogenic contributions such as forest management. The magnitude of Biological Oxygen Demand (BOD) with respect to NH<sub>4</sub><sup>+</sup>-N confirms inputs of organic compounds into some drinking water sources in result of the management practices in water preserved areas. Overall, however, the data obtained demonstrate that for almost all studied watersheds, the water quality for drinking and household supply is within the recommended concentration limits of the WFD and national regulations.

# Particulate contaminant fluxes in the Upper Rhône River

Marina Launay<sup>1,@</sup>, Marina Coquery<sup>2,\*,@</sup>, Helene Angot<sup>2,@</sup>,  
Jerome Lecoq<sup>1,@</sup>

**1** : Hydrologie-Hydraulique (UR HHLY) - **Website**

*CEMAGREF, 5 rue de la Doua, CS70077, 69626 Villeurbanne Cedex - France*

**2** : Milieux aquatiques, écologie et pollutions (UR MALY) - **Website**

*CEMAGREF, 5 rue de la Doua, CS70077, 69626 Villeurbanne Cedex - France*

\* : Corresponding author

Suspended particulate matters (SPM) have been recognized as the main transport pathway for many trace metals and hydrophobic contaminants in river systems. Estimating particulate contaminant fluxes is of huge interest for water-quality managers to identify sources, transport and fate of contaminants at river basin scale and to plan remediation measures. In order to evaluate particulate fluxes of polychlorobiphenyls (PCBs) and mercury (Hg) with minimal uncertainty and to investigate the spatio-temporal variability of these fluxes, a dedicated monitoring network was set up in September 2011 on the Upper Rhône River (France) and on the outlet of its main tributaries. The monitoring strategy relies on continuous water discharge and turbidity measures, and fortnightly measurements of contaminant concentrations together with a specific monitoring of flood events. In order to collect a sufficient amount of SPM to allow for contaminant analysis, continuous-flow centrifugation and integrative sediment trapping were deployed.

This study highlighted that for PCBs and Hg, SPM concentration monitoring is essential during flood events to avoid an underestimation of fluxes. Indeed, SPM concentration appeared to be the most influencing parameter of the flux assessment, as it varied from 1 to 1000 mg/L between base-flow and flood periods. Nevertheless, contaminant concentrations should be accurately studied during hydrological events as they appeared to vary between base-flow and sediment-laden events. Moreover, the grain size distribution was identified as a key parameter to explain contaminant concentration variations during events. Therefore, all particulate contaminant contents should be normalized using particle size distribution data especially when comparisons are needed between contaminant content of particles sampled with different techniques, or sampled in bed deposits. Finally, flux balances are compared at the scale of the river network and over the years.

# Influence of the landfill site on the lake sediments of Vransko Lake, Croatia

Hana Fajković<sup>1,\*,@</sup>, Esad Prohić<sup>1,@</sup>, Lovorka Pitarević  
Svedružić<sup>2,@</sup>, Sanda Rončević<sup>2,@</sup>, Zvonko Habuš<sup>3,@</sup>

**1** : Faculty of science, Department of Geolog (PMF) - **Website**

*Horvatovac 95, 10000 Zagreb - Croatia*

**2** : Faculty of Science, Department of Chemistry (PMF) - **Website**

*Horvatovac 102A, 10000 Zagreb - Croatia*

**3** : ANT - **Website**

*Medarska 69, 10000 Zagreb - Croatia*

\* : Corresponding author

The objective of the study was to investigate the Vransko Lake sediments, and soils from a nearby landfill. Three sediment cores, 50-cm-deep, were sampled in different parts of the lake in order to determine whether there is pollution of the sediments and if it could be linked to the landfill –i.e. if it is higher in its vicinity. Sample DOK-55 is closest to the landfill while DOK-26 is the furthest. The hydrogeological characteristics of the analysed area, from the landfill to the lake, imply a high permeability and porosity, due to the system of fractures and karstification processes. Transport of contaminants is very likely to occur under these conditions. Multi-element (Cu, Pb, Zn, Cd, Ni, Co, Mn, Cr, As, Mo, U, Hg, Ag, Al and Fe) determination by ICP-MS, after Aqua Regia digestion, was performed on a total of 19 samples. Soil sample was also leached with ammonium acetate (1 M), to determine the amount of easily leachable elements. As expected, concentrations of trace metals in the landfill soils were higher than those found in the sediments. Likewise, the results of ammonium acetate leachate also showed high values –i.e. high lixiviation potential. Values of all analysed samples from three different sediment cores and values from the landfill site, including the leachant analysis, are presented in Fig 1. Pollution of the lake sediments with trace metals by the landfill is suggested by: a) spatial geochemical heterogeneity of the sediments throughout the lake, with the higher values of the potentially leachable metals in the core located closer to the landfill; b) larger concentrations of trace metals in the surface layer (0-3 cm) in comparison to deeper, most likely unpolluted, layers (36-38 cm); and c) high concentrations of trace metals in the leachate, which surpass the one from a similar landfill sites.

# The rise of a city; urban lake deposits and pollution transport pathways in Bergen, Norway

Malin Andersson<sup>1,@</sup>, Ola Anfin Eggen<sup>1,@</sup>, Rolf Tore Ottesen<sup>1,@</sup>

1 : Geological Survey of Norway (NGU) - **Website**  
Postboks 6315 Sluppen 7491 Trondheim - Norway

The objective of this study was to investigate the chemical history of the city of Bergen through dating the changes in the concentrations of hazardous substances in urban lake sediments.

32 inorganic elements (of which Fe, Na, Mn, P, Cu, Zn, Pb, Ni, Cd, Cr, As, Hg and S are presented), polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) were analysed in a sediment core that represents 7200 years of accumulation. We also present measured amounts of suspended particles in urban stormwater to determine the effect of some diffuse sources.

The contents of metals and PAH (sum of 16 compounds) were low until the 17th century, when a dramatic increase is noted for most compounds. This is when the city spread to the lake shores and, consequently, the effects of sewage input, urban fires, domestic heating, gasworks and other industry as well as traffic increased. The distribution of PAH-compounds indicates a shift from wood and coal combustion sources towards mixed and petrogenic sources and high-temperature combustion.

PCB concentrations reflect the time period from the introduction of PCB to their banning in Norway (1980), but also suggest active sources present today. Stormwater from the studied, urban catchment (5800 m<sup>2</sup>) transports 800 kg of suspended solids per year.

<sup>14</sup>C dating provides evidence that the sedimentation rate was almost constant until 2700 years ago, when isostatic uplift isolated the waters of the former fjord and the lake was formed, producing a decrease in sedimentation rates. Sediment input increased again with urban and industrial activities. <sup>14</sup>C dating does not provide consistent data for this later period, possibly due to the fact that the lake has been used as a waste site throughout human history. The depth records of several organic compounds, metals and cyanide helped to constrain the chronology of the last few centuries.

# Improving the knowledge of pesticide transfer into groundwater: constraints by a coupled geochemical and pesticide monitoring approach.

Nicole Baran<sup>1,\*,@</sup>, Emmanuelle Petelet-Giraud<sup>1,@</sup>

1 : BRGM. 3 avenue C. Guillemin BP 36009 45060 Orléans Cedex 2 - France

\* : Corresponding author

Enhanced monitoring of groundwater quality over several years has revealed a pesticide contamination of aquifers in North America and Europe, but spatial and temporal fluctuations of pesticides concentrations complicate investigation on pesticide fate and transfer into groundwater. Therefore coupling pesticides and geochemical monitoring help deciphering remaining gaps in knowledge.

The thin thickness of vadose zone of the alluvial unconfined aquifer of Ariège River (~538 km<sup>2</sup>, SW France) makes it vulnerable to contamination due to intensive agriculture. The aquifer is in direct hydraulic connection with rivers Ariège and Hers Vif and probably feeds them during much of the year.

Monthly monitoring of groundwater quality at 16 points in the plain was initiated in March 2009 and is still on-going. It includes some 50 pesticides or metabolites, major ions including nitrate and non-conservative parameters (pH, T, redox potential, EC). A strong spatial variability of the contamination was demonstrated, with predominance of degradation products over parent molecules in some locations. Metolachlor, a pre or early post emergence herbicide and its ionic metabolites present a high occurrence with sharply variables concentrations for given points. Presented results focus on these molecules.

Using the SAM ratio (ratio of metolachlor ESA concentration to the metolachlor concentration) proposed by Philipps et al. (1999), allowed distinguishing several groups according to the SAM values, time-fluctuations and correlation with water level series. Spatially, groundwater geochemical signatures allowed distinguishing the lithology of the different alluvial terraces. Variations of geochemical parameters explain seasonal connection between terraces, local surface-groundwater relations and are also consistent with SAM fluctuations. Potential transfer of waters with different origins and/or according to various mechanisms is thus demonstrated and characterized.

The coupled approach of geochemistry and hydrogeology leads to a better understanding of the spatial and temporal fluctuations of the pesticide concentrations in groundwater at the aquifer scale.

## Impact of a storm event on the transfer of particulate trace metals to the deep sea (NW Mediterranean Sea, Gulf of Lion)

Chloé Dumas<sup>1,\*,@</sup>, Dominique Aubert<sup>1,@</sup>, Xavier Durrieu De Madron<sup>1,@</sup>, Wolfgang Ludwig<sup>1,@</sup>, Jörg Schäfer<sup>2,@</sup>, Claude Estournel<sup>3,@</sup>

**1** : CEFREM , *Université de Perpignan, av. Paul Alduy, 66860 Perpignan - France*

**2** : EPOC, *Université de Bordeaux, Site de Talence Université Bordeaux 1 Avenue des Facultés 33405 TALENCE CEDEX - France*

**3** : Laboratoire d'Aérodologie et d'Océanographie Côtière, *Observatoire Midi-Pyrénées, 14 Avenue Edouard Belin F-31400 Toulouse - France*

\* : Corresponding author

In the NW Mediterranean, energetic hydrodynamical events (such as storms or dense water cascading) contribute to shelf-slope exchanges of sediment bound contaminants, from the continental shelf to the deep basin, mainly through submarine canyons that channelize the exportation of particles.

This study aims at quantifying the Particulate Trace Metal fluxes (PTM) exported through the Cap de Creus canyon during a major storm event (March 2011). Different origins and bioavailability of these PTM should also be examined.

The oceanic cruise CASCADE enabled us to observe the export of particulate matter during this event. Sediment traps were deployed in the canyon during the whole campaign and samples were taken every 2-3 hours. This high frequency sampling allowed the calculation of reliable PTM fluxes. Characterization of the PTM dynamics was done through the determination of enrichment factors and a single extraction procedure was applied to determine the particulate matter sources and to quantify the potential bioavailability of the associated PTM.

Results indicate that the storm did not influence the sediment specific PTM concentrations in the water column or in the sediment traps : although the particulate load is more important during the storm (up to 18,5 mg/L which is 9 times the average) the chemical signature of the PTM is rather similar during the whole period of monitoring. The single extraction procedure revealed that the particles originated mainly from the Rhone river, although this river was not flooding, contrary to the numerous coastal rivers in the Gulf of Lion. This chemical characterization indicates sediment remobilization and exportation from the shelf to the deep sea and no direct contribution from coastal river particles. Significant amounts of PTM were exported during this storm (ex: 23,3 mg/m<sup>2</sup> of Cu of which 48% is potentially bioavailable).

# Inorganic contaminants inputs to the sea from a large urbanized Mediterranean city under various weather conditions

Benjamin Ourse<sup>1,\*,@</sup>, Cédric Garnier<sup>1,@</sup>, Gaël Durrieu<sup>1,@</sup>,  
Stéphane Mounier<sup>1,@</sup>, Dario Omanovic<sup>2,@</sup>, Yves Lucas<sup>1,@</sup>

**1** : Laboratoire PROTEE (PROTEE) - **Website**

*Université du Sud - Toulon - Var: EA3819, BP20132 83957 La Garde - France*

**2** : Ruđer Bošković Institute - for Marine and Environmental Research (IRB) - **Website**

*PO Box 180, 10002 Zagreb - Croatia*

\* : Corresponding author

Progressive anthropization of coastal areas over the world results in changes in the chemistry and biology of the coastal seawaters. Most studies dedicated to Mediterranean rivers input to the sea focused on flood events from large rivers, because storm flows in such area are responsible of most of the annual input to the sea of suspended particulate matter, organic matter and potentially toxic elements. The objectives of the project were (1) to quantify the contaminants brought to the sea due to Marseille city inputs under different weather conditions and (2) to study their dynamics in the coastal zone.

Various sampling campaigns were carried out during dry and wet periods in the main tributaries upstream the Marseille sewage treatment plant, at the outlet at sea and in the freshwater/seawater mixing zone. Dissolved/particulate metals and organic carbon concentrations were determined by voltammetry, HR-ICP-MS and TOC-meter respectively. Batch remobilisation experiments of outlet particles in different salinity ratios were conducted to better apprehend the metal partitioning kinetics between dissolved and particulate fractions in the plume. Finally, on-field vs. lab filtrations were also compared.

Results obtained after lab filtration (~3-4 h after sampling) showed various trends for the studied elements in the salinity gradient, depending on the element and the period. Results obtained after on-field filtration showed that dissolved/particulate metal distributions were not at equilibrium when discharged at sea, resulting in an important and rapid metal desorption in the salinity gradient. Such process, confirmed by lab remobilization experiments, was underestimated using the classical sample treatment protocol. It indicates that contamination of organisms along the coast can be higher than expected. Eventually, these results have evidenced the significant (up to 90%) contribution of treated wastewater on metals discharge to the coastal zone during dry periods, but the greater impact of rivers during wet ones.

# Identification of sensitive parameters in the modeling of SVOCs reemission processes from soil to atmosphere

Vincent Loizeau<sup>1,2,3,\*,@</sup>, Philippe Ciffroy<sup>3,@</sup>, Yelva Roustan<sup>2,@</sup>,  
Luc Musson Genon<sup>1,2,@</sup>

**1** : EDF Recherche et Développement, Département MFEE, 6 Quai Wattier 78401 Chatou - France

**2** : Centre d'Enseignement et de Recherche en Environnement Atmosphérique (CEREA) - **Website** EDF, Ecole des Ponts ParisTech, Université Paris-Est. 6-8 avenue Blaise Pascal, Cité Descartes Champs-sur-Marne 77455 Marne la Vallée Cedex 2 - France

**3** : EDF Recherche et Développement, Département LNHE, 6 Quai Wattier 78401 Chatou - France

\* : Corresponding author

Many studies showed that semi-volatile organic compounds (SVOCs) are subject to Long-Range Atmospheric Transport (LRAT) and that such a transport may occur through a series of deposition-reemission events at the soil surface-air interface. Thus, it appears necessary to take into account the exchange between soil and atmosphere to properly simulate the fate of these pollutants at regional or global scale. The prediction of reemission from soils is however associated with large uncertainties, classified in three main sources: (i) natural variability, including nature of soil and meteorological conditions ; (ii) uncertainty about intrinsic properties of chemicals, which govern the dynamics of chemicals in air and soils ; (iii) model structure, and particularly the discretization of soil compartment.

Considering this background, a major challenge is to identify the most sensitive sources of uncertainty in modelling the reemission of chemicals from soils, in order to know where the priority has to be set for upgrading SVOC dispersion estimation.

To answer this question, a sensitivity analysis was conducted on a soil model by affecting probability density functions for each of model parameters. Four chemicals (Benzo-a-pyrene, PCB-28, Hexachlorobenzene and Lindane) were selected because of their contrasted behaviors in soils.

Results showed that the rank of sensitive parameters depends on the intrinsic properties of the investigated substances, in particular on their mobility potential in soils and their ability to volatilize. Despite such differences, general patterns can however be observed: for all the substances, organic matter content in the soil is one of the most sensitive parameters in the simulation of reemission fluxes. Instead, the number of layers used in the model is less influential. These results allowed defining priorities in LRAT modeling strategy, highlighting in particular that mapping organic matter in soils instead of using a generic value could significantly improve the reemission estimation.



# Tracer based source apportionment of polycyclic aromatic hydrocarbons in PM<sub>2.5</sub> in Guangzhou, southern China

Hai Guo<sup>1,@</sup>, Bo Gao<sup>@</sup>

1 : The Hong Kong Polytechnic University (HKPolyU) - **Website**  
1 Yiu Choi Road - Hong Kong SAR China

PM<sub>2.5</sub> samples were simultaneously collected at six sites in Guangzhou in November–December 2009. Concentrations of 18 polycyclic aromatic hydrocarbons (PAHs) and molecular tracers for vehicular emissions (i.e. hopanes and elemental carbon), coal combustion (i.e. picene), and biomass burning (i.e. levoglucosan) were determined. Three high level episodes were observed during the sampling period, likely due to accumulation effects. Back trajectory analysis revealed that air masses for the three episodes were from eastern inland Pearl River Delta (PRD) region. There was no obvious concentration gradient for total and 5–6 ring PAHs from urban to rural sites. However, 4-ring PAHs exhibited significantly higher levels at rural site than that at urban/suburban sites ( $p < 0.01$ ). BghiP correlated well with hopanes, elemental carbon and picene, indicating vehicular emissions (VE) and coal combustion (CC) were the sources of 5–6 ring PAHs, which were further confirmed by comparing the four tracers/BghiP ratios and IcdP/BghiP ratios in ambient samples with those from source profiles. Positive matrix factorization (PMF) model combined with tracer data was applied to explore the source contributions to PAHs. Three sources were identified by both inspecting the dominant tracer(s) in each factor and comparing source profiles derived from PMF with determined profiles in Guangzhou or in the PRD region. The three sources identified were VE, biomass burning (BB), and CC, accounting for  $11 \pm 2\%$ ,  $31 \pm 4\%$ , and  $58 \pm 4\%$  of the total PAHs, respectively. CC replaced VE to become the most important source of PAHs in Guangzhou, reflecting the effective control of VE in recent years. The three sources had different contributions to PAHs with different ring sizes, with higher BB contributions ( $75 \pm 3\%$ ) to four-ring PAHs and higher CC contributions ( $57 \pm 4\%$ ) to six-ring PAHs such as benzo[ghi]perylene. Temporal variations of VE and CC contributions were probably caused by the change of weather conditions, while temporal variations of BB contributions were additionally influenced by the fluctuation of BB emissions.

# Effect of natural aging on sewage sludge ash characteristics and acid extraction efficiency

Nazaré Couto<sup>1,2,\*,@</sup>, Paula Guedez<sup>1,2,@</sup>, Lisbeth M. Ottosen<sup>2,@</sup>,  
Gunvor M. Kirkelund<sup>2,@</sup>, Alexandra B. Ribeiro<sup>1,@</sup>

**1** : CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, *Caparica, Portugal - Portugal*

**2** : Department of Civil Engineering, Technical University of Denmark, *Lyngby, Denmark - Denmark*

\* : Corresponding author

Incineration of sewage sludge destroys organic contaminants and pathogens while promoting its mass reduction. It is known that incinerated sewage sludge ash (ISSA) properties can vary significantly depending on the characteristics of the catchment area and the applied process in the wastewater treatment plant. However, the storage conditions of ISSA at the incineration plant, before its final destination, may also cause changes in the ash characteristics.

The changes in ISSA characteristics during its storage in an open air facility were studied. ISSA was collected from an incinerator located in Copenhagen, Denmark. The difference in physico-chemical parameters between recently collected and stored ashes (under the influence of environmental parameters such as precipitation, solar radiation and wind) as well as the suitability of acid wash for heavy metal and phosphorus removal were assessed.

Statistically significant differences were observed for some physico-chemical parameters, such as pH, conductivity, water content, loss on ignition and solubility, and in heavy metal concentration namely in Al, Zn and Cu. After acid washing (HNO<sub>3</sub>; 1M), a general decrease in heavy metals concentration was found. Also, 5% of phosphorus was mobilized from ISSA, representing *ca.* 53 g kg<sup>-1</sup> for recently collected ash and 51 g kg<sup>-1</sup> for deposited ash, indicating that even though ashes characteristics change, phosphorus is still available for extraction. In order to its further reuse, a further separation step is needed (e.g. electro-dialytic process, selective precipitation, or ion exchange) as phosphorus was extracted together with heavy metals. Nevertheless, for nutritional constraints this step should account for phosphorus transformation in a plant available form.

***Topic 3***

***Spatial and Temporal Geochemical records of  
Pollution Including Catchment Studies***

***Poster Presentations***

# Landfill fire as source of Dibenzo-p-dioxins and Dibenzofurans in air and lake sediment from Vransko Lake

Hana Fajković<sup>1,@</sup>, Esad Prohić<sup>1,@</sup>, Zvonko Habuš<sup>2,@</sup>

**1** : Faculty of science, Department of Geolog (PMF) - **Website**  
*Horvatovac 95, 10000 Zagreb - Croatia*

**2** : ANT - **Website**  
*Medarska 69, 10000 Zagreb - Croatia*

Lake sediment and air samples from Vransko Lake were analyzed for the presence of Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) compounds. Waste incineration is one of the formation mechanisms for these compounds. A landfill site is located near the lake, and landfill fire occasionally occur accidentally. The first two centimetres of lake sediment were sampled in the summer of 2008 and 2010 to determine whether dry deposition of PCDDs and PCDFs - formed during landfill fire - ended up in the lake. Outdoor air was collected during a 2007 landfill fire for a 5 day period, with a total sample volume of 485,623 m<sup>3</sup>. The air was pumped through an air sampling pump with integrated adsorption unit of polymer resin (XAD), which was later analysed. All analyses were determined by high-resolution gas chromatography - high resolution mass spectrometry (HRGC/HRMS). The total sum of PCDDs and PCDFs in the air was 1940,4 fg/m<sup>3</sup>, with a toxic equivalence of 22,92 fg I-TEQ /m<sup>3</sup>. The total sum of PCDDs and PCDFs in the lake sediments was 17,93 ng/kg (sampled in the year 2008); 17,21 ng/kg and 23,17 ng/kg (sampled in the year 2010). I-TEQ for sediments were 0,046 ng/kg, 0,165 ng/kg and 0,03ng/kg, as follows. The major source of these compounds for humans is through food, since they bioaccumulate. The fish from Vransko Lake is often consumed as the lake is popular with sport fishermen. The determined values of PCDDs and PCDFs in all analysed samples – both sediment and air - were within a tolerable level, but further analysis, especially in a time of landfill fire, as well as analysis of fish tissue would be welcome.

## Multivariate analysis as a tool to evaluate potentially harmful elements (PHE) dispersion in podzols of an industrial area (NW of Portugal)

Manuela Inácio<sup>1,@</sup>, Ana Rita Salgueiro<sup>1,2,@</sup>, Eduardo Ferreira Da Silva<sup>1,@</sup>, Virgínia Pereira<sup>1,@</sup>

1 : Geobiotec, University of Aveiro (Geobiotec), Campus de Santiago, 3810-193 Aveiro - Portugal  
2 : Cerena/DECivil, Av. Rovisco Pais 1049-001 Lisboa, Portugal - **Website**

Since 1950's that the impact in the environment and public health is felt at Estarreja municipality due to the activity of several chemical industries implemented at the Estarreja Chemical Complex (ECC). Located in north central Portugal, the ECC is composed of several chemical industries which are recognized as important sources of Potential Harmful Elements (PHE) inputs into the environment, being the most important essentially related to past industrial activities, namely with the production of sulphuric acid from arsenopyrite roasting and from the chloralkali plant.

Podzols are the most common soil type in the vicinity of ECC, often used as pasture land and agriculture. Due to its particular characteristics, is of great importance to investigate the levels of PHE's and identify their sources, as well as their dispersion mechanisms.

Composite samples of topsoil were collected in an area of approximate 60 km<sup>2</sup>. Samples were dried at 40°C, passed through a 63 µm sieve; extracted with aqua regia and the multi-element analysis was done by ICP-MS in ACME certified laboratory. The results show high levels of PHE in these soils compared to those given in the international guidelines. The maximum concentrations found are above 10,000 mg kg<sup>-1</sup> for As, and above 100 mg kg<sup>-1</sup> for Hg.

The proposed methodology is based in Multivariate Data Analysis: i) primarily was performed a Correlation Coefficient Analysis – which allowed the selection of the PHE's to be used in the second step; ii) a matrix of 15 elements x 85 samples was submitted to Principal Component Analysis, which results identified 4 groups, two of them associated with the production in the ECC; iii) finally Cluster Analysis was applied disclosing 4 groups of samples. The spatial projection of these groups of samples allowed to identify the sewage outlet as the active dispersion mechanisms in the area.

# Monitoring of nutrient and carbon load to the pre-dams of a drinking water reservoir by automatic probes and water samplers

Kurt Friese<sup>1,\*,@</sup>, Larissa Leben<sup>1,@</sup>, Burkhard Kuehn<sup>1,@</sup>, Martin Schultze<sup>1,@</sup>

1 : Helmholtz Centre for Environmental Research - UFZ (UFZ)  
Department Lake Research Brückstr. 3a 39114 Magdeburg - Germany  
\* : Corresponding author

## 1 Importance of the work and objectives

An increase in concentration of dissolved organic carbon (DOC) in surface waters is noticed on the northern hemisphere for over 15 years (Monteith et al. 2007). Also in Germany, a notable increase of DOC concentration can be observed in several reservoirs. Some authors believe that this increase in DOC might be the result of increasing global average temperature. Increasing DOC concentrations are a big threat for waterworks since costs for purification increases simultaneously.

## 2. Methodologies

To identify the sources and pathways of the organic carbon fluxes an extensive observatory was installed in the Rappbode reservoir system, the largest drinking water reservoir in Germany, located in the eastern Harz Mountains. Automatic probes for continuous registration of DOC (via SAC 254nm), nitrate (NO<sub>3</sub>-), electric conductivity (EC), and temperature (T) were deployed in the inflow rivers of the pre-dams. In addition, four automatic water samplers were placed at the four inflows.

## 3. Main results and conclusion

Here, the evaluation of data record from a first 10month period of two inflow rivers (Rappbode and Hassel) are presented. The results showed a high positive correlation of DOC and nitrate concentration and amount of precipitation or discharge, respectively. The concentrations of DOC and nitrate was different in both streams reflecting their different land use within their catchments. The catchment of the Hassel pre-dam delivers higher concentrations of nitrate and DOC by a mixed use of forest (37%), grassland (33%) and agriculture (25%) than the Rappbode catchment which is dominated by forest (> 70%), agricultural use covers only 2% of the area. But since the discharge of the Rappbode is quite larger by a factor of 1.5 the transported load of DOC accumulated to 22.7 t within the observed time period whereas the Hassel transported only 17.3 t of DOC.

# Effect of increased temperature and carbon dioxide concentration in rice volatile emissions in a portuguese paddy field

Nazaré Couto<sup>1,@</sup>, Catarina Oliveira<sup>1,@</sup>, Eduardo P. Mateus<sup>1,@</sup>,  
Marco G. Silva<sup>2,@</sup>, Alexandra B. Ribeiro<sup>1,@</sup>

**1** : CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, *Caparica, Portugal - Portugal*

**2** : REQUIMTE-Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, *Caparica, Portugal - Portugal*

The increase of rice productivity, a crop that is the main staple food for about half of the world's population, is a goal to be achieved in the Mediterranean countries. In fact, as it is estimated that twice as much food will be needed in the years 2000-2025 comparing with 1960s, it is important to study the environmental consequences that can be associated with increased cereal production. Portugal is an important European rice producer with the crop being mainly produced in Mondego, Tejo, Sorraia and Sado Valleys.

Volatile organic compounds (VOC) produced by plants are usually complex mixtures including several different compounds such as esters, phenols, alcohols, aldehydes and terpenoids. These VOC can be responsible by plant susceptibility and/or defence against pathogens or herbivores.

A field campaign between May and October 2012 was carried out aiming to follow the emission of VOC from *Oriza sativa* L. Ariete. The study was carried out in irrigated rice fields located in Salvaterra de Magos (Lisboa e Vale do Tejo region, Portugal) aiming to test the effect of VOC emissions in loamy sand and silty clay soil textures. Open chambers with increased temperature with and without enhanced carbon dioxide concentration were also installed in silty clay soil, aiming to assess the effect of abiotic stress factors in crop emissions.

Solid phase microextraction followed by gas chromatography with mass spectrometer detector (GC/MS) was used for the identification of *O. sativa* VOC in vegetative, reproductive and ripening growth phases. Despite the low quantity of released organic compounds, the influence of soil texture and stress factors will be presented and discussed.

## Sources and historical record of tin and butyl-tin species in a Mediterranean bay (Toulon Bay; France).

Frederique Pougnet<sup>1,\*,@</sup>, Jörg Schäfer<sup>1,\*,@</sup>, Lionel Dutruch<sup>1,\*,@</sup>,  
Cédric Garnier<sup>2,\*,@</sup>, Huy Dang<sup>2,@</sup>, Laurent Lanceleur<sup>1,@</sup>, Jean-Ulrich Mullot<sup>3,@</sup>, Gérard Blanc<sup>1,@</sup>

**1** : Environnements et Paléoenvironnements OCéaniques (EPOC) - **Website**

*INSU, CNRS: UMR5805, Ecole Pratique des Hautes Etudes, Université Sciences et Technologies - Bordeaux I, Observatoire Aquitain des Sciences de l'Univers. Avenue des Facultés - 33405 TALENCE CEDEX - France*

**2** : Processus de Transferts et d'Echanges dans l'Environnement (PROTEE) - **Website**

*Université du Sud - Toulon – Var, Batiment R, Bureau 138 BP 20132 83957 La Garde - France*

**3** : Base Navale de Toulon (LASEM/LCA) - **Website**

*LASEM, BP 61 Toulon Cedex 9 - France*

\* : Corresponding author

Concentrations of inorganic tin (Sn), Tributyltin (TBT), Dibutyltin (DBT) and Monobutyltin (MBT) were measured in sediments of the Toulon Bay, hosting the major French military harbour. In marine environments these species mainly derive from antifouling paints used in various naval domains including military, trade, tourism and leisure. In the past, butyl-Sn contamination has severely impacted bivalve and gastropod populations (mortality, deformations, imposex, etc.) and they are known to accumulate in the aquatic food chain. Anticipating planned dredging, the aim of the present work is to map and evaluate for the first time the recent and historic contamination of these sediments by inorganic and organic Sn species. Surface sediments from 29 sites covering the entire Toulon Bay and two cores from a military area and mussel production zone were analyzed by ICP-MS and GC-ICP-MS using species-specific isotope dilution (TBT, DBT and MBT enriched in <sup>119</sup>Sn) to determine concentrations of inorganic Sn and butyl-Sn.

