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COST ACTION TD1407 Final Meeting



Technology Critical Elements – Sources, Chemistry and Toxicology

2-3April 2019
Zagreb, Croatia

BOOK OF ABSTRACTS

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COST ACTION TD1407 Final Meeting
Technology Critical Elements – Sources, Chemistry and Toxicology

2-3 April 2019

Zagreb, Croatia

Book of Abstracts edited and designed by the organising committee:

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Meeting Program

Tuesday, 2 April

8:30 Registration

9:00 Opening

SESSION 1

General TCEs 1 Detection, Distribution Assessment and Analysis

Chair: Sarah Jane White

Invited talk

9:20 **O1** **Séverine Le Faucheur**, Université de Genève, Switzerland
Addressing the lack of ecotoxicological data for technology-critical metals using QICAR

9:40 **O2** **Clement Levard**, CEREGE – CNRS, France
Critical metal dynamic in the soil-plant system: an opportunity for designing recycling processes?

9:55 **O3** **Brenda Omana Sanz**, Laboratoire d'Océanologie et de Géosciences, Université Lille, France
Accelerating test to assess metal release to the environment from nanowire transparent conducting films

10:10 **O4** **Javier Jiménez-Lamana**, IPREM, Pau, France
Mass spectrometric strategies for the characterization of Technology-Critical Elements (TCE) based nanoparticles and tracking their fate following the uptake and metabolism in plants

10:25 Coffee Break

SESSION 2

Rare earth elements Sources and chemistry

Chair: Kevin Francesconi

10:45 **O5** **Jörg Schäfer**, Bordeaux University, France
Outcomes of the Intercalibration exercise on TCEs in estuarine sediment: a focus on REEs

11:00 **O6** **Maria Dolores Basallote**, University of Huelva, Spain
Source, distribution, toxicity and fate of Rare Earth Elements (REE) in an estuary strongly affected by mining: The Ria of Huelva estuary (SW Spain)

11:15 **O7** **Patricia Neira del Río**, Instituto de Investigaciones Mariñas (IIM-CSIC), Spain
Temporal trend accumulation of platinum and Rare Earth Elements in mussels from an urban beach coastal area

11:30 **O8** **Nadine Weimar**, Jacobs University, Germany
Distribution of rare earth elements and Hf-Nd isotopes between the truly dissolved, nanoparticulate/colloidal and suspended loads of glacial-fed arctic rivers in southern Iceland

11:45 **O9** **Celso Cardoso**, University of Aveiro, Portugal
Recovery of rare earth elements from waters using carbon-based nanomaterials

12:00 Lunch Break

SESSION 3

Platinum group elements Origins, Distribution and concentrations in The Environment

Chair: Antonio Cobelo-García

Invited talk

- | | | |
|-------|------------|---|
| 13:30 | O10 | Sebastien Rauch , Chalmers University of Technology, Sweden
Platinum group elements – Emissions and occurrence in surficial environments |
| 13:50 | O11 | Jörg Schäfer , Bordeaux University, France
The behavior of Pt in coastal/marine environment: what we know today and what we should focus on in the near future |
| 14:05 | O12 | Carlos E. Monteiro , IPMA and CQE/IST-UL, Portugal
Insights on the occurrence and transport of Pt and Rh in Tagus estuary region, SW Europe: from urban into the aquatic system |
| 14:20 | | Coffee Break |
-

SESSION 4

Thallium in the Environment

Chair: Beata Godlewska-Żyłkiewicz

- | | | |
|-------|------------|--|
| 15:00 | O13 | Andrew Turner , University of Plymouth, Plymouth, UK
The geochemistry, bioavailability and toxicity of thallium in the aquatic environment |
| 15:15 | O14 | Carlos Ruiz Cánovas , University of Huelva, Huelva, Spain
Thallium in acid mine drainage (AMD) systems: from the rocks to the Ocean |
| 15:30 | O15 | Andreas Voegelin , EAWAG, Switzerland
Thallium adsorption onto Illite and Mn-Oxides |
-

POSTER SESSION

16:00-18:00

Wednesday, 3 April

SESSION 5

Less studied TCEs: Environmental Behaviour and Speciation

Chair: Andrew Turner

		Invited talk
9:00	O16	Sarah Hayes , U. S. Geological Survey, USA Environmental behavior of tellurium in mine tailings
9:20	O17	Montserrat Filella , University of Geneva, Switzerland Less-studied TCEs in the environment: impact of COST action TD1407
9:35	O18	Josep Galceran , Universitat de Lleida, Spain Indium under scrutiny with AGNES: speciation in solution and dissolution of nanoparticles
9:50	O19	Teba Gil-Díaz , Université de Bordeaux, France Tellurium behaviour in a major European fluvial-estuarine system (Gironde, France): fluxes, solid/liquid partitioning, and bioaccumulation in wild oysters
10:05	O20	Sarah Jane White , US Geological Survey, USA The biogeochemistry of germanium in mine wastes
10:20	O21	Jhy-Chern Liu , National Taiwan University of Science and Technology, Taiwan Subcritical water extraction of indium from indium tin oxide scrap using organic acid solutions
10:35		Coffee Break

SESSION 6

Biogeochemistry of platinum group elements

Chair: Jörg Schäfer

11:00	O22	Sonja Zimmermann , University of Duisburg-Essen, Germany Ecotoxicology of PGE: knowledge, problems, gaps and needs
11:15	O23	Antonio Cobelo-García , IIM-CSIC, Spain The analytical determination of PGEs in environmental samples: recent developments and pending challenges
11:30	O24	Noémie Célariès , Institut de Chimie Moléculaire de Reims, UMR CNRS, France Sorption behavior of Pt-based anticancer drugs in soils
11:45	O25	Monika Sadowska , Faculty of Chemistry, University of Warsaw, Poland Monitoring of traffic-related deposition of palladium in soil
12:00		Lunch Break

SESSION 7

Bioaccumulation and toxicity of rare earth elements

Chair: Sonja Zimmermann

		Invited talk
14:15	O26	Yoshiko Fujita , Idaho Falls, Idaho, USA Interactions of wastewater microorganisms and Rare Earth Elements
14:35	O27	Anna-Lena Zocher , Jacobs University Bremen, Germany Rare earth elements and yttrium in duckweed and fruit bodies of different fungus species
14:50	O28	Laure Giamberini , Université de Lorraine, France A deeper environmental insight in REE exploitations
15:05	O29	Cátia Figueiredo , Marine and Environmental Science Centre, Portugal Lanthanum accumulation, elimination and Lipid and DNA damage in glass eels (<i>Anguilla anguilla</i>) under a warming scenario
15:20	O30	Marie Le Jean , Université de Lorraine, France Ferns for Rare Earth Elements (REE) – Toward deciphering REE transfer to plants using the accumulating fern <i>Dryopteris erythrosora</i>
15:35		Coffee Break

SESSION 8

General TCEs 2: Separation/Extraction Methodologies

Chair: Nevenka Mikac

16:00	O31	Gijs Du Laing , Ghent University, Belgium Recent progress in technologies to remove and recover TCEs from low-concentrated liquid waste and process streams
16:20	O32	Tatjana Trtić-Petrović , University of Belgrade, Serbia Evaluation of task-specific ionic-liquids based aqueous two-phase systems as a separation platform for purification of technology-critical elements
16:35	O33	Eric van Hullebusch , Institut de Physique du Globe de Paris, France Bioleaching and biorecovery of technology critical elements from WEEE
16:50		Closing Remarks, Awards & Goodbye

Poster Session Tuesday, 2 April

-
- P1** Abdou Melina, University of Bordeaux, France
Organotropism and toxicological effects of dissolved platinum in oyster *Crassostrea gigas*
-
- P2** Ayora Carlos, Institute of Environmental Assessment and Water Research, CSIC, Spain
Geochemistry of REE in Acid Mine Drainage: sorption onto basaluminite and schwertmannite
-
- P3** Barciela-Alonso María Carmen, University of Santiago de Compostela, Spain
TCEs determination in dairy products commercialized in Spain
-
- P4** Blaudez Damien, Université de Lorraine, France
Is the Rare Earth Element accumulation trait shared by different *Phytolacca* species?
-
- P5** Blažević Antonela, Department of biology, Zagreb, Croatia
Rare earth fingerprints in edible macrofungi from north-western Croatia
-
- P6** Chen Pei-Jen, National Taiwan University, Taiwan
Investigating environmental fate and toxic mechanisms of monovalent and trivalent thallium in the aquatic environment
-
- P7** Filella Montserrat, University of Geneva, Switzerland
Measuring ultratrace concentrations of germanium species in natural water reference materials by cryotrapping with ICP-MS and ICP-MS/MS detection
-
- P8** Godlewska-Żyłkiewicz Beata, University of Białystok, Poland
Separation and preconcentration of Pt(IV) and Pd(II) from sea water on modified mesoporous silica materials MCM-41
-
- P9** Grabarczyk Malgorzata, Maria Curie-Skłodowska University, Lublin, Poland
Application of stripping voltammetry using cupferron as a complexing agent for the simultaneously determination of Ga(III) and In(III)
-
- P10** Grosjean Nicolas, Université de Lorraine, France
Omics studies to investigate the response of *Saccharomyces cerevisiae* to Rare Earth Elements
-
- P11** Hofmann Annette, Laboratoire d'Océanologie et de Géosciences, Lille, France
Measuring A review on chemical speciation of silver in aqueous and soil environments
-
- P12** Ivanković Dušica, Ruđer Bošković Institute, Croatia
Thallium concentrations in lake water and digestive gland of freshwater bivalves – a field study in two karstic lakes in Croatia
-
- P13** Jiranek Guillaume, University of Geneva, Switzerland
History of TCEs in the Vidy Bay, Lake Geneva
-
- P14** Kińska Katarzyna, University of Warsaw, Warsaw, Poland
An insight into the fate of the platinum group elements in the environment
-
- P15** Klimpel Franziska, Jacobs University Bremen, Germany
Scandium in river water – development of a reliable pre-concentration method and first data for the Weser River, Germany
-
- P16** Lachaux Nicolas, Université de Lorraine, France
Speciation and biological effects of Rare Earth Elements (REE) in freshwater systems
-

P17	Lin Nai-Chun, National Taiwan University, Taiwan Isolation and identification of soil bacteria resistant to gallium and indium in Taiwan
P18	Magdas Dana Alina, National Inst. for R&D of Isotopic and Molecular Technologies, Cluj-Napoca, Romania Elemental and isotopic profiling for food authentication
P19	Mehennaoui Kahina, Université de Lorraine, Metz, France Assessment of chronic toxicity of REE-enriched sediments from a prospective mining area on <i>Myriophyllum alterniflorum</i>
P20	Mertens Jelle, European Precious Metals Federation, Brussels, Belgium Environmental fate and toxicology of Platinum Group Metals: areas for improvement
P21	Mijošek Tatjana, Ruđer Bošković Institute, Croatia Thallium accumulation in the intestinal tissue, homogenate and cytosol of brown trout and Prussian carp from two Croatian rivers
P22	Mikac Nevenka, Ruđer Bošković Institute, Zagreb, Croatia Distribution of some less studied trace elements (Ga, Ge, Nb, Te, Tl, W) and some REE (La, Y) in sediment cores from unpolluted marine and freshwater lakes in Croatia
P23	Ory Jordan, Université de Lorraine, France Investigation of gallium and indium responsive genes in yeast
P24	Pađan Jasmin, Ruđer Bošković Institute and Shimadzu, Croatia Determination of sub-pico-molar levels of platinum in the Krka river estuary (Croatia)
P25	Pandilov Zoran, Ss.Cyril and Methodius University, Skopje, Republic of Macedonia Overview of the industrial applications of Heavy Rare Earth Elements (HREE)
P26	Paulauskas Valdas, Aleksandro Stulginskio Universiteto, Lithuania Thalium in cement kiln dust
P27	Peña-Vázquez Elena, University of Santiago de Compostela, Spain Study of TCEs levels in seaweed from the Galician coast (North West of Spain)
P28	Penezić Abra, Ruđer Bošković Institute, Croatia Detection of arsenic in natural waters by voltammetry
P29	Queralt Ignasi, Institute of Environmental Assessment and Water Research, Spain X-ray fluorescence analysis of Rare Earth Elements: Analytical performance of different instrumental configurations
P30	Romero-Freire Ana, IIM CSIC, Vigo, Spain Characterization of TCEs speciation in natural systems: A critical step for their ecotoxicological risk assessment
P31	Thorat Nanasaheb, University of Limerick, Ireland Studies on toxicology profile of rare earth doped oxide materials
P32	Toller Simone, University of Bologna, Italy Human health vs urban geochemistry during the anthropic times
P33	Trtić-Petrović Tatjana, Vinca Institute of Nuclear Sciences, University of Belgrade, Serbia Seasonal and spatial distribution of technology critical elements in surface sediments of the river Danube

-
- P34** Vedeanu Nicoleta Simona, Iuliu Hatieganu University of Medicine and Pharmacy, Romania
Subacute toxicity study on rats co-exposed to silver and ruthenium (III) ions via water
-
- P35** Vind Johannes, Geological Survey of Estonia, Estonia
Black shale as vanadium resource — an Estonian example
-
- P36** Wardak Cecylia, Maria Curie-Skłodowska University, Lublin, Poland
New, simple, fast and cheap procedure for direct determination of ultra trace concentrations of Ge(IV) in environmental waters
-
- P37** Yam Rita S.W., National Taiwan University, Taiwan
Monitoring ecological impacts of metallic pollution in urban rivers using field-bioaccumulation study of a filter-feeding bivalve
-

Oral Communications

Addressing the lack of ecotoxicological data for technology-critical metals using QICARS. Le Faucheur^{1*}, C. Fortin², J. Mertens³, E. Van Genderen⁴, A. Boullemant⁴, P. G. C. Campbell⁵¹ University of Geneva, Geneva, Switzerland² INRS-ETE, Québec, Canada³ EMPF, Brussels, Belgium⁴ IZA, Durham, NC, USA⁵ Rio Tinto, Paris La Défense, France

Quantitative Ion Character Activity Relationships (QICAR) are models that predict metal effects on organisms based on their intrinsic characteristics. These metal characteristics can be related to their physical properties (molecular weight...), electronic structure (atomic number...), redox properties (oxidation number...), binding properties (ionic radius...) or developed indices (ionic potential...). Reported effects modelled using QICAR have ranged from enzyme activity reduction to mortality. Compared to QSAR (Quantitative Structure-Activity Relationship) applied to the prediction of biological activities of organic molecules, the development of QICAR has been less exhaustive. However, with the increasing use of technology-critical metals (TCM), QICAR could be a useful approach to highlight potential 'problematic' TCM. In the present study, we aimed to develop QICAR based on the total dissolved concentrations and the free ion activities of *data-rich* metals to predict the acute toxicity of TCM towards aquatic organisms.

Toxicological data (EC₅₀) concerning algae, daphnia and fish were compiled for twelve *data rich* metals and nine TCM. Twenty-three metal characteristics were tested as input variables in simple and multiple linear regressions (stepwise approach) to be related to the data-rich metal EC₅₀ values. The lack of binding constants between some TCM and inorganic ligands was overcome with the construction of linear free energy relationships (LFER) between binding constants of two ligands for a series of metals. Fifteen 'best' models were identified to predict the EC₅₀ values for the tested organisms (adjusted $r^2 > 0.8$). Twelve of these models used the covalent index, χ_m^2 , in simple linear regressions, illustrating that a metal's ability to form covalent bond is a good proxy for its toxicity. TCM toxicity prediction was not improved when metal speciation was taken into account, with increasing deviations from the predicted values. This result suggests that the current paradigm for *data-rich* metal uptake and toxicity may not apply to some TCM.

Critical metal dynamic in the soil-plant system: an opportunity for designing recycling processes?

C. Levard*, B. Collin, M. Auffan, J.P. Ambrosi, C. Keller, D. Borschneck, P. Chaurand, V. Vidal, L. Macias Perez, T. Fehlaue, Z. Fekiacova, B. Angeletti, C. Gonneau, J. Rose

CEREGE - CNRS, France

Due to their economic importance (they are present in many emerging applications as renewable energy technologies) and their high supply risk, critical metals (CMs) are the focus of intense researches. In particular, sustainable supply of these metals and impacts for the environment needs to be better investigated. Deciphering their biogeochemical behavior is an efficient starting point to evaluate their potential environmental impact and to develop bio-inspired recovery strategies. In this regard, we aim at understanding the key processes that influence critical metals speciation in biogeochemical cycles, focusing on soil-plant-microorganism interactions as the role of root exudates in the phyto-availability of CMs; the identification of translocation mechanisms from roots to leaves but also leaves secretion of CMs by guttation. Based on this improved understanding of the CMs- biomolecule interactions, we aim at developing environmentally sustainable processes for the recovery of CMs from wastes (without solvents and strong mineral acids) as an alternative to traditional pyro- and hydrometallurgy processes. To do so, we use an interdisciplinary approach mixing microbiology, metagenomic, metabolomic and physical-chemistry using X-ray absorption spectroscopy and X-ray or chemical 2D and 3D imaging techniques. First results on the geochemical behavior of CMs in a natural hotspot in the French Alps and on the extraction of metals from bauxite residues using a bio-inspired extraction protocol will be presented.

Accelerating test to assess metal release to the environment from nanowire transparent conducting films

B. S. Omana^{1*}, L. Lesven², S. Sobanska³, D. Toybou⁴, C. Celle⁴, B. Gilbert⁵, L. Charlet⁶, A. Hofmann¹

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⁴ Univ Grenoble Alpes, CEA, LITEN, DTNM, SEN, LSIN, Grenoble, France

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⁶ Environmental Geochemistry Group; Université Grenoble Alpes, Grenoble, France

The increasing worldwide use of rare metals, including precious metals and critical metals, has an impact on the geochemical cycles of these elements. At all stages of a product life, these metals and their compounds can be released into the environment and come in contact with the biosphere. The use of rare metals in nanomaterials used in high-tech products can have particular issues for environmental impact because of the potentially colloidal nature of these materials implying mobility, high surface reactivity and increased solubility .

We are focusing on silver nanowires (AgNW). These materials are designed to be incorporated in transparent conductive films, in electronics, microelectrodes, heated surfaces, etc. Although they are commonly protected by a coating material, there is a risk for release of dissolved or nanoparticulate compounds either during use or after disposal at end-of-life, because of some degree of permeability of the protective material either at molecular level or because of mechanical or chemical degradation. Since ionic and nanoparticulate Ag is toxic to the biosphere, there is a need for quantifying potential release from these product components .

We developed a method to evaluate the corrosion activity of silver in nanowire transparent conductive films under aqueous environmental conditions. In this method, the corrosion current response obtained from AgNW coated films is quantified. It is shown that there is a consistent link between the current and the coatings' characteristics. The advantage of this approach compared to classical aging studies resides in its much higher speed, 10-20 minutes are sufficient for a diagnostic result. The method is thus seen as an accelerated corrosion test.

We surmise that the method could be easily adapted to conducting films containing speciality elements, in particular the TCEs.

Mass spectrometric strategies for the characterization of Technology-Critical Elements (TCE) based nanoparticles and tracking their fate following the uptake and metabolism in plants

J. Jiménez-Lamana^{*1}, J. Wojcieszek², K. Kinska³, K. Bierła¹, J. Szpunar¹

¹ Institute of Analytical Sciences and Physico, Pau, France

² University of Technology, Warsaw, Poland

³ University of Warsaw, Warsaw, Poland

Technology-Critical Elements (TCE) based nanoparticles (NPs) are being increasingly used, e.g., as catalytic converters in vehicles. As a result, they are being released into the environment, especially in the vicinity of roads, where they can interact with soils and hence with plants. This interaction may lead to some impact on plant physiological processes and eventually to the bioaccumulation of nanoparticles in the animal and human food chain. In this context, the investigation of the behaviour of NPs throughout the whole process of interaction with plants – uptake, bioaccumulation, and translocation – is needed. This presentation will show the results obtained for the interactions of three different type of TCE based NPs (PtNPs, PdNPs and CeO₂ NPs) with plants. By using a multi-technique analytical approach based on mass spectrometry, the behaviour of NPs was investigated throughout the whole process: the stability of NPs in growth media was studied by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS); the bioaccumulation of NPs was determined by conventional ICP-MS after acid digestion; the physicochemical form of the nanoparticles taken up by plants was characterized by SP-ICP-MS after enzymatic digestion in different plant tissues, including above ground organs; the new species created within the plant as a result of the dissolution/oxidation of NPs were characterized and identified by liquid chromatography techniques coupled to ICP-MS and electrospray ionization Orbitrap MSn (ESI Orbitrap MSn). Finally, the perspective of using trapped ion mobility/time of flight spectrometry (timsTOF) to further study the interactions between TCE ions, released from nanoparticles, and metal chelators in plants (such as, e.g., nicotianamine) will be explained.

Outcomes of the intercalibration exercise on TCEs in estuarine sediment: a focus on REEs

J. Schäfer^{1*}, A. Coynel¹, A. Marache¹, A. Lerat¹, A. Cobelo-García²

¹ Bordeaux University, France

² CSIC Vigo, Spain

The current significant gaps in our knowledge and understanding of TCEs are mainly explained by their typical ultra-trace concentrations and the sometimes complex environmental matrices, making their analytical determination extremely difficult and/or time-consuming. In the frame of the COST Action TD-1407 "Network on Technology-Critical Elements the community has performed an intercalibration exercise on TCEs in estuarine sediment from the Gironde Estuary, France. Among other elements, REEs were blind analyzed in subsamples by more than 15 laboratories in various countries to (i) set reference values for this sediment, (ii) check analytical performances of the different methods applied and (iii) evaluate the most appropriate currently available procedure (digestion, analytical set-up) for the determination of REE. The presentation addresses systematic differences in the results obtained and their relation with digestion methods (Aqua Regia extraction vs total digestion) and/or analytical equipment (single quad ICP-MS, ICP-MS-MS and HR-ICP-MS, NAA).

Source, distribution, toxicity and fate of Rare Earth Elements (REE) in an estuary strongly affected by mining: The Ria of Huelva estuary (SW Spain)

M. D. Basallote*, C. R. Cánovas, M. Olías, Ra. Pérez-López, F. Macías, J. M. Nieto

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Mining activities enhance metal mobility from rocks. One of the most outstanding examples is the sulfide mining, which causes the oxidation of sulfide leading to the generation of acid mine drainage (AMD). During these reactions, extremely acid and metal-rich (i.e. Fe, Cu, Zn, Pb, etc.) leachates are released into the water bodies, causing the deterioration of water quality in mining areas. The high acidity released during sulfide oxidation also causes the dissolution of host rocks, which leads to increased concentrations of elements commonly enclosed in host rocks such as Al, Ca, Mg, Na, and REE. This study analyzes the REE sources, distribution, toxicity and fate in an estuary heavily affected by AMD from sulfide mining; the Ria of Huelva estuary, which is mainly characterized by a sharp pH gradient (from 3 to 8), due to the confluence of the acidic Tinto and Odiel rivers. To address this issue, several samplings has been performed in AMD sources, river streams and along the estuary under different hydrological regimes (i.e. dry and rainy season). Characterized AMD sources indicated that sulfide oxidation is an important driver of REE into water bodies and concentration up to several ppm were found in different mine sites. These elements exhibit a quasi-conservative behavior from the mine sites to the estuary as a result of the low pH values found in the rivers (from 2 to 4). However, a non-conservative behavior is observed during mixing processes between acidic river waters and alkaline seawater, where a progressive depletion of these elements in solution is observed around pH 4.5, similarly to the depletion of Al. At this pH range, REE are partitioned into the particulate matter, which may settle and be deposited in the estuarine sediments or be transported outside the estuary to the Gulf of Cádiz through the particulate matter.

Temporal trend accumulation of platinum and Rare Earth Elements in mussels from an urban beach coastal area

P. N. del Río^{1*}, A. Cobelo-García¹, J. Santos-Echeandía²

¹ IIM-CSIC, Spain

² IEO, Spain

Little is known about the biogeochemical cycle of Technology-Critical Elements, since they are not generally included in environmental pollution assessment or biomonitoring strategies. Anthropogenic impacts and changing oceanographic conditions affect the biogeochemical cycles of Technology-Critical Elements. The coastal ecosystem is especially vulnerable to alterations due to the effects of global change; here we will focus on changes produced in the last two decades in wild marine organisms in platinum and Rare Earth Elements concentrations.

Anthropogenic emissions of platinum have increased significantly in recent decades, especially after the incorporation of automobile catalytic converters. To verify if this affects to the levels of this metal in organisms, a temporal series of mussels collected in an urban beach of the city of Vigo (Spain) has been analyzed.

We also studied the behavior of the Rare Earth Elements in this same time series to verify how the changing hydrographical conditions affect the distribution of these elements.

Distribution of rare earth elements and Hf-Nd isotopes between the truly dissolved, nanoparticulate/colloidal and suspended loads of glacial-fed arctic rivers in southern Iceland

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² BGR, Marine Resource Exploration, 30655 Hannover, Germany

Rare Earth elements and Yttrium (REY) and Hf and Nd isotopes are used as geochemical tools in geoscientific studies of the Earth (near-)surface environment. The distribution of particle-reactive elements such as REY and Hf in river water reflects, amongst others, the geology and the climate of the catchment. The actual REY (and Hf) flux into the ocean is affected by the association of these elements with specific “physical pools” in river water: (i) suspended particles ($>0.2\ \mu\text{m}$), (ii) nanoparticles and colloids, NPCs ($0.2\ \mu\text{m} - 10\ \text{kDa}$), and (iii) the truly dissolved fraction ($<10\ \text{kDa}$).

In our study, we investigated the REY distribution in these different physical pools and its change between 2010 and 2016 in the glacial-fed Markarfljót and Þjorsá rivers (MR and TR, respectively), in Iceland.

Both rivers show low concentrations of dissolved organic carbon (MR: $0.50\ \text{mmol kg}^{-1}$; TR: $0.48\ \text{mmol kg}^{-1}$), that is typical of glacial-fed rivers. The shale-normalised REY patterns of the dissolved ($<0.2\ \mu\text{m}$) and of the particulate ($>0.2\ \mu\text{m}$) pools in both rivers are very similar and show LREYSN depletion and small positive EuSN anomalies, due to the presence of mafic particulates and NPCs (e.g. [1]). La/Yb ratios decrease and Y/Ho ratios increase as progressively finer particles are removed from the river water via (ultra)filtration. This corroborates recent studies which suggest that the REYSN patterns of the truly dissolved pools of river water and seawater are very similar [2,3]. This suggests that the typical REYSN pattern of seawater develops already on the continent during terrestrial weathering, but only becomes visible when particulates and NPCs are removed during mixing of river water and salt water in estuaries. The decoupling of Hf and Nd isotopes, that is typically observed in seawater results from incongruent terrestrial weathering of evolved continental crust and should, therefore, not be observed in river waters in Iceland due to the mafic lithology and the young age of the catchment rocks in Iceland.

References

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- [2] Merschel, G. et al. (2017) *Geochim. Cosmochim. Acta* 213, 383-399.
- [3] Pourret, O. and Tuduri, J. (2017) *Scientific Reports* 7, Article number: 5857.

Recovery of rare earth elements from waters using carbon-based nanomaterials

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Society has never been so much dependent on electronic and electric devices as it is today. As a result, e-waste has become a worldwide problem due to environmental changes associated with the incorrect treatment and storage of e-waste and because the amount of e-waste is increasing each year. Also, electrical and electronic devices are dependent on rare earth elements (REEs). Currently, they are considered as “vitamins” of modern industry. However, high demand and limited resources of REEs, combined with the environmental problems associated with their exploration, enforce the development of new ways to recover these elements from e-waste and wastewaters. Development of low-cost techniques and materials to recover these valuable elements from e-waste is important to resolve the above issues. In this way, the main objective of this work was to develop an efficient carbon-based composite towards the REEs recovery. Since most of the sorption studies reported in the literature were performed with ultrapure waters spiked with tens to hundreds mg/L of single REE, the objective is to study the recovery from waters of different matrices to remove environmental realistic concentrations. Two different carbon-based nanomaterials were synthesized and evaluated for the REEs (La, Ce, Nd, Eu, Gd, Tb, Dy and Y) recovery capacity, using different amount of sorbent and in the presence of different type of waters. In ultrapure water, average recovery percentages of 47% to 97% were obtained, in mineral water, these recoveries were around 100% and in saline water, the recoveries decrease to ca. 50 to 60% using 100 mg/L of sorbents. Results were adjusted using kinetic models and the sorption mechanism that better described the results was chemisorption. The application of the nanocomposites tested for the recovery of REEs from aqueous solutions confirms that the carbon-based composites have a great potential to be used in this field.