Tin and butyl-Sn concentrations in the bay varied over 4 orders of magnitude, depending on the distance to the shipyards. The common spatial distribution of total Sn (1300 to 112000 µg/kg), TBT (<0.5 to 2700 µg/kg), DBT (<0.5 to 1800 µg/kg) and MBT (0.5 to 1000 µg/kg), similar to that of other contaminants in the Bay (e.g. Hg, Pb, Cu), the Enrichment Factors, the low degradation and the historical records of butyl-Sn species, support the scenario of a strongly polluted marine environment with exportation of polluted sediment to the open Mediterranean. Low degradation and the historical records of butyl-Sn species in two <sup>210</sup>Pb-dated sediment cores, representative of the Northern Bay, are consistent with the relatively recent use of TBT by military shipyards and confirm maximum pollution during the 1970s, which will persist in the anoxic sediments for several centuries. Resuspension of extremely contaminated subsurface sediments by the scheduled dredging will probably result in mobilization of important amounts of butyl-Sn species in the water column, highlighting the need for thorough monitoring with respect to existing French dredging guidelines (GEODE). All these results suggest that the contaminant cocktail in the Toulon Bay presents a severe risk for this coastal ecosystem.



# Silver in urban wastewater discharged into the fluvial Gironde Estuary: Concentrations, fluxes and potential impact.

Victoria N. Deycard<sup>1,@</sup>, Laurent Lancelleur<sup>1,@</sup>, Jörg Schäfer<sup>1,@</sup>,  
Gérard Blanc<sup>1,@</sup>, Alexandra Coynel<sup>1,@</sup>, Cécile Bossy<sup>1,@</sup>, Lionel  
Dutrich<sup>1,@</sup>, Alexandre Ventura<sup>2,@</sup>

**1** : Transferts Géochimiques des Métaux à l'interface continent océan UMR EPOC 5805 (TGM) -  
**Website**

*Université Bordeaux 1, Av. des facultés 33405 Talence cedex - France*

**2** : Lyonnaise des Eaux, Agence Diagnostic Assainissement

*Lyonnaise des Eaux, Agence Diagnostic Assainissement Centre Régional Aquitaine F-33029,  
Bordeaux - France*

Based on daily (24h-cumulated, flow-weighted, during 3 weeks) samples from the entries and the outlets of the two major wastewater treatment plants of the Bordeaux agglomeration located on the Garonne Branch of the Gironde Estuary, we compared daily Ag concentrations and fluxes to those transported by the Garonne River during low discharge. Average dissolved (60 ng/L; max: 400 ng/L) and particulate (3 mg/kg; max: 17 mg/kg) concentrations in wastewater effluent were clearly higher than average dissolved (2 ng/L; max: 5 ng/L) and particulate (1 mg/kg; max: 5 mg/kg) concentrations in the Garonne Branch.

Particulate influent Ag concentrations at Clos de Hilde and dissolved influent Ag concentrations measured at both plants were highly variable and did not directly depend on rain events, suggesting that these Ag inputs are source-specific making Ag a good urban tracer in Bordeaux wastewater. Minimum total (8.2 g/d) and dissolved (4.3 g/d) Ag fluxes in the Garonne Branch were representative of low discharge periods and were lower than average total (24 g/d; i.e. 0.003 g/inhab/yr) and dissolved (11 g/d; i.e. 0.001 g/inhab/yr) Ag fluxes released by the two major WWTPs. This means that urban Ag inputs via WWTPs may significantly increase concentrations and fluxes in the fluvial Gironde Estuary and impact water estuarine water quality, increasing Ag exposure of local commercial aquatic species such as shrimp and fish.

# Heavy metals migration features in urban landscapes of Ulaanbaatar city

Olga Sorokina<sup>1,@</sup>, Natalia Kosheleva<sup>1,@</sup>, Nikolay Kasimov<sup>1,@</sup>

**1** : Faculty of Geography, Lomonosov Moscow State University (Faculty of Geography, MSU) - **Website**  
119991, Russian Federation, Moscow, GSP-1, Leninskie gory, Faculty of Geography - Russia

The purpose of the study is to assess the environment contamination with heavy metals (HMs) in Ulaanbaatar which population exceeds 1 million (1/2 of Mongolian population). Various media were sampled to detect technogenic geochemical anomalies: aerosols (132 samples), snow (21), poplar leaves (82), soils (108). Concentrations of 20 the most dangerous HMs were measured using ICP method. Results were processed using geochemical methods, cluster and factor analysis, and mapping.

Air contamination in Ulaanbaatar is manifested in high concentrations of Pb and particle matters especially during cold seasons. Extremely high air pollution levels are registered in the city center because of mountain relief and temperature inversions.

Snow water analysis shows that HMs fall out predominantly in solid fraction but the most contrasting anomalies form in dissolved one. By springtime the most polluted areas are ger (Mongolian traditional dwelling) and industrial districts. Combustion temperature causes different composition of fly ash from thermal power plants (TPPs) and ger stoves. TPPs emissions include As-Bi-Zn-Th-Fe-Co-Cr-Cu group and spread over large distances because of high chimneys whereas ger stoves emissions include Be-Cd-Mo-Sb-Sr-V group that falls out near gers.

Poplar leaves contamination characterizes atmospheric state during vegetation season. Distribution of Cr, Zn, Cu, As, Cd in leaves shows that they concentrate near pollution sources because of their low migration capacity whereas Pb and V anomalies form at greater distances from sources because of their atmospheric migration. The strongest biogeochemical transformation is observed in industrial zone and near highways.

Soils accumulate pollutants during long-term period, fix them from solid fraction of snow water and reflect influence of technogenic sources. Many HMs have low migration capacity in Ulaanbaatar soils. Pb-Zn-Cd-Cu accumulate mainly in soils near highways, As-Sr-V – TPPs and gers, Co-Ni-Cr – building plants. Mo in anionic form migrates to river valleys.

## The Emperors mercurial elements – heavy metal pollution in a bog near Hadrian's Wall

Anke Kuttner<sup>1,@</sup>, Dmitri Mauquoy<sup>1,@</sup>, François De Vleeschouwer<sup>2,3,@</sup>, Tim Mighall<sup>1,@</sup>, Eva Krupp<sup>4,@</sup>

**1** : University of Aberdeen

*Department of Geography & Environment, School of Geosciences, University of Aberdeen, Elphinstone Road, Aberdeen, AB24 3UF - United Kingdom*

**2** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**3** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

**4** : University of Aberdeen

*Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, AB24 3UE - United Kingdom*

To effectively place pollution signals into an archaeological context, it is important to separate those derived from natural sources from those of anthropogenic activities. This study aims to decouple sources and processes involved in enrichment of heavy metals in a 3500-year record from a bog in the vicinity of Hadrian's Wall and the Northern Pennine Orefield. For this purpose several geochemical elements were determined indicative of different sources and processes alongside Pb, Zn, Cu, As, and Hg. To extract the different fractions influencing their distribution we used enrichment factors (EF) and applied principal component analysis (PCA) to the dataset. Average concentrations are: Pb, 25.3µgg-1; Zn, 8.9µgg-1; Cu, 2.0µgg-1; As, 1.0µgg-1; Hg, 31.0ngg-1. The highest concentrations, approximately 13x, 9x, 8x, 10x and 6x respectively, date into the first half of the 19th (As) and 20th century (Pb, Cu, Hg, Zn). The PCA extracted 7 components. Generally, at least two components are necessary to elucidate the heavy metal distribution. Only 56% of the variance in copper is explained by the PCA, with 44% related to some unknown source/process. Zinc, As and Pb are related to pollution (second component), but Hg and Cu are more closely associated with organic matter (fourth component). Four phases of pollution have been identified: I, ~2350-1500calBP; II, ~1050-700calBP; III, ~500-350calBP; IV, 250calBP-present. Peaks in other metals do not always correspond with Pb, but appear to be associated with possible climate changes reconstructed using biological proxies. Elevated Cu EF also occur during the Bronze Age (~3150-2800calBP). The pattern of Pb pollution is in accordance with previous studies, although it can be attributed to both anthropogenic and natural sources. The enrichment during the late Iron Age and Roman period suggests that the Northern Pennine Orefield was exploited for metals. The interpretation of Zn, As, Cu and Hg requires more attention.

# Impact of Urbanisation on Carbon Sequestration in Forest Parks: a comparative assessment between Bulgaria and Scotland

Miglena Zhiyanski<sup>1,@</sup>, Andrew Hursthouse<sup>2,@</sup>, Vanya Doichinova<sup>@</sup>

1 : Forest Research Institute-BAS, Sofia - Bulgaria

2 : School of Science, University of the West of Scotland (UWS) - **Website**  
PA1 2BE, Paisley - United Kingdom

The process of urbanization creates unique urban ecosystems and urbanized soils. Urban areas currently make up about 4% of the world's terrestrial surface, and urban growth continues at an unprecedented rate. Due to high pollution load and the dynamic effect of climate change in the urban environment, the green infrastructure comes under increasing stress. The potential is for urban forest areas to offer a significant contribution in mitigation of CO<sub>2</sub> at a small scale, but little is known about the interaction with urban soils, increasingly recognized as a sink for inputs of urban pollutants.

This study focuses on determining the influence of changing soil conditions, driven by urbanization, on carbon storage in forest parks. It compares soil properties with carbon stocks, nutrient availability and potentially toxic element loads. Experimental sites were established in three contrasting regions Sofia and Sandanski (Bulgaria) and Glasgow (UK), with contrasting urban characteristics. Sampling sites in the studied regions were distinguished as: urbanized (U – for Sofia; S – for Sandanski, G - Glasgow) and control non-urbanized (NU - for Sofia; NS – for Sandanski; NG - Glasgow). In each of them the following components of ecosystems: soil, forest floor, grass coverage and aboveground tree vegetation were examined.

The key difference was the higher values of carbon stored in soils of urban forest parks compared with the control plots. In urban soils of Sofia carbon stocks varied within 80 ÷ 125 tC ha<sup>-1</sup>, for Sandanski 44 - 88 tC ha<sup>-1</sup>, for Glasgow 76 - 120 tC ha<sup>-1</sup>, with non-urbanized control sites: 53 - 103 tC ha<sup>-1</sup> for the Sofia region, 32 - 39 tC ha<sup>-1</sup> for the Sandanski region, 56 - 100 tC ha<sup>-1</sup>. For the tree carbon stock, it was higher in non-urbanized sites, because of higher tree density in these plots. The results for aboveground biomass carbon stock in urban sites varied 34.5 - 61.7 tC.ha<sup>-1</sup> for Sofia, 36.5 tC.ha<sup>-1</sup> for Sandanski, and 45.2 - 60.8 tC.ha<sup>-1</sup> for Glasgow and in Non-Urban sites: 33.9 - 67.5 tC.ha<sup>-1</sup>, 34.0 - 67.8 tC.ha<sup>-1</sup> and 57.3 tC.ha<sup>-1</sup> respectively.

Dependencies between carbon sequestration in soils and specific soil characteristics (soil pH, textural fractions, PTE concentrations) were studied using PCA. The analyses of the results obtained showed that carbon sequestration in urban forest parks depended more on management activities than degradation by poor soil quality/toxicity under current exposure conditions.

# **New method to assess glyphosate speciation in soils and sediments**

Mathieu Canton<sup>1,@</sup>, Marc Lucotte<sup>1</sup>

**1** : Université de Québec à Montréal (UQAM)  
*201 avenue Président Kennedy, Montréal, QC, H2X 3Y7 - Canada*

Glyphosate is the main herbicide used in industrial farming. It permits no till practices and the cultivation of some genetically modified organisms. It is known to have high affinity to soil where it is bounded to metal complex, clays and soil organic matter. Alkaline extractions with NaOH or KOH are frequently used in glyphosate soil analyses but the recovery rate varied in different soils due the multiple substrates used by glyphosate. The aim of this study was to test several extractions on different soils and sediments to highlight glyphosate speciation in Brazilian oxisoil and river sediment. Analyzes were performed with GC-ECD and Enzyme Linked Immuno Sorbent Assay. CaCl<sub>2</sub> solution extracts the mobile fraction available trough solid and liquid phases equilibrium. Alkaline solution extracts the fraction bounded to clays and organic matter. Citrate dithionite bicarbonate solution extracts glyphosate loosely and strongly bounded to iron and aluminium oxi hydroxides. Ascorbic acid solution extracts glyphosate loosely bounded to amorphous iron and aluminium oxi hydroxides. The recovery rates are close to zero with CaCl<sub>2</sub> solution. The best recovery rates, close to 100%, were obtained for the both extractants specific to iron and aluminium oxi hydroxides. It means that glyphosate is mainly bounded to amorphous oxi hydroxides. The recovery rate of alkaline digestion is intermediate suggesting that clays and organic matter are not the main substrate in Brazilian soils. This work is a first step to determine the speciation and the reactivity of sorbed glyphosate in soils and sediments and to study the behavior of nutrient in enriched glyphosate soils.

# Carbon and Nitrogen Isotope Characterization of the Ayuquila Watershed's Sediment and Macrofauna

Carlos Palomera-Garcia<sup>1,@</sup>, Leah Bendell<sup>2,@</sup>

**1** : Centro Universitario de la Costa Sur, Universidad de Guadalajara (CUCSur-UdG), *Independencia Nacional 151 Autlan de Navarro, Jal. - Mexico*

**2** : Simon Fraser University (SFU). *Department of Biological Sciences 8888 University Dr, Burnaby, BC V5A 1S6 - Canada*

Multiple stressors have affected the Ayuquila Watershed in Jalisco, Mexico. Despite an on-going water quality monitoring program no evidence exists on how land use activities have affected its aquatic communities. The objectives of this study through the use of stable isotope analysis were: 1) to identify sources of organic matter, 2) to characterize the food webs on each site based on the isotopic signatures, and then 3) to relate the sources of organic matter and resulting food webs to adjacent land use activities. Benthic macroinvertebrates, fishes, and sediment were sampled in two rivers along a gradient of agriculture, forest, and agriculture, and their isotopic signatures characterized. Sampling was done during the rainy and dry field seasons in 2007 and 2008. Temporal and spatial differences were noted in the isotopic values obtained, with a higher isotope range variation in the dry season. Between-season comparisons were statistically significant for both isotopes in faunal tissues. Stable C isotope analysis indicated that organic matter was influenced by forest C3 and/or autochthonous sources rather than from surrounding agricultural vegetation. However, d15N were close to ratios known from sewage and animal waste. NMDS ordination grouped the sites based on d15N suggesting that human and animal sewage have more influence than specific land use activities in the aquatic communities. d15N values reflected the assimilation of suspended organic matter which placed invertebrate collectors above fish and invertebrate predators on the river's food web. This study confirmed known point and non-point sources of nitrogen pollution which are having an impact in the river's faunal communities. These results pinpoint the need for further management practices to improve the water quality and reduce the impact to the biota and surrounding human communities.

# Assessing heavy metal sources by the combined use of geochemical and geophysical data: Application to the Pontaut old mining area at the Garonne river headwaters, Aran Valley, Spain

Ignasi Queralt<sup>1,\*,@</sup>, Marc Gil<sup>2,@</sup>, Albert Casas<sup>2,@</sup>, Eva Margui<sup>3,@</sup>

**1** : Institute of Earth Sciences Jaume Almera, CSIC, Barcelona, Spain (ICTJA-CSIC), *Solé Sabarís s/n, 08028 Barcelona - Spain*

**2** : Univ. of Barcelona. Dep. of Geochemistry, Petrology and Geological Prospection, *Martí Franqués s/n, 08028, Barcelona - Spain*

**3** : Univ. of Girona. Dep. of Chemistry, *Campus de Montilivi, 17003 Girona - Spain*

\* : Corresponding author

Previous studies at the Lot-Garonne fluvial system reported important inputs of heavy metals (Zn, Pb, Cd and Cu) into the Gironde estuary. This historic pollution has had an important socio-economic impact, especially for the bivalve' production which can reach heavy metals content up to 50 times higher than those produced at clean coastal areas. Sources of pollution (mainly Cd and Zn) entering the Gironde estuary were attributed to abandoned industrial areas in the midlands of the fluvial system. However, additional sources can be found at headwaters where ore deposits were mined for centuries.

The Aran Valley (Central Pyrenees, Spain) was during hundred years an important mining district for zinc (sphalerite) and lead (galena) recovery. Mining activity finished approximately at 1950's. Nowadays tailings, mine galleries and some open pits remain abandoned being potential sources of pollution to the water streams. Near Pontaut village was placed the main factory for the production of mineral concentrates, at the immediacy of Garonne river stream.

Remains of these mining activities and their metal transfer to waters and vegetation have been studied by means of geochemical, mineralogical and geophysical methods. By the combined use of X-ray spectroscopies (XRF, XRD), leaching tests, chemical analysis (ICP-MS) and electrical tomography we can properly assess the origin of the metal supply to the surrounding environment and the extent of the dumping site area. Detailed geochemistry reveals that cadmium is found in the sphalerite ores whilst arsenic and copper are related with lead concentrates. Delivery of metals to the running waters depends on the formation of secondary minerals such as smithsonite (ZnCO<sub>3</sub>), goslarite (ZnSO<sub>4</sub>·7H<sub>2</sub>O), anglesite (PbSO<sub>4</sub>) and related minerals. Differences on solubility of these minerals under different weather conditions control the release of metals to water. Geophysical methodologies such as electrical tomography were used to delimit the extent of the mining wastes remaining at the area.

# **Impact of ancient mining site on air quality under Mediterranean climate : Study case of the Pb-Zn-Cd Jebel Ressas mining site (Tunisia).**

Manel Ghorbel<sup>1,@</sup>, Marguerite Munoz<sup>2,@</sup>, Fabien Solmon<sup>3,@</sup>

1 : Laboratoire Ressources Minérales et Environnement (RME). *Faculté de Sciences de Tunis el Manar, 2092 Tunis - Tunisia*

2 : Laboratoire Géosciences Environnement Toulouse (GET). *CNRS : UMR5563, Observatoire Midi Pyrénées, Université de Toulouse, CNRS, IRD, 14 avenue E. Belin, F-31400 Toulouse - France*

3 : International Center of Theoretical Physics (ICTP). *Strada Costiera 11, 34014 Trieste - Italy*

## *1. Introduction*

Pb-Zn-Cd Tunisian mining sites are usually nearby villages and farmlands. Fine grained treatment wastes were dumped close to the ancient miners' village nowadays dedicated to farming. Under Mediterranean climate, these wastes are prone to wind erosion and may generate metals bearing-dust potentially transferred towards habitations and farmlands. Hence population may be exposed via dust inhalation and ingestion.

In order to assess the impact of remaining wastes on the air quality, both calculated estimations and in situ measurements in Jebel Ressas village (30km south of Tunis) were performed to determine airborne metal concentrations over a 20km<sup>2</sup> area and to compare them to air quality standards.

## *2. Methodology*

Metallic contamination transfer by wind process was studied during one month in summer season when wind erosion is likely the most effective.

An aerosol sampler was used to collect PM<sub>10</sub> on a terrace roof in Jebel Ressas village close to the treatment dumps. Aerosols were collected on filters replaced every 24 hours and filtered air volumes were registered. Pb and Cd were analyzed by ICP-MS after total acid digestion.

An emission model coupled to a transfer model (FDM) was used to calculate airborne PM<sub>10</sub> concentrations on a rack of receiving points around the dump source using local meteorological data and physical properties of the emission source (grain size, aerodynamic roughness...).

## *3. Main results and conclusion.*

Average measured concentrations of airborne Pb and Cd in the sampling point are respectively 0.039 and 0.0004 µg/m<sup>3</sup> for PM<sub>10</sub>. A good correlation of calculated with measured values validates the model.

Modeled concentrations show that NW side of the source is the most contaminated where WHO guidelines for Pb and Cd are exceeded up to 1200m. Contamination is also spread towards N, SW and SE directions including the village but on lower distances from the source.



## **Spatial and temporal variation of Pt concentration in PM<sub>2.5</sub> in the Metropolitan Area of Mexico City**

Ofelia Morton Bermea<sup>1,@</sup>, Elizabeth Hernández Alvarez, Omar Amador Muñoz, María Elena García Arreola<sup>2,@</sup>, Lida Martínez Trejo<sup>@</sup>

**1** : Universidad Nacional Autónoma de México (UNAM). *Ciudad Universitaria, México D.F. C.P 04510 Mexico - Mexico*

**2** : Universidad Autónoma de San Luis Potosí (UASLP). *Av. Dr. Manuel Nava 5 Instituto de Geología Zona Universitaria San Luis Potosí CP 78240 Mexico - Mexico*

Emissions of Pt-containing particulates, derived from the abrasion and deterioration of automobile catalyst has resulted in their increase in urban environments. Nowadays, about four million vehicles in Mexico City use catalytic converters, which means, that their impact should be considered.

In order to evaluate the contribution of Pt to environmental pollution of the Metropolitan Area of Mexico City, airborne particles  $\leq 2.5 \mu\text{m}$  (PM<sub>2.5</sub>) were collected at five different sites in the urban area (northwest, northeast, center, southwest, southeast). Samples were collected on April 2011 (dry-warm season), August 2011 (raining season) and December 2011 (dry-cold season). Platinum determinations were carried out by inductively coupled mass spectrometry (ICP-MS). The highest mass concentration for the many elements was observed at northeast, which is one of the most heavily traffic exposed sites in Mexico City.

Average Pt concentration in the analyzed particulated matter are  $46.32 \pm 27.03 \text{pg m}^{-3}$  in the dry-warm season,  $69.04 \pm 30.84 \text{pg m}^{-3}$  in the raining season and  $93.3 \pm 19.46$  in the dry-cold season. A clear Pt enrichment of samples collected in the dry-cold season is observed, however no spatial trends is evident.

## Origin of atmospheric trace elements using rare earth elements and lead isotopes: lichens monitoring in a mountain volcanic area (the Puy-de-Dôme, France)

Adrien Claustres<sup>1,2,\*,@</sup>, Yannick Agnan<sup>1,2,\*,@</sup>, Nathalie Sejalon-Delmas<sup>1,2,@</sup>, Gaël Le Roux<sup>1,2,@</sup>, Anne Probst<sup>1,2,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

Human activities impact significantly the natural balance of biogeochemical cycling resulting in environmental contamination, particularly with trace metals. The atmosphere is one of the major ways of dispersion of such elements before their deposition. Lichens are known to integrate these elements and to be good tools for atmospheric trace metal biomonitoring. We investigated trace metal contamination in Puy-de-Dôme region, a volcanic area in central France. The main objective was to determine the origin of accumulated elements.

For this purpose, lichens have been collected on field and digested with nitric and fluorhydric acids for total metal concentrations and lead isotopes analysis with ICP-MS. We combined multivariate statistical analysis, rare earth elements (REE) patterns and elements ratio to assess the origin of trace elements. Lead isotopes ratio allowed a particular investigation on lead sources along an altitudinal transect.

The results indicated that in lichens REE, Al, Ti, Fe, As, Cr and Ni mainly originated from regional natural soil erosion. This was also supported by REE patterns which were similar to those of the local bedrocks and by the low enrichment factors. In contrast, high enrichment factors of Pb, Cd, Zn, Sb and Sn suggested an origin from both local and long-range anthropogenic emissions. Indeed, Pb isotopic ratio revealed the multiple sources of Pb: the natural geochemical background and an anthropogenic contribution from gasoline. The anthropogenic lead contribution was estimated to vary between 42% and 70%, with highest value near the road climbing the Puy-de-Dôme volcano.

## **Is thallium in peat a good indicator of anthropogenic contamination? Examples from Czech sites with contrasting pollution histories**

Vojtech Ettler<sup>1,@</sup>, Martin Mihaljevic<sup>1,@</sup>, Ales Vanek<sup>2,@</sup>, Milan Zuna<sup>1,@</sup>

**1** : Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, *Albertov 6, 128 43 Praha 2 - Czech Republic*

**2** : Department of Soil Science and Soil Protection, Faculty of Agrobiolgy, Food and Natural Resources, Czech University of Life Sciences Prague, *Kamycka 129, 165 21 Praha 6 - Czech Republic*

In recent years, the behaviour and fate of thallium (Tl) in the environment have received increasing attention. Besides other trace metals, it has been seldom studied in peat, lake sediment, tree rings and other geochemical archives to reconstruct historical deposition/accumulation rates. The purpose of this study is to investigate the Tl distribution and accumulation rates in Czech peatbogs with contrasting anthropogenic loads and to compare them with those of other metals/metalloids.

Nine peat cores (max. depth 40 cm) were sampled in the mountain areas of the Czech Republic (6 cores in the northern part affected by emissions from coal-burning power plants and 3 in the pristine southern part). In addition, 3 cores were collected close to the Pb mining and smelting area of Pribram. Cores were <sup>210</sup>Pb dated and trace metals/metalloids were measured in the digests by ICP-MS.

Maximum Tl concentrations in peat were significantly higher in the polluted northern areas (1.16 mg/kg) and close to the Pb smelter (0.83 mg/kg) than in the pristine area (0.45 mg/kg). Thallium distribution well correlated with other metals (Pb, Hg) and metalloids (As, Sb). Thallium enrichment factors (EFs) calculated against Sc reached the maximum value of 17 indicating significant input of anthropogenic Tl. Thallium accumulation rates in peat varied between 20 and 50  $\mu\text{g}/\text{m}^2/\text{y}$  until 1930s, followed by a significant increase related to industrial activities in the northern part of the Czech Republic (up to 290  $\mu\text{g}/\text{m}^2/\text{y}$  in 1980s). In contrast, maximum Tl accumulation rate at the pristine site was 88  $\mu\text{g}/\text{m}^2/\text{y}$ . Data from the vicinity of Pb mines/smelter indicated higher accumulation rates even in the second half of the 19th century (between 50 and 200  $\mu\text{g}/\text{m}^2/\text{y}$ ) followed by a significant decrease in late 1970s as a result of more efficient flue gas cleaning technology installed in the smelter during this period.

# A peat bog record of atmospheric heavy metals deposition from the North Shore of the St. Lawrence Estuary, Quebec.

Steve Pratte<sup>1,\*,@</sup>, Alfonso Mucci<sup>2,@</sup>, Michelle Garneau<sup>3,@</sup>

**1** : GEOTOP & Département des Sciences de la Terre et de l'Atmosphère, UQAM  
*Montreal, Qc, H3A 3P8 - Canada*

**2** : GEOTOP & Department of Earth and Planetary Sciences, McGill University  
*Montreal, Qc, H3A 2A7 - Canada*

**3** : GEOTOP & Département de Géographie, UQAM  
*Montreal, Qc, H3A 3P8 - Canada*

\* : Corresponding author

Ombrotrophic peat bogs provide reliable historical records of atmospheric metal deposition, in particular for lead [1]. In comparison to Pb, the behaviour of other trace metals in peat bogs is not as well understood. To date, most studies were carried out in Europe and served to document various periods of anthropogenic activities. In contrast, records of atmospheric metal deposition in North America are still scarce. The present study focuses on the reconstruction of the recent history of trace metal deposition from a peat bog on the North Shore of the St. Lawrence Estuary.

A one meter core was collected, sub-sampled at 1-cm interval and analysed to reconstruct the recent history of atmospheric metal deposition. Here we present the deposition history of atmospheric As, Cd and Pb as well as stable Pb isotopes (204, 206, 207 208). Core chronology was established using 210Pb for the surface horizons and 14C for the deeper sections. Isotopic signatures were compared to the isotopic composition of North American major lead-bearing ores and modern aerosol for U.S. and Canada (1994-1999).

Results show that anthropogenic concentrations of Pb, As and Cd increased sharply from the beginning of the 19th through the 20th century, to reach a maximum between 1950 and 1970. Since the early 70's, metal concentrations have decreased rapidly, following the ban on leaded gasoline and other mitigation procedures, but have not reached pre-industrial levels. Stable Pb isotopes reveal that atmospheric Pb sources were dominated by coal burning during the first half of the 20th century and replaced by leaded gasoline afterwards. Lead isotopes also suggest that leaded gasolines have been replaced by other sources of atmospheric lead since leaded gasolines ban.

[1] Shotyk *et al.* (1996) *Earth Planet Sci Lett.* **145**, 1-7.

# Assessment of Aquatic Environment of Bhindawas Wetland, Jhajjar Haryana (India)

Sunil Kumar<sup>1,@</sup>, Rajesh Dhankhar<sup>@</sup>

1 : Dept. of Environmental Sciences, Maharshi Dayanand University Rohtak - **Website**  
Dept. of Environmental Sciences, Maharshi Dayanand University Rohtak, Haryana - India

Bhindawas wetland is spread over an area of 1074 acres in Jhajjar district of Haryana state, India. Environmental quality of Bhindawas wetland is degrading day by day because of pollution created by surrounding agricultural fields and drain no. 8. Lake is infested specially by aquatic plants. The other major problems in lake are eutrophication, siltation and ecological succession. The present study was undertaken to analyse the variation in physico-chemical quality of water, heavy metal content in sediment and macrophytic plants. Ten sites were selected for water sampling. The field data (temperature, dissolved oxygen and pH) were measured in forenoon at the sites in the year 2011. The water samples were filtered and analyzed according to American Public Health Association (APHA, 1998). Sediment samples and macrophytic plants were analyzed according to Allen (1989). Water quality revealed that turbidity and phosphate were high in the wetland water. Phosphate and nitrate were varied from 0.132-0.26 mg/l and 0.121-0.25 mg/l which cause eutrophication in the wetland. Other parameters of water were present in the normal range. 50% of sediment samples were alkaline in nature having maximum pH 8.19. Organic carbon was varied from 0.696 to 1.33%. Soluble cations, exchangeable cations, total cations in sediments were present in good quantity. The values of heavy metals (Fe, Zn, Cu, Ni, Pb, Cr & Cd) were within the prescribed limit as given by Canadian sediment quality guidelines for the protection of aquatic life. It was also noted that *Eichhornia crassipes* was good accumulator for zinc and copper, while *Ipomea aquatica* was excellent absorber of calcium and magnesium in wetland water. *Salvinia molesta* was found rich in potassium. This study will help into formulation of proper environmental management plan for the wetland.

## Accumulation of radionuclides and trace elements in wetlands near former uranium mines

Alicia Cuvier<sup>1,2,3,@</sup>, Gael Le Roux<sup>2,3,@</sup>, Laurent Pourcelot<sup>1,@</sup>

**1** : Institut de Protection et de Sûreté Nucléaire IPSN, CEA

*IRSN, Cadarache Bat 153, 13108 St Paul-lez-Durance - France*

**2** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**3** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

Recent studies have detected an increased accumulation of radionuclides and trace elements in the vicinity of former mines, mainly due to the predominant direction of stream water resulting from run-off and water discharge from the mine (Vera Tomé et al 2002). Given that wetland properties (enrichment in organic matter or anoxic conditions) can contribute to the accumulation and release of contaminants, the aims of our study are: 1/ to determine the speciation of the accumulated radionuclides and elements, 2/ to understand the environmental properties involved in the accumulation, and 3/ to characterize major forms of radionuclides (uranium and radioactive daughters) and trace elements in the different sites of accumulation to try predicting their potential release. Two former uranium mining sites, Bertholène (Aveyron) and St Alban sur Limagnole (Lozère), and, for the sake of comparison, a naturally uranium enriched soil, located in SW France, have been chosen for this multi-scale study. The elaboration of detailed metric maps will help to choose representative sampling sites in enriched areas. Different methodological approaches, like sequential extraction and mineralogical studies (XRD, SEM, EXAAF), will be performed on selected grain-size fractions to determine speciation and trapping mechanisms of contaminants. The potential release from the soils will also be considered by sampling soil water. Peat age dating with <sup>14</sup>C bomb pulse and <sup>210</sup>Pb will allow to reconstruct the chronology of deposition of uranium and trace elements in relation to mining activities. First results obtained on a peatland close to the open mine of Bertholène showed a significant increase of some trace elements in peat samples with estimated ages younger than 1962 AD. For example, vanadium concentrations increase from 16 mg\*kg<sup>-1</sup> to 44 mg\*kg<sup>-1</sup>, being this large accumulation surely related to the specific composition of Bertholène's ore –rich in vanadates in the oxic zone.

## Reconstructing historical atmospheric mercury deposition in Western Europe: The case study of the ombrotrophic Misten peat bog (Belgium)

Mohammed Allan<sup>1,@</sup>, Gael Le Roux<sup>2,3,@</sup>, Jeroen Sonke<sup>4,@</sup>,  
Natalia Piotrowska<sup>5,@</sup>, Jarek Sikorski<sup>5,@</sup>, Maurice Streef<sup>6,@</sup>,  
Nathalie Fagel<sup>1,@</sup>

**1** : AGEs Argiles, Géochimie et Environnement sédimentaires, Département de Géologie, Université de Liège, Allée du 6 Août B18 Sart Tilman B4000 – Liège - Belgium

**2** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**3** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

**4** : Laboratoire Geosciences Environnement Toulouse (GET)

Midi-Pyrenees Observatory (OMP) 14 avenue Edouard Belin 31400 Toulouse - France

**5** : Department of Radioisotopes, GADAM Centre of Excellence, Institute of Physics, Silesian University of Technology, Gliwice - Poland

**6** : PPM, Département de Géologie, Université de Liège, Allée du 6 Août B18 Sart Tilman B4000 – Liège - Belgium

Four peat cores (01W, 04W, 05W and 06W) were collected in 2008 in the Misten bog (Hautes-Fagnes Plateau, East Belgium) and studied for their mercury content over the past 1500 years. Elementary content analyses were reported in regard with a  $^{210}\text{Pb}$ - $^{14}\text{C}$  age models in order to estimate the spatial variability in the mercury accumulation rates, the historical record being further compared to other European records. In addition, pollen stratigraphy was used to check the validity of the age depth model and the immobility of mercury in the acrotelm and the catotelm zones. Mercury concentrations in the four cores ranged from 16 to 1100  $\mu\text{g kg}^{-1}$ , with the maxima between 840 and 1100  $\mu\text{g kg}^{-1}$ . The average Hg accumulation rate before the influence of human activities (from 500 to 1300 AD) was  $1.8 \pm 1 \mu\text{g m}^{-2} \text{y}^{-1}$  ( $2\sigma$ ). Maximum Hg accumulation rates ranged from 90 to 200  $\mu\text{g m}^{-2} \text{y}^{-1}$  between 1930 and 1980 AD. Based on comparisons with historical records of anthropogenic activities in Europe and Belgium, the predominant regional anthropogenic sources of Hg during and after the Industrial Revolution were coal burning and smelter Hg emissions.

## Radionuclides from uranium mining tailings in a mountain catchment area, Reboleiro, Portugal

Fernando Carvalho<sup>1,@</sup>, João Oliveira, Margarida Malta<sup>@</sup>

1 : Instituto Superior Técnico/Instituto Tecnológico e Nuclear (IST/ITN)  
E.N. 10 2686-953 Sacavém

Four old uranium mines with exposed mining tailings were operated during the last century in the mountain valley of Reboleiro village, near Trancoso, North of Portugal. Environmental radioactivity surveys were carried out in the valley to assess radioactivity and radiological risk to the public. Radionuclide concentrations in the mining waste piles near Reboleiro were as high as  $19\,090\pm 472$  Bq/kg (dw) of  $^{238}\text{U}$ ,  $13\,540\pm 1370$  Bq/kg of  $^{226}\text{Ra}$  and  $16\,170\pm 790$  Bq/kg of  $^{210}\text{Pb}$ , which can be compared with agriculture soils of the valley that displayed concentrations of  $458\pm 13$ ,  $490\pm 64$  and  $524\pm 19$  Bq/kg for the same radionuclides, respectively. Surface runoff and percolation of rain water and mine drainage over time raised radioactivity levels in the Stream Ribeira do Paul and in some irrigation wells in the valley. Radionuclides in soils, agriculture products and drinking water were determined. Drinking water distributed by the public network is supplied by an artificial lake in the region, not affected by uranium mine drainage, and displayed  $^{238}\text{U}$ ,  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  concentrations of  $19.1\pm 0.7$ ,  $9.3\pm 0.5$ , and  $142\pm 5$  mBq/L, respectively. Water from wells and bore holes in the Reboleiro valley displayed variable concentrations with a maximum of  $4205\pm 184$  mBq/L,  $30\pm 1$  mBq/L, and  $61\pm 2$  mBq/L for  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$ , respectively. Radionuclide concentrations in agriculture products also varied widely with location. For example in lettuce leaves,  $^{238}\text{U}$  concentrations varied from  $57\pm 4$  mBq/kg (ww) in a reference site up to  $3534\pm 93$  mBq/kg(ww) in a kitchen garden at the Reboleiro village. Weathering of uncovered mine tailings allowed for dissolution and transport of several uranium series radionuclides, particularly the more soluble ones such as uranium and radium, to the surface stream and sub-surface aquifer.



# **Geochemistry of the major elements and fluorine in the waters of the coastal Ghannouche – Gabes (Gulf of Gabes). Impact of phosphogypsum waste.**

Rim Ben Amor<sup>1,@</sup>, Gueddari Moncef<sup>@</sup>

1 : F.S.T., *campus universitaire, 2092, Tunis, Tunisia - Website*

The coastal Ghannouche- Gabes (GG) is situated on the east coast of Tunisia. Since the 70's it has had an important industrialization especially after the installation of the chemical complex for the treatment of phosphates. These industries that are regrouped around the port of trade in Ghannouche, cause many environmental problems, because of the importance and the composition of their gaseous emissions (sulphurous and fluoric gas), wastewater and solid waste, that are poured directly into the sea. This solid waste is a phosphogypsum (PG); PG is an acidic by-product produced by the phosphate fertilizer industry during the production of phosphoric acid from phosphate rock. This by-product is rich in gypsum, fluorine, phosphorus, and heavy metals. These elements constitute a danger to the environment.

Our study area is characterized by continental shelf very extensive and *Posidonia oceanica*. But since the year's 70, we note a regressive evolution of these herbal colonies essentially after a discharge of urban and industrial waste.

The coastal GG is characterised by the importance of hydrodynamics factors. Indeed, the mainstream from NE sector induced a longshore N-S. The tidal amplitudes can reach 2,38m.

This work has for main objectives to study the geochemistry of major elements and fluorine in the surface waters of coastal GG by spatiotemporal tracking, and evaluate the impact of phosphogypsum waste on the quality of these waters.

To reach these objectives, samples of surface waters were taken from GG coastal. These samples made the object of measures of some physical-chemical parameters and the analysis of major elements and fluorine.

The main results gotten show that sodium, potassium and the chloride have a similar geochemical evolution. They are preserved in solution and are not affected by Phosphogypsum waste. The contents of these elements vary in the space with constant Na/Cl et K/Cl ratio. The concentrations of sulphate and calcium are influenced by the Phosphogypsum waste. Indeed, the concentrations of these two elements are highest around of the trade port and tend to decrease towards the open sea, the north and the south of the study area. The highest contents of sulphate and calcium in this zone would be bound to the dissolution of the Phosphogypsum waste. It is confirmed by the results of the mineral saturation index that show that the waters on the coastal GG are under saturated with respect to gypsum mineral. The concentration of magnesium vary from 1,2 to 1,7 g/l. This variation would be controlled by the ionic association Mg-SO<sub>4</sub><sup>2-</sup>, Mg-HCO<sub>3</sub> and Mg-F and by the biologic activity. Areal distribution of bicarbonates is under influence of the pH, of the exchanges with the atmosphere, of the dissolution – precipitation of CaCO<sub>3</sub> and of the biologic activity. Fluorine would be implied in the precipitation of the fluorite mineral in the influence zone, where waters have raised concentrations of fluorine and are saturated to super saturated with respect to fluorite.

# Environmental impacts of abandoned coalfields on surface and ground waters in Şile, Istanbul / Turkey

Yüksel Orgun<sup>1,@</sup>, Meltem Sungur<sup>1,@</sup>, Cemile Erarslan<sup>1,@</sup>, Ali Tutay<sup>2,@</sup>

1 : ITU - Turkey

2 : Istanbul University - Turkey

Coal mining negatively affects the environment and cause serious environmental and human health problems in terms of water and soil pollution. To determine the environmental impact of coal, trace element concentration may be used as reference. The study area, Avcıkoru (Şile), was the most important coal mining area in Istanbul region until 1990s. After the coal reserves run out, coal fields were abandoned without any remediation and several artificial lakes occurred in the region. The aim of the study is to investigate the effect of coal on surface and ground waters by measuring parameters (pH, Eh, EC and others) in situ and trace element concentrations of the water samples.

The Avcıkoru coals display lignite and subbituminous coal characteristics. The average humidity value, volatile matter, ash, total S and gross calorific value (on dry bases) are 32.26%, 27%, 39.06%, 3.97%, 5740 kcal/kg, respectively. The observed dominant sulfur mineral in the coal is pyrite having framboidal structure. To determine trace element content (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Th, U, V, Zn etc.) of the coal, 10 coal ash samples were analyzed by ICP-MS. According to the analysis, concentrations of potentially harmful elements in coal samples are higher than World's average. For example As, Cd, Ni and V range from 41.75 to 987.67µg/g, 5.1 to 60.05µg/g, 1.95 to 866.08 µg/g and 165 to 592.22µg/g, respectively.

To represent the wet and dry periods, water samples were collected from 8 artificial lakes, and 11 springs and 2 wells. In artificial lakes pH, Eh and EC range from 2.71 to 4.31, 148 to 244 mV and 783 to 4080µs/cm in dry periods and from 2.72 to 5.84, 55 to 224 mV and 537 to 2850 µs/cm in wet periods, respectively. For spring and well- waters, pH, Eh and EC range from 5.52 to 7.48, -42 to 73 mV and 81.5 to 710 µs/cm in dry season and range from 5.48 to 7.5; -29 to 74 mV and 56 and 1346 µs/cm, in wet season, respectively. Trace element content (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Th, U, V, Zn etc.) of water samples were analyzed by ICP-MS. Obtained result show that all parameters of artificial lake samples are higher than those of wells and springs waters. For instance, in artificial lakes As, Cd, U, Pb, Mn and Ni mean values are 2.7µg/l, 5.2µg/l, 9.9µg/l, 17µg/l, 4600µg/l and 430µg/l, respectively. Whereas, for wells and springs water, As, Cd, U, Pb, Mn and Ni mean values are 1.0µg/l, 0.07µg/l, 0.12µg/l, 0.02µg/l, 8.3µg/l, 16.2µg/l, respectively.

Our results showed that the abandoned coalfields negatively affect the waters and this effect decreases gradually further away from the coal field.

## Heavy metals accumulation in the Upper Litani Basin soils

Samira Korfali<sup>1,2,@</sup>, Mey Jurdi<sup>2</sup>, Nabil Amacha<sup>1</sup>

1 : Environmental Unit, Litani River Authority , PO Box 11 3732, Beirut, Lebanon - Lebanon

2 : Department of Environmental Health, Faculty of Health Sciences, American University of Beirut, PO box 11-0236, Beirut, Lebanon - Lebanon

Great concern has been expressed over the problem of soil contamination with heavy metals due to rapid industrialization and urbanization. Such metals can accumulate in plants and animals and eventually in humans through the food chain. There are a number of factors that contribute to heavy metal contamination in agricultural soils including deficient management of solid waste, waste water discharge, irrigation with contaminated water, use of fertilizers and pesticides. The aim of this study is to quantify the levels of metals in soils of Upper Litani Basin, these soils are subjected to all above mentioned factors, specifically irrigation by polluted Litani River. Based on the reconnaissance survey, soils were collected from 24 sites along the Litani River flow, and 12 sites irrigated by Canal 900 withdrawn from the Qarraoun Dam along river. Metals in soils (Mo, Pb, As, Zn, Cu, Ni, Co, Mn, Cr, Ba, Hg, Cd) were analyzed using EDXRF technique; pH, %TC, %TOC were also tested. Data revealed the following ranges for heavy metals in soils and % of samples exceeding the international guidelines: Mn (123-1226 mg/kg)-67 % , Cu (23-147 mg/kg) 8% , Cr (32-272 mg/kg)-92%, Pb (nd-174 mg/kg)-4%, Hg (nd-8 mg/kg)-38 % , Cd (nd-15 )-25%, and As (6-28 mg/kg)-84 % . In canal soils: Mn (307 -1133 mg/kg) 86 % , Cu (36-73 mg/kg) 25 % , Cr (120-350 mg/kg)-100 % , Pb (nd-13), Hg (nd-9 mg/kg)-25 % , Cd (nd-14 mg/kg)-25 % , As (9-26 mg/kg)-92 % . These striking findings of high level of accumulation of toxic metals (Cr, Cd, Hg, As) in soils and consequent in plants pose a major health threat to consumers. Additionally this could impact the economy of such rural communities and constitute a challenge to be addressed. Hence environmental intervention to ensure quality and sustainability of the River should be immediately implemented by all stakeholders.

# Spatial distribution of lead in surface and deep sediments of the semi-enclosed bay influenced by the anthropogenic activity (Kastela Bay, Croatia)

Ivanka Lovrencic Mikelic<sup>1,\*,@</sup>, Krunoslav Skaro<sup>2,@</sup>

**1** : Rudjer Boskovic Institute (RBI) - **Website**  
*Bijenicka cesta 54 10 000 Zagreb - Croatia*

**2** : Hydrographic Institute of the Republic of Croatia (HHI) - **Website**  
*Zrinsko-Frankopanska 161, 21 000 Split - Croatia*

\* : Corresponding author

The area around the Kastela Bay is heavily exposed to anthropogenic activities representing the sources of contaminants to the bay. We studied the spatial distribution of lead in the sediments at three depths (0–5 cm, 5–10 cm, 40–50 cm), to determine i) whether lead disperses in the bay or it accumulates on the localized sites and ii) to establish the sediment condition regarding pollution.

Samples were collected on 95 sampling stations disposed in a regular grid covering the bay. Lead concentrations were measured by the energy dispersive X-ray fluorescence technique. Enrichment factors were calculated to differentiate natural and anthropogenic origin of lead. The reference element was aluminium and the reference material was the unpolluted, preindustrial sediment from the Kastela Bay. The degree of sediment pollution was also assessed using geoaccumulation indices and comparing lead concentrations with recommended values of the sediment quality guidelines. Maps of lead concentrations, enrichment factors, and geoaccumulation indices were presented.

Lead concentrations were in the range <1.6–142 mg/kg. Maximum content was higher than the upper limit of guidelines recommended values (30.2 mg/kg or 50 mg/kg). Mean values of enrichment factors were in the range 3.5–6.9 and the maxima in the range 23–68, suggesting the presence of lead from anthropogenic sources. Mean values of the geoaccumulation indices were in the range -0.065–1.6 and maxima in the range 3.9–5.4. This points to very polluted to extremely polluted sediment levels. The east part of the bay is the most polluted one. The area of polluted sediments increases with decreasing sediment depth. Lead distribution was found to depend on sediment grain size, sampling depth, and location of point pollution sources. Lead is generally dispersed in the Kastela Bay but accumulates only on a few sites.

# Determination of U and Pu isotopes in an ombrotrophic peat core and implications for post-depositional migration of fallout radionuclides

Francesca Quinto<sup>1,@</sup>, Erich Hrnccek<sup>1,@</sup>, Michael Krachler<sup>1,\*,@</sup>,  
William Shotyk<sup>2,@</sup>, Peter Steier<sup>3,@</sup>, Stephan Winkler<sup>3,@</sup>

**1** : European Commission-Joint Research Center, P.O. Box 2340, 76125 Karlsruhe - Germany

**2** : University of Alberta, Department of Renewable Resources - Canada

**3** : University of Vienna, VERA Laboratory, Währinger Strasse 17, 1090 Vienna - Austria

\* : Corresponding author

Uranium isotopes (<sup>234</sup>U, <sup>236</sup>U, <sup>238</sup>U) and Pu isotopes (<sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>242</sup>Pu) were analyzed in an ombrotrophic peat core from the Black Forest, Germany, representing the last 80 years of atmospheric deposition. The reliable determination of ultra-traces of these isotopes was only possible using ultra-clean laboratory procedures and accelerator mass spectrometry. The vertical profile of the <sup>236</sup>U/<sup>238</sup>U isotopic ratios along the ombrotrophic peat core represents the first observation of the <sup>236</sup>U bomb peak in a terrestrial environment. Re-deposition of global fallout derived <sup>236</sup>U with an average <sup>236</sup>U/<sup>238</sup>U isotopic ratio of  $(7.1 \pm 0.4) \times 10^{-7}$  in the top layers of the core was observed.

The mean <sup>240</sup>Pu/<sup>239</sup>Pu ratio of  $0.19 \pm 0.02$  (N=32) in the peat layers was in good agreement with the accepted value of 0.18 for global fallout in the Northern Hemisphere. This finding is largely supported by corresponding and rather constant <sup>241</sup>Pu/<sup>239</sup>Pu ( $0.0012 \pm 0.0005$ ) and <sup>242</sup>Pu/<sup>239</sup>Pu ( $0.004 \pm 0.001$ ) ratios. Since the Pu isotopic composition characteristic for global fallout was also identified in peat samples pre-dating the period of atmospheric atom bomb testing (AD 1956 - AD 1980), migration of Pu within the peat profile is clearly indicated.

Comparing the abundances of the global fallout derived <sup>236</sup>U and <sup>239</sup>Pu along the peat core, the post depositional migration of Pu clearly exceeds that of U. However, the cumulative <sup>236</sup>U/<sup>239</sup>Pu ratio of  $0.39 \pm 0.20$  is in agreement with previous studies on the global fallout U and Pu.

## Distribution and enrichment of selected elements in sediments of the Ergene River, Turkey

Mihri Hallı<sup>1,@</sup>, Erol Sari<sup>2,\*,@</sup>, Mehmet Kurt<sup>3,@</sup>

**1** : Ethnography and Archeology Museum. *Meydan Mahallesi Kadirpaşa Mektep Sokak No:7 22020 Edirne - Turkey*

**2** : İstanbul University - **Website**

*Institute of Marine Science and Management, Müşküle sokak no 1, 34134 İstanbul - Turkey*

**3** : Mersin University. *Advanced Technology Education, Research and Application Center, Çiftlikköy Kampusu 33343 Yenisehir/ Mersin - Turkey*

\* : Corresponding author

The aim of this study was to establish the distributions of selected elements (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) as well as to assess the extent of anthropogenic inputs into the Ergene River, (Turkey). The river receives both treated and untreated municipal and industrial discharges generated in and around the cities of Tekirdağ, Kırklareli and Edirne (Turkey). Freshly deposited sediment samples collected from twenty four stations of the river and its tributaries, were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after total digestion. The accuracy of the determinations was checked by analyzing the reference material NIST SRM 2710. The contamination of the sediments was assessed on the basis of enrichment factor (EF) and to corresponding sediment quality guidelines (SQGs) effects range low/effects range median. Because no regional geochemical background values for metals are available. We adopted the geochemical average shale values for EF calculation. The range and average concentrations measured in mgkg<sup>-1</sup> were 40610 - 96090 (74868 ±11730) for Al, 115 - 517 (248 ±101) for As, 955 - 3037 (1621 ±493) for Cr, 23 -203 (65 ±46) for Cu, 13950 - 41790 (28251 ±7373) for Fe, 133 - 865 (352 ±167) for Mn, 19 - 155 (70 ±35) for Ni, 77 - 145 (100 ±15) for Pb, 258 - 966 (483 ±177) for V and 74 - 388 (189 ±101) for Zn. Intensification of agricultural and industrial activities within the river basin have caused considerable increase of heavy metals such as As (EF=41), Cr (EF=17), Pb (EF=5), V (EF=4) and Zn (EF=3) in the surface sediments of the Ergene River. Arsenic and Cr appeared to be the pollutants with the greatest potential to cause adverse effects on biota, while Cu, Pb and Zn may adversely affect some benthic species occasionally, as suggested by the SQGs.

# Interaction of Air Masses between Mountain Summit and Foot

Hai Guo<sup>1,@</sup>

1 : The Hong Kong Polytechnic University (HKPolyU) - **Website**  
1 Yiu Choi Road - Hong Kong SAR China

To advance our understanding on the factors that affect photochemical pollution at different elevations in mountainous areas, concurrent field measurements were conducted at a mountain site (957 m a.s.l) and an urban site at the foot of the mountain in Hong Kong. The mixing ratios of air pollutants CO, SO<sub>2</sub> and NO-NO<sub>2</sub>-NO<sub>x</sub> were greater at the foot of the mountain (i.e. Tsuen Wan, TW) than near the summit (i.e. Tai Mao Shan, TMS), except for ozone. In total, only 1 O<sub>3</sub> episode day was observed at TW, whereas 21 O<sub>3</sub> episode days at TMS. The discrepancy of O<sub>3</sub> at the two sites was attributed to the mixed effects of NO titration, vertical meteorological conditions, regional transport and mesoscale circulations. The lower NO levels at TMS and the smaller differences of “oxidant” O<sub>x</sub> than O<sub>3</sub> between the two sites suggested that variations of O<sub>3</sub> at the two sites were partly attributed to different degree of NO titration. Analysis of vertical structure of meteorological variables revealed that the inversion layer at the range of altitudes of 500~1000m might be another factor that caused the high O<sub>3</sub> levels at TMS. Furthermore, analyses of the wind fields and the levels of air pollutants i.e. CO, NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> in different air flows indicated that high O<sub>3</sub> concentrations at TMS were somewhat influenced by regional air masses from the highly polluted Pearl River Delta region. Particularly, the diurnal profiles and correlations of gaseous pollutants suggested influence of mesoscale circulations, confirmed using the Master Chemical Mechanism moving box model (Mbox) and the Weather Research and Forecasting (WRF) model. By investigating the correlations of observed O<sub>3</sub> and NO<sub>x</sub><sup>\*</sup>, and the ratios of VOC/NO<sub>x</sub>, it is concluded that photochemical O<sub>3</sub> formation was VOC-sensitive or both NO<sub>x</sub> and VOC-sensitive at TMS, while it was VOC-sensitive at TW.

## Impact of Douro vineyards to surface water quality

Anabela Cachada<sup>1,\*,@</sup>, Sara Barbosa<sup>2,@</sup>, Pedro Pato<sup>1,@</sup>, Ana Dias<sup>2,@</sup>, Carla Patinha<sup>2,@</sup>, Amélia Reis<sup>2,@</sup>, Eduardo Ferreira Da Silva<sup>2,@</sup>, Armando Duarte<sup>1,@</sup>

**1** : CESAM & Department of Chemistry, University of Aveiro, Aveiro, Portugal (CESAM), *University of Aveiro Campus de Santiago 3810-193 Aveiro - Portugal*

**2** : Geobiotec, University of Aveiro (Geobiotec), *Campus de Santiago, 3810-193 Aveiro - Portugal*

\* : Corresponding author

The use of agrochemicals in vineyards is a potential source of many chemical compounds to several ecosystems and might affect their quality and functions. The Demarcated Region of Douro (Portugal) runs along the Douro River with vineyards frequently located on steep slopes of narrow valleys. Under the peculiar topography of this region, runoff and erosion processes may enhance the transport of pollutants and act as a potential source to surface water. To evaluate this impact, a research project (DVINE) is being carried out to assess the impacts of viticulture in the surface water quality. Sampling was located in a region draining to tributaries with a dam reservoir, where surface water samples were collected. General characterization of samples showed alkaline pH (from 7.73-9.28), temperatures ranging from 22.3-25.9 °C and conductivity ranging from 124-192 µS/cm. Bicarbonate ranged from 24.0-43.4 mg L<sup>-1</sup>, chloride from 12.9-20.9 mg L<sup>-1</sup>, nitrate from 1.4-5.5 mg L<sup>-1</sup> and sulphate from 9.2-10.3 mg L<sup>-1</sup>. Differences between sampling stations were observed with the highest values found in the tributaries. Glyphosate, an herbicide currently used in the region, was below detection limit (<0.10 µg L<sup>-1</sup>) in all samples. Further analysis will evaluate the presence of other herbicides (terbutylazine), fungicides (cymoxanil, folpet, mancozeb, metalaxyl, penconazole) and insecticides (chlorpyrifos, deltamethrin) also used in this region. In addition, the presence of formerly used pesticides considered as priority substances, under the scope of Water Framework Directive (endosulphan, DDT and simazine), will be also evaluated. The assessment of the impact of wine-growing practices in the Douro Region in the surface water quality will contribute to raise awareness among winegrowers to the importance of sustainable winegrowing practices.



## A 6 years survey of trace metals in atmospheric deposition in the Cap Béar (NW Mediterranean, Gulf of Lions)

Dominique Aubert<sup>1,\*,@</sup>, François Bourrin<sup>1,@</sup>, Nicole Delsaut<sup>1,@</sup>,  
Stéphane Kunesch<sup>1,@</sup>, Christophe Menniti<sup>1,@</sup>

**1** : Centre de Formation et de Recherche sur les Environnements Méditerranéens (CEFREM UMR 5110 CNRS/UPVD) - **Website**

*Université de Perpignan, Université de Perpignan 52 av. Paul Alduy, 66860 Perpignan - France*

\* : Corresponding author

The Cap Béar station (SW of Perpignan) is monitored since 2007 in order to quantify the amount of atmospheric trace metals (mainly Cd, Pb, Cu, Zn, Ni, Al) exported to the Gulf of Lions (NW Mediterranean). This is a rather natural site, weakly affected by local human activities. The initial device was a simple system made of a high-density polyethylene (HDPE) bottle connected to a HDPE funnel that allowed collecting total atmospheric deposition every month. In the frame of the SOERE MOOSE (Mediterranean Ocean Observing System of Environment), the configuration has moved toward an automated one (ARS 1000 equipment, MTX Italia SPA) that made possible to discriminate between dry and wet deposition at a 14 day's sampling period. Particles are separated from the dissolved fraction (or soluble fraction in the dry deposition) by filtration using HCl pre-washed 0.45µm nitrate cellulose membranes. Before ICP-MS analysis, total deposition samples and particles are fully digested in an acid mixture (HF+HCl+HNO<sub>3</sub>). The results show that particulate deposition is by far the most important contributor to trace metal fluxes. Massive deposition of Al is frequently observed and originates almost entirely from Saharan dust deposition (Guieu et al., 2010) that occurs during southern winds episodes. Ni and Pb follow more or less the same pattern and also show Ni/Al and Pb/Al ratios typical for Saharan dust evidencing a natural origin for both elements. Cu fluxes show seasonal variations with high fluxes in spring and summer and lower fluxes during the other part of the year. This is the result of local agricultural practices in the surrounding vineyards that use Cu in the "bouillie bordelaise" as fungicide to fight downy mildew. If looking at other monitoring sites on the French Mediterranean coast, fluxes of trace metals in the Cap Béar are often significantly lower (typically one order of magnitude).