Platinum group elements – Emissions and occurrence in surficial environments

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The platinum group elements (PGEs; i.e. Pt, Pd, Rh, Ir, Ru, Os) are used in applications ranging from automobile exhaust catalysts to medicine and consumer electronics. The first report of PGE emissions dates from the 1970s, when automobile exhaust catalysts were introduced to alleviate urban pollution. However, despite decades of research, emission rates from different sources, environmental pathways and speciation still remain poorly understood. In addition, most research has focused on Pt, Pd and Rh and little is known about Ir, Ru and Os. This presentation provides an overview of current knowledge and recent research on the occurrence of PGEs in surficial environments.

PGEs are released from automobile exhaust catalysts, with additional sources including metal production activities, hospital effluents and industry producing catalysts, as well as possible secondary emissions. As a result, elevated PGE concentrations have been found in urban and roadside environments (e.g. airborne particles, road dust, roadside soil, lake sediments). The speciation of PGEs in the environment remains unknown, but there is evidence that a fraction of emitted PGEs is soluble or bioavailable. In addition, the occurrence of fine PGE particles (e.g. nanoparticles found in urban air and road dust) is causing the dispersion of PGE at local regional and global scales.

The behaviour of Pt in coastal/marine environment: what we know today and what we should focus on in the near future

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Platinum (Pt) has been increasingly applied in specific technical applications for several decades, and this Technology Critical Element metal represents an emerging metallic contaminant. The presence of Pt in coastal environments is still very poorly documented, but the few existing studies suggest the presence of measurable anthropogenic Pt signals in different coastal systems. As such, Pt may have the potential to serve as a tracer of modern urban (medical, traffic) sources. The presentation addresses dissolved and particulate Pt distributions and historical records in sediment and marine bivalves (“mussel watch”) from different coastal sites in the Mediterranean and the Atlantic coast as well as potential transfer pathways to marine organisms.

Insights on the occurrence and transport of Pt and Rh in Tagus estuary region, SW Europe: from urban into the aquatic system

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Platinum-group elements are contaminants of emerging concern in aquatic environments, potentially bioavailable and posing hazardous impacts. Considering the limited understanding of Pt and Rh behaviour in Tagus estuary (Lisbon, Portugal), over the past years three Iberian research groups brought new insights on the occurrence and cycling of those elements in the estuarine environment. This work presents the data recently gathered. Several sets of sediment samples were collected in Tagus estuary and simultaneously analysed for Pt and Rh by adsorptive cathodic stripping voltammetry. All data were compared with ancillary parameters .

Surface sediment samples (n=72) were used to evaluate the sources, pathways and spatial distribution of Pt and Rh in Tagus estuary. Accordingly, four distinct areas were outlined: the background, waste- (WWTP) and pluvial waters discharge sites, motorway bridges and industrialised areas. Concentrations ranged 0.18 – 5.1 ng Pt g⁻¹ and 0.019 – 1.5 ng Rh g⁻¹, with two main origins identified: industrial activities and automotive catalytic converters (ACC). Background levels (median) were 0.55 ng Pt g⁻¹ and 0.27 ng Rh g⁻¹.

Three sediment cores were collected at two industrial sites and in the Natural Reserve of the estuary in order to evaluate the industrial signature of Pt and Rh, previously to the implementation of ACC in the early 1990s. Higher concentrations were found in deeper layers than in surface sediments and this was more pronounced at BRR. In addition, an evaluation of the mechanisms responsible for the retention of both elements in those sediment layers was performed.

This work is also focused on the transfer of Pt and Rh from the urban area to the estuary through a WWTP discharge under tidal influence. The possible recirculation and exchanges with the adjoining coastal area will be studied using the hydrodynamic model of Tagus estuary, improved with dissolution and complexation experimental data.

The geochemistry, bioavailability and toxicity of thallium in the aquatic environment

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Thallium is a rare but highly toxic heavy metal that has been classified as an EPA priority pollutant. Despite its toxicity, very little information exists on the environmental behaviour of Tl and, in particular, its mobilisation, impacts and fate in aquatic systems. This may be attributed to the relatively low economic value of the metal and, until recently, difficulty associated with its analysis at trace levels in natural samples. This presentation reports on measurements of Tl in the hydrosphere of southwest England, performed by the latest generation of quadrupole ICP-MS. Specifically, concentrations of Tl in water, sediment and biota are given for fresh and brackish water environments. The results reveal that the principal sources of Tl to the region are from disturbed sulphidic metal deposits, where Tl occurs as discrete minerals or in conjunction with other minerals (e.g. chalcopyrite), and that concentrations are greatest (up to several $\mu\text{g L}^{-1}$) in systems affected by acid mine drainage. Since the principal species of the metal in aquatic systems (Tl^+) is a biogeochemical analogue of the potassium ion, interactions with sediment are relatively low. Moreover, chemical differences between Tl^+ and other, bivalent heavy metal ions means that conventional, industrial means of metal remediation (e.g. flocculation of hydroxides) are not applicable. The toxicity of Tl has been evaluated by determining its effect on the chlorophyll fluorescence quenching of the estuarine macroalga, *Ulva lactuca*. Toxicity is shown to be greater than equivalent concentrations of Ag^+ , widely regarded as the most toxic metal ion in brackish waters. It is suggested that Tl is able to pass through the cell membrane via Na-Cl-K porters but that K^+ itself has little impact in ameliorating the uptake and toxicity of Tl, at least in this alga. Implications for the monitoring and regulation of Tl in surface waters are discussed.

Thallium in acid mine drainage (AMD) systems: from the rocks to the Ocean

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Thallium (Tl), classified as a non-essential element, is also a highly toxic element classified as priority pollutant by the U.S. Environmental Protection Agency. Thallium minerals are very rare in nature, but Tl is an abundant minor component in different minerals such as alkali micas, feldspars and sulfides. The weathering of rocks containing these minerals leads to the release of this metal in soils, waters and sediments. Concentrations ranging from 0.08 to 1.5 mg/kg are commonly found in soils while an average concentration of 7 ng/L of Tl can be considered in rivers worldwide. However, the existence of anthropogenic activities may lead to a drastic increase of Tl levels in these environmental compartments. A significant example is the sulfide and coal mining, which generate acid mine drainage (AMD) processes, giving rise to large fluxes of dissolved and particulate Tl into the hydrosphere. This work reports the distribution of thallium in different environmental compartments (i.e. rocks, rivers, estuaries and Ocean) of a system heavily affected by AMD; the Iberian Pyrite Belt (IPB), one of the largest concentrations of polymetallic massive sulfide deposits in the world. The IPB has been intensively exploited for Cu, Au, Ag, among others, since ancient times, leaving a huge environmental legacy, which causes the contamination by metals of main water courses. Based on results obtained in the IPB for the last 10 years by our research group during extensive samplings in rocks, rivers, and ocean/estuaries, the mobility and fate of Tl across the IPB will be discussed.

Thallium adsorption onto illite and Mn-OxidesS. Wick¹, B. Baeyens², M. M. Fernandes², J. Peña³, A. Voegelin^{1*}¹ EAWAG, Switzerland² Paul Scherrer Institute, Switzerland³ University of Lausanne, Switzerland

Thallium (Tl) is a highly toxic trace element with a diverse biogeochemical behavior. In the environment, Tl occurs mainly as Tl(I) and, to a lesser extent, as Tl(III). Tl(I) can substitute K in minerals such as mica due to its similar ionic radius. High contents of Tl can occur in Mn-oxide deposits. Based on these geochemical observations, illite and birnessite have long been assumed to be key adsorbents for Tl in soils. Using X-ray absorption spectroscopy (XAS) to determine the speciation of Tl in geogenically Tl-rich soils, we confirmed the importance of Tl(I) uptake by illite and the association of Tl(III) with Mn-oxides [1]. In subsequent laboratory experiments, we studied the adsorption of Tl(I) onto purified illite [2]. Adsorption isotherms in various background electrolytes and covering large ranges of dissolved Tl(I) concentrations could be modelled using a 3-site cation exchange model for illite. XAS provided evidence for the importance of non-specific and high-affinity uptake mechanisms. More recently, we measured Tl adsorption isotherms for different Mn-oxides (phyllo- and tectomanganates). Using XAS, we assessed the oxidation state of adsorbed Tl as a function of Mn-oxide type and loading as well as the mode of Tl(III) binding on hexagonal birnessite. Ultimately, we aim to combine our models for Tl adsorption onto illite and Mn-oxides to describe the impact of these minerals on the adsorption and solubility of Tl in soils.

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Environmental behavior of tellurium in mine tailings

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Tellurium (Te) is a critical element that is increasingly used in high technology applications, including solar panels and thermoelectric devices. Tellurite (Te^{IV}) is generally considered to be more toxic than tellurate (Te^{VI}), but thermodynamic datasets differ in their prediction of the dominant oxidation state under surficial conditions. This highlights the utility of direct field observation of Te behavior under a variety of environmental conditions. Tellurium is enriched in gold-silver telluride deposits, but is not recovered and historic mine tailings contain elevated Te concentrations at several locations across the western United States. Eight mine sites were selected to represent a climate gradient from arid to alpine in order to assess Te behavior under a wide variety of climatic conditions. Tellurium concentrations in mine waste vary between 6 and 900 mg kg^{-1} ; further characterization was performed using x-ray diffraction, x-ray absorption spectroscopy, micro-focused x-ray fluorescence mapping, electron microprobe analysis, and physiologically-based extraction tests.

At Delamar, a semi-arid site in Nevada, x-ray absorption analysis reveals that Te is primarily present in tailings that contain up to 290 mg Te kg^{-1} as Te^{VI} with low (13-18%) gastric bioaccessibility. Microprobe analysis shows a complex assemblage of primary and secondary Te-bearing minerals, although Te is primarily associated with iron (oxy)hydroxides. Tailings at Vulcan, CO, an alpine climate, contain up to 150 mg Te kg^{-1} with low gastric bioaccessibility (8%). Yet, interestingly, an efflorescent salt sampled contains 900 mg Te kg^{-1} , present as Te^{VI} , with high bioaccessibility (~100%). Additional characterization of these samples is ongoing, but the gastric bioaccessibility in the tailings is highly variable (2-100%), suggesting differences in the Te-hosting phases and other factors controlling Te release. This study provides a better understanding of Te behavior under a broad range of environmental conditions, which is important when assessing the potential human health and environmental implications.

Less-studied TCEs in the environment: impact of COST action TD1407

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The elements considered as being technologically-critical vary among classifications and change with time. However, some elements that do not belong to any group with common chemical characteristics (e.g. platinum group elements, rare-earths) appear in all classifications. Some of these 'orphan' or 'less-studied' elements have been the object of particular attention in the COST action TD1470, namely Nb, Ta, Ga, In, Ge and Te. Our understanding of their environmental behaviour was, and still is, limited. However, work fostered by this COST action has significantly improved the situation by promoting community awareness, identifying main bottlenecks, facilitating new research and, more importantly, creating a solid pool of expertise. We can proudly state that this COST action marks a before and after concerning these elements. In this communication, progress, grey areas, the network created and future initiatives will be presented.

Indium under scrutiny with AGNES: speciation in solution and dissolution of nanoparticles

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The free ion concentration of amalgamating elements with negative standard redox potential can be efficiently measured with the electroanalytical technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping)[1-2]. Free concentrations of Zn, Cd and Pb have been determined in a variety of matrices ranging from river water to wine or soil extracts. A new AGNES methodology has been implemented for the measurement of free indium, for both the traditional Hanging Mercury Electrode [3] and the Thin Mercury Film/Rotating Disk Electrode [4]. Speciation of indium in solutions with oxalate and nitrilotriacetic acid indicates that current stability constants in NIST database are not very accurate. The determination of the lability degree of complexes with an ancillary electroanalytical technique allow to optimize the deposition times. AGNES can also be applied to dispersions without any previous separation of the solid or colloidal phases, so it is suitable for providing relevant information about the behaviour of nanoparticles, avoiding usual artefacts which can impact on other analytical techniques. The analysis of dispersions of In_2O_3 nanoparticles in background electrolyte and in synthetic seawater confirms a marked reduced solubility when compared to bulk $\text{In}(\text{OH})_3$. The dissolution can be characterized as following a very slow kinetics (e.g. after a couple of weeks, equilibrium is not yet reached).

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Tellurium behaviour in a major European fluvial-estuarine system (Gironde, France): fluxes, solid/liquid partitioning, and bioaccumulation in wild oysters

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Tellurium (Te) is a Technology Critical Element (TCE) with largely unknown environmental behaviour, especially in continent-ocean interface systems. This is due to the lack of studies in aquatic environments and to analytical challenges limiting the determination of its naturally low (ultra-trace) environmental levels. We performed a comprehensive study of Te in the Lot-Garonne-Gironde fluvial-estuarine system to better understand seasonal variations, solid/liquid partitioning (K_d), gross fluxes, estuarine dynamics, and transfer to wild oysters at the estuary mouth. A temporal record (2014-2017) of dissolved (Ted) and particulate (Tep) Te concentrations at five sites in the Lot-Garonne River system shows little differences between sites, with average $\sim 1 \text{ ng L}^{-1}$ and $\sim 50 \text{ } \mu\text{g kg}^{-1}$ respective concentrations. Watershed Ted and Tep follow parallel seasonal patterns, resulting in constant partitioning ($\log_{10} K_d \sim 4.75 \text{ L kg}^{-1}$), with constant annual gross dissolved fluxes ($\sim 15.0 \text{ kg y}^{-1}$) and variable gross particulate fluxes (from 6.50 to 140 kg y^{-1}) entering the Gironde Estuary. Estuarine reactivity in contrasting hydrological conditions (from flood to drought) suggest that estuarine hydrological residence times strongly affect Tep behaviour. Historical records (1984-2017) of Te in wild oysters at the estuary mouth vary from 1.33 to 2.89 $\mu\text{g kg}^{-1}$ dry weight (d.w.), without any clear long-term trend. This study provides rare knowledge on Te environmental dynamics in aquatic systems, suggesting that, although no current anthropogenic sources were identified in the economically developed Lot-Garonne-Gironde fluvial estuarine system, there is a non-negligible bioaccumulation in wild oysters at the estuary mouth.