# Factors controlling the sediment and organic carbon transport during flood events in the Oka river catchment (Basque Country, Northern Spain)

Luis Montoya-Armenta<sup>1,\*,@</sup>, Estilita Ruiz-Romera<sup>1,@</sup>, Miren Martinez-Santos<sup>2,@</sup>, Iñaki Antigüedad<sup>2,@</sup>, Borja Muñoz-Leoz<sup>1,@</sup>

1 : University of the Basque Country, *Department of Chemical and Environmental Engineering, Alameda de Urquijo s/n, E-48013 Bilbao - Spain*

2 : University of the Basque Country, *Department of Geodynamics, Barrio Sarriena s/n, E-48940 Leioa - Spain*

\* : Corresponding author

This study was conducted at the Oka river catchment, located in Urdaibai Estuary (Biosphere Reserve), of great ecological importance for Basque Country. The aims of the work are: (i) to determine the relationship between precipitation, discharge, suspended sediment and organic carbon yield during flood events for three hydrological years (2009-2012), (ii) to analyze the temporal variability of these parameters, (iii) to quantify the specific suspended sediment and organic carbon yield. A hydrometeorological station installed at the catchment outlet allowed continuously capture data from: precipitation, discharge, turbidity and physicochemical parameters. The regression relationship between field turbidity and solid suspended concentration (SSC) measured in the laboratory was established with a linear function:  $SSC = 0.971 \cdot \text{Turbidity}$  ( $R^2=0.94$ ). The total export SS, DOC and POC were estimated in 2267.5 t, 104.2 t and 53.2 t, representing 71.85, 3.30 and 1.68 t km<sup>-2</sup> y<sup>-1</sup> respectively, as mean for the three years in study. Higher DOC values compared to POC ones could be attributed to less erosion in the Oka catchment, due to soils are covered with pastures and forests, which provides a high content of DOC produced by litter decaying. In this study, POC% decreases with CSS increasing following a hyperbolic relationship. Low POC% associated with CSS between 20 and 2000 mg L<sup>-1</sup> can be recognized as allochthonous origin and attributed to soil erosion during periods of high flow. Statistical analyses showed that total precipitation, flood discharge and total water yield, were the major factors controlling SS, POC and DOC transport from the catchment. High seasonal, annual and inter-annual variability in SS, DOC and POC transport occurred in the catchment. Sediment was mainly transported during autumn-winter, when frequent flood events of high magnitude and intensity occurred. However, exceptional flood events occur during different seasons of the year, influencing the transport of sediments and associated contaminants.

***Special Session 1***  
***Frontiers in Mercury Biogeochemistry***  
***Oral Presentations***

# Methylation of mercury in the ocean: Insights from measurements and models

Robert Mason<sup>1,@</sup>

**1** : Department of Marine Sciences, University of Connecticut (UConn)  
*1080 Shennecossett Rd, Groton, CT 06340 - United States*

The primary aim of this presentation is a review and synthesis of the field and laboratory measurements and modeling studies examining the net methylation of mercury in the open ocean waters, and the main bioaccumulation pathways for human exposure. The presentation will discuss briefly the potential sources of methylated Hg (both monomethylmercury (CH<sub>3</sub>Hg) and dimethylmercury (CH<sub>3</sub>)<sub>2</sub>Hg)) to ocean waters, and the potential changes in methylated Hg concentrations over time due to human activity. The talk will then focus on in situ formation, which primarily occurs in conjunction with organic matter degradation, and both biotic and photochemical degradation. The talk will discuss a number of studies in the water column of the Atlantic, Pacific, Indian and polar oceans, as well as in major seas (e.g. Mediterranean) and coastal waters which have enhanced our understanding of the distributions of methylated Hg in the oceans, and elucidated the mechanisms that control their formation and degradation. Similarities and differences in concentrations, distribution and the potential mechanisms and potential pathways of formation will be discussed. Information from rate studies, based primarily on isotope tracer approaches, will be collated and contrasted with the insights gained from interpretation of field data and mass balance modeling. These comparisons will focus on highlighting the important factors that need to be considered when applying incubation data to field studies, and will attempt to reconcile differences between the various datasets. Finally, the information will be used to further refine the mass balance for CH<sub>3</sub>Hg in the upper ocean, and will highlight the important pathways of formation and degradation in the ocean. The talk will highlight needed future research and discuss approaches to furthering our understanding of methylated Hg cycling in the ocean, especially in terms of the CH<sub>3</sub>Hg that is accumulating in seafood consumed by humans and other wildlife.

## How do bacteria methylate mercury?

Alexander Johs<sup>1,\*,@</sup>, Jerry Parks<sup>1,@</sup>, Mircea Podar<sup>1,2,@</sup>, Romain  
Bridou<sup>3,@</sup>, Richard Hurt<sup>1,@</sup>, Steven Smith<sup>3,@</sup>, Stephen  
Tomanicek<sup>1,@</sup>, Yun Qian<sup>1,@</sup>, Stephen Brown<sup>1,2,@</sup>, Craig  
Brandt<sup>1,@</sup>, Anthony Palumbo<sup>1,@</sup>, Jeremy Smith<sup>1,2,@</sup>, Judy  
Wall<sup>3,@</sup>, Dwayne Elias<sup>1,2,@</sup>, Liyuan Liang<sup>1,@</sup>

**1** : Oak Ridge National Laboratory (ORNL) - **Website**  
1 Bethel Valley Road Oak Ridge, TN 37831 - United States

**2** : University of Tennessee, Knoxville (UTK) - **Website**  
Knoxville, TN 37996 - United States

**3** : University of Missouri, Columbia, MO 65211 - United States

\* : Corresponding author

Methylmercury is a potent neurotoxin produced in natural environments from inorganic mercury by anaerobic bacteria. However, until now the genes and proteins involved have remained unidentified. We have identified a two-gene cluster, *hgcA* and *hgcB*, required for mercury methylation by *Desulfovibrio desulfuricans* ND132 and *Geobacter sulfurreducens* PCA. In either bacterium, deletion of *hgcA*, *hgcB*, or both genes abolishes methylation activity. The genes encode a putative corrinoid protein, HgcA, and a 2[4Fe-4S] ferredoxin, HgcB, consistent with roles as a methyl carrier and an electron donor required for corrinoid cofactor reduction, respectively. Among bacteria and archaea with sequenced genomes, gene orthologs are present in confirmed methylators but absent in nonmethylators, suggesting a common mercury methylation pathway in all methylating bacteria and archaea sequenced to date.

## Marine methylmercury production and marine boundary exchange – results of the 2012 GEOTRACES West Pacific PANDORA cruise

Lars-Eric Heimbürger<sup>1,@</sup>, Jeroen Sonke<sup>1,@</sup>, David Point<sup>2,@</sup>,  
Christelle Lagane<sup>2,@</sup>, Marie Labatut<sup>3,@</sup>, Catherine Pradoux<sup>3,@</sup>,  
Francois Lacan<sup>3,@</sup>, Catherine Jeandel<sup>3,@</sup>, Alexandre  
Ganachaud<sup>4,@</sup>, Gérard Eldin<sup>3,@</sup>

1 : Geosciences Environment Toulouse (GET), CNRS : UMR5563, 14 avenue Edouard Belin, 31400, Toulouse - France

2 : Geosciences Environment Toulouse (GET), IRD : UR154, 14 avenue Edouard Belin, 31400, Toulouse - France

3 : Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (LEGOS), CNRS : UMR5566, 14 avenue Edouard Belin, 31400, Toulouse - France

4 : Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (LEGOS), IRD : UR065, 14 avenue Edouard Belin, 31400, Toulouse - France

Is methylmercury (MeHg) primarily formed *in situ* in the oceanic water column or is it produced in marginal sediments and subsequently advected into the open ocean? To answer this outstanding question we measured MeHg and total mercury (tHg) in a highly dynamic zone where boundary exchange is important, the Coral and Solomon Seas (0-20°S, 145-165°E). Here, a broad westward current extending from the equator to 30°S, the South Equatorial Current splits upon arriving at the major islands and archipelagoes of Fiji (18°S, 180°E), Vanuatu (15-20°S, 168°E), and New Caledonia (18-23°S, 165°E), resulting in a complex system of western boundary currents and zonal jets that feed the Coral and Solomon Seas [1]. We present vertical profiles (to 1300m-depth) for tHg and MeHg that were sampled in summer 2012 on RV Atalante. The 9 profiles consist of 89 unfiltered acidified (HCl 0.4%, v:v) samples. MeHg (MMHg+DMHg) was analyzed via isotope dilution GC-SF-ICP-MS after derivatization with propylborate and extraction into hexane. tHg concentrations vary only little at all stations (mean=0.90±0.18pM, range=0.55-1.69pM, n=87). The vertical tHg profiles show neither surface enrichment nor indications for sedimentary sources. Also MeHg vertical distributions are similar at all stations (mean=0.17±0.14pM, range=DL-0.42pM, DL=0.01pM, n=89). MeHg concentrations are generally low (0.043±0.021pM, n=39) at the surface (0-200m), increase gradually from 200 to 400m-depth (0.195±0.103pM, n=21) to reach their maximum below 400m-depth, (0.337±0.034pM, n=29). The fact that MeHg and tHg distributions are relatively homogeneous in this dynamic zone and comparable to what is observed eastward in the open Equatorial Pacific [2, 3] suggests that MeHg is formed *in situ* in the oceanic water column and that boundary exchange has little or no influence on Hg dynamics.

[1] Gasparin et al. DSR 2011

[2] Mason et al. ER 2012

[3] Mason and Fitzgerald DSR 1993

## Archived open sea dolphins tell us about the fate of Hg in North Pacific Ocean

Takaaki Itai<sup>1,@</sup>, Yusuke Yasuda<sup>1,@</sup>, Shin Urakami<sup>1,@</sup>, Tomohiko Isobe<sup>1,@</sup>, Sawako Horai<sup>2,@</sup>, Tadasu Yamada<sup>3,@</sup>, Yuko Tajima<sup>3,@</sup>, Shinsuke Tanabe<sup>1,@</sup>

**1** : Center for Marine Environmental Studies, Ehime University, 2-5, Bunkyo-cho, Matsuyama, Ehime 790-8577 - Japan

**2** : Faculty of Regional Science, Tottori University, Koyama-minami 4-4-1, Tottori 680-8551 - Japan

**3** : National Museum of Nature and Science, Hyakunin-cho 3-23-1, Shinjuku-ku, Tokyo 169-0073 - Japan

Mercury cycling in the Pacific Ocean has gained significant attention in recent years, especially with regard to raising mercury emissions from Asia. Uncertainty exists concerning whether increases in anthropogenic emissions over time might have caused increased mercury bioaccumulation in the biota in this region. Marine mammals have the highest potential to accumulate Hg, because of their long life span and higher trophic positions in marine food chains. In this study, we examined accumulation features and temporal trends of trace element levels in the liver and brain of striped dolphin (*Stenella coeruleoalba*, n = 48) and Melon headed whale (*Peponocephala electra*, n=69) which migrate in the range of temperate and tropical regions by the influence of the warm Kuroshio Current. Stranded or bycaught species have been collected from coastal regions of Japan since 1977 to 2011. These samples after collection were stored under -25 °C in the environmental specimen Bank (es-Bank), Ehime University. Hepatic Hg levels ranged from 6.5 - 1100 and 12 - 1240 µg g<sup>-1</sup> (DW) in striped dolphin and Meron-headed whale, respectively. These Hg levels varied depending on the size of individuals. Multiple linear regression analysis which aimed to correct effect of body size indicated significant increase of total Hg level in striped dolphin ( $p < 0.01$ ) and organic Hg level in Meron-headed whale ( $p < 0.05$ ). This result implied temporal increase of Hg level in offshore regions of Japan. Mercury in the brain of striped dolphin and Melon-headed whale correlated positively with hepatic Hg level, and ranged from 1.4 - 84 and 4.3 - 81 µg g<sup>-1</sup> (DW), respectively. These levels are comparable to the concentrations that were found to cause various toxic effects in animal experiments suggesting that increasing Hg level in open ocean will possibly induce ecotoxicological effects on cetaceans.

# Mercury Stable Isotope Fractionation in Alaskan Marine Top Predators

Jeremy Masbou<sup>1,\*,@</sup>, David Point<sup>2,@</sup>, Jeroen Sonke<sup>3,@</sup>, Paul Becker<sup>4,@</sup>

**1** : Geosciences Environment Toulouse (GET), CNRS-IRD-UPS, 14 avenue Edouard Belin 31400 Toulouse - France

**2** : Geosciences Environment Toulouse (GET), IRD, 14 avenue Edouard Belin, 31400, Toulouse - France

**3** : Observatoire Midi-Pyrenees (OMP), CNRS : UMR5563, 14 avenue Edouard Belin, 31400, Toulouse - France

**4** : National Institute of Standards and Technology (NIST), Hollings Marine Laboratory, Charleston, South Carolina - United States

\* : Corresponding author

With a long residence time in the atmosphere, anthropogenic gaseous Hg(0) emissions are able to reach remote Arctic regions carried by atmospheric circulation. Unique Arctic Hg depositional conditions, river Hg inputs and marine/wetland ponds methylation are potentially at the basis of record Hg concentrations in Arctic top predators, present a health risk for northern people due to their consumption of these traditional foods. On top of that, the complex link between anthropogenic Hg emissions and Arctic biota Hg levels is likely influenced by climate change. Recent work by our group on Hg stable isotopes in Alaskan seabird eggs illustrated the control of sea ice cover on Hg cycling. Complementary mammal measurements have been made to document the temporal and geographical variations in Hg stable isotope signatures of Alaskan marine foodwebs. Mercury stable isotope analyses were conducted in liver samples of 55 beluga whales (*Delphinapterus leucas*), 53 ringed seals (*Phoca hispida*) and 15 polar bears (*Ursus maritimus*) collected since 1988. Large variations in Mass Dependent Fractionation (MDF) and Mass Independent Fractionation (MIF) are observed between species and within species stocks. Combining Hg isotope observations with ecological parameters such as  $\delta^{15}\text{N}$  or  $\delta^{13}\text{C}$ , we are able to explain how mammal habitat use and associated diet are affecting mercury isotopes signatures. Belugas appear very sensitive to these parameters and individuals from each stock show significantly different MIF signatures. As for seabird eggs, north to south MIF gradients appear for all species, confirming the role of sea ice cover in modulating Hg photochemistry. This is also supported by significant temporal Hg MIF trends (1988-2002) observed in ringed seal livers. In contrast Hg MDF shows potential for tracing food web connectivity as illustrated for polar bears and their direct ringed seal diet. We point out Hg stable isotopes high potential for understanding Hg biogeochemical cycle in Arctic Region.



## **Species specific mercury isotopic composition during chemical and biological methylation pathways**

David Amouroux<sup>1,@</sup>, Vincent Perrot, Maria Jimenez-Moreno, Caiyan Feng, Julien Barre, Emmanuel Tessier, Sylvain Bérail, Mathilde Monperrus, Zoyne Pedrero<sup>@</sup>

**1** : Laboratoire de Chimie Analytique, Bio-inorganique et Environnement (LCABIE-IPREM), CNRS : UMR5254, 2 Avenue P.Angot, Hélioparc Pau Pyrénées, 64053 Pau cedex 9 - France

Many scientific discussions are to date arising on the potential processes controlling the formation, bioaccumulation and metabolism of methylated mercury (Hg) species. To study the environmental chemistry and advanced transformations of mercury, combined molecular and isotopic signatures should provide new information to better constrain its biogeochemical fate and ecotoxicological impact. The species specific isotopic composition (SSIC) of Hg can also be relevant to quantify environmental processes and track pollution sources in complex ecosystems and provide a new dimension for environmental risk assessment. The recent development of Hg isotopic ratio measurements in environmental samples (i.e. mass dependent and independent isotopic fractionation mechanisms) have suggested that photochemical demethylation is probably a major control of MeHg extent in surface waters, as further reflected in the Hg isotopic composition of the food chain. The main objective of our work was to combine the information on the molecular speciation of Hg and on the isotopic composition of its related compounds, methylated mercury (MeHg, DMeHg) and inorganic mercury (IHg), as well as the transformation extent of these chemical forms (methylation / demethylation). This new information has been collected using Gas Chromatography hyphenated to Multicollector ICPMS and during both laboratory methylation experiments and analysis of specific food chain samples accumulating significant amounts of methylated Hg species (plants, fishes, mammals). The results obtained demonstrate that specific isotopic composition in species is influenced by several mechanisms depending largely on the transformation kinetic and extent for both mass dependent and mass independent fractionations. Biological metabolism is involving significant mass dependent fractionation, while mass independent fractionation was consistent and mainly linked to MeHg turnover in the aquatic environments.

# Climate controls the fluctuations of fish mercury levels in Québec lakes

Marc Lucotte<sup>1,\*,@</sup>, Serge Paquet<sup>1,@</sup>, Matthieu Moingt<sup>1,@</sup>

1 : UQAM (GEOTOP), CP8888, suc Centre-Ville, Montreal, QC, H3C3P8, Canada - Canada

\* : Corresponding author

The compilation of data bases of Québec Ministry of Environment, Hydro-Québec, COMERN strategic network as well as Environment Canada's CARA research program allowed us to reconstruct the history of total mercury levels (Hg) over the 1979-2011 period in two predatory fish species most consumed in mid-northern Québec (Canada): northern pike (*Esox lucius*) and walleye (*Sander vitreus*). We present results for a series of 82 large lakes frequently fished by sport fishers. In order to compare different years and lakes among each other, we calculated fish flesh Hg levels at standardized lengths. We run our statistical analysis considering 20 GIS variables (lake order, watershed slopes, drainage density, mining sites, vegetation cover, geological substratum) and 15 climatic variables (monthly precipitations, temperatures, and sulfate deposition). Climatic factors such as annual mean temperatures and winter precipitations could explain 60% of the variations of walleye Hg levels. In turn, these climatic variables appeared to strongly control walleye growth rates. In addition, logging activities equivalent to at least 20% of the watershed surface every 10 years could explain 15% of the variations of walleye Hg levels. The influence of mining activities in lakes watershed appeared to be masked by the dominant climatic conditions and eventual logging activities. In fact, walleyes caught in lakes heavily impacted by mining activities such as Chibougamau and Matagami lakes presented some of the lowest Hg levels at standardized length. 35% of the variations of pike Hg levels could be explained by the nature of the watershed, rather steep slopes having a positive influence on the bioaccumulation of the heavy metal in that fish species. Watershed characteristics (10 to 20% slopes and higher fraction of the watershed covered by mixed forest) was in turn linked to fish growth rates, which by itself explained 45% of the variations of pike Hg levels.

## **Methylmercury and total mercury in boreal stream waters: Highly variable yet fairly predictable from climatic variables**

Markus Meili<sup>1,\*,@</sup>, Peder Blomqvist<sup>2,@</sup>, Hjalmar Laudon<sup>2,@</sup>, Kevin Bishop<sup>3,@</sup>

**1** : Dept. of Applied Environmental Science (ITM), *Stockholm University, SE-106 91 Stockholm - Sweden*

**2** : Dept. of Forest Ecology and Management, *Swedish University of Agricultural Sciences, SE-901 83 Umeå - Sweden*

**3** : Dept. of Aquatic Sciences and Assessment, *Swedish University of Agricultural Sciences, SE-752 44 Uppsala - Sweden*

\* : Corresponding author

Alarming high levels of methylated mercury in fish from remote freshwaters have been reported for decades, particularly from boreal and tropical forest regions. A key step to bioaccumulation is the transformation of atmospheric mercury into aqueous methylmercury, occurring preferentially in suboxic zones such as wetlands, sediments, and soils. Over the past years, the small-scale variability of total mercury (THg) and methylmercury (MeHg) concentrations in boreal runoff waters has been monitored at intervals of hours-weeks and over distances of 0.1-10 km by repeated synoptic sampling in >20 small streams during full annual cycles. Both MeHg and THg turned out to be highly correlated to water level (and flow rate), but showed opposite trends indicating enhanced mobilisation of THg (together with DOC) but dilution of MeHg at increasing flow. Correspondingly, the degree of methylation (MeHg/THg) can vary hundredfold among neighbouring sites within weeks. Most of the huge variability was temporal, due to rapid fluctuations that were highly synchronized among streams, and could be explained by water-level-dependent changes in the flow pathways of entering groundwater. However, beyond episodic fluctuations in groundwater mixing, evaluations revealed a seasonal component, suggesting that the net methylation of mercury was lowest in winter, increased exponentially over the whole growing season, and peaked around the time of freezing shortly before collapsing back to winter values. An explanation of such a pattern may be found in a biotic activity depending on nutrient availability and suboxic niches rather than temperature alone. Irrespective of mediating mechanisms, both seasonal and episodic patterns suggest a strong yet nontrivial climatic control (sensitivity) of both THg and MeHg concentrations in surface waters.

## Effects of organic ligands on photolytic redox transformation of mercury

Liyuan Liang<sup>1,@,\*</sup>, Alexander Johs<sup>1,\*,@</sup>, Feng He<sup>1,@</sup>, Hao-Bo Guo<sup>1,@</sup>, Baohua Gu<sup>1,@</sup>

**1** : Oak Ridge National Laboratory (ORNL) - **Website**  
*One Bethel Valley Rd. Oak Ridge, TN 37831 - United States*

\* : Corresponding author

Photochemical reduction of divalent mercury, Hg(II), is an important pathway in producing elemental Hg(0) in open waters and contributes to Hg cycling in the environment. This redox transformation is affected by aqueous and surface species, such as the naturally dissolved organic matter (DOM) because of its aromatic moieties that pertain light-absorbing characteristics. How DOM mediates the photochemical reduction of Hg(II) is not yet clear. In this study, we systematically investigated effects of the structural arrangement and stoichiometry of reactive functional groups in DOM on photochemical reduction of Hg(II), by using analogs including salicylic acid, 4-hydrobenzoic acid, anthranilic acid, 4-aminobenzoic acid, and phthalic acid. Photochemical reduction of Hg(II) is influenced not only by the neighboring functional groups but also their positioning on the aromatic benzene ring. The rates were found to increase in the order of anthranilic acid > salicylic acid > phthalic acid by varying neighboring functional groups from amine, hydroxyl, to carboxyl on benzoic acid. The substitution position of the functional groups affected reduction rates in the order: anthranilic acid > 4-aminobenzoic acid and salicylic acid > 4-hydroxybenzoic acid. Analyses of ultraviolet (UV) light absorbance of these DOM analogs indicate that the Hg(II) reduction rate is positively correlated to their UV absorption. Quantum chemical calculations suggest that upon photoexcitation, a  $\pi\sigma^*$  transition localized at the -NH<sub>2</sub> or -OH groups of the benzoic acid leads to the formation of a -NH $\cdot$  or -O $\cdot$  radical respectively, via the H-atom detachment. The calculations also indicate that in the presence of DOM, the Hg(II) reduction rate may be enhanced through a radical pathway. This work contributes to the understanding the role of DOM in Hg photochemical transformation and geochemical cycling in the environment.

## Methylmercury production in urban wastewater and fluxes into the fluvial Gironde Estuary (France)

Victoria N. Deycard<sup>1,\*,@</sup>, Laurent Lancelleur<sup>1,@</sup>, Jörg Schäfer<sup>1,@</sup>,  
Gérard Blanc<sup>1,@</sup>, Mathieu Masson<sup>2,@</sup>, Alexandra Coynel<sup>1,@</sup>,  
Cécile Bossy<sup>1,@</sup>, Lionel Dutrich<sup>1,@</sup>, Alexandre Ventura<sup>3,@</sup>

**1** : Transferts Géochimiques des Métaux à l'interface continent océan UMR EPOC 5805 (TGM) - **Website**

*Université Bordeaux 1, Av. des facultés 33405 Talence cedex - France*

**2** : Université de Genève Sciences II - **Website**

*10, route de Suisse CP 416 1290 Versoix - Switzerland*

**3** : Lyonnaise des Eaux, Agence Diagnostic Assainissement

*Lyonnaise des Eaux, Agence Diagnostic Assainissement Centre Régional Aquitaine F-33029, Bordeaux - France*

\* : Corresponding author

Monomethylmercury (CH<sub>3</sub>Hg) and inorganic Mercury (HgII) concentrations were measured in the fluvial part (Garonne Branch, March 2008-May 2009) and along the salinity gradient of the macrotidal and highly turbid Gironde Estuary, southwest France (6 cruises, Nov. 2005-Nov. 2007). Additional water samples were collected hourly at the entry and the exit of a major Wastewater Treatment Plant (WWTP) treating ~35% of the wastewater of Bordeaux (1 million inhabitants) during one day and on-board a vessel anchored at a fixed station on the Garonne Branch, close to the WWTP.

Results showed an influence of the maximum turbidity zone and associated high-suspended particulate matter concentrations on CH<sub>3</sub>Hg concentrations. Dissolved CH<sub>3</sub>Hg concentrations in WWTP effluent showed an increase in CH<sub>3</sub>Hg/HgII ratios from 6% to 22% suggesting CH<sub>3</sub>Hg production during the treatment process. Assuming constant CH<sub>3</sub>Hg concentrations in WWTP effluent, wastewater CH<sub>3</sub>Hg fluxes into the Garonne Branch are up to 5% of riverborne CH<sub>3</sub>Hg flux (3.2 g/d) during low discharge. During summer drought, limited renewal of the ("stagnant") water masses oscillating in the fluvial estuary within the Bordeaux Agglomeration suggests that urban CH<sub>3</sub>Hg inputs together with high temperature, high turbidity and organic matter release favor accumulation and persistence of CH<sub>3</sub>Hg in the fluvial estuary.

# In-situ analysis of mercury traces in water by electrochemical sensor using gold nanoparticles

Laure Laffont<sup>1,2,3,\*,@</sup>, Teddy Hezard<sup>1,@</sup>, David Evrard<sup>1,\*,@</sup>, Katia Fajerweg<sup>4,@</sup>, Philippe Behra<sup>2,@</sup>, Pierre Gros<sup>1,@</sup>

1 : LGC, Université Paul Sabatier - Toulouse III, CNRS : UMR5503, 118, route de Narbonne 31062 Toulouse Cedex 9 - France

2 : LCA, INRA : UMR1010, Institut National Polytechnique de Toulouse – INPT, 4 allée Emile MONSO B.P. 44362 31432 TOULOUSE Cedex 4 - France

3 : RTRA, STAE, 23 avenue Edouard Belin 31400 Toulouse - France

4 : LCC, Université Paul Sabatier - Toulouse III, CNRS : UPR8241, 205, route de Narbonne 31077 - Toulouse cedex 04 - France

\* : Corresponding author

Since the middle of the 20<sup>th</sup> century, mercury (Hg) has been considered as a major pollutant because of its high (eco)toxicity, which causes significant human health and environmental risks. Hg monitoring in the aquatic system is necessary to better understand its transport and transformations in the environment.

Many spectroscopic methods offer selectivity and good sensitivity with respect to Hg(II) trace determination, such as cold vapor atomic absorption spectroscopy for example. However these methods, which involve expensive devices and require complicated sampling procedures, are not easily transposable for *in situ* analysis.

In this context, electrochemical sensors represent an interesting alternative due to their low cost, ease of use, low energy requirements and simple procedures and the possibility they offer to build portable systems. Gold (Au) is a very common electrode material due to its strong affinity for Hg. Electrode surface modification by Au nanoparticles (AuNPs) has been of great interest in the last decade.

In this study, we report the analytical performances of an electrochemical sensor for Hg(II) using a glassy carbon electrode functionalized by electrodeposited AuNPs. Hg(II) is first preconcentrated by electrochemical reduction into Hg(0) and further deposition onto the electrode and then analyzed by re-oxidation step. The sensitivity was studied as a function of chloride concentration in order to mimic freshwater, groundwater and seawater. The sensor sensitivity first increased as a function of Cl<sup>-</sup> concentration and then decreased due to progressive Cl<sup>-</sup> adsorption on AuNPs which inhibited Hg(0) deposition. Maximal sensitivity (close to 0.7  $\mu\text{A nMHg(II)}^{-1}\cdot\text{min}^{-1}$ ) was recorded for around 0.09 M Cl<sup>-</sup>. The analytic response was linear in the range of 100 pM to 4 nM with limit of detection close to 70 pM in HCl 0.01 M for 5 min preconcentration.

***Special Session 1***  
***Frontiers in Mercury Biogeochemistry***  
***Poster Presentations***

# Determination of femtomolar levels of methylmercury in sea-water by isotopic dilution gas chromatography sector field inductively coupled plasma mass spectrometry

Christelle Lagane<sup>1,@</sup>, Lars-Eric Heimbürger<sup>2,@</sup>, David Point<sup>1,@</sup>,  
Laure Laffont<sup>2,@</sup>, Jérémy Masbou<sup>2,@</sup>, Frédéric Candaudap<sup>2,@</sup>,  
Bastien Thomas<sup>3,@</sup>, Daniel Cossa<sup>4,@</sup>, Joël Knoery<sup>3,@</sup>, Jeroen  
Sonke<sup>2,@</sup>

**1** : Geosciences Environment Toulouse (GET), IRD, 14 avenue Edouard Belin, 31400, Toulouse - France

**2** : Geosciences Environment Toulouse (GET), CNRS : UMR5563, 14 avenue Edouard Belin, 31400, Toulouse - France

**3** : Laboratoire Biogéochimie des contaminants métalliques (LBCM) - **Website**

IFREMER - Laboratoire Biogéochimie des Contaminants Métalliques rue de l'Île d'Yeu 44311 NANTES Cedex 3 - France

**4** : Laboratoire Biogéochimie des contaminants métallique (LBCM) - **Website**

IFREMER - Centre de Méditerranée LBCM Zone Portuaire de Brégaillon CS 20330 83507 La Seyne sur Mer cedex - France

Monomethylmercury (MMHg) accumulates to harmful levels along the marine food chain. Determinations of MMHg in sea-water are still scarce mainly due to analytical limitations that did not allow detecting ultratrace concentration levels, in the femtomolar range. Three techniques are used today to measure MMHg in sea-water and of which all imply a derivatization step: cryofocussing hydrate generation [1], ethylation [2] and propylation [3]. Determination of MMHg in sea-water by species-specific isotope dilution, derivatization by propylation, and detection via gas chromatography–inductively coupled plasma mass spectrometry (ID-GC-ICP-MS) was shown to be most promising [3]. We improved the performance of this method by optimizing the coupling between a gas chromatograph and a high resolution sector field inductively coupled plasma mass spectrometry (Element XR). Participation on recent international intercalibration exercises confirmed the performance of this method in terms of detection limits, accuracy and precision. We applied this method to samples from the recent Polarstern cruise ARK XVI/3 TranArk to the central Arctic Ocean (09/2011). A vertical profile was measured in parallel at the GET laboratory via ID-GC-SF-ICP-MS and at the IFREMER laboratory in Nantes via cryofocussing hydrate generation and detection via atomic fluorescence spectroscopy [4]. We will discuss the results of this comparison as well as precision, detection limit and blank levels.

[1] Stoichev et al. 2002. J Environ Mon **4**: 517-521

[2] Bloom 1989. Can Jour of Fish Aqua Sci **46**(7): 1131-1140

[3] Monperrus et al. 2005. Anal Bioanal Chem **381**(4): 854-862

[4] Cossa et al. 2003. IFREMER eds Quae



# Temporal variations of atmospheric gaseous elemental mercury and its relation with others pollutants and meteorological parameters at a French coastal Mediterranean site

Nicolas Maruszczak<sup>1,\*,@</sup>, Benoist De Vogüé<sup>1,@</sup>, Bastien Thomas<sup>2,@</sup>, Sabine Castelle<sup>1,@</sup>, Joël Knoery<sup>2,@</sup>, Daniel Cossa<sup>3,@</sup>

**1** : Laboration Environnement Ressources Provence-Azur-Corse (LER-PAC) - **Website**  
*IFREMER - Centre de Méditerranée Laboratoire Environnement Ressources Provence Azur Corse Zone Portuaire de Brégaillon CS 20330 83507 La Seyne sur Mer cedex - France*

**2** : Laboratoire Biogéochimie des contaminants métalliques (LBCM) - **Website**  
*IFREMER - Laboratoire Biogéochimie des Contaminants Métalliques rue de l'île d'Yeu 44311 NANTES Cedex 3 - France*

**3** : Laboratoire Biogéochimie des contaminants métallique (LBCM) - **Website**  
*IFREMER - Centre de Méditerranée LBCM Zone Portuaire de Brégaillon CS 20330 83507 La Seyne sur Mer cedex - France*

\* : Corresponding author

As a part of the GMOS European project, we continuously monitored atmospheric gaseous elemental mercury (GEM) between January 2009 and March 2010, and between January and December 2012, at a coastal Mediterranean site (La-Seyne-sur-Mer, France). Data on air temperature, wind speed, wind direction, and humidity were also collected as supporting meteorological parameters. Levels of others pollutants (O<sub>3</sub>, CO, NO<sub>x</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>) were also monitored. From January 2009 to December 2009, GEM was measured directly and continuously (using a portable automated Mercury analyzer "Gardis-5" (measurement every 10 minutes)). From January 2012 to December 2012, GEM was determined using a Tekran Model 2537A (measurement every 5 minutes). Between January 2009 and March 2012, levels of GEM ranged from 1.15 to 5.73 ng.m<sup>-3</sup> (average 2.20 ± 0.54 ng.m<sup>-3</sup>), and GEM concentration between January 2012 and December 2012 ranged from 1.19 to 6.15 ng.m<sup>-3</sup> (average 2.2 ± 0.6 ng.m<sup>-3</sup>). A diel variation of GEM is observed and attributed to anthropogenic activities within the city (urban and/or industrial). A variation of a similar amplitude is observed with the lowest GEM levels in summer and the highest during winter. This seasonal phenomenon is common to other monitored air pollutants and is usually explained as the result of the dispersion of pollutants in the atmospheric boundary layer. The highest observed GEM concentrations were associated with air masses from the urban area of the Rhône valley (regional source, 100 km away) and the more local anthropogenic source (urban area of La Seyne-sur-Mer, 1-10km away). Indeed, a significant positive correlation with other compounds associated with anthropogenic activities (CO, NO<sub>x</sub>, O<sub>3</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>) is observed.

## Main features of Hg distribution in lichens in the Russian (sub-)Arctic

Vladimir Shevchenko<sup>\*</sup>, Jeroen Sonke<sup>1,@</sup>, Oleg Pokrovsky<sup>@</sup>

**1** : Observatoire Midi-Pyrenees (OMP), CNRS : UMR5563, 14 avenue Edouard Belin, 31400, Toulouse - France

**\*** : Corresponding author

Many publications show that Arctic fauna is polluted by mercury (Hg) higher than fauna of other regions. Among other reasons, this may result from Atmospheric Mercury Depletion Events (AMDE), which occur during springtime at polar sunrise.

In our work we used lichens to estimate atmospheric fallout of Hg over land. Lichens absorb substances, including trace elements, through dry and wet deposition, and have been widely used as biomonitors. We studied concentration of Hg in terricolous (mostly of genera *Cladonia* and *Cetraria*) and fruticose epiphytic (mostly of genera *Alectoria*, *Usnea* and *Bryoria*) lichens collected in 2004–2012 in the Russian (sub-)Arctic from Kola Peninsula to Chukchi Peninsula. About 155 samples were collected. The unwashed lichen samples were air-dried and homogenised to a fine powder in an agate crusher. Lichen samples were analyzed for their Hg content by using Direct Mercury Analyzer Milestone DMA-80.

Hg concentrations ranged from 13 to 5987 ng/g. Epiphytic lichens had significantly higher Hg levels (median is 280 ng/g for 25 samples) than terricolous lichens (median is 33 ng/g for 132 samples). The Hg mainly arrives to the sampling sites as a result of long-range atmospheric transport. No evident pollution from industrial point sources was found. The highest values of Hg content were found in fruticose epiphytic lichens *Bryoria* in the southern part of the Taimyr Peninsula (from 2185 to 5987 ng/g) and near the lower course of Lena River (1159 ng/g). These high values of Hg content are interpreted as the result of AMDEs in high-latitude areas of Eastern Siberia.

In conclusion, the lichens could be used as biomonitors of Hg deposition from atmosphere and fruticose epiphytic lichens are better indicators of Atmospheric Mercury Depletion Events.

# The Pic du Midi Observatory - A new high altitude site for atmospheric Hg research

Jeroen Sonke<sup>1,@</sup>, Xuewu Fu, Bastien Sauvage, Francois Gheusi<sup>@</sup>

**1** : Observatoire Midi-Pyrenees (OMP), CNRS : UMR5563, 14 avenue Edouard Belin, 31400, Toulouse - France 14 avenue Edouard Belin, 31400, Toulouse - France

The Pic du Midi Observatory in the French Pyrenees Mountains (2877m) was built in 1878. It is one of the oldest, permanently occupied astronomical, meteorological and atmospheric observatories well known for its ozone observations that have shown a five-fold increase since 1878. Since 2010 we have been adapting the atmospheric chemistry platform for Hg research. After climatizing lab space, and securing a pressurized argon supply and clean power, an automated Tekran Hg speciation system was installed indoors in 2011. A newly commercialized Tekran 1104 heated manifold supplies clean outside air to the inside 1130 module inlet. The manifold makes possible the year-round observation of atmospheric Hg speciation, even under extreme conditions of ice riming, -40°C and 150 km/h winds. A full year of Hg speciation observations shows the frequent (23) intrusion of free tropospheric air masses that are accompanied by gaseous oxidized Hg peaks up to 500 pg/m<sup>3</sup>. Hg speciation dynamics also depend strongly on meteorological conditions such as wind direction and cloud cover. In parallel to Hg speciation, we have been developing manual sampling methods for compound-specific stable isotopic composition (CSSIC). The isotope signatures of gaseous and particulate Hg species may inform on the sources and transformations of Hg in the upper atmosphere. The atmospheric chemistry platform hosts parallel, automated observations of ozone, CO, NO<sub>x</sub>, black carbon, particle numbers, UV and meteorology. Manual sampling of total carbon, CO<sub>2</sub>, CH<sub>4</sub>, and water isotopes is performed on a bi-weekly basis. Hg speciation observations will be made available to the community through GMOS. The Pic du Midi Observatory can host research teams for prolonged periods of time, under excellent living conditions. The goal of this presentation is to solicit researchers with an interest in the atmospheric chemistry of Hg or other related compounds to join us at the Observatory for new and innovative collaborative research efforts.

## Relation of fish consumption to biomarkers of mercury, selenium and arsenic exposure from Mediterranean women

Ana Miklavčič<sup>1,@</sup>, Anica Casetta<sup>2,@</sup>, Janja Snoj Tratnik<sup>1,@</sup>, Darja Mazej<sup>1,@</sup>, Mladen Krsnik<sup>3,@</sup>, Marika Mariuz<sup>2,@</sup>, Katia Sofianou<sup>4,@</sup>, Zdravko Špirić<sup>5,@</sup>, Fabio Barbone<sup>2,@</sup>, Milena Horvat<sup>1,@</sup>

1 : "Jožef Stefan" Institute, *Department of Environmental Sciences, "Jožef Stefan" Institute, Ljubljana - Slovenia*

2 : University of Udine, *Unit of Hygiene and Epidemiology, University of Udine, Udine - Italy*

3 : Institute of Clinical Chemistry and Biochemistry, *University Medical Centre Ljubljana, Institute of Clinical Chemistry and Biochemistry, Ljubljana - Slovenia*

4 : Institute of Child Health, *Institute of Child Health, "Aghia Sophia" Children's Hospital, Athens - Greece*

5 : Institute for Applied Ecology, *Institute for Applied Ecology, Oikon ltd., Zagreb - Croatia*

In order to assess mercury (Hg), selenium (Se) and arsenic (As) exposure in Mediterranean area, total mercury (THg), monomethylmercury (MeHg), Se and As levels were measured in umbilical cord blood and breast milk from Italian (n=900), Slovenian (n=584), Croatian (n=234) and Greek (n=484) women. THg, MeHg, As, and Se levels were also determined in mother's blood samples from Italy and Croatia. In addition, THg and MeHg were determined in women's hair from all the countries and As levels were determined in urine samples from Italy, Croatia and Greece. Apart from the consumption of other food items, frequencies of fish consumption were assessed with detailed food frequencies questionnaires, because fish can represent an important source of mercury, selenium and arsenic in humans. The highest levels of Hg and As were found in cord blood (Med(Hg) =5.8 ng/g; Med(As) =3.3 ng/g) and breast milk (Med(Hg) =0.6 ng/g; Med(As) =0.8 ng/g) from Greek women, while the highest Se levels were found in cord blood (Med=113 ng/g) and mother's blood (Med=117 ng/g) from Italy. Significant linear correlations were found between different biomarkers of Hg, As, Se exposure. In addition, a significant relation was found between frequencies of total fish consumption and Hg, As and Se biomarkers of exposure, possibly explaining the correlations between determined elements in cord blood, mother's blood or breast milk. Moreover, the differences of As and Hg exposure between countries were probably due to different amounts of fish consumption and consumption of different species of fish with different origin.

# Mercury biogeochemistry in the extreme high altitude Lake environments of the Bolivian altiplano

Lucia Alanoca<sup>1,@</sup>, Mathilde Monperrus<sup>2,@</sup>, David Amouroux<sup>2,@</sup>,  
Emmanuel Tessier<sup>2,@</sup>, David Point<sup>1,\*,@</sup>

**1** : Géosciences Environnement Toulouse (GET) - **Website**

CNRS: UMR5563, Observatoire Midi-Pyrénées, Université Paul Sabatier - Toulouse III, IRD: UR234, 14 avenue Edouard Belin 31400 Toulouse - France

**2** : Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE-IPREM), CNRS : UMR5254, 2 avenue P. Angot Helioparc Pau Pyrenees 64053 Pau - France

\* : Corresponding author

Lake ecosystems of the Bolivian Altiplano are characterized by relatively shallow waters, intense primary productivity and extreme physicochemical gradients (intense UV radiations and low dissolved oxygen contents due to the high altitude (3700 m)). Previous studies reported for the first time very high monomethylmercury (MMHg) concentrations in organisms of this extreme region. This raised the question of the origin of this potent neurotoxin, and its biogeochemistry in the context of the extreme lake environments.

The production of MMHg is a key process driving Hg bioaccumulation in food webs. Methylation and demethylation are thus major transformation pathways regulating the net production and cycling of MMHg. In this sense, Hg species concentrations and Hg methylation/demethylation potentials (<sup>199</sup>Hg and <sup>201</sup>Hg stable isotopic tracers) were determined in sediment, water and periphyton compartments of Lake Uru Uru during the dry and wet seasons.

Methylation and demethylation potentials were found similar comparing dark controls vs diurnal conditions demonstrating the minor role of photochemical reactions for both transformations in the water column. The transformation potentials suggested a greater reactivity during the dry season in the northern part of the Lake. Biotic mediated mechanisms were suspected to be the main drivers of mercury species transformation. Modeled net Hg methylation, using transformation potentials and species concentrations indicated that both periphyton and sediment compartments represented the main source for MMHg production in Lake Uru Uru. This work represents the first data on Hg species concentrations and transformation potentials from a lacustrine environment of the Altiplano Region. The results demonstrate that the intense biological turnover and biofilms (ie *titora* plant) occurring in these aquatic environments promote the production of the MMHg and its further trophic transfer in the upper food chain.

## **Biomethylation potential of cationic mercury by microbial biofilm versus planktonic cells and surface sediment**

Paul-Philippe Remy<sup>1,@</sup>, Jörg Schäfer<sup>2,@</sup>, Laurent Lanceleur<sup>2,@</sup>,  
Frédéric Jorand<sup>1,@</sup>

**1** : LCPME, CNRS : UMR7564, Université de Lorraine, 405 rue de Vandoeuvre, 54602, Villers-lès-Nancy - France

**2** : EPOC, CNRS : UMR5805, Université Bordeaux 1, Av. des facultés 33405 Talence cedex - France

Mercury (Hg) is considered as a major pollutant with serious potential environmental and human health consequences especially in his methylated form (CH<sub>3</sub>Hg<sup>+</sup>) which is easily bioaccumulated and biomagnified across the trophic chain in aquatic environments. Mercury methylation in aquatic systems is mainly linked to the growth of several anaerobic microbial communities, including iron reducers, sulfate reducers and methanogens while demethylation, i.e. the opposite process is both biotically and abiotically driven. Most of these works focused on pure microbial cultures, but the role of biofilms, i.e. the most common life form of microorganisms in aquatic systems, in Hg methylation remains poorly documented. Some previous work has shown clearly higher Hg methylation potentials in biofilms than in water column. In contrast, others consider that plankton microorganisms could be more efficient methylating actors than biofilm consortia (e.g. in an anoxic tropical lake), suggesting high variability depending on the aquatic system sampled.

This study aims at evaluating the Hg methylation potential of biofilm consortia *versus* planktonic cells in the water column and surface sediment of an eutrophic pond (temperate climate). Isotopically spiked (<sup>199</sup>Hg<sup>2+</sup>) water, sediment and biofilm were incubated during seven days and analyzed for <sup>199</sup>CH<sub>3</sub>Hg<sup>+</sup> by GC-ICP-MS. Cell numbers were combined with methylation potentials to assess specific methylation (<sup>199</sup>Hgmethylated.cell<sup>-1</sup>). Both, structurally intact and scattered biofilms were compared to understand the role of biofilm organization and composition (e.g.: exopolymeric substances and other constituents) in Hg methylation. The results showed that structurally intact biofilm consortia had higher specific Hg methylation potentials and suggested that under the present experimental conditions planktonic cells had lower specific methylation.

## Reactivity of biomineralized versus chemically synthesized FeII-FeIII green rusts with cationic mercury

Paul-Philippe Remy<sup>1,@</sup>, Alice Hazotte<sup>1,@</sup>, Anne-Sophie Sergent<sup>1,@</sup>, Christophe Cloquet<sup>2,@</sup>, Nicolas Estrade<sup>2,@</sup>, Khalil Hanna<sup>3,@</sup>, Frédéric Jorand<sup>1,@</sup>

**1** : LCPME, CNRS : UMR7564, Université de Lorraine, 405 rue de Vandoeuvre, 54602, Villers-lès-Nancy - France

**2** : CRPG, CNRS : UMR7358, Université de Lorraine, 15 rue Notre Dame des Pauvres 54501 Vandoeuvre les Nancy - France

**3** : ENSCR, CNRS : UMR6226, Institut des Sciences Chimiques de Rennes, Avenue du Général Leclerc, CS 50837 F-35708 RENNES Cedex 7 - France

Green rusts (GRs) are mixed ferrous–ferric minerals found as corrosion product of Fe<sup>0</sup> among many anoxic environments. They are known to be very reactive and play a key role in the redox cycling of iron. These compounds can be synthesized by chemical co-precipitation of Fe<sup>II</sup> and Fe<sup>III</sup> species or from bioreduction of ferric oxides by iron reducing bacteria. While previous works were mainly focused on the reactivity of chemically synthesized GRs, no study, to our knowledge, has reported on the reactivity of biogenic GRs towards organic or inorganic contaminants. The biogenic GR is known to be more stable over time than those chemically synthesized probably due to the presence of exo-polymeric substances or bacterial cells surrounding the crystals.

This work is devoted to compare the reactivity of chemically (GR(CO<sub>3</sub><sup>2-</sup>) and GR(SO<sub>4</sub><sup>2-</sup>)) and biologically synthesized GR against the cationic mercury (Hg<sup>II</sup>). Reductive transformation of cationic mercury was monitored by ICP-AAS. Results show that both abiotic and biotic carbonated GR can reduce Hg<sup>2+</sup> to Hg<sup>0</sup>. The biomineralized carbonated GR(CO<sub>3</sub><sup>2-</sup>) appeared to be equivalently reactive to the chemically synthesized counterparts. However, the reductive ability towards methyl red used as a model organic compound, was found strongly dependent on the type of GR (ChemGR vs BioGR).

The disparity between the inorganic' and organic' reduction tests, and the effect of stabilizing agents on the GR reactivity were discussed.

***Special Session 2***  
***Bioaccessibility of Pollutants in Soils and  
Vegetables***  
***Oral Presentations***



# Developments in the estimation of human exposure to potentially harmful substances in soil using bioaccessibility measurements

Mark Cave<sup>1,@</sup>

1 : British Geological Survey (BGS) - **Website**  
Keyworth Nottingham NG12 5GG - United Kingdom

Since the early reports of the use of in-vitro extraction methods to mimic the human ingestion bioaccessibility of potentially harmful elements in soils [1], the increasing need for accurate estimates of exposure for human health risk assessments has driven research into the development of these methods. The key criteria for bioaccessibility methods are: to produce similar results to in-vivo trials; but are also practical and reproducible for contaminated land testing laboratories. Currently these include the relative bioaccessibility leaching procedure (RBALP) [2] and the in-vitro gastro intestinal (IVG) [3] methods in the US and the method developed by the Bioaccessibility Research Group of Europe (BARGE) known as the Unified BARGE method (UBM) [4]. The presentation will give an overview of the developments in these methods with particular emphasis on the European UBM method to show the method has been validated against an animal model, undergone inter-laboratory trials and been used on a regional and national level within the UK.

1. Ruby, M.V., et al., *Development of an in-Vitro Screening-Test to Evaluate the in- Vivo Bioaccessibility of Ingested Mine-Waste Lead*. Environmental Science & Technology, 1993. **27**(13): p. 2870-2877.
2. Drexler, J.W. and W.J. Brattin, *An in vitro procedure for estimation of lead relative bioavailability: With validation*. Human and Ecological Risk Assessment, 2007. **13**(2): p. 383-401.
3. Basta, N.T., et al., *The effect of dosing vehicle on arsenic bioaccessibility in smelter-contaminated soils*. Journal of Environmental Science and Health Part A, 2007. **42**(9): p. 1275 - 1281.
4. Denys, S., et al., *In Vivo Validation of the Unified BARGE Method to Assess the Bioaccessibility of Arsenic, Antimony, Cadmium, and Lead in Soils*. Environmental Science & Technology, 2012. **46**: p. 6252-6260.

# Soil mineralogy and its effect on oral bioaccessibility of Ni and Cr in soils overlying basalt lavas, Northern Ireland

Siobhan Cox<sup>1,\*,@</sup>, Merlyn Chelliah<sup>1,@</sup>, Alastair Ruffell<sup>2,@</sup>,  
Jennifer Mckinley<sup>2,@</sup>

1 : Queen's University Belfast (QUB), *School of Planning, Architecture and Civil Engineering, David Keir Building, Queen's University Belfast, Belfast, BT9 5AG - United Kingdom*

2 : Queen's University Belfast (QUB), *School of Geography, Archaeology and Palaeoecology, Queen's University Belfast, BT7 1NN - United Kingdom*

\* : Corresponding author

Geological soil parent material is often the source of elevated levels of potentially toxic elements (PTEs) in soils. In some areas, the total concentrations of these PTEs are at concentrations which exceed regulatory guidelines for protection of human health. PTEs of geogenic origin are often present within the soil matrix in forms that are not bioavailable to humans in significant concentrations. Oral bioaccessibility testing can be used to quantify the amount PTE that is accessible to humans in these cases. A previous study used non-specific sequential extraction coupled with chemometric analysis (CISED) to determine the distribution of Ni and Cr amongst soil components in 3 soil samples overlying Palaeogene basalt lavas in Northern Ireland, but without quantitative data relating to soil mineralogy, interpretation of the role of mineralogy on the oral bioaccessibility of Ni and Cr was inconclusive. This paper presents the findings of quantitative x-ray diffraction (QXRD) analysis of bulk mineralogy for 12 soil samples. Petrographic analyses (including scanning electron microscopy (SEM)) carried out on selected soils are further applied to substantiate the QXRD analysis. Results are related to oral bioaccessibility and CISED analyses to determine the effect of soil mineralogy on oral bioaccessibility of Ni and Cr. The geochemistry and preliminary XRD analysis of these soils identified minerals including montmorillonite, mica, clinocllore, hematite, diopside and weathered feldspars. Initial SEM analysis identified Cr in an iron rich mineral along with Mg, Al, Ti and Fe, however Ni was not detected. It is expected that characterizing soil mineralogy will demonstrate the effect that soil weathering plays in the bioaccessibility of both Ni and Cr.

# Earthworm: a multifunction tool for biomonitoring and refunctionalization of polluted soils

Thibaut Lévêque<sup>1,2,\*,@</sup>, Yvan Capowiez, Yann Foucault<sup>1,2</sup>, Eva Schreck, Marina Couveignes, Camille Dumat<sup>1,2 @</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

**(1) Importance of the work and objectives.** Reach regulation requires the study of pollutants fate and impact on the biosphere and the development of new tools for sanitary risk assessment. In that context, human bioaccessibility in vitro tests are performed on polluted soils to estimate pollutants bioavailability. From another side, earthworms could modify pollutants bioavailability in soils by their bioturbation activities. One scientific question is therefore: does metal bioaccumulation in earthworm correlated with metal bioaccessibility?

**(2) Methodologies.** Several experiments are performed to: (A) Estimate the difference of metals bioaccessibility and bioavailability between polluted soils influenced by earthworm bioturbation or not. (B) Correlate metal bioaccumulation in earthworms with human bioaccessibility. Various historically polluted soils by atmospheric deposition of particles from metal recycling activities and two contrasted earthworm species: *L. terrestris* (ecologically relevant) and *E. fetida* (international standard for ecotoxicology tests) are used for controlled and field experiments. Before and after bioturbation: i) metal bioaccessibility will be determined by in vitro UBM test; ii) metal uptake by earthworms will be measured. iii) microscopy (MEB-EDS) and spectroscopies (Raman, XRF and EXAFS) are used to perform elementary maps and determine potential changes in metal speciation and compartmentalization.

**(3) Main results and conclusions.** Strong influence of metal speciation and soil characteristics was observed on pollutant uptake by earthworm: variations of a factor of five. Moreover, metal bioaccessibility was significantly modified by earthworm bioturbation (factor three). Currently ongoing experimentations will acquire data from pollutant concentrations in earthworms and bioaccessibility in relation with soil organic matter in particular. Statistical analysis and formulation of a model for predicting human bioavailability will then be developed.

# Development and application of an in-vitro tracheobronchial bioaccessibility protocol for lead in the < 10 um (PM10) size fraction

Ndokiari Boisa<sup>1,@</sup>, Graham Bird<sup>2,@</sup>, J. Dean<sup>3,@</sup>, Nwabueze Elom<sup>3,@</sup>, Jane Entwistle<sup>4,\*,@</sup>, Simon Kemp<sup>5,@</sup>

**1** : Department of Geography, Faculty of Engineering and Environment, *Northumbria University, Newcastle upon Tyne, NE1 8ST - United Kingdom*

**2** : School of Environment, Natural Resources and Geography, *Bangor University, Bangor, Gwynedd, LL57 2UW - United Kingdom*

**3** : Department of Applied Sciences, Faculty of Health and Life Sciences, *Northumbria University, Newcastle upon Tyne NE1 8ST - United Kingdom*

**4** : Department of Geography, Faculty of Engineering and Environment - **Website** *Northumbria University, Newcastle upon Tyne, NE1 8ST - United Kingdom*

**5** : British Geological Survey, *Keyworth, Nottingham, NG12 5GG - United Kingdom*

\* : Corresponding author

The inhalation pathway can be a significant route through which potentially harmful elements (PHEs) can enter the human body, particularly when the particle size distribution of the sample is dominated by the < 10 um fraction (PM10) and in contexts where high total suspended solids prevail in the ambient environment. This paper presents research on the development of an *in-vitro* simulated epithelial lung fluid (SELF) extraction procedure for the tracheobronchial compartment of the respiratory tract and an application of this protocol as part of a human health risk assessment of Pb in Mitrovica, Kosovo. Mitrovica is an area of particular concern with exposure to Pb indicated by the presence of highly elevated concentrations of Pb in blood and hair samples (WHO, 2004; Runow, 2005). Our results suggest that tracheobronchial bioaccessibility is maximised after 96 hours and the role of metal-binding proteins (e.g. albumin) is highlighted. In the samples from Mitrovica, *in-vitro* tracheobronchial bioaccessibility ranged between 0.02 to 11.0% across a range of topsoils, smelter wastes and mine tailings. Samples with no X-ray diffraction observable Pb-bearing phases indicated the highest mean % bioaccessibility, and 21% of the samples investigated indicated a higher bioaccessibility in the SELF compared with the unified BARGE oral bioaccessibility protocol (Wragg et al., 2009). Notwithstanding the outstanding issue of *in-vivo* validation, daily inhalation exposure to Pb was estimated. One approach to assess the potential health effect associated with this exposure is to calculate the hazard quotient (HQ) (USEPA, 2005). Based on total Pb concentration in PM10, all study sites except Roma Mahalla indicated HQ values above 1; implying the possibility of negative health effects at those sites. However using the SELF bioaccessible Pb concentration in PM10, all samples indicated HQ values <1.

## References

- Runow, K.D., 2005. Investigation of the heavy metal load in refugee camps with Mitrovica in Kosovo: results of the hair analyses. Institute for Functional Medicine, Wolfhagen.
- USEPA, 2005. Human health risk assessment protocol for Hazardous Waste Combustion Facilities. EPA530-R-05-006. Office of Solid Waste and Emergency Response, U.S. EPA Region 6.
- Wragg, J., Cave, M., Taylor, H., Basta, N., Brandon, E., Casteel, S., Gron, C., Oomen, A., Van De Wiele, T., 2009. Inter-laboratory Trial of a Unified Bioaccessibility Procedure. British Geological Survey, Open Report, OR/07/027.
- WHO, 2004. Preliminary Report on Blood Lead Levels in North Mitrovica and Zvecan July 2004. WHO, Pristina.

# Influence of the epicuticular wax on the foliar metal uptake in the case of *Brassica oleracea* exposed to industrial atmosphere particles fallouts

Sophie Sobanska<sup>\*</sup>, Damien Cuny, Tian Tian Xiong<sup>1,2</sup>, Camille Dumat<sup>1,2,@</sup>, Vincent Dappe, Eva Schreck, Annabelle Austruy<sup>1,2,@</sup>

**1** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**2** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

\* : Corresponding author

Nowadays, numerous fine and ultra-fine metallic particulate matters (PM) are emitted in the environment by industrial activities such as ferrous and non-ferrous smelters including lead recycling facilities. These PM emissions increase in the atmosphere with the use of more effective filters in facilities [1]. Edible vegetables cultivated nearby these industries may be contaminated by metal rich industrial fallouts and thus, may represent a sanitary risk for population through the vegetable consumption. Studying the metal uptake by vegetables is of prime importance to evaluate the sanitary risk when vegetables are contaminated by atmospheric fallouts. Soil-vegetable transfer of metals is well documented whereas few are known about atmosphere-vegetable transfer [2]. According to Schreck et al. (2012)[3], the cuticular wax seems to be involved in the mechanisms of PM uptake occurring in the phyllosphere.