The biogeochemistry of germanium in mine wastesS.J.O. White^{1*}, L.A. Schaider², J.P. Shine³, N.M. Piatak¹, R. McAleer¹, S. Hayes¹, R.R. Seal II¹¹ USGS, USA² Silent Spring Institute, USA³ Harvard T.H. Chan School of Public Health, USA

Germanium (Ge) is an element critical to new energy, defense, and communications technologies, and its use is rapidly expanding. Ge is produced from both coal fly ash and as a byproduct of zinc (Zn) sulfides. The mining and smelting of Zn sulfides appear to be currently and historically one of the largest sources of Ge to the environment; Ge has been disposed of as waste from production of primary commodities for hundreds of years. However, the life cycle of Ge is poorly understood, including partitioning and speciation during mining processes and environmental behavior. To understand the biogeochemical cycling of Ge related to mining, we characterized mine wastes (chat) at the Tar Creek Superfund Site in Oklahoma, USA, where historical mining of sphalerite (ZnS) and galena (PbS) has left wastes elevated in lead (Pb), Zn, and cadmium (Cd) that present human health concerns. Ge is elevated in the chat at this site compared to average crustal values (1.4 ppm). Small chat particles (<37 μ m) contain higher concentrations of Ge (9-17 ppm) than large particles (>0.5 mm) (2-4 ppm), a similar pattern to Pb, Zn, and Cd distributions. The mineral phases that host Ge are critical determinants of Ge's mobility, bioaccessibility, and potential for Ge recovery from the chat. Preliminary mineral accounting using x-ray diffraction, electron microprobe analyses (EMPA), synchrotron-based x-ray fluorescence (XRF) mapping, and x-ray absorption spectroscopy (XAS) suggests that Ge is present in sphalerite (ZnS) (<90 – 750 ppm), hemimorphite ($\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$) (BDL to 2200 ppm), and quartz (below detection of EMPA, but detectable with XRF/XAS), phases with significant differences in solubility. Ongoing work to understand Ge distribution among these phases, and Ge incorporation mechanisms into each phase will help inform not only the environmental implications of Ge at mining sites, but also potential for recovery and our understanding of ore formation.

Subcritical water extraction of indium from indium tin oxide scrap using organic acid solutions

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Indium (In) and its compounds have been extensively used in the manufacture of thin film transistor liquid crystal display (TFT-LCD) in the form of indium tin oxide (ITO). However, In is a by-product commodity from primary ones of aluminum and zinc without its individual reserve. Therefore, the recovery of In from secondary resources has received extensive study. Yet, traditional technologies involve significant amount of strong acid and energy and may not be environmentally friendly. A novel technology using subcritical water extraction (SWE) was applied to extract indium (In) from waste indium tin oxide (ITO). Four types of organic acid, including acetic acid, gluconic acid, citric acid, and etidronic acid were used for this purpose at solid to liquid ratio (S/L) of 10 g/L. Neither acetic acid nor gluconic acid yielded effective extraction of In from ITO. When 1 M of citric acid was used, 35.99% In was extracted at 100°C within 30 min, while 57.28% and 70.71% were extracted at 125°C and 150°C, respectively, as pressure varied from 12 to 19 kg/cm². Regarding effect of acid strength, it was found that 50.77% In was extracted at 0.1 M of etidronic acid, and it increased to 96.31% and 97.54% at 0.5 and 2.0 M, respectively. Complex formation between In and organic acid played a significant role in the extraction reactions. Compared with conventional extraction methods, SWE was more effective using less concentrated acids and required shorter reaction time .

Ecotoxicology of PGE: knowledge, problems, gaps and needs

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This presentation summarizes the current knowledge on the lab-based ecotoxicity of platinum group elements (PGE) with a focus on Pt, Pd and Rh, which are used in automobile catalysts. Among the three PGE, most studies were performed with Pt whereas information on the effects of Pd and Rh is scarce. The range of PGE concentrations applied in these exposure studies usually exceeded current environmental concentrations by far. Moreover, most studies focused on acute effects on single test organisms. Data on long-term exposure to environmentally relevant concentrations are missing. Furthermore, in most experiments, effects were related only to the nominal exposure concentration and information on the real exposure concentration was often insufficient or even absent. Sometimes the speciation of the metal used for exposure was unclear and generally speciation changes during the experiment were not considered at all although it is clear that metal speciation can considerably affect metal uptake and toxicity. For both, the quantification of environmentally relevant PGE concentrations in different matrices as well as the determination of the metal speciation, reliable analytical methods allowing for high throughput are needed. So far, PGE toxicity was tested only for a limited number of test species with focus on aquatic organisms. Toxicological effects were observed at different organisational levels (molecule, cell, individual). However, information on populations, communities and ecosystems is lacking and also the mode of action is not yet understood. Toxicity differs among the various test species and toxicological endpoints with lowest LOEC values (lowest observed effect concentration) were reported so far for changes in the heartbeat rate of embryos of Ramshorn snail and zebra fish. However, as most studies were performed under different, generally non-standardized conditions, the comparability and reproducibility of the experiments and thus a comparison between different experiments are problematic.

The analytical determination of PGEs in environmental samples: Recent developments and pending challenges

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The Platinum Group Elements (PGEs), which include platinum (Pt), palladium (Pd), iridium (Ir), rhodium (Rh), osmium (Os) and ruthenium (Ru), are amongst the rarest trace elements in the Earth's crust with concentrations generally at or below the ng g^{-1} level. Since the introduction of catalytic converters in motor vehicles in the late 80's – early 90's, containing several grams of Pt, Pd, and Rh in different ratios, an increase in their concentrations in a variety of environmental matrices has been reported.

In order to improve our understanding of the environmental biogeochemistry of the PGEs, analytical methods allowing their accurate determination are required and, accordingly, significance improvements have been attained in the last decades. Voltammetric methods have been successfully applied for waters and solid sample digests, but are mainly restricted to the determination of Pt. Inductively-Coupled Plasma Mass Spectrometry (ICPMS) is, in general, the method of choice for the determination of PGE in a variety of environmental matrices. Typical quadrupole-based apparatus offer detection limits, at best case scenarios (e.g. low matrix samples, absence of interferences, etc.) at the 0.1-10 ppt level for these elements; superior configurations (e.g. Sector-Field ICPMS) further improves its detection capabilities. However, a critical limiting factor in the determination of PGEs by ICPMS is the presence of interference-forming elements (e.g. Sr, Y, Cu, Hf, Pb) which are generally present in the samples at several orders of magnitude higher than the PGEs, many of which cannot be resolved even when using high-resolution ICPMS. Therefore, the use of different approaches (e.g. matrix separation) to eliminate or at least minimize the problems arising from these interferences is required, thus making the procedure time consuming and not suitable for routine analysis.

This talk will discuss the main recent advances for the accurate and interference-free determination of PGEs (e.g. new matrix separation and preconcentration methods, advantages of new instruments – e.g. Triple-Quad ICPMS, etc.) as well as the pending challenges that need to be considered for further development (e.g. availability of suitable environmental CRMs, inter-laboratory and inter-method comparison, reduction of analysis time with the aim of routine analysis, allowing the study of certain PGEs – for which no analytical procedure is currently available in natural waters – in aquatic systems).

Sorption behavior of Pt-based anticancer drugs in soils

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Countries are currently facing socio-economic environmental public health challenges which create the need for shared strategies to inform and support a transition towards a sustainable economy. Technology Critical Elements (TCEs) are of great importance in the development of emerging key technologies, hence their increasing use. However, their environmental consequences imply complex processes which threaten the human and environmental health, and thus need to be studied. Among those TCEs, the Platinum Group Elements (PGEs) are widely used in different industries, including for instance the pharmaceutical industry, where Pt-based drugs are used to treat cancer. However, when excreted by the human bodies, these compounds reach the urban wastewaters, then wastewater treatment plants (WWTP) where they are not sufficiently removed, and are therefore found in the environment. Indeed, they can be present either in WWTP effluents, which can be used for field crops or greenhouses irrigation, or in sewage sludges, which can be applied onto soils.

Our work aimed at studying the behavior of platinum-based compounds used in human medicine in different soils. Sorption experiments as a function of different parameters were carried using the batch technique. The role of contact time, pH, concentration, organic matter and limestone contents was assessed. Experiments were also performed on a sewage sludge and the corresponding sludge-amended soils to evaluate the impact of sludge use as soil amendment. Finally, preliminary solid-state ^{195}Pt NMR experiments were conducted to bring more insight into the sorption mechanism of these compounds.

Monitoring of traffic-related deposition of palladium in soil

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One of the main sources of platinum group elements emission to the environment are car converters, which now contain palladium as the dominant metal. The amount of PGEs increases especially in road dust and roadside soils. Determination of Pd in such samples is a great analytical challenge because of very low Pd content (below 0.2 ppm) and a complex matrix causing interferences. Thus, monitoring based on quartz sand has been proposed as an alternative. As quartz matrix is simpler to study than soils, PGEs can be more easily determined by methods suitable for trace analysis, such as ICP MS and voltammetry. However, the ICP MS method often fails, because Pd suffers from severe spectral interferences, and the analytical needs exceed the possibilities of stripping voltammetry. Therefore, it is necessary to preconcentrate Pd and separate the interfering ions (Cd, Zn, Cu, Ni, Pb). Solid phase extraction (SPE) is commonly used for that purpose, and Cellex-T is one of the most suitable sorbents for effective PGEs extraction. Palladium is then eluted with thiourea solution. Unfortunately, the presence of thiourea strongly influences voltammetric measurements, and determination of Pd is possible only after decomposition of thiourea. Thus, the complete procedure of sample preparation for Pd determination in quartz sand includes sample digestion in *aqua regia*, separation of Pd from a complex matrix simultaneously with its 10-fold preconcentration (SPE) on anion-exchanger Cellex-T, and Pd elution with thiourea/HCl solution followed by mineralization of the eluate in conc. nitric acid. The recovery is very satisfying ($98 \pm 3\%$) and the proposed methodology can be applied for Pd determination in quartz sand samples containing 2-300 ppb Pd.

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Interactions of wastewater microorganisms and Rare Earth Elements

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Increased environmental fluxes of rare earth elements (REE) resulting from their expanded recovery, usage and disposal have led to their designation, along with other technology critical metals (e.g., In, Ga, Ge), as “emerging contaminants”. Little is known about potential impacts of increased REE on natural or engineered ecosystems. We have been examining interactions of REE with microorganisms, specifically those involved in wastewater treatment, in pure and mixed cultures, under aerobic and anaerobic conditions. To date we have conducted experiments with yttrium, europium, samarium, and gadolinium, applied individually at concentrations ranging from micromolar to millimolar. For the pure cultures tested thus far, in batch reactors, we have observed that the effects of REE additions vary between the different bacterial species, and sometimes for a given bacterium, the effect (or non-effect) appears to depend on the growth state. Observed impacts on microbial activity can also differ between individual REE. In anaerobic sludge (mixed culture) continuous bioreactors supplied with Y or Gd at low micromolar concentrations for >2 months, bulk microbial activity measurements such as methane or carbon dioxide production do not appear to be significantly impacted by REE additions. However, phylogenetic analysis indicates that some changes in microbial community composition may have been induced. Such changes could affect long-term function and treatment performance. REE impacts are likely highly dependent on chemical speciation in the particular environmental matrices.

Rare earth elements and yttrium in duckweed and fruit bodies of different fungus species

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Information on uptake and fractionation of rare earth elements and yttrium (REY) by fungi and plants is limited and often ambiguous. However, a better understanding of the biogeochemical behavior of REY is important because anthropogenic REY concentrations in the environment have increased due to the growing use of REY in high-tech products and processes.

Here, we present REY concentrations for fungal fruit bodies (*Boletus edulis*, *Imleria badia*, *Suillus luteus*), individual compartments of *Suillus luteus* fruit bodies (cuticle, flesh of cap, tubes & pores, stipe) and duckweed naturally grown in lake water and aquarium water. Total REY concentrations are in the ug/kg range (dry matter) for all samples. Duckweed shows higher REY concentrations than ambient water. The shale-normalized REY patterns are rather flat but differ depending on the environment in which the duckweed grew. While duckweed grown in lake water shows a pattern resembling the lake water pattern, the pattern of duckweed grown in aquarium water shows negative Ce and positive La and Y anomalies, similar to the tap water used for preparing the aquarium water .

Whole fruit bodies of different fungus species grown at the same site and corresponding individual compartments are characterized by similar smooth shale-normalized REY patterns with positive Y anomalies. Highest total REY concentrations are shown by the mushroom cuticles. Beside the positive Y anomaly, the REY patterns of the mushrooms are very similar to those of ambient soils. Like many ectomycorrhizal fungi, *Suillus luteus* produces siderophores which can induce fractionation of the REY. However, soil leaching experiments with the siderophore desferrioxamine B suggest that this does not affect the REY distribution observed in *Suillus luteus*. The absence of significant REY fractionation combined with the similarity of mushroom and soil patterns suggests that fungal fruit bodies may have potential as archives of tracers in geochemical exploration.

A deeper environmental insight in REE exploitations

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Rare earth elements (REEs) have become a highly valuable commodity due to their increased use in high-tech products and medical applications. In the current geopolitical and economical context, (re)opening of mining facilities for REE extraction is being explored in several countries. Mining of REE may result in their dispersal from indigenous rocks to soils, sediments, water and possibly biota. In recent years, their environmental behavior has attracted increasing attention, studying their cycling and geochemistry, but their potential ecotoxicological effects require further investigation. Although they show the same behavior during natural processes owing to their similar chemical properties, there is no a clear consensus which support that they have also a predictable pattern of (eco)toxicity. This project focuses on if and how (re)opening of REE mines will alter the normal ecology of organisms at the sediment-water interface. We established a widely applicable conceptual approach to assess the environmental impact of REE mining and to estimate the maximum concentrations without impact. This research includes: characterization and sampling of a prospective REE-rich mining areas in Quebec; identification of the major properties that can affect REE availability in natural sediments; assess the release of REEs from rocks and study of REE toxicity to different test organisms. First results show that, the content in rocks and adjacent sediment-water bodies does not necessary match implying a potential transport of REE. REE availability in sediments is very low compared to the total content and show correlations with grain size, content in Mg, Fe and Al, whereas eluviations derived from a rock-leaching process show contrasting toxicity results for the different organisms. Our findings suggest that REE could be leaching towards the sediment-water interface in mining areas. As they bear toxic effects more studies should be carried out to assess LN toxicity, and to define ecological safety levels.