In this present work, we investigated the role of epicuticular wax on the particle uptake by vegetable leaves by cultivating *B. oleracea* plants grown with and without epicuticular wax. Vegetables were exposed to Pb-smelter-derived particles during 43 days. Leaves were harvested, analyzed by ICP-MS and then compared. The leaf surfaces were characterized by spectroscopic and imaging techniques (MEB-EDX, TOF-SIMS and Micro Raman) to investigate the role of epicuticular wax on the uptake and speciation of metal-rich particles. The total concentration of lead measured in leaves with and without cuticular wax was found to be 150 higher than in uncontaminated vegetable leaves. However the total amount of lead is similar for both experiments (287 mg.kg<sup>-1</sup>). Microscopic and spectroscopic investigations do not show any significant differences between the two vegetables. These preliminary results would show that the epicuticular wax would not play a key role in the foliar transfer of lead-enriched particles.

[1] Zhang et al., 2005, J. Aerosol Science 36 211–233.

[2] Uzu et al., 2010, Environ. Sci. and Technol., 44, 1036-1042.

[3] Schreck et al., 2012, Sci. of Total Environ., 427-428, 253-262.

## Exposure assessment of sequestered organic compounds in polluted sites and soils: use of a juvenile animal model to estimate their relative bioavailability.

Matthieu Delannoy<sup>1,\*,@</sup>, Agnès Fournier<sup>1,@</sup>, Guido Rychen<sup>1,@</sup>,  
Cyril Feidt<sup>1,@</sup>

1 : Unité de Recherche Animal et Fonctionnalités des Produits Animaux (URAFPA) - **Website**  
Université de Lorraine, INRA: USC340. 2 Avenue Forêt de Haye – 54 518 Vandoeuvre-lès-Nancy,  
France

\* : Corresponding author

Exposure assessment of polychlorinated biphenyls (PCBs) contaminated soils is a critical issue in terms of human health, especially since little reliable information on transfer of PCBs to humans *via* involuntary soil ingestion is available. Indeed, young children with their hand-to-mouth activity may be exposed to contaminated soils. The current study addresses the impact of soil organic matter (OM) condensation on bioavailability of sequestered NDL-PCBs. Three artificial soils (AS) were prepared according to OECD guideline 207. One standard soil (SS), containing no organic matter, and two amended versions of this SS with fulvic acid (FA) or activated carbon (AC) were prepared to obtain 1% organic mass. This study involved fourteen juvenile male swine as a physically close model of young children. Animals were randomly distributed into 4 contaminated groups (3 replicates) and a control one (2 replicates). During 10 days, the piglets were fed AS or a corn oil spiked with 19 200 ng of Aroclor 1254 per g of dry matter (6 000 ng/g of NDL-PCBs) to achieve an exposure dose of 1 200 ng NDL-PCBs.Kg-1 of BW per day. After 10 days of oral exposure, NDL-PCBs concentrations in adipose tissue, liver and muscles were determined by GC-MS, after extraction and purification. Variance analyses were performed on NDL-PCBs levels in tissues as repeated measures using mixed procedure of SAS software. A Significant treatment effect and two distinct groups of treatments were found: on one hand oil, SS and FA, on the other hand control and AC. This study highlights that condensed OM (AC) strongly reduces bioavailability whereas the less condensed one (FA) does not seem to have a significant effect. This result has to be considered as a first step for further relative bioavailability studies involving mixture of different humic substances.

# Mineralogy, solid-phase distribution and human oral bioaccessibility of Pb in outdoor dusts of Estarreja, Portugal

Carla Patinha<sup>1,@</sup>, Amélia Reis<sup>1,@</sup>, Ana Dias<sup>1,@</sup>, Yves Noack, Samuel Robert, Mark Cave<sup>@</sup>

1 : Geobiotec, University of Aveiro (Geobiotec)  
Campus de Santiago, 3810-193 Aveiro - Portugal

Estarreja is a vulnerable region since is heavily contaminated (soils, sediments, air and water) and is characterized by a mixed agriculture/urban land use. Unlike other Portuguese cities, besides the typical urban anthropogenic metal sources, Estarreja is also under the strong influence of the Chemical Complex, which includes several chemical industries, such as a chlor-alkali plant and other chemical plants producing anilina, nitrobenzene, PVC, isocyanide polymers of aromatic base and polystyrene polymers for thermal isolation.

For five decades, several of these industries have discharged its solid residues in an improvised park in the surrounding areas.

Due to the proximity to large populations, contaminated urban soils can pose significant direct risks to human health through dust inhalation, soil and dust ingestion, and dermal contact (Luo et al., 2011). For outdoor activities in playgrounds or recreational areas, oral ingestion is normally the critical pathway of exposure for children (Ljung et al., 2007).

The objective of this study is to determine the concentrations, oral bioaccessibility and solid-phases forms of Pb in outdoor spaces used by children. To achieve these aims several methodologies were applied: SEM, UBM (Unified Bioaccessibility Method) BARGE method, Chemical Selective Extraction.

Results show that: the total concentration of Pb range from 19.8 and 552 mg/Kg; the Bioaccessible fraction, expressed as a percentage of the total concentration in the dust, range from 29.8 to 97.7%; in general, the major Pb-phases are, by decreasing order, exchangeable and acid soluble fractions > residue> Fe-oxides> Fe-oxyhydroxides> oxidasible> Mn-oxyhidroxides.

Pb in outdoor dusts of Estarreja raise some health concern due to the high concentrations that are bioaccessible and to the fact that exposure is likely to occur.

## References

Luo, X. S., Yu, S., Li, X. D. (2011). Distribution, availability, and sources of trace metals in different particle size fractions of urban soils in Hong Kong: implications for assessing the risk to human health. *Environ. Polut.* 159, 1317-1326.

Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M. (2007). Bioaccessibility of metals in urban playground soils. *J Environ Sci Health Part A*, 42, 1241–1250.

# The importance of incorporating human bioaccessibility of potentially harmful elements in the solid-phase in health risk assessment studies: the case of lead in urban soils of Lisbon, Portugal

Amélia Reis<sup>1,@</sup>, Carla Patinha<sup>1,@</sup>, Ana Dias<sup>1,@</sup>, Mark Cave<sup>2,@</sup>,  
Joanna Wragg<sup>2,@</sup>, Eduardo Da Silva<sup>1,@</sup>, António Sousa<sup>3,@</sup>

1 : Geobiotec, University of Aveiro (Geobiotec), *Campus de Santiago, 3810-193 Aveiro - Portugal*

2 : British Geological Survey (BGS), *Keyworth, Nottingham, NG12 5GG - United Kingdom*

3 : CERENA, Technical Superior Institute (CERENA), *Av. Rovisco Pais, 1049-001, Lisbon - Portugal*

This paper discusses some results from a land-use (soil from urban recreational areas) versus vulnerable organism (children aged under 12 years old) target survey carried out in the city of Lisbon, Portugal. The main objectives are: (i) to interpret the results of the oral bioaccessibility testing for Pb in soils; and (ii) assessing the site-specific exposure and non-carcinogenic risk of Pb, to children while playing outdoors. Samples were taken at 51 locations distributed across the city, depending on the location of public parks, public gardens, playgrounds and schools. Pseudo-total Pb concentrations in soils were determined by ICP-MS; bioaccessible concentrations of Pb were determined in a selected set of 19 samples from the total under study using the Unified Bioaccessibility Method (UBM) developed by the Bioaccessibility Research Group of Europe (BARGE). The bioaccessible fraction (Bf%) of Pb in the soil was calculated as the ratio between the highest UBM extracted concentration and the Pb total concentration. Estimation of exposure and non-carcinogenic risk is based on the guidelines proposed by the US EPA (2009).

The results show that Pb total concentrations range from 6-441 mg kg<sup>-1</sup> and have a median value of 108 mg kg<sup>-1</sup>; bioaccessible concentrations (G-phase) range from 6-197 mg kg<sup>-1</sup> and have a median value of 60 mg kg<sup>-1</sup>. Samples with the highest values of bioaccessible Pb do not correspond to samples with the highest Bf%. The adjustment on the exposure estimate (*Average Daily Intake*) by incorporating oral bioaccessibility in the estimation of the *Hazard Quotient* has led to a significant variation in the risk ranking of the studied sites. Taking a *Hazard Index (HI)* = 1 as the safety level (US EPA, 2009) and considering ingestion as the only pathway of exposure, the results show that the soils under study can be considered safe as the  $HI < 1$ .

## References

U.S. Environmental Protection Agency (EPA), (2009). Highlights of the child-specific exposure factors handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/R-08/135.



## Speciation and bioaccessibility of Pb, As and Sb from soccer fields and sediments river near old mining environment

Grégoire Pascaud<sup>1,@</sup>, Thibaut Lévêque<sup>2,3,@</sup>, Marilyne Soubrand<sup>1,@</sup>, Salma Boussen<sup>4,@</sup>, Emmanuel Joussein<sup>1,@</sup>, Camille Dumat<sup>2,3,@</sup>

**1** : Université de Limoges, GRESE. *Université de Limoges: EA4330, 123 avenue Albert Thomas, 87060 Limoges. - France*

**2** : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

**3** : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

**4** : Université de Tunis El Manar, laboratoire des Ressources Minérales et Environnement. *Faculté des Sciences, Tunis - Tunisia*

Abandoned mine sites can often contain a large amounts of waste materials enriched with metals and metalloids. The dispersion in the environment of these contaminants throughout wind and water erosion is a major concern for vegetation, water resources and human health. In this context, this study is focused on an old Pb-Ag mine located in French Massif central. Mine tailings (220m<sup>2</sup>×50m×4m) are Pb-, As- and Sb-enriched (e.g. up to 38000 mg Pb kg<sup>-1</sup>, 600 mg As.kg<sup>-1</sup>). The heavy metals concentrations observed are all above the PNECsoil values for each element studied inducing a major health and ecotoxicological hazard. Moreover the risks are amplified by (i) the scare of vegetation cover, (ii) small tailing process particle size and (iii) the presence of a river and a soccer field near the tailing, which are directly subject to tailing run-off during the rain periods and erosion. Local populations can therefore be exposed to heavy metals throughout various scenarios.

The global aim of this study is to estimate Pb-, Sb- and As-(eco)toxicity risks relative to contaminant dispersion. Seven samples of materials (soils, tailings and sediments) were collected. Contaminants compartmentation and speciation were evaluated by BCR and mineralogical characterization (XRD and SEM-EDS). Moreover the health risk was determined by bioaccessibility tests.

Different As, Sb and Pb speciations were observed in the studied solid samples: As and Sb are located in the residual fraction, then relatively stables whereas Pb is associated to exchangeable, reducible and oxidable fractions.

The mean bearing phases for heavy metals are beudantite, anglesite, iron oxyhydroxydes and organic matter-clays mixture. Accordingly to speciation observed, Pb and As bioaccessibility respectively correspond to 48% and 23% of the total amounts in the solid studied samples. The risks to the human health consecutively to ingestion will be discussed in relation to bioavailability of pollutants.

## **POLLUSOL 2 project: large scale investigation of soil-to-plant and soil-to-human exposition pathways in urban areas nearby industrial area in Wallonia**

Julie Leclercq<sup>1,\*,@</sup>, Gilles Colinet<sup>2,@</sup>, Hugues Titeux<sup>3,@</sup>, Benoit Pereira<sup>3,@</sup>, Philippe Sonnet<sup>3,@</sup>

**1** : SPAQuE - **Website**

*Boulevard d'Avroy, 38/1 4000 LIEGE - Belgium*

**2** : ULg-GxABT - **Website**

*Passage des Déportés, 2 5030 GEMBLoux - Belgium*

**3** : UCL - **Website**

*Place de l'Université, 1 1348 LOUVAIN-LA-NEUVE - Belgium*

\* : Corresponding author

Since 2007, SPAQuE, with the assistance of four universities in Belgium (UCL-ELIE, UMONS, ULg-GxABT and ULg-Aquapôle), has investigated urban areas in Wallonia (Belgium). Data were collected within residential gardens, woodland and rural areas. The objectives of this project were to map background concentrations in soils and groundwater and to develop tools aiming at improving estimation of soil-to-plant and soil-to-human transfers.

1126 soil, 1341 vegetables and 435 groundwater samples were collected and analyzed. Seventeen inorganic and 33 organic pollutants were analyzed in soil, 16 inorganic and 16 organic pollutants in vegetables and 20 inorganic and 74 organic compounds in groundwater.

The presentation will focus on the tools developed for predicting soil-to-human and soil-to-plant transfers.

To study human bioaccessibility, the Unified BARGE (Bioaccessibility Research Group of Europe) Method was applied on 307 soils samples for 8 inorganic pollutants.

The BARGE test results show that the gastric bioaccessibility increases in the following sequence: Cr and Ni (<15%), As, Co and Cu (20-30%), Zn and Pb (45-55%) and Cd (> 80%). Intestinal bioaccessibility is substantially lower, except for arsenic. The variability between the measured bioaccessibility values was low.

More complex prediction models of bioaccessibility involving soil parameters have been developed but the observed Mean Absolute Deviation (MAD) (<6%) are similar to those obtained using averages.

Within the Risk Assessments, the bioaccessibility (P95) at the gastric stage were selected for estimating the total bioaccessibility of all contaminants, apart from arsenic (precautionary principle).

To estimate soil-to-plant transfer, several chemical extractants were tested (CaCl<sub>2</sub>, EDTA, DPTA and Mehlich 3 methods) and soil and plant analysis were performed after field sampling and pot experiments.

Regarding soil-to-plant transfer, data analysis showed that it's rare to have a clear correlation between soil and plant concentrations. For the four different types of vegetables (leaves, roots, fruits and tubers), we nevertheless built several prediction equations valid for the range of concentrations encountered in urban gardens in Wallonia.

# Bioaccessibility of metals/metalloids from soils and waste materials from mining and smelting areas in Africa

Vojtech Ettler<sup>1,@</sup>, Martina Vitkova<sup>1,@</sup>, Bohdan Kribek<sup>2,@</sup>, Martin Mihaljevic<sup>1,@</sup>

1 : Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2 - Czech Republic

2 : Czech Geological Survey, Geologicka 6, 152 00 Praha 5 - Czech Republic

Dry climate and strong winds are believed to be responsible for ingestion and inhalation of contaminated dust particles in areas affected by mining, mineral processing and smelting. The aim of this study is to evaluate the bioaccessibility of metals (Co, Cu, Pb, Zn) and As from soils and waste materials (fly ashes, slag dust) originating from the metal mining and smelting areas of Zambia (the Copperbelt Province) and Namibia (the Tsumeb area).

We adopted *in vitro* methods based on simulated gastric fluid (SGF; 0.4 M solution of glycine adjusted to pH 1.5) and simulated lung fluid (SLF). Topsoils (n = 107) were sampled in both mining- and smelter-affected areas and were subjected to SGF. The contaminant bioaccessibilities from smelter fly ashes (n = 2) and dust from slag crushers (n = 1) were investigated in both fluids.

The contaminant concentrations in topsoils were generally 2 to 7× higher in the smelting area compared to ore mining and processing area, indicating significant effect of smelter dust fallout. Higher bioaccessibilities were observed for As and Pb (up to 100% of the total concentration), whereas those of Co, Cu and Zn were below 83%. For smelter dusts the maximum bioaccessibilities in SLF were relatively low (Co 16%, Cu 2%, Zn 1.2%, As 2.9%), whereas values higher than 20% were obtained for SGF (e.g., Co 80%, Cu 50%, Zn 77%, As 83%). The obtained data indicate that a severe health risk related to topsoil particles ingestion and/or smelter dust particles ingestion/inhalation should be taken into account. In particular, Co and Cu exceed tolerable daily intake (TDI) if a model based on 100 mg of ingested and inhaled dust (soil) per day is applied. This study was supported by the Czech Science Foundation (P210/12/1413) and IGCP project no. 594.

## Relative bioavailability of soil-bound chlordecone in growing lambs.

Stefan Jurjanz<sup>1,\*,@</sup>, Catherine Jondreville<sup>1,@</sup>, Maurice Mahieu<sup>2,@</sup>, Agnès Fournier<sup>1,@</sup>, Harry Archimede<sup>2,@</sup>, Guido Rychen<sup>1,@</sup>, Cyril Feidt<sup>1,@</sup>

**1** : Unité de Recherche Animal et Fonctionnalités des Produits Animaux (URAFPA) - **Website**  
*Université de Lorraine, INRA: USC340. 2 Avenue Forêt de Haye – 54 518 Vandoeuvre-lès-Nancy, France - France*

**2** : Unité de Recherches Zootechniques (URZ) - **Website**  
*INRA: UR143. Centre Antilles-Guyane, Domaine Duclos - Prise d'Eau, 97170 Petit-Bourg - France*

\* : Corresponding author

The insecticide chlordecone was used until 1993 in banana plantations on the French West Indies. The high persistence of this organochlorine compound has resulted in the contamination of certain agricultural soils. It has been shown that free range reared animals would ingest soil, sometimes in considerable amounts. Thus, grazing animals can ingest contaminated soils. Therefore it would be necessary to know the availability of contaminants ingested together with the soil along grazing in order to evaluate the safety of the produced food.

A heavily polluted Andosol (26 mg/kg dry soil), sampled in Guadeloupe, was used for the experiment. Twenty eight weaned lambs, four control animals and 24 treated lambs were carried out in the experiment. Three doses of chlordecone (2, 4 or 6 mg/kg BW) were supplied orally through two matrices (soil-bound or via spiked oil). Each treatment was repeated on four animals which received the fixed doses orally during 15 days. After slaughtering, blood and fat samples were taken and their concentrations in chlordecone were determined.

In the two target tissues, the response of chlordecone concentration to ingested chlordecone increased linearly, but the dose-response did not differ between soil-bound and oil-spiked exposure of the animals. Thus, the bioavailability of chlordecone present in soil relative to chlordecone present in oil did not differ from 1. Therefore it can be concluded that chlordecone, despite its high affinity for andosol, will not be retained in the digestive tract of ruminants when they ingest contaminated soil during grazing.

Thus, the very high availability of soil-bound chlordecone makes that ingestion of polluted soils by grazing animals must be considered as a main contributor to the risk of contamination of animal products.

# Soil to plant transfer of uranium series radionuclides

Fernando Carvalho<sup>1,@</sup>, João Oliveira, Margarida Malta<sup>@</sup>

1 : Instituto Superior Técnico/Instituto Tecnológico e Nuclear (IST/ITN)  
E.N. 10 2686-953 Sacavém

Soil to plant transfer of radionuclides belonging to the uranium decay series was investigated in the center-North region of Portugal where there is a legacy of about 60 old uranium mine sites. Soil-to-plant transfer factors (TF) are needed and used worldwide to perform radiological risk assessments to members of the public through ingestion of diet. This investigation encompassed several areas ranging from fields near the old uranium mine of Cunha-Baixa (Mangualde) to reference fields in the region. In the area impacted by mining waste and acid mine drainage at Cunha-Baixa  $^{238}\text{U}$ , of  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  concentrations in surface soils (<63  $\mu\text{m}$  fraction) were  $10111 \pm 267$ ,  $4452 \pm 274$ , and  $4899 \pm 162$  Bq/kg (dw), respectively, while soil of a reference area in Marialva do Castelo showed concentrations at  $386 \pm 12$ ,  $713 \pm 81$ , and  $390 \pm 15$  Bq/kg for the same radionuclides, respectively. Agricultural products grown in the same areas, encompassing for example potato, carrot, lettuce, pumpkin and apple were analyzed for uranium series radionuclides. Results show that  $^{226}\text{Ra}$  usually is the radionuclide most concentrated by plants. Other radionuclides, including thorium and uranium isotopes,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  are less concentrated in plants particularly in the aerial parts, leaves and fruits. However,  $^{226}\text{Ra}$  concentrations and soil to plant transfer factor (TF) do not seem a constant. The contribution of soil and irrigation water as factors to radionuclide accumulation in plants is discussed and soil to plant transfer ratios are calculated and compared with values available in literature and currently used in dose assessment to the population.

***Special Session 2***  
***Bioaccessibility of Pollutants in Soils and***  
***Vegetables***  
***Poster Presentations***

# Lead (Pb) paint bioaccessibility after two years residence in soil columns spiked with phosphate

Andrew Hunt<sup>1,@</sup>, Dhary Alkandary<sup>@</sup>

**1** : University of Texas at Arlington, Geology Dept. (UTA) - **Website**  
500 Yates Street Arlington, TX 76019 - United States

Phosphate addition is a promising approach to remediating Pb-contaminated soils. Its efficacy with Pb-paint containing soils has not been investigated

In soil column trials, an "A" horizon soil was spiked with various Pb-paints, and then phosphate (as Apatite II) was either added, or not, to the soil columns. Eight Pb-paints were evaluated, these paints contained Pb-pigment in several forms (e.g., PbCO<sub>3</sub>, Pb-oxide, and PbSO<sub>4</sub>), and various extenders plus other pigments (e.g. Zn-oxide, Ti-oxide, quartz, dolomite, calcium carbonate, Cr, Fe). Paints were ground and passed through a < 250 μm mesh, and mixed with soil at 2% w/w. Apatite II was added (and mixed) at 5% w/w. Three times weekly 10 ml of Milli-Q water was added to each column. Soil from each column was collected at various times for *in vitro* bioaccessibility testing. Testing utilized a simulated gastric fluid to assess the amount of Pb that could potentially be mobilized in the human stomach following ingested. The assay involved rotating 1g of soil in 100ml of fluid (HCl plus glycine mix at pH 2.5) in polypropylene bottles in a water bath at 37 °C for 1hr. Extracted Pb was measured by ICP-AES. Soils were also examined by SEM/EDX.

Here we report on 7 separate soils removed from the columns at 24 months. Extraction data showed reduced Pb availability in all the phosphate amended soils. These reductions were 38%, 30% 24%, 13% 13% 10% and 1% (for paints (our numbering) 7, 8, 60, 12, 58, 12, and 76 respectively). Pb-phosphate particles were observed by SEM in the amended soils. We posit that bioaccessibility variations were due to the form of the Pb in the paints.

The suitability of using apatite II to immobilize Pb in Pb-paint contaminated soil (by forming the sparingly soluble Pb-phosphate mineral phases) appears to be justified.

## Lead (Pb) bioaccessibility measured in soil spiked with Pb-based paint and with phosphate

Andrew Hunt<sup>1,@</sup>

**1** : University of Texas at Arlington, Geology Dept. (UTA) - **Website**  
500 Yates Street Arlington, TX 76019 - United States

The threat posed by Pb in soil for pediatric populations continues to be a public health issue. Reducing the bioavailability of Pb in soil through the addition of phosphorus to the soil is a promising method for reducing the exposure threat.

Here we assess how an *in vitro* bioaccessibility extraction is affected by different types of Pb-bearing paint in a low Pb soil that has either been amended with a phosphate product (Apatite II) or not. Thirteen Pb-bearing paint samples were ground and passed through 250 and 100 µm nylon meshes. Samples nominally in vitro test. Either the paint alone was subject to extraction, or it was mixed with 0.9g of soil and then extracted, or the paint/soil mix was amended with Apatite II on a 5% w/w basis and extracted. Samples were analyzed in duplicate. Extraction involved rotating samples in 100ml of simulated gastric fluid (HCl plus glycine mix at pH 1.5) in polypropylene bottles in a water bath at 37 °C for 1hr. Extracted Pb was measured by AAS. Residues and original paints were examined by SEM/EDX, and the latter also analyzed by XRD.

Instrumental analysis identified several forms of Pb in the paints (e.g., PbCO<sub>3</sub>, Pb-oxide, PbSO<sub>4</sub>), and various other pigments (e.g. Zn-oxide, Ti-oxide, quartz, dolomite, calcium carbonate). The extraction mobilized approximately an order of magnitude less Pb from the paint/soil mix than was extracted from the paint-only sample. The difference in the amount of Pb extracted from the paint/soil mix compared to the paint/soil/phosphate mix was minimal. The presence of soil clearly influenced the degree of paint-Pb extraction.



# Innovative environmental applications of attapulgite clay

Ariadne Argyraki<sup>1,\*,@</sup>, Vassilis Zotiadis<sup>2,@</sup>

**1** : Ariadne Argyraki, *Faculty of Geology and Geoenvironment, University of Athens, Greece - Greece*

**2** : Vassilis Zotiadis, *Edafomichaniki S.A. Em. Papadaki, Athens - Greece*

\* : Corresponding author

We present a series of laboratory and field, pilot- scale applications of attapulgite clay as an amendment for the stabilization of metals in contaminated soil and sewage sludge. Attapulgite's structure together with its fine particle size and fibrous habit are responsible for its high specific surface area and sorption properties. A pilot scale application of attapulgite clay as a binder for in situ stabilization of toxic metals in contaminated land showed significant reduction in the water leachable metal fraction (Cu: 17%, Pb: 50%, Zn: 45%, Cd: 41%, Ag: 46%, As: 18%, Mn: 47%, Ba: 45%, Sb: 29%). In a second pilot scale environmental application, an innovative attapulgite "Geosynthetic Reactive Clay - GRC" was designed and developed for "capping" and "stabilization" of toxic metals in contaminated soil. Also, laboratory scale experiments with fresh sewage sludge from a municipal water treatment plant showed that addition of attapulgite clay in sludge, significantly reduced the leachable concentrations of phenol, DOC, Hg, Cu, Mo, Pb, Se, As, Zn and pathogen population over a 4 weeks observation period. The developed soil remediation techniques are promising and cost-effective under present market conditions. Concerning treatment of sewage sludge, attapulgite clay is an effective additive that could enhance the composting procedure creating an environmental added value, final compost product.

# **Bioaccessibility of metals and metalloids in polluted vegetables in relation with exposure conditions: foliar and/or root uptake**

Tian Tian Xiong<sup>1,2</sup>, Annabelle Austruy<sup>1,2</sup>, Vincent Dappe, Sophie Sobanska, Eva Schreck, Thibault Leveque<sup>1,2</sup>, Christophe Laplanche<sup>1,2</sup>, Marie-José Tavella<sup>1,2</sup>, Camille Dumat<sup>1,2,@</sup>

1 : Université de Toulouse; INP, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement); ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

2 : CNRS; EcoLab; 31326 Castanet Tolosan, France - **Website**

## **(1) Importance of the work and objectives:**

At the global scale, the quality of plants cultivated in farms or kitchen gardens in relation to the quality of the environment is an important research subject. Nowadays, metal recycling and production processes release a large proportion of ultra-fine particules enriched with metals and metalloids (PM) into the atmosphere. Foliar pollutants uptake due to PM depositions can strongly influence plant quality. In such cases, the risk for human and animal health regarding the ingestion of polluted plants should be considered.

## **(2) Methodologies:**

Several controlled, field experiments and model development are performed in EcoLab in order to study the foliar and/or root transfers of metals and metalloids from complex process PM and reference compounds: (i) which interactions exist between the two ways of metal transfer? What are the bioaccessibility and phytotoxicity of metals in function of transfer way? After 3 weeks of growth in a phytotron, plants (salad and cabbage) are exposed (shoot and/or roots) to inorganic pollutant (Pb, Cu, Cd, Sb). Four plants are harvested all the 5 days to evaluate the kinetic of transfer; measures of biomass and gas exchanges are performed. Pollutants contents in roots and leaves are then measured.

## **(3) Main results and conclusions:**

In addition to the root transfer, a strong foliar uptake of various metals was observed. Previous experiments and modelling showed that additive ecotoxicity can exist between the two ways of exposure. Due to foliar exposure, photosynthetic activity and plant biomass were respectively reduced by 3 and 2 in comparison with references. Bioaccessibility depends of exposure way, metal and plant nature (maximum variation of a factor 3 was observed) . Our results carry therefore important highlights to improve environmental and sanitary risk assessment in various contexts like polluted urban area (big towns in China), kitchen gardens near industries.

## Relative bioavailability of tropical volcanic soil-bound chlordecone in piglets.

Cécile Bouveret<sup>1,@</sup>, Guido Rychen<sup>1,@</sup>, Sylvain Lerch<sup>1,@</sup>,  
Catherine Jondreville<sup>1,@</sup>, Cyril Feidt<sup>1,\*,@</sup>

**1** : Unité de Recherche Animal et Fonctionnalités des Produits Animaux (URAFPA) - **Website**  
*Université de Lorraine, INRA: USC340. 2 Avenue Forêt de Haye – 54 518 Vandoeuvre-lès-Nancy, France*

\* : Corresponding author

The application of Chlordecone (CLD), a chlorinated polycyclic ketone pesticide, until 1993 in the French West Indies, has resulted in long-term pollution of agricultural soils and consequently in potential contamination of food resources. The aim of this study was to assess the impact of two tropical volcanic soils, an andosol and a nitisol, on CLD availability in piglet, using the relative bioavailability (RBA) approach. These Two batches of surface (A horizon) tropical volcanic soils were collected in former banana fields in Martinique, where CLD was commonly spread before 1993. Concentrations of CLD in soils were of 4.6 and 2.4 mg.kg<sup>-1</sup> of fresh matter for andosol and nitisol, respectively. Bioavailability of CLD present in each soil relative to CLD present in oil was estimated from CLD concentrations in liver and subcutaneous fat, by means of the slope ratio method. For both soils and relative to an oil matrix, RBA was close to 100% indicating that CLD was not retained in the soil matrices during the piglet digestive process. Additionally, after a 14-days exposure period, liver and subcutaneous fat CLD concentrations exceeded the maximum residue limit (10 µg.kg<sup>-1</sup> of fresh matter and 100 µg.kg<sup>-1</sup> of fat for liver and subcutaneous fat, respectively) beyond a CLD ingestion of 2.1 and 6.8 µg CLD.kg<sup>-1</sup> of body weight per day, respectively. Thus, rearing practices in CLD contaminated areas should limit involuntary soil ingestion by farm animals.