Lanthanum accumulation, elimination and Lipid and DNA damage in glass eels (*Anguilla anguilla*) under a warming scenario

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Rare Earth elements (REEs) comprise elements from lanthanum to lutetium that together with yttrium and scandium are considered by the European Union as Critical Metals and are emergent contaminants of great economic interest and concern as they are of critical importance for numerous groundbreaking environmental technologies and high-technology products. Transfer to aquatic ecosystems is expected to increase, however, little information is known about their potential impacts in marine biota, which highlights the urgency towards understanding the biogeochemical behavior and ecotoxicology of REEs.

Considering the endangered conservation status and the economic relevance of the European eel (*Anguilla anguilla*) and the vulnerability of early fish life stages to contaminants, we exposed glass eels, through water, to an ocean warming scenario (OW; $\Delta +4^{\circ}\text{C}$; 18°C and 22°C) and to an environmentally relevant concentration (360 ng.L^{-1}) of lanthanum (La), one of the most abundant REEs, for 5 days (plus 5 days of depuration). The major aim of this study was to assess the accumulation and elimination of La in eel's body parts (head, viscera and body) under a warming scenario and evaluate lipid peroxidation, heat-shock response, DNA damage (body) and the quantification of acetylcholinesterase (head).

The results revealed that lanthanum-exposed glass eels under OW accumulated significantly higher concentrations than control organisms. This accumulation was tissue-dependent and peaked in the first days in contact with the contaminant. Accumulation was higher in the viscera, followed by the skinless body and ultimately in the head, possibly as a protective mechanism to cope with La neurotoxicity. Heat shock response was thermo-regulated with exposed glass eels to OW + La producing significantly higher heat shock proteins. Evidence of lipid and DNA damage was found, which were supported by alterations in acetylcholinesterase levels in the head. Further investigation is needed towards understanding the biological effects of REEs.

Ferns for Rare Earth Elements (REE) – Toward deciphering REE transfer to plants using the accumulating fern *Dryopteris erythrosora*

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The increasing demand for rare earth elements (REEs) mainly driven by new-technologies, together with their current low recyclability, allow to consider them as emerging contaminants. The REE group includes the lanthanides, plus yttrium and scandium, and can be split, according to their atomic mass, into light REEs (LREEs) and heavy REEs (HREEs). Although broadly present at moderate levels in the Earth crust and in soils (approximately 100 ppm), REEs can reach higher concentrations. Indeed, soils around REE mining sites in China can bear up to 4.67×10^3 ppm REEs. Evidences for REE transfer and impact on living organisms have been reported. However, no data are currently available to identify cellular targets or molecular effectors involved in REE transport across biological membranes. In order to uncover the black box of REE uptake and transfer mechanisms, we searched for environmental models among REE accumulating ferns. Furthermore, the identification of new REE accumulators, well adapted to temperate climates, could bring out candidates for environmental friendly remediation techniques or agromining. To that end, a collection of sixty rustic fern species was screened, including the REE accumulating species *Dryopteris erythrosora*. It highlighted contrasted behaviors between genera, allowing us to sort out those ferns into distinct accumulating categories. Interestingly, LREEs and HREEs were not uniformly transferred to the fronds, suggesting either a different bioavailability of LREEs vs HREEs or different specific transfer systems for the two groups of REEs. After preliminary μ XRF experiments showing LREE and HREE distribution in the fronds, more in-depth studies of the different tissues of the ferns using synchrotron facilities will give insights about the different REE specific absorption, transfer and fractionation in plants. Combined with the use of Next-Generation Sequencing technologies, this study will help to fill the knowledge gap regarding REE transfer from the soil to the plant compartment.

Recent progress in technologies to remove and recover TCEs from low-concentrated liquid waste and process streams

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Critical and precious metals are essential in many modern applications. Their migration from solid to liquid streams is ubiquitous during industrial manipulation of the raw materials. The resulting (waste) waters are characterized by low concentrations and varying chemical composition. Hence, treatment technologies should cope with such specific system conditions and physico-chemical properties of the critical and precious metals when elaborating a removal and/or recovery strategy. This review will provide an overview of the present status and outlook on technologies that are or can be used to recover critical metals from solution, including cementation, precipitation, reduction, ion exchange, solvent extraction, electrochemical methods and adsorption. Special attention is given to adsorption technology, which is considered as one of the most promising metal recovery options owing to its facile implementation, low cost, high availability and high removal efficiencies even at low target metal concentrations. Novel sustainable and high-performing adsorbents with high potential are particularly addressed. Key directions are suggested to tackle existing challenges in the field and improve sustainability of future material cycles.

Evaluation of task-specific ionic-liquids based aqueous two-phase systems as a separation platform for purification of technology-critical elements

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Technology-critical elements (TCEs) are crucial components for developing new technologies. The increasing demand for high-purity TCEs has spurred the development of purification and separation platforms to recover these valuable elements. With the aim to develop removal platforms more benign and efficient than those studied hitherto, we assessed novel aqueous biphasic systems (ABSs) based on cholinium and imidazolium ionic liquids (ILs) for the extraction of selected lanthanides (Ln = Er, Dy, Eu, Nd, Gd, La, Lu, Sm and Tb) from water matrices. The ILs used in this research (cholinium piccolinate, ChPik; cholinium pentate, ChDTPA; choilinium lactate, ChLac; cholinium anthranilate, ChAnt; 1-hexadecyl-3-methylimidazolium saccharinate, C16mimSac and 1-butyl-3-methylimidazolium saccharinate, C4mimSac) are soluble in water, generate ABSs with appropriate water-soluble constituents, and contain anions that have a high affinity for Ln cations.

The distribution coefficients of lanthanides acquired for ChPik, ChDtpa and ChLac based ABSs were in the range from 19 to 623, meaning that all Lns preferentially migrated to the IL-rich phase following the order ChPik < ChDtpa < ChLac for La, Nd, Sm and Eu, while for Gd, Tb, Dy, Er and Lu the order was ChPik < ChLac < ChDtpa. K values of Lns in the case of ChAnt/PPG ABS were around 1. A downward trend of K values was observed for ChPik/PPG and ChLac/PPG as the atomic masses of the metals increased, while the change of K for ChDtpa/PPG ABS with molar masses was steadier. High extraction efficiencies (>99%) of Lns were achieved for the IL-rich phase for ChPik, ChDtpa and ChLac based ABSs.

Imidazolium based ILs with saccharinate anion were considerably less effective for Ln extraction; extraction efficiencies were <30% in the case of C16mimSac/KCl, while the C4mimSac/K₂CO₃ system was completely ineffective.

Bioleaching and biorecovery of technology critical elements from WEEE

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Rapid growth in manufacturing of electronic devices has generated large quantities of waste electrical and electronic equipment (WEEE) in recent years. Worldwide annual WEEE growth rate has been estimated at 8.8% (2004–2011), increasing to 17.6% (2011–2016) and total production estimated as 93.5 million tons in 2016 alone (Baldé et al., 2017). The United Nations Environment Program (UNEP) and European Union (EU) have classified several metals such as Ga, In, W, Nd, Pd, Ta, REE etc., as critical raw materials for the EU economy based on their supply risk and economic importance. Hence, secondary sources for these elements, also called technology critical elements (TCE), have to be looked for. TCE containing E-wastes (spent magnets, spent batteries, spent liquid crystal display (LCD) and spent fluorescent lamps), can be considered as promising secondary sources for these elements. This presentation will focus on the bioleaching and biorecovery of the following TCE (Nb, Ta, Ga, In, Ge and Te). Indeed, biotechnologies can be seen as a promising alternative to the current industrial best available technologies. This presentation will present the current frontiers in TCE recovery from WEEE using biotechnology, the biochemical fundamentals of these bio-based technologies and discuss recent research and development activities. These technologies encompass biologically induced leaching (bioleaching) from various matrices, biomass-induced sorption (biosorption), and bioelectrochemical systems.

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Poster Communications

Organotropism and toxicological effects of dissolved platinum in oyster *Crassostrea gigas*

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Despite platinum (Pt) expanding use and increasing release in the coastal environment, few studies cover the transfer of this Technology Critical Element (TCE) to biota and its associated potential toxicity. Oysters (*Crassostrea gigas*) from an unpolluted estuary were exposed to the stable isotope ¹⁹⁴Pt in seawater at a range of concentrations (50, 100, and 10 000 ng·L⁻¹ Pt) during 35 days. Seawater was renewed daily and spiked to respective nominal Pt concentrations for two replicate series. Control conditions were also monitored. Fifteen oysters from each tank were sampled and dissected after 3, 7, 28 to 35 days of Pt exposure. Different endpoints were investigated throughout the exposure period being (i) Pt distribution between the different organs (organotropism) through analyses by ICP-MS, and (ii) modification of biomarkers at cellular (lipofuscin and lipid content, Black Silver Deposit accumulation) and tissue (digestive gland integrity) levels. Organotropism study revealed that gills, and to a lesser extent mantle, show the greater Pt accumulation. A linear increase in Pt levels occurred in all the organs investigated (i.e. digestive gland, gonads, gills, mantle, and muscle) with the exposure period. In oysters exposed to Pt concentrations of 10,000 ng·L⁻¹, significant biomarker impairments were detected, with a clear toxicological impact at cellular levels. They reflect altered lipofuscin and neutral lipid contents, as well as intra-lysosomal metal accumulation. These observations suggest the activation of excretion (detoxification) mechanisms, including Pt elimination through faeces and clearly support the importance of the digestive gland in the response to direct Pt exposure. The present work contributes to improve our understanding of Pt accumulation and biomarker responses in marine bivalves. Such effects of emerging metallic contaminant such as Pt and other TCEs in aquatic organisms may be used as integrative tools between environmental monitoring and toxicological assessment.

Geochemistry of REE in Acid Mine Drainage: sorption onto basaluminite and schwertmanniteA. Lozano¹, C. Ayora^{1*}, A. Fernández-Martínez², F. Macías³¹ Institute of Environmental Assessment and Water Research, CSIC, Barcelona, Spain² Institute of Earth Sciences, CNRS & Univ. Grenoble-Alpes, Grenoble, France³ Department of Earth Sciences, University of Huelva, Spain

The geochemistry of Rare Earth Elements (REE) has been investigated in natural streams and in mine areas during the last decades. Most of these studies agree that REE are mobile in acidic waters and they transferred to a solid phase when pH increases. However, there is no agreement on the pH range, on which precipitates can retain REE and the mechanisms responsible for the retention. A field survey conducted in the Odiel river, SW Spain showed that pH values higher than 5, REE, Cu, Al and Fe concentrations in the river were lower than expected from a theoretical mixture because they were trapped in the precipitates. For pH below 4, however, only schwertmannite ($\text{Fe}_8\text{O}_8\text{OH}_6\text{SO}_4$) and no basaluminite ($\text{Al}_4\text{SO}_4\text{OH}_{10}\cdot 5\text{H}_2\text{O}$) precipitated. Then, REE, Cu and Al behaved conservatively and Fe does not, indicating that REE are trapped in the Al but not in the Fe solid phase. These observations are perfectly consistent with the REE accumulation in the Al-rich precipitates in the AMD treatment systems. Taking into account these observations, sorption experiments with synthetic basaluminite and schwertmannite at different pH were performed in the laboratory. For Lanthanides and Yttrium, sorption edge took place at pH higher than 5, whereas Sc sorption started at pH 4. A surface complexation model is proposed to explain the retention mechanism onto these two precipitates. Both minerals, schwertmannite and basaluminite showed similar sorption behavior. However, as its formation occurs at pH lower than 4, no REE elements are sorbed on schwertmannite.

TCEs determination in dairy products commercialized in Spain

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TECs are released to the environment due to the high number of applications in the industry and can be accumulated along the trophic chain to reach the human being through the diet.

The objective of this study is the analysis of TCEs in dairy products commercialized in Spain to assess the exposure levels of the population to these elements. The samples were digested with nitric and sulfuric acid using microwave energy and the analysis of these elements was then carried out by inductively coupled plasma-mass spectrometry (ICP-MS).

The analytical performance of the method was studied. Calibration was performed using the standard addition method in a concentration range from 0 to 100 $\mu\text{g L}^{-1}$. The method was sensitive (LODs ranging from 0.02 ngL^{-1} (^{175}Lu) to 31.6 ngL^{-1} (^{115}In)), precise (RSD < 3%), and accurate (recovery percentages 86-112 %). The method was applied for TCEs determination in milk, cheese, cream and yogurt samples. Cerium, gallium and thallium showed the largest concentrations, and were the elements present in the biggest number of samples. Meanwhile germanium, indium, platinum, rhodium and tellurium haven't been detected in any of the analyzed samples.

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Is the Rare Earth Element accumulation trait shared by different *Phytolacca* species?

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A fast increase in the demand and production of Rare Earth Elements (REEs) has been observed over the past decades because of their diverse uses in new technologies, green energies and medical devices. Moreover, the lack of recyclability for these elements, their spreading as fertilizers in China along with the high concentrations found in mining areas lead REEs to be considered as emerging pollutants. Although these elements are not essential to plants, REE can be detected at low concentrations in plant tissues. However, a few number of plant species are able to accumulate REE. One of the best examples is *Phytolacca americana* (pokeweed). This plant, first identified as a manganese hyperaccumulator, was further reported as a REE accumulator. *Phytolacca americana* is a fast growing and high-biomass producing plant that can reach 3 m height, making this plant a good candidate for the remediation of REE-contaminated sites. Given that the Mn hyperaccumulation trait was reported for different species of *Phytolacca*, and that REE accumulation ability is shared by several *Carya* species, we aimed at revealing whether REE accumulation is a monophyletic trait among *Phytolacca* genus by investigating 5 representative species. Our analyses revealed how REE accumulation in those *Phytolacca* species modified the macro- and micro-elemental composition of roots and shoots, to allow a better understanding of REE absorption/translocation mechanisms. Additional analyses were performed to investigate the effects of REE exposure on plant growth and morphology, and on physiological parameters related to metallic stress.

Rare earth fingerprints in edible macrofungi from north-western Croatia

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Macrofungi (macroscopic fungi) take up elements from a substrate via spacious mycelium. Even though the mechanisms of assimilation and transportation of REEs in fungi are still poorly known, literature data suggest that macrofungi have the ability to accumulate higher concentrations of rare earth elements than some vascular plants. This can be of considerable importance in edible fungi, which, if frequently consumed, can present a potential source of REE in the human diet.

The present study aims to investigate levels and distribution of rare earth elements, including Y, (REY) in fruiting bodies of edible fungi collected from the north-western part of Croatia. According to the Geochemical Atlas of Europe, the study area is characterised by naturally elevated levels of REYs. This provides an opportunity to study the distribution and fractionation of REY in edible fungi under initially elevated levels of rare earths in local soils. During the sampling campaign, an attempt was made to collect different edible fungal species from this area. A total of 20 samples, representing 15 edible species from the phylum Basidiomycota, was collected and analyzed by High Resolution Inductively Coupled Plasma Mass Spectrometry for the total concentration of rare earth elements, including Y. The obtained concentrations, with ΣREY ranging from 0.019 mg kg⁻¹ to 0.452 mg kg⁻¹, are similar or slightly lower compared to literature values for the macrofungal species. The results point to large variability between different studied species with regards to their ability for rare earth elements uptake and suggest that some other factors, in addition to the total soil REY concentrations, influence accumulation of this group of elements in the fruiting bodies of macrofungi.

Investigating environmental fate and toxic mechanisms of monovalent and trivalent thallium in the aquatic environment

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Thallium (Tl) is a technology critical element frequently used in the new or developing technologies of electronic, optical, semi-conductive and superconductive industries etc. The anthropic processes of Tl entering the aquatic environment include from its mining, usage (e.g., coal combustion and cement production) and disposal (e.g., wastewater discharge from those high-tech manufactures). Tl is also classified as a priority pollutant by the U.S. EPA, as it has high toxicity to mammals. Tl exists in the environment as monovalent (Thallous, Tl(I)) or trivalent (Thallic, Tl(III)) state. Tl(I) is thought to be more thermodynamically stable than Tl(III); however, recent studies indicate occurrence of Tl(III) in surface water, and it seems much more toxic than Tl(I) to aquatic organisms. However, the environmental transformation between Tl(I) and Tl(II) in natural water matrices and their toxicities to the higher trophic levels of aquatic organisms such as fish remain unclear. We have developed two analytical methods including high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) and anodic stripping voltammetry (ASV) for assessing Tl speciation and fate in environmental water samples. To investigate toxic mechanisms of Tl, we used medaka (*Oryzias latipes*) fish as a model organism to assess the transcriptome of two Tl species using next generation sequencing (NGS) analysis. Differential gene expression profiles showed that Tl(I) significantly induced cholesterol synthesis, steroid hormone metabolism and phase I metabolism related genes. The Tl-altered transcriptional expression was confirmed by qPCR and related enzyme activities. The correlation between Tl speciation and toxicity in medaka fish is under further investigation.

Measuring ultratrace concentrations of germanium species in natural water reference materials by cryotrapping with ICP-MS and ICP-MS/MS detection

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Germanium is an element among so called technologically critical elements, quite rare in nature, but increasingly used and vital for modern technologies needed for modern communication, computing or the production of clean energy. Increased use also brings increasing demand for analytical methods for accurate Ge determination and speciation analysis at ultratrace levels in environmental samples. Inorganic Ge levels in unpolluted natural waters are in single or low tens of pg/L for freshwater and in low pg/L range in seawater, and methylated germanium species are below pg/L in freshwater and up to 20 pg/L in seawater. Analysis at those levels still pose a considerable challenge. Most of the published data have been obtained by hydride generation (HG) coupled to cryotrapping (CT) and either graphite furnace-AAS and recently also ICP-MS detection. With the fast progress of analytical methodology such as reaction cell ICP-MS and especially ICP-MS/MS technology, the analytical procedures need to be revisited for accurate analysis.

A semi-automated HG-CT-ICP-MS system originally developed for arsenic speciation analysis [1] was adopted for Ge speciation analysis. After optimization of reaction conditions for individual species, compromise conditions found. HG was performed from 0.25M TRIS buffer (pH 6) +0.005M EDTA reaction medium. Higher NaBH₄ concentration (3%) and addition of 1% L-cysteine to the samples as reaction modifier were found crucial for efficient HG of methylated germanes. Deionized water was identified as the main source of elevated iGe blanks. Limits of detection below 0.1 pg/L for all species were achieved. Results for river water reference material SLRS-4 agree well with so far published values; also SLRS-6 and seawater reference materials NASS-7 and CASS-6 were analyzed.

Pilot experiments of HG-CT with ICP-MS/MS detector will be presented.

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Separation and preconcentration of Pt(IV) and Pd(II) from sea water on modified mesoporous silica materials MCM-41Ż. Arciszewska¹, B. Leśniewska¹, I. Nowak², B. Godlewska-Żyłkiewicz^{1*}¹ University of Białystok, Institute of Chemistry, Białystok, Poland² Adam Mickiewicz University, Faculty of Chemistry, Poznań, Poland

Platinum group elements (PGEs) are widely used in various branches of industry, especially in the production of automotive catalytic converters and electronic, chemical and fuel manufacturing. All these applications caused increase of PGEs content in environmentally relevant matrices, such as roadside dust, soils, sea water and marine organisms. Direct determination of Pt and Pd in environmental samples by spectroanalytical techniques is difficult due to insufficient sensitivity of these techniques and/or their susceptibility to spectral and matrix interferences. In most cases, the accurate results of analysis could be obtained when the efficient procedure of matrix separation was introduced before a detection step. A new solid phase extraction procedure for the preconcentration and separation of Pt and Pd from sea water before their spectrometric determination is proposed in this work. A novel sorbent mesoporous silica MCM-41 modified with 3-merkaptopropyltrimetoksysilane was used as the column filling. The analytes were separated in a dynamic mode. Parameters influencing the retention and elution processes, such as pH of sample solution, kind, concentration and volume of eluent, and flow rates of sample and eluent were optimized. The recovery of Pt and Pd from the studied sorbents was quantitative even in the presence of a high excess of sodium and potassium chlorides. The developed method was applied for the determination of both analytes in spiked sea water samples.

Application of stripping voltammetry using cupferron as a complexing agent for the simultaneously determination of Ga(III) and In(III)

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The importance of the procedure for simultaneous determination of Ga(III) and In(III) in environmental water samples results from the fact that both gallium and indium have recently gained much interest and are essential in high-technology industries, mainly for manufacturing semiconductor and electronic devices. Consequently with such keen demand, the levels of these elements in the environment are gradually increasing.

Stripping voltammetry is one of the most favorable techniques for the determination of metal ions because of their low cost and high sensitivity. The unusually high sensitivities are based on the fact that the analyte is pre-concentrated on the working electrode as a complex of the determined metal. As it was shown in earlier investigations, Ga(III) and In(III) form electrochemically active complexes with cupferron what makes possible voltammetric determination of these elements with low detection limit [1,2]. This study will focus on the development of the first adsorptive voltammetric procedure for the simultaneous determination of gallium and indium. In order to obtain the best shape and separation of gallium and indium peaks on voltammogram we studied the influence of various experimental parameters (e.g. pH, composition of the supporting electrolyte, cupferron concentration, accumulation potential and time). In the optimized conditions the detection limits were below 10 nM for Ga(III) and In(III). The method was satisfactorily applied to the simultaneous quantification of gallium and indium in environmental water samples collected from eastern areas of Poland.

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Omics studies to investigate the response of *Saccharomyces cerevisiae* to Rare Earth Elements

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The Rare Earth Elements (REEs) group gather 17 chemical elements including 15 lanthanides, Yttrium and Scandium. As part of the Technical Critical Elements (TCEs), they are of high importance in high-tech domains ranging from renewable energies to medicine. Although many investigations have been carried out to find innovative ways to supply the rising demand for these elements, the effects of the increasing release of these new emerging contaminants in the environment is still poorly documented. Furthermore, the few existing studies on biota often mention controversial effects and therefore reflect the lack of knowledge on the impact of REEs at the cellular level. Thus, we adopted high throughput strategies to study REE stress responses on several model organisms, at the cellular and molecular levels.

In order to build a strong basis of the impact of these elements, to identify key genes, proteins, pathways and compartments involved in a REE stress as well as their translocation, we used the well-known eukaryotic model organism *Saccharomyces cerevisiae*. We used three complementary large-scale omics methods, focusing on different steps of the cellular response, which consist of the screening of a genome-wide mutant collection on several REEs, transcriptional analyses (RNA-seq), as well as proteomic analyses (shot-gun) under REE stress. These methods allowed to pin point the major role of the cell wall and plasma membrane organization, but also of the endocytic pathway and the sphingolipid biosynthesis, in the REE response in *S. cerevisiae*. The unique metallic stress response triggered on this model organism by these REE elements, and the differences observed between the REEs tested, set up an important foundation in the understanding of the potential impact of REEs on eukaryotic organisms at the cellular and molecular levels.

A review on chemical speciation of silver in aqueous and soil environments

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Silver ! Although about 50 % of world wide silver consumption goes into production of coins, bullions and jewelry, and constitutes national reserves, another 50 % goes into industry, where it is mostly used in electronics, photovoltaics, photography, medical and purification products and to an ever increasing part as nanomaterial in functional goods [1]. In these products silver is exploited for its specific properties of being a very good electric conductor with good corrosion resistance as well as being an antibacterial agent. In the numerous applications where tiny amounts of silver are used per unit product, this silver is often not recycled and it is widely dispersed in all types of waste, ending up in effluents, fly ash and waste water treatment sludges.

While discharge of silver to the waste stream occurs mainly through the metallic (nano)-particulate form, final sink of the element in the environment is limited to a small number of chemical species, in particular AgCl and more so Ag₂S that has extremely low solubility. However, since sulfide and silver are redox sensitive species, continued dynamic changes in silver speciation are possible in environments with changing oxygen levels, microbial activity and photoreactivity. Based on literature, we will review silver speciation in soil and aqueous environments and focus in particular on the role of natural organic matter and redox potential in promoting speciation changes of silver and maintaining reactions where the toxic Ag⁺ emerges again and again.

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Thallium concentrations in lake water and digestive gland of freshwater bivalves – a field study in two karst lakes in Croatia

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Thallium is nonessential and highly toxic metal. It has high water solubility and shows the tendency of accumulation in living organisms. As a priority pollutant, it should be monitored both in water and in the organisms. So far, there are relatively few studies of Tl bioaccumulation in freshwater bivalves, especially in karst waters.

We have studied Tl accumulation in the digestive gland of freshwater bivalves *Anodonta* spp. from two karst lakes in Croatia, Brljan and Visovac. The lakes are integral part of the Krka River ecosystem. Brljan Lake is situated upstream from Visovac Lake and is consequently more affected by the pollution of wastewaters from the Town of Knin. In Visovac Lake, organisms were sampled in shallow (1-3 m, VS) and deep (~13 m, VD) part of the lake, and at Brljan Lake only in shallow part (2-4 m, BR). In addition to Tl, we also analyzed the content of 23 trace elements and 4 macro elements in digestive gland in order to detect possible coaccumulation of Tl with other elements. Metals were determined by HR ICP-MS.

Concentrations of dissolved Tl in water were very low in both lakes (5-6 ng/L). Whole digestive gland tissue of bivalves from VS location had about ten times higher Tl concentrations (0.039 µg/g) compared to the other two locations (0.004 and 0.005 µg/g at VD and BR location, respectively). Thallium concentration ranges in the cytosolic fraction of digestive gland were as follows: BR: 0.0008-0.004 µg/g, VS: 0.0002-0.0009 µg/g and VD 0.0004-0.0008 µg/g. Correlation analysis confirmed specific coaccumulation patterns at each of the investigated locations. Obtained results indicate low Tl exposure by water and suggest the need for further sediment research as a potential source of Tl for these bivalves.

History of TCEs in the Vidy Bay, Lake Geneva

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TCEs is a group of chemical elements that include lanthanides, platinum group elements (Pt, Pd, Rh, Os, Ir, Ru) plus Ga, Ge, In, Te, Nb, Ta and Tl 1. Despite an increased use in recent years, little is known about these elements, particularly regarding their environmental behaviour.

To increase our knowledge about TCEs, a dated sediment core from the Vidy bay in Lake Geneva has been analysed for TCEs and other trace elements. Indeed, this core had been previously analysed for some elements and physico-chemical parameters 2.

Some TCEs show a contamination pattern over the past century. It may be linked to water discharged in the bay, particularly from the waste water treatment plant of the nearby city.

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An insight into the fate of the platinum group elements in the environment

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The assessment of elements influence into the environment and the living organisms is possible only, if we have procedures that allow reliable determination of analytes at a sufficiently low level. Moreover, the complexity of the sample matrix and necessity of analyte preconcentration very often require additional steps in sample preparation process. To monitor PGEs in soil samples received from the monitoring plots distributed along high-ways and exposed to traffic-related contamination developed sample preparation procedures were used. Particular attention was paid to the application of adsorptive stripping voltammetry, which, due to low limits of quantification, can be an alternative method to inductively coupled plasma mass spectrometry.

The deposition of PGEs in the roads vicinity makes that they can be taken up and accumulated by plants, which may cause disturbances in their proper functioning. Therefore the influence of PGEs on the growth and morphology of *Sinapis alba* L. was studied. The hydroponically cultivated plants were exposed to the presence of various platinum, palladium and rhodium salts as well as their nanoparticles. The total content of xenobiotics in plant tissues and the presence of PGEs nanoparticles were monitored. Furthermore, hyphenated techniques – liquid chromatography with different detection modes were applied to study induction of stress metabolites and formation of PGEs complexes in plants.

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Scandium in river water – development of a reliable pre-concentration method and first data for the Weser River, Germany

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Scandium is classified as critical raw material by the European Union, emphasizing its importance for modern economies. While its behaviour in magmatic systems is well understood, there are only a few studies on its behaviour in earth surface systems like rivers. It is especially important to improve this understanding, because Sc mining from laterites in Australia is expected to start soon. As Sc has not yet been mined. This will soon lead to a wider usage of Sc in industry, (e.g. for Al-Sc alloys in the transportation industry) and together with the mining and beneficiation operations themselves, to an increased release of Sc into the environment.

In general, concentrations of dissolved Sc in river water are very low (ppt range) Sc is bound to nanoparticles/colloids and suspended particles. One of the challenges in analysing Sc in river water is its low concentration requiring a pre-concentration before analysis. The NOBIAS Chelate PA1 (Hitachi) has been used to pre-concentrate a range of trace metals including rare earth elements and yttrium (REY) and Sc from seawater, but not from freshwater .

This poster aims at presenting a reliable pre-concentration protocol for the quantitative determination of Sc and REY at ultra trace element concentrations in freshwater samples using the NOBIAS Chelate PA1. Additionally, first Sc data for the Weser River in Germany will be presented and compared to the REY data.