***Special Session 3***

***Arsenic: Current Issues, of Speciation,  
Environmental Behavior, and Human Health  
Impacts***

***Oral Presentations***

# Arsenic removal from groundwater by household sand filters in Vietnam

Andreas Kappler<sup>1,@</sup>, Katja Nitzsche<sup>1,@</sup>, Michael Berg<sup>2,@</sup>, Pham Thi Kim Trang<sup>3,@</sup>, Pham Hung Viet<sup>3,@</sup>, Sebastian Behrens<sup>1,@</sup>

**1** : Geomicrobiology, Center for Applied Geoscience, University of Tuebingen, *Sigwartstraße 10, 72076 Tübingen - Germany*

**2** : Eawag, Swiss Federal Institute of Aquatic Science and Technology, *Dübendorf - Switzerland*

**3** : Center for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science, *Hanoi - Vietnam*

Worldwide more than 100 million people ingest detrimental concentrations of arsenic by consuming groundwater contaminated from natural geogenic sources. Many Asian countries, in particular Vietnam, Bangladesh, India, and Cambodia are known to be affected by high groundwater arsenic concentrations as a result of reducing aquifer conditions. Household sand filters are simple to operate and remove most of the arsenic from the groundwater containing arsenic and ferrous iron with an iron/arsenic ratio of at least 50 leading to As values of

Although household sand filters are an effective technical solution for mitigating arsenic exposure, not much is known about microbial iron, manganese, and arsenic redox transformations occurring in the filters and their effect on filter efficiency. Here I will present data on microbial community analysis in such filters with a focus on Fe-, Mn-, and As-oxidizing and -reducing microorganisms. Geochemical analyses of water samples and mineralogical analyses of minerals are used to identify the main biogeochemical processes occurring in the filter and to evaluate filter performance on different time scales. Our research aims to better understand the microbial and chemical redox transformation processes that drive arsenic/manganese/iron mineral interactions in household sand filters and to give recommendations for improved filter use and filter material disposal.

[1] Berg *et al.* (2006) *Environ. Sci. Technol.* **40**, 5567-5573. [2] Kleinert *et al.* (2011) *Environ. Sci. Technol.* **45**, 7533-7541.

# How do mine waters affect the natural arsenic geochemistry in glacial till and bedrock? - A case study of Kittilä Suurikuusikko gold mine in Finland

Soile Backnäs<sup>1,\*,@</sup>, Kaisa Turunen<sup>1,@</sup>, Antti Pasanen<sup>1,@</sup>

**1** : Geological Survey of Finland (GTK), P.O.Box. 1237, FIN-70211 Kuopio - Finland

**\*** : Corresponding author

Areas with bedrock abundant in ore minerals have naturally high amount of harmful elements in soil as well as in ground and in surface waters. After the beginning of the mining also the anthropogenic contamination specially related to mine waters tends to increase. Thus, it is important to estimate the effects of mining activity and water treatment methods to the natural background when assessing the long term effects to the surrounding environment.

Due to gold bearing arsenopyritic ore, the arsenic concentrations in the Kittilä municipality and in the Central Finnish Lapland are naturally high. In this study natural and anthropogenic arsenic geochemistry in Suurikuusikko gold mine at Kittilä, Finland was characterized using mineralogical studies (MLA, XRF) and different extraction methods (hot aqua regia, ammonium oxalate and acetate extractions). Altogether 24 glacial till and bedrock samples were analyzed. In addition 13 water samples were taken from tailings seepage, mine dewatering, and ground and surface waters. Water samples were analyzed for total and soluble metal and metalloids concentrations, anions, DOC, TOC, pH, redox and alkalinity. At the mine site, mine waters are treated by introducing them to natural peat wetlands. PHREEQC was used in modeling the effect of the mine waters to natural arsenic geochemistry of glacial till and weathered bedrock underlying the wetlands.

The results show that the arsenic chemically adsorbed in weathered bedrock and glacial till have significant impact in the arsenic emissions from the Suurikuusikko mine. Anthropogenic arsenic from mine waters increases the proportion of chemically adsorbed and bioavailable arsenic in the soil at mine site and therefore increases potential risk for the environment. According to the modeling study the dissolution of natural arsenic and formation of secondary precipitates depends on the chemistry of the mine waters and arsenic related mineralogy in soil and bedrock.

## **Arsenic concentrations in aggregate resources and constructions sites in arsenic rich areas in Finland**

Timo Tarvainen<sup>1,@</sup>, Paavo Härmä<sup>1,@</sup>, Birgitta Backman<sup>1,@</sup>, Tarja Hatakka<sup>1,@</sup>, Jouko Vuokko<sup>1,@</sup>, Heikki Nurmi<sup>1,@</sup>, Outi Pyy<sup>2,@</sup>, Pirjo Kuula-Väisänen<sup>3,@</sup>, Kirsti Loukola-Ruskeeniemi<sup>4,@</sup>

**1** : Geological Survey of Finland (GTK) - **Website**  
*P.O.Box 96, FI-02151 ESPOO - Finland*

**2** : Finnish Environment Institute (SYKE) - **Website**  
*Mechelininkatu 34a, FI-00251 HELSINKI - Finland*

**3** : Tampere University of Technology (TUT) - **Website**  
*PO Box 527, FI-33101 Tampere - Finland*

**4** : Ministry of Employment and the Economy (TEM) - **Website**  
*PL 32, 00023 VALTIONEUVOSTO - Finland*

EU Life+ project ASROCKS started in September 2011. The main objective of the project is to provide guidelines and risk management tools for the exploitation of natural aggregate resources, crushed bedrock, sand and gravel, in areas with naturally elevated arsenic concentrations in bedrock and soil in the Tampere-Häme region, southern Finland. In addition, guidelines are also developed for the re-use of aggregates in construction areas with higher than average arsenic concentrations. The guidelines and tools produced during the project are targeted both for the aggregate producers and environment authorities.

In areas with naturally elevated arsenic concentrations such as the Tampere region arsenic typically resides in the soil, near the surface of the underlying bedrock. Arsenic does not cause major risks for human health unless the soils are disturbed for example during groundworks. Therefore it is important to ensure that arsenic won't be transported to groundwater or surface waters during major groundworks or excavations in crushed rock aggregate production. Long-term use of drinking water containing high concentrations of arsenic may cause health risks.

In the first phase of the project, ten production sites for crushed bedrock aggregates, seven sand and gravel excavation sites and four construction sites were selected for sampling of rock, soil, aggregate products, groundwater and surface water. The variation of As concentrations was higher in the crushed bedrock aggregates than in sand and gravel products. Elevated As concentrations were measured from some sulphide bearing veins and from surfaces of cracks in bedrock. The highest As concentrations in bedrock (up to 916 mg/kg) were measured from a planned construction site. Only small part of the total As concentration was easily leachable. Arsenic concentrations in groundwater were without exception lower than the guide value 10 µg/l designated for household water.

## **Arsenic behaviour in coastal sediments - an analytical and modelling approach**

Duc Huy Dang<sup>1,@</sup>, Erwan Tessier<sup>1,@</sup>, Véronique Lenoble<sup>1,@</sup>,  
Julia Vouge<sup>1,@</sup>, Gaël Durrieu<sup>1,@</sup>, Dario Omanovic<sup>2,@</sup>, Jean-  
Ulrich Mullot<sup>3,@</sup>, Stéphane Mounier<sup>1,@</sup>, Cédric Garnier<sup>1,@</sup>

**1** : Laboratoire PROTEE (PROTEE) - **Website**

*Université du Sud - Toulon - Var : EA3819, BP20132 83957 La Garde - France*

**2** : Ruđer Bošković Institute - Center for Marine and Environmental Research (IRB) - **Website**

*PO Box 180, 10002 Zagreb - Croatia*

**3** : LASEM-Toulon, Base Navale de Toulonn LASEM-Toulon, BP 61, 83800 Toulon - France

Sediments from Toulon bay (NW Mediterranean Sea) are hugely contaminated by numerous pollutant species (e.g. metals/metalloids, PAH). Pollutant transfer to the water column constitutes a possible risk, especially for micro-organisms, which have to be investigated. In such context, analytical and modelling approaches were carried out to better understand arsenic dynamics and fate in sediments, at the water/sediment interface, and its remobilisation during resuspension events (e.g. dredging). Core sediments were sampled throughout the bay at different seasons to characterize porewaters (physical/chemical parameters, diagenesis tracers and major/trace concentrations) and solid sediments (major/trace contents, selective extractions and carrier phases identification). A 1D steady-state modelling approach (PROFILE) was used to fit the elements' profiles, estimating depth reaction intervals and reaction rates. Thermodynamic simulation (PHREEQC) was also performed to (1) calculate the elements' speciation and (2) simulate the dissolved/particulate As fractionation, by providing the main geochemical reactions and processes occurring in sediments to the database. The obtained dissolved profiles showed significant variations between campaigns, suggesting different diagenesis activities probably linked to the varying input of "fresh" organic matter (e.g. plankton bloom). Within these variations, the coupling of experimental and modelling approaches demonstrated that As dynamic is (1) strongly controlled by iron cycling in the subsurface sediments and (2) significantly influenced by dissolved/particulate organic matter in sulfidic sediments. Finally, batch experiments performed on surface and deep sediments, associated with water sampling carried out during dredging operations, allowed studying arsenic remobilisation during sediment resuspension, which can constitute another pathway to the evaluated diffusive fluxes from the sediment to the water column. This study confirms the suitability of coupled experimental/modelling tools in order to highlight arsenic behaviour in coastal sediments, influenced by its own speciation and its interactions with the chemical environment (sediment carrier phases, dissolved species).



# Comparison of arsenic geochemistry and ecological risks at two geologically different mine sites in Finland

Kaisa Turunen<sup>1,@</sup>, Soile Backnäs, Antti Pasanen<sup>@</sup>

1 : Geological Survey of Finland (GTK) - **Website**  
P.O.Box. 1237, FIN-70211 Kuopio - Finland

In extractive and industrial minerals arsenic is a common element that cannot be avoided in mining activities. Anthropogenic activities can affect the behavior and form of arsenic by changing the chemistry and oxidizing conditions of water and soil. Therefore, areas naturally poor in arsenic may still have elevated concentrations in solid wastes or drainage and create a serious threat to human health and ecological risk for the environment. Thus, in assessing the anthropogenic impact and ecological risks, it is important not only to determine total arsenic concentrations, but also to consider the geological background and the form of arsenic. In this study the geochemistry of natural and anthropogenic arsenic was characterized by analyzing soil, sediment, peat and humus samples taken from two geologically different mining sites in Finland. The bedrock of the study sites was either naturally rich in arsenic (Suurikuusikko gold mine in Kittilä), or poor in arsenic, but having arsenic-rich calcinate tailings (YARA industrial site in Siilinjärvi). The samples were analyzed by using hot aqua regia, nitric acid, ammonium oxalate and ammonium acetate extractions. Ecological risks were determined by comparing the measured concentrations of the humus, peat and sediment samples to measured background concentrations in order to calculate the risk quotients. At both sites, the percentages of chemically adsorbed oxalate extractable fractions and easily mobilized, bioavailable acetate extractable fractions of arsenic were elevated compared to the background values. According to the risk quotients, the arsenic concentrations in humus and lake bottom sediment at YARA industrial site are elevated and exceed the background concentrations. At Kittilä, elevated concentrations were measured in peat samples taken from wetlands receiving the tailings seepage waters. The results indicate an increase in anthropogenic arsenic pollution and despite the geological background, mining activities have increased the ecological risks by changing arsenic into more soluble and mobile forms

# Health risk estimate for groundwater and soil contamination in the Slovak Republic – a convenient tool for identification of risk areas

Katarina Fajcikova<sup>1,\*,@</sup>, Veronika Cveckova<sup>1,@</sup>, Stanislav Rapant<sup>1,@</sup>

1 : State Geological Institute of Dionyz Stur (SGIDS) - **Website**  
*Mlynska dolina 1 81704 Bratislava - Slovakia*

\* : Corresponding author

A health risk estimate for environmental exposure of residents represents a convenient tool for identifying risk elements that can have a negative impact on human health as well as risk areas where adverse health effects can be expected. This presentation deals with estimation of the health risk to residents living in the Slovak Republic of exposure to contaminated groundwater and soils. The objective of this work was quantification of health risk for inorganic contaminants and further identification of potential risk areas within the country based on map visualization. Risk levels were quantified according to the methodology of "Health Risk Assessment" established by the US EPA. Two main toxic effects were assessed, chronic and carcinogenic, in relation to ingestion of contaminated groundwater and soil by resident population in the Slovak Republic (adults, children). The quantification of health risk was based on available national geochemical data for those chemicals found in groundwater and soils for which relevant quantitative information on their toxic effects to humans exist and is well-known (reference doses, cancer slope factors). Map interpretation of results was performed in the form of surface visualization of health risk levels for the whole territory of Slovakia (grid map) as well as for the administrative units of the country (as mean values). The results of health risk estimation indicate that arsenic and antimony pose the highest chronic risk for adults in case of groundwater and for children in case of soils. Arsenic was identified as a cancer risk in some areas in the case of groundwater and soils. The identified risk areas were mainly those with naturally increased contents of As and Sb in geological environment.

The presentation is supported by the EU financial instrument LIFE+ and contribution of Ministry of the Environment of the Slovak Republic ([www.geology.sk/geohealth/](http://www.geology.sk/geohealth/)).

# Experimental assessment for release of As in sediments of the Shinaki Dam receiving neutralized sulfate-rich acidic river water in Kusatsu, central Japan: Roles of organic acids and bacterial sulfate reduction

Kosei E. Yamaguchi<sup>1,2,\*,@</sup>, Izumi Ito<sup>1,@</sup>, Tomomi Yoshino<sup>1,@</sup>, Eri Tanaka<sup>1,@</sup>, Shunta Hashimoto<sup>1,@</sup>

1 : Department of Chemistry, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510 - Japan

2 : NASA Astrobiology Institute (NAI), (virtual institute) - United States

\* : Corresponding author

Originating from the Kusatsu-Shirane volcanic district in the central Japan, the Yukawa River is acidic (pH = ~2) and rich in sulfate because of natural oxidation of sulfide in its source hot spring area. For nearly fifty years, the river water has been neutralized by adding pulverized CaCO<sub>3</sub> in suspension at its mid-downstream. The Shinaki Dam was constructed to precipitate and store the treated sediments for assurance of water quality. However, because the sediments have been filling the dam, they are dredged and transported to nearby mountains for dumping by local government. Those sediments are expected to contain significant amount of As, because of its high concentration in the river water (up to 10 mg/L) and co-precipitation with Fe(OH)<sub>3</sub> produced by increase in pH from ~2 to ~5 upon neutralization. Because As would cause serious environmental and health problems, chemical stability of the As-rich dumped sediments needs to be guaranteed; however, environmental acids such as acid rain and organic acids and microbial processes such as bacterial sulfate reduction (BSR) in anaerobic environments would enhance dissolution of Fe(OH)<sub>3</sub> to release adsorbed As. It is therefore important to investigate the stability of the dumped sediments. We performed a series of laboratory experiments to quantitatively assess the extent of As release (1) by leaching the sediments with various reagent-grade organic acids (acetic, oxalic, formic, and citric acids) and natural organic acids and (2) upon bacterial sulfate reduction. We found that almost all As adsorbed onto the Fe(OH)<sub>3</sub> in the sediments was released by leaching within three days (formic and oxalic acids were the most effective media for As liberation), and that an appreciable amount of As was released upon BSR (through reductive dissolution of As-rich Fe(OH)<sub>3</sub>). This study has important implications for storing As-contaminated sediments for water quality assurance.

# Statistical tools for assessing the potential risk of elevated geogenic arsenic in groundwaters

Luis Rodríguez-Lado<sup>1,\*,@</sup>, C. Annette Johnson<sup>2,@</sup>, Michael Berg<sup>2,@</sup>

**1** : Departamento de Edafología e Química Agrícola, University of Santiago de Compostela (USC) - **Website**

*Fac. de Biología, Campus Universitario Sur 15782 Santiago de Compostela (La Coruña) - Spain*

**2** : Swiss Federal Institute of Aquatic Science and Technology (EAWAG) - **Website**

*Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf - Switzerland*

\* : Corresponding author

It has been estimated that over 100 million people in Central, South and Southeast Asia are at risk of exposure to unusually high natural levels of arsenic in drinking water. Due to the sheer size of the affected regions, the complete screening of the millions of potentially affected wells to determine the spatial occurrence and magnitude of the As contamination remains unaffordable. Predictive modelling has been used as a sound tool to identify areas at risk for high As where field data is not available. It identifies relationships between As concentrations from field observations and related environmental conditions, represented by geospatial information at sampled locations, that can then be applied to predict elevated (>10 µg/L) geogenic As contents in areas where no groundwater studies exist. We present an analysis of the suitability of some different predictive geostatistical methods – from ordinary kriging to multinomial logistic regression and multinomial committee methods – to determine the spatial domain of the health risk associated with elevated As in groundwaters in some Asian countries. Ordinary kriging is only suitable when an elevated density of field As measurements is available, leading to high prediction errors and unrealistic spatial predictions when used on sparse datasets. Multinomial logistic regression has been found to be suitable for risk analyses on sparse data, allowing, in addition, to ascertain the geochemical processes involved in the release of As. However, the predictions rely exclusively on the data used to calibrate the model, and the underlying spatial uncertainty associated with the predictive model cannot be quantified. This constraint can be solved by using committee multinomial logistic regression algorithms, which provides a stable modelling framework to evaluate the potential risk of elevated geogenic As in groundwaters.

## **As fractionation and distribution in mine wastes and stream sediments in the Asturias Hg mining district (Northwestern Spain)**

**Jorge Loredo**<sup>1,\*,@</sup>, **Veronica Silva**<sup>1,@</sup>, **Rodolfo Fernandez-Martinez**<sup>3,@</sup>, **Raquel Larios**<sup>3,@</sup>, **Almudena Ordoñez**<sup>1,@</sup>, **Isabel Rucandio**<sup>3,@</sup>

**1** : Univeristy of Oviedo, *Independencia, 13. Oviedo, Asturias - Spain*

**2** : CIEMAT, *Avenida Complutense, 40. Madrid - Spain*

**\*** : Corresponding author

Mercury mining in Asturias (northern Spain) has been carried out since Roman times. The most important mines used extractive operations in the 19th and 20th centuries and they were definitively abandoned in 1974. Specific and non-specific arsenic minerals are present in the paragenesis of the Hg ore deposit. A significant geochemical dispersion of Hg and As throughout the area has occurred by mobilization from the abandoned mines and spoil heaps, and because of pyrometallurgical processes. Arsenic mobility and availability in the environment are strongly affected by the association of As with solid phases in soils and sediments. On the other hand, surface area plays an important role in controlling As distribution and transport in sediments. It has been established that finer fractions are associated with the highest As accumulation and mobility in soils and sediments. The objective of this study is to examine phase associations of As in the finest grain size fractions of mine wastes and stream sediments collected in the surroundings of mine tailings from two abandoned mine sites (La Soterraña and Los Ruedos mines). For this purpose an arsenic-selective sequential procedure which distributes As content into seven phase associations, was investigated. This methodology has been applied to the finest grain size fractions of a waste sample from La Soterraña site and to a stream sediment sample from Los Ruedos site. Results showed that both sites have relatively low As presence in the most mobile forms. As is predominantly linked to amorphous Fe oxyhydroxides, coprecipitated with Fe and partially with Al oxyhydroxides and associated with structural material in La Soterraña site. At Los Ruedos site, As incorporated into amorphous Fe oxyhydroxides is the predominant fraction, representing more than 80% of total As.

## Determination of arsenic bioavailability in contaminated soils

Karen Bradham<sup>1,@</sup>, Kirk Scheckel<sup>1,@</sup>, Gary Diamond<sup>2,@</sup>, Brad Miller<sup>1,@</sup>, David Thomas<sup>1,@</sup>

1 : United States Environmental Protection Agency (US EPA) - **Website**  
109 TW Alexander Drive, MD-D205-05, Research Triangle Park, NC 27711 - United States  
2 : SRC Inc, New York - United States

Accurate estimation of soil arsenic bioavailability underlies reliable estimation of human health risks from ingestion of arsenic-contaminated soil. Therefore, reliable and inexpensive tools are needed to determine soil metal bioavailability. This study evaluated inexpensive methods for assessing metal bioavailability in soil as a means to improve human exposure estimates and potentially reduce remediation costs. Residential soils affected by mining or smelting activity, NIST standard reference materials, and a new EPA reference material were evaluated for arsenic bioavailability, bioaccessibility, and speciation. We will present results of an extended set of soils (> 20), including multiple assays of the same soils, which provide a quantitative assessment of reproducibility of mouse assay results. This study also included comparison of results from the mouse assay with results from a swine and monkey assay applied to the same test soils. Bioavailability estimates for identical soils (9 test soils and 3 standard reference materials [SRMs]) assayed in mice and swine were statistically correlated and the two assays yielded nearly identical estimates for 3 SRMs (mouse/swine ratio ranged from 0.86–1.00). Arsenic speciation in soils was examined using the Materials Research Collaborative Access Team's (MRCAT) beamline 10-ID, Sector 10 at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Argonne, IL and As bioaccessibility was determined using a simplified gastric extraction. AsV species were the dominant arsenic forms in most test soils and in SRMs while other soils had appreciable levels of AsIII sulfide or ore species. Arsenic bioaccessibility was highly correlated with the in vivo assay results ( $R^2=0.92$ ). Methods described in this presentation serve as highly cost effective and reproducible methods for improving arsenic risk assessments by providing site-specific assessments of arsenic in soils.

# Fate of arsenic during microbial reduction of arsenic-bearing biogenic and abiogenic Fe(III) oxyhydroxides

E. Marie Muehe<sup>1,\*,@</sup>, Lukas Scheer<sup>1,@</sup>, Guillaume Morin<sup>2,@</sup>,  
Birgit Daus<sup>3,@</sup>, Andreas Kappler<sup>1,@</sup>

**1** : Geomicrobiology, University of Tuebingen, Sigwartstr. 10, 72076 Tuebingen - Germany

**2** : Environmental Mineralogy, Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), Université Pierre et Marie Curie - Paris VI, Campus Jussieu, Tour 23, 5e étage, couloir 23-24, 4 place Jussieu, 75005 Paris - France

**3** : UFZ- Helmholtz Centre for Environmental Research, Groundwater Remediation, Permoserstr. 15, 04318 Leipzig - Germany

\* : Corresponding author

Arsenic (As) in contaminated groundwater and soil enters the human food chain (in)directly via drinking water, plants and animals, and negatively affects the health of humans. Fe(III) (oxyhydr)oxide minerals have a high sorption affinity for As and many studies have investigated the (bio)geochemical processes that are involved in the mobilization (release) and immobilization (removal) of As from Fe(III) oxyhydroxides in As-contaminated aquifers and soils. The main mechanism relevant for As mobilization is considered to be the reductive dissolution of As-bearing Fe(III) (oxyhydr)oxides. However, research has focused on the reactivity of abiogenic Fe(III) (oxyhydr)oxides, yet in nature biogenic Fe(III) (oxyhydr)oxides, precipitated by Fe(II)-oxidizing bacteria are also present. These biominerals consist of different Fe mineral phases that are associated with cell-derived organic matter (CDOM), which changes the biogeochemical properties compared to their abiogenic equivalents. In this study we followed As mobility and Fe mineralogy during reduction of As-bearing biogenic and abiogenic Fe(III) minerals by *Shewanella oneidensis* MR-1. We found that microbial reduction of As(III)-bearing biogenic Fe(III) (oxyhydr)oxides released more As than reduction of abiogenic Fe(III) (oxyhydr)oxides. In contrast, As was immobilized more effectively by secondary Fe minerals during Fe(III) reduction of As(V)-loaded biogenic than abiogenic Fe(III) (oxyhydr)oxides. SEM-EDX mapping showed that As(V) was localized to a phosphorous-containing secondary Fe mineral phase and further XAS-analysis revealed that As(V) was able to replace phosphate in the phosphate-bearing Fe(II) mineral vivianite. During sterile incubation of minerals and after microbial Fe(III) reduction stopped, As(V) was mobilized from biogenic Fe(III) (oxyhydr)oxides by sorption competition with phosphate and CDOM. Our data shows that the presence of CDOM significantly influences As mobility during reduction of Fe(III) minerals and we suggest that it is essential to consider both biogenic and abiogenic Fe(III) (oxyhydr)oxides to further understand the environmental fate of As.

# Fate and mobilization of arsenic on nano-TiO<sub>2</sub> in soil columns with sulfate-reducing bacteria

Chuanyong Jing<sup>1,\*,@</sup>, Suqin Liu<sup>@</sup>

**1** : Research Center for Eco-Environmental Sciences, 18 Shuang Qing Road, Beijing - China

\* : Corresponding author

Arsenic remediation using nanomaterials has attracted increasing attention worldwide, whereas its potential release from spent nanomaterials in reducing environments is presently underappreciated. To investigate the redox transformation and mobility of As adsorbed on nano-TiO<sub>2</sub> in the subsurface, we inoculated a sulfate-reducing bacterium (SRB), *Desulfovibrio vulgaris* DP4, in a soil column and added the As(V)-TiO<sub>2</sub> suspension in the influent groundwater matrix. Multiple complimentary characterization techniques were also employed including synchrotron-based STXM,  $\mu$ -XRF, and XANES. The 97-d batch incubation results demonstrated that As(V) was desorbed and subsequently reduced to As(III) in aqueous solution. Reduction of As(V) to As(III) was coupled to the conversion of sulfate to sulfide and lactate to acetate. STXM results provided the direct evidence of appreciable As(III) on TiO<sub>2</sub>. XANES analysis indicated that 15~28% As precipitated as orpiment. In the effluent of soil columns, As(III) accounted for 21 $\pm$ 7% of the total dissolved As during the 51-d column experiments, whereas no As(III) was detected in the abiotic control. The  $\mu$ -XRF analysis suggested that the nano-TiO<sub>2</sub> with As was mainly retained in the influent front and its transport was negligible. Our thermodynamic pE-pH calculation and XANES analysis demonstrated that biogenic magnetite as a secondary iron mineral was responsible for As retention in the soil column. While SRB restrained the release of dissolved As, it facilitated the transport of particulate As with biogenic magnetite. Our results demonstrate that SRB could facilitate desorption, as well as reduction of As(V) under reducing conditions. With the high mobility of nanomaterials, the fate and transport of associated pollutants would be greatly changed compared with bulk minerals. Our molecular level observation provides insightful knowledge of As mobilization at the nano-TiO<sub>2</sub> and water interface undergoing oxic to anoxic changes, and highlights the key role of SRB in the fate of As in the presence of nanomaterials.



## **Manganese and arsenic release induced by progressive hypoxia in Lake Biwa, Japan**

Takaaki Itai<sup>1,@</sup>, Yuika Hyobu<sup>1,@</sup>, Michio Kumagai<sup>2,@</sup>, Shinsuke Tanabe<sup>1,@</sup>

1 : Center for Marine Environmental Studies, Ehime University, 2-5, Bunkyo-cho, Matsuyama, Ehime 790-8577 - Japan

2 : Lake Biwa Environmental Research Institute, 5-34 Yanagasaki, Otsu, Shiga 520-0022 - Japan

Enrichment of Mn and As in the surface of sediment has been reported from various lakes in the world. This enrichment is generally caused by the precipitation/adsorption of MnO<sub>2</sub> and arsenate after upward diffusion of Mn<sup>2+</sup> and arsenite. Lake Biwa is a typical example, in which clear enrichments of Mn and As within the thin surface enriched layer (< 2 cm) of sediments were observed. However, progressive hypoxia recently reported from the lake can induce release of these elements into water column. In order to reveal the dynamics of Mn and As in the lake bottom, we made geochemical survey through determination and speciation of Mn and As in sediment, porewater and lake bottom water. According to our estimation, total Mn and As in the enriched layer of Lake Biwa was roughly 10000 and 240 tons, respectively. These amounts are ca. 1800 and 12 times respectively higher than the inventory of these elements in Lake Biwa water, suggesting that releasing a portion of Mn and As from the enriched layer can be a cause of large increase of these elements in lake water. The flux of Mn and As from the lake sediment to the water column were estimated to be 3400 - 16000 and 400 - 1800 mg m<sup>-2</sup> year<sup>-1</sup>, respectively. The fluxes were higher in the deeper part of the lake in which the sediment characteristics were more reducing than in the shallower part. With progressive hypoxia, this flux should increase. If 40% of the Mn was released from the enriched surface layer, and then completely mixed in whole lake, the Mn level in the water could reach 600 µg/L which corresponds to lethal levels of some crustaceans and insects. Although such an extreme situation is unlikely, continuous monitoring Mn and As levels is important to safeguard the lake ecosystem and food supply.