Speciation and biological effects of Rare Earth Elements (REE) in freshwater systems

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Rare Earth Elements (REE) became essential in high- and green-technology applications. Their increasing production and use have led to the release of anthropogenic REE in the environment, including aquatic systems. However, little is known about the ecotoxicology of REE, particularly in complex systems, preventing the implementation of regulatory thresholds.

To understand better the speciation and biological effects of REE, we conducted acute ecotoxicological assays on several freshwater species belonging to different food web levels: the green microalga *Raphidocelis subcapitata* (ISO 8692, 2012), the crustacean *Daphnia magna* (ISO 6341, 2012), the bivalve *Corbicula fluminea* and the fish *Danio rerio* (OCDE 203, 1992). We test three elements representative of the REE group: neodymium (Nd), gadolinium (Gd) and ytterbium (Yb) alone and in mixture. The assays were performed in absence and presence of dissolved organic matter (DOM: 8 mg/L of dissolved organic carbon including 6.8 mg/L fulvic acid).

First results show comparable effective concentrations (EC_x) for Nd, Gd and Yb, which suggests a similar toxicity pattern among all REE. The presence of DOM tended to decrease the bioaccumulation and consequently the toxicity of REE. These results should be considered in environmental risk assessment. In the future we will realize mesocosm experiments in order to reproduce exposure conditions closer to the environment.

Isolation and identification of soil bacteria resistant to gallium and indium in Taiwan

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Gallium (Ga) and indium (In) are metal elements belonging to the group IIIA in the periodic table, and present in trace amount in the Earth's crust. Due to their utilization in high-tech industries in Taiwan, occasional higher concentrations of Ga or In in ground water near Hsinchu Science Park, where many semiconductor companies/factories are located, were reported, indicating their potential risk to environmental and human health. Soil microorganisms usually provide good resources to ameliorate impacts on the environments caused by metal contamination. The purpose of this study was to identify candidate bacteria with capability of reducing toxicity of Ga and In in the environment. Using nutrient agar containing Ga or In, we obtained 6 and 18 bacterial isolates on each medium based on colony morphology. Further investigation confirmed that 11 isolates are resistant to 200mg L⁻¹ of Ga, but only 2 isolates could survive in 100mg L⁻¹ of In. Among those metal resistant isolates, Ga-resistant strains were all identified as *Burkholderia* spp. whereas In-resistant isolates were identified as *Luteibacter* sp. and *Stenotrophomonas* sp., respectively, based on 16S rDNA sequence analysis. Surprisingly, these two In-resistant isolates also showed moderate degree of resistance to Ga. Identification of bacteria tolerant to toxicity of technology critical elements in this study supplies not only potential agents for bioremediation, but also bacterial materials for further study of the mechanism underlying metal tolerance as a base to develop better strategies for treatment of Ga or In contamination in the future.

Elemental and isotopic profiling for food authentication

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The significant increase of consumer interest for food products, having a well proved traceability, has determined the development of combined analytical methods to differentiate among different products categories as function of: geographical origin, animal or vegetal species differentiation, organic products vs. conventional growing conditions. The price difference among distinct categories of apparently similar food types has created a financial enticement to mislabel and try to pass off cheaper products as premium commodities. Stable isotope ratios of so-called bio-elements ($^2\text{H}/^1\text{H}$; $^{18}\text{O}/^{16}\text{O}$; $^{13}\text{C}/^{12}\text{C}$; $^{15}\text{N}/^{14}\text{N}$) in association with elemental profiling and chemometric methods were successfully used for differentiation among distinct food and beverages categories. The experimental data processing was made by applying chemometric techniques: first Analysis of Variance (ANOVA), followed by Pearson correlation and Linear Discriminant Analysis (LDA). In this study, the association potential of isotopic and elemental profiling, for the food discrimination, according to: geographical origin, species type and agricultural practices of different commodities was presented and discussed.

Assessment of chronic toxicity of REE-enriched sediments from a prospective mining area on *Myriophyllum alterniflorum*

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Rare earth elements (REE) are strategic compounds increasingly used in emerging technologies. Their future exploitation with opening new mining areas contribute to their increased mobility and will influence their fate and effects in the environment. Despite the growing number of studies on REE toxicity, their effects on aquatic organisms is not fully understood. Moreover, their effects on organisms living in the sediments and more specifically aquatic plants, remain scarce. Hence, the aim of the current study is to assess the chronic toxicity of naturally REE-enriched sediments on *Myriophyllum alterniflorum*. Effects on growth, pigment and phenolic compound content and dry matter content are assessed along with uptake and translocation of REE to various plant parts. The experiment is performed in a water-sediment system. *M. alterniflorum* from axenic cultures are used for the present study. Plants are exposed to two REE-enriched sediments for 6 weeks; namely N2 and B4, and control sediment. N2 and B4 were collected in North Quebec, Canada. They were selected based on their parent materials. The physico-chemical analyses showed that B4 contains the highest amount of REE and has the highest fine grain fraction. The first results show that both sediments lead to a growth inhibition in term of length and fresh biomass. The plants exposed to REE-enriched sediments present longer roots than those of the control sediment. This could be linked to a lack of nutrients in contaminated sediments, or interactions between REE and plant nutrients. These results may indicate a phyto-available fraction of REE from the sediments that leads to significant changes in plant growth behavior, and may also hint on a potential transfer of REE through the food web chain. The present study provides first insights on REE behavior between sediments and plants, and their potential chronic toxicity on aquatic organisms around prospective mining areas.

Environmental fate and toxicology of Platinum Group Metals: areas for improvement

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Platinum Group Metals (PGMs) are widely used in everyday life (electronics, catalysts, jewelry...). Under the EU REACH Regulation, there is the obligation for industry to do an assessment for each substance put on the EU market. Therefore, industry reviews the available scientific data, and performs additional testing -where needed- to create a REACH compliant dossier. However, during the dossier preparation and finalization, it is noticed there are still areas for improvement for the PGMs. Some illustrations:

1/ It is known that PGMs have strong coordination properties to (in)organic ligands. As such, it can be expected that a re-speciation occurs in the environment (like in water or soil solution), depending on their physico-chemical properties. However, this environmental speciation remains an understudied field, as well as the effects of various coordination structures of a metal on the toxicity to living organisms.

2/ There are toxicity data available in public literature. However, data are only for a limited amount of substances and are for acute toxicity endpoints only. Chronic toxicity and field data are rare, although they are most relevant. Also, data have mostly been generated for aquatic media, whereas data in real sediments and soils are often lacking.

3/ Bioaccumulation data are available for some PGMs. However, bioaccumulation data for metals in higher organisms often show an inverse relationship with exposure concentration, and trophic dilution processes are observed for other metals. Also, the role of the metal coordination structure on their bioaccumulation is unclear. The metals' industry is continuously investing in further developing relevant scientific principles in order to allow proper and reliable assessments worldwide. In this perspective, a communication of the main areas for improvement and pending question marks to the interested and specialist scientific community could be welcomed.

Thallium accumulation in the intestinal tissue, homogenate and cytosol of brown trout and Prussian carp from two Croatian rivers

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Thallium is a rare heavy metal but its high toxicity, water solubility and tendency of bioaccumulation made it a US EPA priority pollutant. It is generally present in the environment at low levels but human impact has increased its content so it should be strictly monitored in the environment.

Accordingly, Tl levels were measured in brown trout from the karst Krka River and Prussian carp from the lowland Ilova River, both inhabiting the area affected by the industrial waste outlets. We compared Tl distribution among intestinal tissue, its homogenate and cytosolic fraction since whole tissue concentrations do not necessarily reflect metabolically available and potentially toxic metal levels, but rather the total accumulation. Cytosolic fractions, containing sensitive biomolecules, lysosomes and microsomes, reflect biologically and trophically available metal levels in the organisms. Thallium concentrations were measured by HR ICP-MS in digested tissue, homogenates and cytosols of fish intestine in two seasons (autumn, spring) and two sites (reference, polluted).

In all intestinal fractions Tl concentrations were around 20-30 times higher in trout than carp, i.e. 19-47 µg/kg in tissue and homogenate and 9-31 µg/kg in cytosol of brown trout; 1.2-2.1 µg/kg in tissue and homogenate and 0.5-0.9 µg/kg in cytosol of Prussian carp. Despite these differences, ratio of Tl levels between homogenates and whole tissues was comparable in both species (0.86-1.03). On the other hand, the ratio between cytosolic and total Tl concentrations ranged 0.5-0.7 in brown trout and 0.3-0.5 in Prussian carp depending on the sampling site and/or season.

Therefore, Tl is partly present in the metabolically available fraction of fish intestine, which could potentially be toxic. Although Tl concentrations in the river water were comparable between the karst and lowland rivers (4-9 ng/L), Tl bioaccumulation showed species-, season- and site-specific differences.

Distribution of some less studied trace elements (Ga, Ge, Nb, Te, Tl, W) and some rare earth elements (La, Y) in sediment cores from unpolluted marine and freshwater lakes in Croatia

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Vertical profiles of some less studied trace and rare elements (Ga, Ge, Nb, Te, Tl, W, La, Y), including also some of technology-critical elements, were studied in sediment cores taken in marine and freshwater lakes located within protected areas in Croatia. The marine lake (the Lake Mir) is a part of the Nature Park Telascica, and represents a small, shallow marine lake situated in the south-eastern part of the Dugi otok Island in a karstic landscape of the eastern Adriatic coast. The freshwater lakes (the Plitvice Lakes), a pristine hydrological system of sixteen karst lakes, are situated in a sparsely populated area of the northwestern Dinarides, central Croatia, and are included on the UNESCO World Natural and Cultural Heritage List. These lakes are not directly exposed to the anthropogenic influence, so it is interesting to study such environmental archives and evaluate the existence of possible temporal trends of concentrations of less studied trace elements. Undisturbed sediment cores, between 50 and 100 cm long, were collected using the Uwitec gravity corer and subdivided into 2 cm segments. After drying and homogenization samples were digested in a microwave oven by a two-step total digestion procedure and the trace elements were analyzed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICPMS). Quality control of the used analytical method was verified by the analysis of available geological certified reference materials (CRM) certified for the content of less studied trace elements. In the paper vertical profiles and geochemical behavior of less studied elements will be discussed in comparison with chosen major and trace elements which can serve as indicators of terrigenous and anthropogenic influences and sedimentation processes.

Investigation of gallium and indium responsive genes in yeast

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New technologies require the ever-increasing use of technology-critical-elements (TCEs) such as gallium and indium, with essential physico-chemical properties, implying a fortiori, the increasing metal contamination of the environment. Gallium and indium share the same electronic configuration and oxidation state as aluminum. However, only a few studies mention their effects on eukaryotic organisms, limiting the understanding of the cellular pathways and functions involved in their toxicity and detoxification mechanisms. *Saccharomyces cerevisiae*, a well-known eukaryotic model, was used to perform a tolerance/sensitivity screen for gallium, indium and aluminum by using a knock-out mutant collection. The tolerance and sensitivity levels of mutants for the genes and functions identified during the screening allowed to establish their involvement's degree in the response to these metals. The analysis of the over-represented functions for each of these elements was done by the study of GO-terms (Gene Ontology). As a result, a higher toxicity of indium, close to that of aluminum, was observed with a lower toxicity of gallium. We have observed common responses to these metals, but also gallium and indium specific responses. In addition, comparison with data from other screening studies in the literature has revealed specific mechanisms. The use of the eukaryotic model *Saccharomyces cerevisiae*, which has many orthologous genes with humans, could provide insights in the effect of these TCEs on human health.

Determination of sub-pico-molar levels of platinum in the Krka river estuary (Croatia)

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Platinum (Pt) abundance and distribution on the Earth's surface mainly depends on anthropogenic activities, which accounts for ~80% of Pt fluxes [1], whereas ~45% of produced Pt is used for catalytic converters in cars. Insufficient data on Pt distribution, behaviour and role in aquatic environment placed Pt on the list of potentially eco-toxic elements [2]. One of the reasons for scarce Pt data is extremely low concentration of Pt (<1 pM) in natural waters. Analysis of Pt in natural water requires extremely sensitive analytical techniques, among few, ICP-MS with preconcentration step [3] and catalytic stripping voltammetry [4] are the most widely used. In order to increase the sensitivity using voltammetric analysis, we tested second, third and fourth derivative signal transformation [4]. By using derivative signal transformation and adapted voltammetric procedure we obtained limit of detection (LOD) for real samples of 15 fM, which is even lower than we reported previously [4]. Optimized method was used to determine Pt distribution in the Krka River estuary. Horizontal and vertical profiles (salinity <1 to 39) of Pt were examined in discrete and composite samples. Measured concentrations of Pt are extremely low (<1 pM), among the lowest concentrations found in literature for estuarine systems and ocean waters. Concentrations of Pt gradually increased towards sea end-member, with slight deviation from the conservative mixing line in the region of the urbanized area (Šibenik town) during summer period. In analysed samples Pt was mainly present in dissolved form.

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Overview of the industrial applications of Heavy Rare Earth Elements (HREE)

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The Rare Earth Elements (REE) are a group of chemical elements that exhibit a range of special (some unique) properties which are used in many modern and “green” technologies. The International Union of Pure and Applied Chemistry defines the Rare Earth Elements as the 15 lanthanides together with yttrium and scandium. The REEs are subdivided into Light Rare Earth Elements (LREE) and Heavy Rare Earth Elements (HREE), although authors disagree on which elements are assigned to each group. In this paper, the following elements are included in the HREE group: terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The HREE group are some of a range of strategic elements that have not been exploited in significant quantities, but which are now attracting new interest because of likely new sources and potential use in new technologies. HREEs are less abundant than the LREE and are thus of higher value. Some HREE are listed as critical as the use of these elements is outstripping supply. This paper gives a short overview of the use of Heavy Rare Earth Elements (HREE) in modern industrial applications.