## Natural arsenic behaviour in the Alpine/Mediterranean Var River watershed

Aurélie Barats<sup>1,\*,@</sup>, Gilbert Féraud<sup>1,@</sup>, Cécile Potot<sup>1,@</sup>, Violaine Philippini<sup>1,@</sup>, Yves Travi<sup>2,@</sup>, Gaël Durrieu<sup>3,@</sup>, Michel Dubar<sup>4,@</sup>, Roland Simler<sup>2,@</sup>

**1** : Université de Nice Sophia-Antipolis, Institut de Chimie de Nice (ICN), UMR CNRS 7272  
28 avenue de Valrose, 06108 Nice Cedex 2 - France

**2** : Université d'Avignon et des Pays du Vaucluse, Laboratoire d'Hydrogéologie (EMMAH), UMR UAPV, 33 rue Louis Pasteur, 84000 Avignon - France

**3** : Université de Toulon, Laboratoire PROTEE, EA 3819, 83957 La Garde - France

**4** : Université de Nice Sophia-Antipolis, Laboratoire CEPAM (UMR CNRS 7264), 24 avenue des Diables Bleus, 06357 Nice Cedex 4 - France

\* : Corresponding author

The behaviour of arsenic (As) in waters from the Var River watershed (southeastern France), a typical Alpine/Mediterranean river, was examined with the aims: (i) to clearly identify the distribution and the origin of As in the waters, (ii) to determine the As fluxes to the Mediterranean sea, and (iii) to highlight eventual non conservative As behaviours, *i.e.* transfers between aqueous or solid phases. Waters were sampled along the Var River and its tributaries, during different hydrological regimes. Rocks of various geological natures were also sampled. Total As concentrations were determined by ICP-MS in the dissolved phase of river or drinking waters (<0.45 µm) and in rocks. In the upper part of the whole Var River basin, high As concentrations occur both in river waters (maximum 263 µg.L<sup>-1</sup>) and in waters used as drinking resource (above the European limit of 10 µg.L<sup>-1</sup> and maximum 70 µg.L<sup>-1</sup>). In the lower part, As concentrations in the Var River are lower and averaging, in 2009, 2.7 µg.L<sup>-1</sup> (weekly monitoring). This As content is (i) significantly higher than the world-average baseline (0.83 µg.L<sup>-1</sup>), and (ii) not related to anthropogenic inputs but exclusively related to a natural geochemical background induced by the occurrence of As-rich rocks (Hercynian metamorphic rocks and Permian argillites). Taking the average annual Var discharge into account, the only dissolved As inputs provide, in 2009, 4.2 tons of As to the Mediterranean Sea. An original graphical interpretation of a mixing model (developed in the PhD of Cécile Potot in 2011) reveals some As non conservative behaviours during the groundwater recharge by the river and some river mixing. These As transfers are thought to be related to the amount and the nature of the solid phase.

## **Arsenate sorption onto episammic biofilms developed on streambed sediments. Influence of phosphate presence**

Diego Martiñá Prieto<sup>1,\*,@</sup>, Rosa Devesa-Rey<sup>2,@</sup>, Francisco Díaz-Fierros<sup>1,@</sup>, M<sup>a</sup> Teresa Barral Silva<sup>1,@</sup>

**1** : University of Santiago de Compostela (USC) - **Website**

*Dpt. Soil Science and Agricultural Chemistry. Fac. Farmacia. Campus Vida. 15782. Santiago de Compostela – Spain. - Spain*

**2** : Defense University Center, Escuela Naval Militar, *Defense University Center, Escuela Naval Militar, Plaza de España 2, 36920 Marín, Spain - Spain*

\* : Corresponding author

Arsenic is potentially toxic to humans in the environment. It is of great interest to develop new methods to mitigate As spread, by means of eco-friendly tools. The main aim of this study was to assess As (V) adsorption capacity onto episammic biofilm-sediment systems as a potential bioremediation tool, evaluating the effect of presence of equimolar P concentrations. A natural biofilm was grown during 15 days onto 8 g of riverbed sediment, using 60 mL of natural river water as nutrient supplier. In order to determine adsorption isotherms, 60 mL of different initial As concentrations (A0) (0, 5, 25, 50, 100, 250 and 500 µg/L) were added to the systems. Sediment samples without biofilm were prepared as controls following the same treatment of the other samples. Equilibrium As concentrations were measured by ICP-MS. The same procedure was employed to determine As sorption isotherms with the presence of equimolar P concentrations. The average percentage of As adsorbed with respect to A0 for sediment and biofilm-sediment system was of  $78.9 \pm 3.5$  and  $96.9 \pm 6.6$  %, respectively. The P presence decreases As sorption capacity of sediment up to 25 % at higher initial concentrations. In contrast, in systems containing biofilms As adsorption increased slightly at higher concentrations due to P presence. The results highlight the positive effect of biofilm on the As sorption by sediment, at the studied concentrations. Adsorption isotherms were satisfactorily adjusted by Freundlich and Langmuir models, presenting Freundlich model higher values of R<sup>2</sup> in all cases. The maximum adsorption capacity of the sediment and biofilm-sediment system given was of 6.6 and 6.8 µg/g, respectively, and in the case of P presence was of 4.5 and 7.8 µg/g, respectively. In conclusion episammic biofilms are efficient tools to improve sediment As sorption capacity, showing more significant effect with P presence.

## Bacterial oxidation of arsenopyrite

Nurgul Celik Balci<sup>1,@</sup>, Meryem Menekse<sup>2,\*,@</sup>, Nevin Karaguler<sup>2,\*,@</sup>, Serra Gul<sup>1,\*,@</sup>, M Sonmez<sup>3,\*,@</sup>

**1** : Department of Geological Engineering (ITU) - **Website**

*Ayazaga Campus 34469 Maslak Istanbul - Turkey*

**2** : Department of Molecular Biology and Genetics (ITU) - **Website**

*Ayazaga Campus 34469 Maslak Istanbul - Turkey*

**3** : Department Metallurgical and Materials Engineering (ITU) - **Website**

*Ayazaga Campus 34469 Maslak Istanbul - Turkey*

\* : Corresponding author

Oxidation of arsenopyrite can release As into the environment which is toxic in the environment at even low concentration . Despite the common occurrences in natural conditions, and environmental risk , our knowledge is limited about the effect of physical conditions of oxidizing environments and microbial processes on weathering of arsenopyrite. Microbial processes and physical conditions controlling oxidation of arsenopyrite and As release were examined at laboratory and field conditions in detail. The laboratory experiments were set up as biological and chemical at various temperature (4,10, 25oC) and pH conditions (pH 2,4) to elucidate the effect of physical conditions and microbial processes on oxidation kinetic of arsenopyrite.

The greater As concentration was measured in the experiments carried out with microorganism under oxygen –rich, acidic conditions. With decreasing pH and higher temperature. As concentration increased indicating fast weathering kinetic of arsenopyrite. The similar release kinetics between Fetot and As were determined in the early stage of biological experiments. With time, increasing Fe(III)aq concentration and Fe precipitation caused As removal from the experimental solution suggesting that Fe (oxy-hydro)oxides produced by biological reactions may regulate release and transport of As from the source. These determinations are consistent with our SEM analysis. During the field studies carried out at Balıkesir-Balya Pb-Zn Mine waste site, high As concentration were measured both in the acidic surface water and in the sediments around the waste site and the spring. Consistent with this, secondary As bearing minerals such as scorodite, paulmooreite Adamite and Koritnigite were also determined in the same sediment samples. Molecular biological techniques carried out in the mine wastes and the surface sediments of spring located around the waste revealed a diverse microbial population indicating that the similar biogeochemical reactions to the experimental one may occur in the field site.

***Special Session 3***  
***Arsenic: Current Issues, of Speciation,  
Environmental Behavior, and Human Health  
Impacts***  
***Poster Presentations***

## Temporal assessment of As spatial distribution in soils in the vicinity of Panasqueira mining area (Portugal)

Ana Rita Salgueiro<sup>1,2,\*,@</sup>, Paula Helena Ávila<sup>3,@</sup>, Carla Candeias<sup>1,@</sup>, Rita Melo<sup>4,@</sup>, Eduardo Ferreira Da Silva<sup>1,@</sup>

1 : Geobiotec, University of Aveiro (Geobiotec), *Campus de Santiago, 3810-193 Aveiro - Portugal*

2 : Cerena/DECivil - **Website**

*Av. Rovisco Pais 1049-001 Lisboa - Portugal*

3 : LNEG - National Laboratory of Energy and Geology (LNEG) - **Website**

*Rua da Amieira Apartado 1089 4466-901 S. Mamede de Infesta - Portugal*

4 : URS Corporation - **Website**

*Juan de Mariana, 17 B, 2a planta. Madrid 28045 - Spain*

\* : Corresponding author

The Panasqueira hydrothermal mineralization (central Portugal) hosted by metasediments with quartz veins rich in ferberite, is the biggest Sn-W deposit of the Western Europe, and has been in operation since 1896 to present. The economic exploitation has been focused on wolframite, cassiterite and chalcopyrite. The mining and beneficiation processes produce arsenic-rich mine wastes contained in several tailing ponds (~2 Mm<sup>3</sup>) and impoundments (~10,5 Mm<sup>3</sup>). These tailings and impoundments are exposed to atmospheric conditions leading to the formation of AMD leaches due to water percolation.

The first soil campaign (75 samples) was carried on in 2004. Several elements showed high contents, being As one of the most concerning due to a maximum of 831 mg kg<sup>-1</sup>, 24 times higher than local background.

The second soil campaign (64 samples) was carried on in 2010, at two depths: (A) superficial soil - anthropogenic influence and (B) at 15cm depth – geogenic influence. Arsenic maximum content in A soil is similar to the one found in 2004 – 708.7 mg.kg<sup>-1</sup> – while the B soil presents a maximum of 350.4 mg.kg<sup>-1</sup>. However, median values are very similar 77.1 and 68.3 mg.kg<sup>-1</sup>. The enrichment index discloses that the contamination is much higher in A than in B soil samples. Contamination factor reveals that for both depths the study area is considered very high contaminated.

The two temporal scenarios show that, on a superficial analysis, As in soil did not decreased in time being still retained. Comparing the two depths A soils revealed to be more contaminated, probably due to wind action and surface water drainage.

Soils are very prone to contamination from hydrological sources and also from atmospheric sources, however when soils are the receptor of tailings drainage coming from metal mining and smelting this waste disposal causes a major impact on soils, posing serious environmental concerns.

# Geochemical mapping of Arsenic contamination in surface water in the Quadrilátero Ferrífero region, Minas Gerais, Brazil

Raphael Vicq<sup>1,\*,@</sup>, Mariangela Garcia Praça Leite<sup>1,@</sup>, Fellipe Pinheiro Chagas Mendonça<sup>1,\*,@</sup>, Hermínio Arias Nalini Jr<sup>1,@</sup>

1 : Universidade Federal de Ouro Preto (UFOP) - **Website**

*Rua do Aleijadinho, 34. Bairro Antônio Dias. Ouro Preto. Minas Gerais. 35.400-000 - Brazil*

\* : Corresponding author

Arsenic contamination is a public health issue and population exposure to arsenic through contaminated drinking water is a reality in more than 70 countries, mainly developing countries. In Brazil, in the Quadrilátero Ferrífero region, Minas Gerais, arsenic is mainly associated with greenstone belts, quartz-carbonate veins and auriferous sulfides (pyrite). Allied to arsenic's high concentrations in the rocks, its release into the environment has increased over the last 300 years due to the extraction of gold. Across the region, the concentrations of As can reach more than 2000 µg/L in surface waters, while 10 µg/L is the limit set by WHO and recommended by Brazilian legislation. However, despite being a vulnerable region, there has been no detailed geochemical mapping of surface water of the Quadrilátero Ferrífero region. To achieve this aim, all the 3rd order geographical basins of the Quadrilátero Ferrífero were defined, totaling 512 sections of rivers; water samples were collected following the methodology recommended by the USEPA, and As concentrations determined by ICP-OES. Arsenic concentrations up to 235 µg/L were found in das Velhas river basin, in the Rio Acima and Nova Lima municipalities, 48 µg/L in the Conceição river basin, and 183 µg/L in the Carmo river basin in Ouro Preto and Mariana. At 52 sites, 11% of the total sampled, arsenic levels were above the recommended limit. Most of the contaminated sites were located in rural communities, where the populations are predominantly low-income, subject to dietary deficiency and without proper sanitation. These populations are likely to be particularly susceptible to arsenic-related health effects.

# Removal of arsenic from contaminated groundwater by goethite adsorption in the presence of the arsenite-oxidizing bacterium *Aliihoeflea* sp. strain 2WW

Patrizia Zaccheo<sup>1,\*,@</sup>, Anna Corsini<sup>2,@</sup>, Lucia Cavalca<sup>2,@</sup>,  
Vincenza Andreoni<sup>2,@</sup>, Gerald Muyzer<sup>2,3,@</sup>

**1** : Dipartimento di Scienze Agrarie e Ambientali - Produzione, Territorio, Agroenergia - Università degli Studi di Milano (DiSAA), *Via Celoria 2 - 20133 Milano - Italy*

**2** : Dipartimento di Scienze per gli Alimenti, la Nutrizione e l'Ambiente - Università degli Studi di Milano (DeFENS), *Via Celoria 2 - 20133 Milano - Italy*

**3** : Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, *Science Park 904, 1098 XH Amsterdam - Netherlands*

\* : Corresponding author

Contamination of aquifers with As has raised great concern, because of serious risks to human health. The revised drinking water standard for arsenic imposes a 10 µg L<sup>-1</sup> threshold limit, which has boosted research efforts to remove As efficiently. Arsenic has a high affinity for adsorption to metal oxides, with As(V) being more effectively adsorbed than As(III). Consequently the oxidation of As(III) to As(V) is a prerequisite for achieving As concentrations below the threshold. Bio-oxidation of As(III) by microorganisms has recently received attention as a sustainable alternative to the use of chemical oxidants.

The aim of our work was to improve the removal of As from groundwater by oxidizing As(III) to As(V) followed by adsorption to goethite. For this purpose, we first isolated an arsenite-oxidizing bacterium, *Aliihoeflea* sp. strain 2WW, from a biofilm treating contaminated groundwater, and subsequently investigated the As(III) oxidation capability of this strain. The experiments were conducted in Tris-HCl 5 mM (pH 7.2) containing 200 µg L<sup>-1</sup> of As, using As(III)-induced and non-induced resting cells. As(III) and As(V) adsorption capability of goethite was evaluated by using 4 g L<sup>-1</sup> goethite and increasing As concentrations (25-800 µg L<sup>-1</sup>). Finally we tested the As-removal efficiency of the combined 2WW-goethite system on a synthetic contaminated water and a contaminated groundwater sample. Resting cells of an As(III)-induced culture of 2WW were able to oxidize completely 200 µg L<sup>-1</sup> of As in 8 hours, while non-induced cells oxidized As in 24 hours. Subsequently, results from the As-adsorption experiments showed that goethite removed almost the complete 200 µg L<sup>-1</sup> of As(V) from the solution, while for As(III) only 75% was adsorbed.

Our results indicate that As(III) oxidation by *Aliihoeflea* sp. strain 2WW combined with goethite adsorption is an efficient approach for the removal of As from contaminated groundwater.



## Arsenic and mercury speciation and bioaccessibility in plants and soils from mining sites

Jorge Loredo<sup>1,\*,@</sup>, Rodolfo Fernandez-Martinez<sup>2,@</sup>, Raquel Larios<sup>2,@</sup>, Veronica Silva<sup>1,@</sup>, Almudena Ordoñez<sup>1,@</sup>, Isabel Rucandio<sup>2,@</sup>

1 : Univeristy of Oviedo, *Independencia*, 13. Oviedo, Asturias - Spain

2 : CIEMAT, *Avenida Complutense*, 40. Madrid - Spain

\* : Corresponding author

The determination of arsenic and mercury speciation and availability for plants grown in polluted soils is important for understanding the uptake, transfer and accumulation processes of these pollutants in plants as well as for evaluating toxicity and risk. As and Hg speciation and availability were evaluated in soils and plants from two sites affected by mining and roasting activities. The studied areas were two abandoned Hg mines in Northwestern Spain: La Soterraña and Los Ruedos. Aerial parts and roots were separated in the plant samples. Speciation studies were performed after the application of specific and suitable extraction methods for each element species. HPLC-ICP-MS was used to determine the four more common arsenic species in terrestrial plants (As(V), As(III), MMA and DMA) whereas HPLC-CV-AFS was employed to separate and determine Hg(II) and Me Hg species. In addition, soil to plant transfer factor, based on total (TF) and available content (TF<sub>avail</sub>) in soils were evaluated for the studied plants.

Arsenic speciation results showed that As (III) and As (V) are present in all studied plant tissues. As(V) was the predominant species in all samples. Organic arsenic species (DMA and MMA) were found only in plants from La Soterraña mining site. Mercury speciation showed that inorganic mercury clearly prevails in the studied plant tissues for the two mining sites. Higher availability was found for arsenic in the two studied sites. Little differences were found in transfer factor for all the samples. However available transfer factor demonstrated that *Calluna Vulgaris (L) Hull* was the plant with the highest ability to extract arsenic from the corresponding soil. These data are relevant in order to estimate risks associated with the potential consumption of vegetation at these sites and eventual affections to the trophic chain.

# Heavy metals in agricultural topsoils affected by Trepca mine in the Mitrovica region, Republic of Kosova

Milihate Aliu<sup>1,2,3,\*,@</sup>

1 : University of Prishtina, *Besim Rexhepi* nn 70000 Ferizaj - Albania

2 : Geological survey of Slovenia, *Dimičeva 14*, 1000 Ljubljana - Slovenia

3 : Institute of Chemistry, Faculty of Science, *POB 162*, 1001 Skopje - Macedonia

\* : Corresponding author

Heavy metals are known to have adverse effects on the environment and human health.

OBJECTIVES of this study were: a) determine the contents of the heavy metals arsenic (As), cadmium (Cd), chromium (Cr), Cobalt (Co), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) in the agricultural topsoil of the Mitrovica region, Republic of Kosovo, and b) identify the origin of heavy metal and possible enrichment of heavy metal in the agricultural topsoil of investigated area.

METHODOLOGY: For this purpose, 99 agricultural topsoil samples were collected and the contents of metals were determined by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS: The concentration ranges were: As 3.2 - 3880 mg/kg, Cd 0.1 - 47 mg/kg, Cr 7 - 1060 mg/kg, Co 3.7 - 156 mg/kg, Hg 0.04 - 8.1 mg/kg, Ni 7.6 - 2568 mg/kg, Pb 42 - 3450 mg/kg, Zn 720 - 12000 mg/kg. According to the New Dutchlist contents of metals exceeded the action values by 3 times for Cr, 4 times for Cd, 12 times for Ni, 16 times for Zn, 65 times for Pb and up to 70 times for As. The contents of Co and Hg are in agreement with optimum values specified in the New Dutchlist. The results of factor analysis group As, Cd, Hg, Pb and Zn in F1 and Co, Cr and Ni in F2.

CONCLUSION: For As, Cd, Hg, Pb and Zn the highest contents in agricultural topsoil can be related directly to mining and smelting activities in the area while the Co, Ni and Cr contents are dominated by the parent material. The presence of heavy metals in agricultural topsoil indicates the potential for pollution transfer from this media to the food chain.

## Intermittent irrigation and arsenic bioavailability in rice cultivation

Gunnar Jacks<sup>1,@</sup>, Maria Lagerstroem<sup>2,@</sup>, Elin Lavonen<sup>3,@</sup>, Aziz Hasan<sup>4,@</sup>

**1** : KTH (Royal Institute of Technology) (KTH) - **Website**  
*KTH, Brinellvagen 28, SE-100 44 Stockholm - Sweden*

**2** : Oceanography, Rutgers Univ., *Rutgers Univ. New Brunswick NJ 08901-8521 - United States*

**3** : Swedish University of Agricultural Sciences (SLU) - **Website**  
*Swedish University of Agricultural Sciences SE-750 07 Uppsala - Sweden*

**4** : Dept. of Geology, Dhaka University, *Dept. of Geology, Dhaka University Dhaka 1000 - Bangladesh*

Arsenic is mobilized into the shallow groundwater in the Bengal delta in Bangladesh and in West Bengal in India through reductive dissolution of iron oxyhydroxides with adsorbed arsenic. About 0.9 M shallow wells are used for irrigation of rice. Rice is a significant source of human arsenic intake, up to 50 % under some conditions. Intermittent irrigation is a type of irrigation used today in NE China and in the Indian peninsula where water is often scarce. As the redox-conditions are important for the bioavailability of arsenic, we compared, in Bangladesh, the bioavailability and uptake of arsenic in rice in conventional and intermittent irrigation. Redox conditions in soil were studied by soil water sampling with suction lysimeters and speciation of arsenic into As(III) and As (V) and with redox indicators of polished carbon steel plates and steel plates painted with lead oxide. Redox levels were assessed by the presence of rust, visibly not corroded surfaces and deposition of magnetite on the steel plates mirroring different redox levels. On the lead oxide painted plates sulphate reduction was observed as formation of black lead sulphide. Intermittent irrigation was found to promote significantly more oxidizing soil conditions in terms of lower As(III)/As (V) ratios consistent with the observations from the redox indicators. The arsenic content in rice was low and not significantly different in the conventional and the intermittently irrigated plot. This might be because the field used was a virgin one not previously used for rice cultivation, and the arsenic content was initially low.

# The effect of plants in the arsenic co-occurrence of two sites in Loa River basin

Manuel Bugueño<sup>1,\*,@</sup>

1 : Departamento de Ingeniería Hidráulica y Ambiental, Pontificia Universidad Católica de Chile Av. Vicuña Mackenna 4860, Macul Código Postal 6904411 Santiago - Chile

\* : Corresponding author

Arsenic (As) contamination in the Loa River is an environmental problem that limits the use of water in one of the most arid places on earth. We compared the fluvial sediments from two contrasting lower Loa River basin sites with different geochemical environments. The two sites correspond to Sloman dam, which has no macrophytes and has low organic matter (OM), and the Quillagua oasis, which is 23 km downstream from Sloman and has a higher OM content and is rich in macrophytes. Analysis of 12 sediment cores showed that As in Quillagua oasis was present and showed a significant correlation with OM ( $r=0.85$ ,  $p<0.001$ ), indicating that the first superficial 5 cm of sediments contained the higher As concentration (1528 mg/kg d.w.). On other hand, pore water analysis showed that As is 2-100 times less concentrated (1 to 0.02 mg/kg) compared to column water in Quillagua oasis (2 mg/kg). In contrast, the Sloman site showed no significant correlation between As and OM ( $r=0.278$ ,  $p=0.235$ ), had less As in sediments (262 mg/kg d.w.) but more As in pore water (0.2 to 1.9 mg/kg). Elemental analysis of the macrophyte *Scirpus americanus* from Quillagua showed that this plant accumulated As mainly in the roots (341 mg/kg). Scanning microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) confirmed that the As was fixed in the superficial of roots. In conclusion, these data show that plants from the Quillagua oasis are actively fixing As in the roots, and suggest that both macrophytes and OM control the immobilization and accumulation of As in the arid Loa River basin.

## ***PARTICIPANTS LIST***

<b>Last Name</b>	<b>First Name</b>	<b>Pages</b>
Abdelmalek	Mohammed	
Agnan	Yannick	77, 78, 114
Alanoca	Lucia	149
Aliu	Milihate	194
Alkandary	Dhary	167
Allan	Mohammed	119
Amouroux	David	16, 137, 149
Ander	L.	79
Andersson	Malin	92
Argyraki	Ariadne	7, 169
Aubert	Dominique	94, 129
Austruy	Annabelle	21, 67, 157 170,
Backnäs	Soile	174, 177
Baran	Nicole	69, 93
Barats	Aurélie	186
Beaumelle	Léa	43
Ben Amor	Rim	121
Besse	Jean-Philippe	41
Boisa	Ndokiari	11, 156
Bonmatin	Jean Marc	49
Bour	Agathe	63
Bradham	Karen	182
Briant	Nicolas	62, 74
Bugueño	Manuel	196
Cave	Mark	79, 153, 159, 160
Celik Balci	Nurgul	188
Chereau	Gaétan	62, 74
Claustres	Adrien	85, 114
Coquery	Marina	39, 41, 90
Couto	Nazaré	56, 98, 103
Cox	Siobhan	8, 154
Crippa	Laura	61
Cuvier	Alicia	118
Cveckova	Veronika	33, 34, 178
Dabrin	Aymeric	39
Dang	Duc Huy	176
de Lima	Edmilson	
De Vleeschouwer	Francois	1, 57, 85, 107
Delannoy	Matthieu	158
Deycard	Victoria	105, 141
Dufour	Cécile	1
Dumat	Camille	12, 19, 21, 22, 58, 67, 71, 155, 157, 161, 170
Entwistle	Jane	11, 156

<b>Last Name</b>	<b>First Name</b>	<b>Pages</b>
Erkan	Nuray	<b>65</b>
Ettler	Vojtech	<b>115, 163</b>
Fajcikova	Katarina	33, 34, <b>178</b>
Fajković	Hana	<b>91, 100</b>
Feidt	Cyril	158, <b>164, 171</b>
Foster	Simon	
Foucault	Yann	21, <b>67, 71, 155</b>
Francesconi	Kevin	2
Friese	Kurt	102
Gandois	Laure	<b>57, 78, 87</b>
Gibson	Gillian	
Goix	Sylvaine	<b>10, 71</b>
Gulamussen	Noor	32
Guo	Hai	<b>97, 127</b>
Härmä	Paavo	175
He	Mengchang	<b>29</b>
Heimbürger	Lars-Eric	1, 85, <b>134, 144</b>
Hernández-Terrones	Laura	60, <b>64</b>
Hiiob	Mariina	<b>35</b>
Houecande	Orianne	<b>24</b>
Hunt	Andrew	<b>167, 168</b>
Hursthouse	Andrew	13, 14, 27, <b>40, 89, 108</b>
Itai	Takaaki	<b>26, 135, 185</b>
Jacks	Gunnar	<b>44, 195</b>
Jing	Chuanyong	<b>184</b>
Johs	Alexander	<b>133, 140</b>
Jorand	Frederic	150, 151
Jurjanz	Stefan	164
Kappler	Andreas	<b>173, 183</b>
Kim	Tak Hyun	<b>28</b>
Knights	Katherine	<b>6</b>
Korfali	Samira	<b>123</b>
Kosheleva	Natalia	<b>82, 106</b>
Krachler	Michael	<b>125</b>
Kumar	Sunil	117
Laffont	Laure	16, <b>142, 144</b>
Lagane	Christelle	134, <b>144</b>
Le Roux	Gael	<b>57, 85, 87, 114, 118, 119,</b>
Leclercq	Julie	<b>162</b>
Lemière	Sébastien	<b>42, 54</b>
Lévêque	Thibaut	21, 71, <b>155, 161,</b>
Li	Xiangdong	<b>9</b>
Loizeau	Vincent	<b>96</b>

<b>Last Name</b>	<b>First Name</b>	<b>Pages</b>
Loredo	Jorge	181, 193
Lovrencic Mikelic	Ivanka	124
Lucotte	Marc	109, 138
Mai Phuong	Tran Thi	46
Mansaray	Makawu	
Martiñá Prieto	Diego	55, 187
Martinez Cortizas	Antonio	83, 84
Martinez-Santos	Miren	37, 130
Maruszczak	Nicolas	145
Masbou	Jeremy	136, 144
Mason	Robert	132
Matijević	Lana	38
Mattielli	Nadine	76
Maurice	Laurence	1, 16, 22
McIlwaine	Rebekka	8
McIntosh	Roslyn	13
Mehra	Aradhana	20
Meili	Markus	80, 139
Mendonça	Fellipe	191
Mighall	Tim	83, 84, 107
Morton Bermea	Ofelia	113
Mouchet	Florence	47, 48, 63, 69
Muehe	E. Marie	183
Mundalamo	Rejune	81
Munoz	Gabriel	59
Munoz	Marguerite	112
Nava	Viridiana	60, 64
Nganje	Therese	14
Nriagu	Jerome	5
Orgun	Yüksel	122
Ortega	Daniela	60, 64
Oshidero	Sunday	
Oursel	Benjamin	95
Özden	Özkan	66
Palmer	Sherry	31
Palomera-Garcia	Carlos	110
Pampura	Tatiana	80
Pascaud	Grégoire	161
Patinha	Carla	128, 159, 160
Pinelli	Eric	47, 48, 57, 63
Pougnet	Frederique	104
Pourkhabbaz	Alireza	73
Pourkhabbaz	Hamidreza	73



<b>Last Name</b>	<b>First Name</b>	<b>Pages</b>
Pratte	Steve	<b>116</b>
Probst	Anne	57, 77, 78, <b>80</b> , 85, 114,
Probst	Jean-Luc	
Quayle	Colee	
Queralt	Ignasi	<b>111</b>
Rapant	Stanislav	<b>33, 34</b> , 178
Reid	John	
Reis	Amélia	128, 159, <b>160</b>
Remy	Paul-Philippe	<b>150, 151</b>
Resongles	Eléonore	
Rodgers	Kiri	<b>27</b>
Rodríguez-Lado	Luis	<b>180</b>
Romić	Marija	38
Salgueiro	Ana	<b>101, 190</b>
Sanei	Hamed	<b>88</b>
Sari	Erol	<b>126</b>
Saria	Rayenne	<b>47</b>
Sarioglu Cebeci	Meltem	<b>50</b>
Scanlon	Ray	6
Shevchenko	Vladimir	<b>146</b>
Sobanska	Sophie	19, <b>157</b> , 170
Sonke	Jeroen	16, 85, 119, 134, 136, 144, 146, <b>147</b>
Sorokina	Olga	106
Stefanowicz	Anna	68
Stewart	Alex	<b>17, 23</b>
Swartjes	Frank	<b>15</b>
Tarvainen	Timo	<b>175</b>
Teisserenc	Roman	87
Turunen	Kaisa	174, <b>177</b>
Udatný	Martin	<b>25</b>
Velizarova	Emiliya	<b>89</b>
Verneuil	Laurent	<b>48</b> , 63
Wagener	Angela	<b>45, 53</b>
Xiong	Tian Tian	19, <b>21</b> , 157, <b>170</b>
Yamaguchi	Kosei	<b>179</b>
Zaccheo	Patrizia	61, <b>192</b>
Zaoui	Lillia	<b>52</b>
Zhang	Chaosheng	<b>30, 70</b>