Thallium in cement kiln dust

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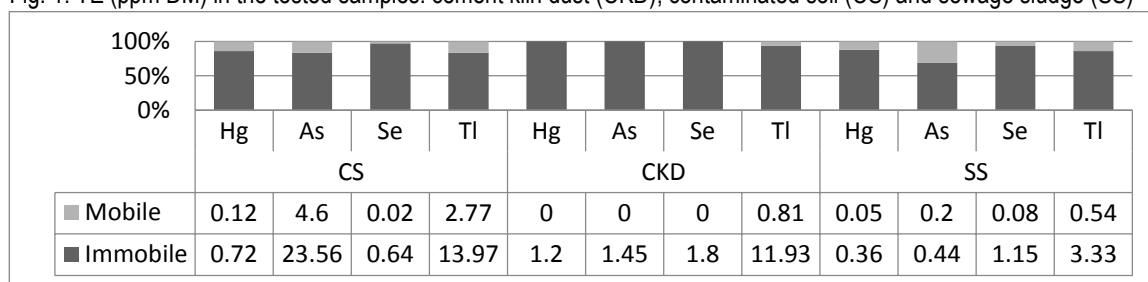
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Thallium (Tl) minerals are rare in nature, thus Tl is often excluded from the list of metals to be analysed despite of its high toxicity [1]. Thallium does not have such economic value as other trace elements (TE) – only about 15 tons is produced worldwide annually. But it is estimated that 2000-5000 tons of Tl per year are mobilized by various industrial processes. Considerable amounts of Tl can be released into the atmosphere from coal-burning power plants, oil refineries, metal smelting, cement production and other industries [2]. Since Tl compounds are volatile at high temperatures, they are not efficiently retained by electrostatic precipitators or other emission control facilities [3]. Aim of this study was to determine concentrations of Tl (alongside with Se, As, Hg) in cement kiln dust (CKD) originated at JSC 'Akmenes Cementas' (Lithuania), to evaluate its mobility as EDTA extractable fraction as well as bioavailability by lettuce cultivated on Tl enriched growing media.

CKD was sampled from electrostatic precipitators of cement manufactory as pyro-processing particulate emissions. It consists of fine mineral particles captured by air cleaning installations after the dehydration of cement ingredients in rotary kiln at high temperatures ($\approx 1500^\circ\text{C}$). Contaminated soil (CS) was taken at a territory of a former sleeper impregnation plant of "Lithuanian Railways". Sewage sludge (SS) was sampled at Kaunas (Lithuania) wastewater TP after dewatering in centrifugation unit. Mean concentration of Tl in CKD samples (taken twice per month during 6 month period) was 11.0 ppm (STDEV 1.49), min and max concentrations ranging from 7.9 up to 12.8 respectively, Tl in CS samples – 15.1 ppm DM (STDEV 2.02), min and max – 11.8 and 16.7. Data on the total (*aqua regia* extractable) and mobile (as EDTA-extractable) concentrations of Tl, As, Se and Hg in CKD and initial mixture components are presented in Fig. 1.

Fig. 1. TE (ppm DM) in the tested samples: cement kiln dust (CKD), contaminated soil (CS) and sewage sludge (SS)



CS and SS samples were mixed with CKD to produce stabilized mixtures with 20% immobilising additive; these were used as growing media for Tl phytoextraction in greenhouse conditions.

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Study of TCEs levels in seaweed from the Galician coast (North West of Spain)

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Seaweeds are a source of essential minerals but, they also can concentrate non-essential elements from the surrounding seawater. Therefore, seaweed can be used for monitoring the levels of pollution. The interest in the analysis of the elemental composition of edible seaweed has also increased in recent years, due to the rise in their consumption by western population.

The objective of this study is the analysis of TCEs in edible seaweed from the Galician coast. These elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS) after microwave acid digestion with nitric acid and hydrogen peroxide. The measurements were performed in KED mode (collision cell with He) and applying mathematical corrections to minimize the interferences.

Calibration was performed using the standard addition method in a concentration range from 0 to 100 $\mu\text{g L}^{-1}$. The analytical characteristics of the method (limits of detection, analytical recovery, reproducibility...) were also evaluated. The method was applied to TCEs determination in several types of seaweed samples (brown, red, green) commercialized in Spain.

Acknowledgements

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Detection of arsenic in natural waters by voltammetry

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Biogeochemical controls on arsenic (As) cycles/speciation have been studied for many years, yet little is known about As dynamics in coastal waters. Arsenic is a metalloid ubiquitous in the environment, with its sources being of natural and anthropogenic origins. It is classified as a Group 1 carcinogenic substance (1) and presents a public health risk impacting over 70 countries worldwide, which makes monitoring of As concentrations in the aqueous environments a priority. Arsenic in the water environment is mainly present in the form of inorganic trivalent (As(III) - more toxic) and pentavalent (As(V) – less toxic) oxyanions.

Arsenic can be detected by using voltammetry (2-4). In this work an antifouling gel coated gold microelectrode (GIME) was used for direct quantification of the fractions of As(III) and As(V) available for bio-uptake, using an on board voltammetric setup during a one-week scientific cruise in the Gironde Estuary in the SW France. The concentrations of As(III) and As(V) in the fraction size considered to be available for uptake were between 0.7 and 3.4 nM and between 0.9 nM and 22.9 nM, respectively, while the total dissolved concentrations of As(III) and As(V) were between 0.93 and 5.85 nM, and between 13.05 and 36.2 nM, respectively.

Optimization of the system for detection of arsenic at natural pH, the differences between on board conducted measurements and complementary laboratory analyses contributing to the validation of the GIME measurements, and a deeper understanding of the distribution of arsenic species in the estuary will be presented.

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X-ray fluorescence analysis of Rare Earth Elements: Analytical performance of different instrumental configurations

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X-ray fluorescence (XRF) spectrometry is a powerful tool for the direct analysis of solid material that has been used since early 80's for the determination of minor and trace elements, such as rare earth elements, in minerals and rocks .

Wavelength-dispersive XRF (WDXRF) has been classically used for the analysis of rare earth elements but development of new detection systems with better efficiency and resolution in the spectrum enable the use of energy-dispersion XRF (EDXRF). At present, WDXRF and different configurations of EDXRF are used for the analysis of pressed powder pellets or fused glassy beads containing REEs.

The advantage of XRF is the direct analysis of solid material, without sample digestion, which could be presented directly as powder or pressed pellet. The disadvantage could be a high error and a high average lower limit of detection (LLD) of about 2–10 ppm .

Obtaining reliable analytical results can only be achieved through careful selection and optimization of the spectral lines. Usually the REE's are evaluated through the L-lines located in the region from 4 to 10 KeV. However, this region is characterized for the presence of other major, minor or trace elements such as Ti, Cr, Mn, Fe, Ni, Cu or Zn and many overlaps should to be corrected by spectral deconvolution. The use of alternative REEs lines at high energies could be an option but high energy excitation is required and no much instrumentation can work at the necessary power.

We analysed REE's content in rocks, mining wastes and precipitates of acid mine waters by using different XRF instrumental configurations. Results are compared with those reported using ICP analysis procedures.

Characterization of TCEs Speciation in natural systems: A critical step for their ecotoxicological risk assessment

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The current development of new technological and energy-related applications has increased the use and demand of the Technology-Critical Elements (TCEs), and therefore their potential input to the environment. Thus, a significant scientific effort is currently being made on the assessment of their environmental impact. In this study we compared different assays (ecotoxicological, cyto-genotoxicity and toxicokinetic tests) performed with TCEs for different aquatic media and organisms. Results obtained suggest that: i) non-steady state speciation conditions are usually observed for several TCEs in short-term experiments (e.g. Pt, Gd); ii) the presence of certain ligands (e.g. phosphates), may lead to precipitation of insoluble TCEs complexes at elevated concentrations (e.g. Gd) and may lead to erroneous ecotoxicological interpretations; iii) the interaction in metal mixtures (e.g. Ce, Gd, Lu), as they are usually present in nature, reveal synergistic/antagonistic effects. Results presented in this study show that TCEs, after few days added to different media, does not reach speciation equilibrium conditions and is impacted by presence of other compounds (e.g. metals, complexing ligands) in the media. Therefore, misleading ecotoxicity data may result without a clear understanding of the complexation and reaction kinetics of TCEs in natural aquatic systems.

Studies on toxicology profile of rare earth doped oxide materials

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Rare earth doped oxide materials have interesting physical and chemical properties that can be implemented in various technological and biomedical applications. These materials are currently being investigated for memory devices, battery applications in technological field. On the other hand these materials are intensively studied for various biomedical applications such as cancer cell imaging agents, MRI contrast agents, drug delivery and therapy. The toxicity of such material is a prime concern towards their translation into real field application. In the current study we synthesised various rare earth doped magnetic oxide materials and studied their toxicology profile on various cells as well as on blood. Materials showing toxicity that is dependent on elemental composition and nano surface properties. We believe this study will set a guideline for such type of material's translation to real field applications.

Human health vs urban geochemistry during the anthropic times

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Following the need to deliver innovation in the epoch that most currently refers to as Anthropocene we have undertaken joint research on medical geochemistry that combines a flair for methods development deriving from our different scientific background. At the BiGeA Department (University of Bologna) much work has been done on waste management and critical raw materials recovery from incinerators ashes, with the stimulating discussion at the CA15115 (MINEA), especially in working group n. 3. Our research on geochemistry extends to the environmental characterisation and impact assessments (at Ravenna Campus of Environmental Sciences) until the reach of molecular biology and cancer research (at the National Cancer Institute CRO, University of Trieste, Aviano).

Here we report our comparative analysis of urban environmental processes and human health issues that can serve as a starting point for further studies during the anthropic times. In particular, we explore the linkers between the environmental issues related to landfill and municipal solid waste incinerators and the incidence of human health threats. The geographic boundary of the study is the highly urbanised area of the Emilia-Romagna region, Italy. We believe that we can take advantage of this workshop in Zagreb to create a link between different sectors and try to find a common language to work together.

Seasonal and spatial distribution of technology critical elements in surface sediments of the river Danube

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In this paper, the seasonal distribution of the selected elements including technology-critical elements (TCE) in the river sediments was investigated. The samples were collected from 1141 km to 846 km of the Danube River and three tributaries on this way in the following periods: April 2016, September 2016 and April 2017. The heavy metal concentration in the sediments connected with hydro-power dam and accumulation of sediments in the reservoir systems Iron gate I and Iron gate II were analyzed.

River sediments were collected from the river bottom at the central and the deepest part using an Ekman grab sampler and air-dried in a thin layer in the dark at room temperature (23 ± 1 °C). After drying, the samples were homogenized using a pestle and mortar and sieved through a 1-mm sieve to ensure sample homogeneity. All samples were analyzed applying Instrumental Neutron Activation Analysis and ICP techniques. Principal Component Analysis (PCA) and Power transformation as a pretreatment method were applied for analysis of experimental data.

It was found that the increase in the amount of sediment in the reservoir prior to the dam Iron gate I was accompanied by an increase in the concentration of the following metals: antimony, arsenic, chromium, europium, neodymium and samarium. Also, it was found that the concentrations of the investigated elements were lower in September in comparison with April, which is due to the lower water level in that period and therefore to the smaller amount of accumulated sediments.

Subacute toxicity study on rats co-exposed to silver and ruthenium(III) ions via water

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Ruthenium is one of the rare earth elements, often used in electronics, as a catalyst, in medicine, for jewelry or in computers industry. It is also considered today one of the so called *critical element* as it is often used in technology, but without knowing sufficiently about its toxic effect. Silver on the other hand is well known for its antiseptic, antibacterial or immunostimulant properties, being used for this reason in medicine to obtain silver nanoparticles for therapeutic aim. The combination of ruthenium with silver compounds may be an alternative for platinum based anti-cancer drugs which are known to have a high toxicity.

The present study investigated the co-exposure to ruthenium (III) on the subacute toxicity of silver ions in rats after daily administration of low doses for 28 days by oral gavage. Three groups of Wistar rats were used for this aim (n=6): M - the negative control group, Ag - the treated group with AgNO₃ (9 mg/kg) and Ag+Ru – the treated group with AgNO₃ (9 mg Ag⁺/kg) and RuCl₃ (2,25 mg Ru³⁺/kg). The subacute toxicity was investigated by: 1) the evaluation of several specific biochemical and hematological parameters after 14 and 28 days of exposure, 2) the evaluation of specific oxidative stress biomarkers from liver and kidney, 3) histopathological investigation of liver and kidney tissue samples after 28 days of exposure, and 4) silver and ruthenium concentration determination in urine, liver and kidney parenchyma after 14 and 28 days of exposure.

The obtained results show that subacute exposure to low doses of silver ions slowly changes some of the oxidative stress biomarkers (MDA, GSH and GSH/GSSG ratio) without affecting the other investigated parameters. The co-exposure to low doses of ruthenium (III) mitigated the oxidative stress caused by silver ions. This is the first *in-vivo* study investigating the toxic effect of co-exposure in low doses of silver and ruthenium ions, and the obtained results may justify further research on this subject mainly on some possible competitive mechanism investigation.

Black shale as vanadium resource — an Estonian example

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Black shales are fine-grained sedimentary rocks rich in organic matter and several metals. Some of the significant high-concentration metals are uranium (U), molybdenum (Mo), vanadium (V), zinc (Zn), lead (Pb), but occasionally also such valuable metals as the PGE-s, gold (Au) and rhenium (Re). Typically, the metalliferous black shales have been exploited as a resource of U or oil/gas, and thus they have been called two-fold energy resources. Hereby we present an updated overview of the Estonian black shale deposit with an emphasis on the critical element V.

The Estonian black shale (known as graptolitic argillite or earlier dictyonema shale) was also exploited for the extraction of U in the 1950-s for a short period. Because the black shale deposit occurs nearly on 1/3 of the country's territory, huge potential for metallic resources (V, U, Mo, Zn, etc.) is evident. With the recent increase in the V prices, it has been acknowledged that it can be the most valuable constituent of black shale, proportionally about 85% when comparing the current U, Mo, Zn and V prices. The "order of magnitude" reserve of V as vanadium pentoxide is estimated over 88 million tons. V is one of the 27 critical raw materials listed by the European Commission and thus the Estonian deposit or similar black shale deposits in Sweden or elsewhere could provide the necessary resources. Nevertheless, black shales have the potential to be the sources for many critical and non-critical materials.

New, simple, fast and cheap procedure for direct determination of ultra trace concentrations of Ge(IV) in environmental waters

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Germanium belongs to the group of elements of critical technological importance due to the development of modern industry. Among the others it is used in the manufacture of semiconductors, lasers, special optical glasses and in the production of infrared sensing and identification systems. As a result, the world production of germanium products is now increasing and the level of it in the environment is beginning to rise, so it is necessary to develop sensitive, low-cost and simple procedures for determining germanium in environmental samples.

This communication provides a simple and fast procedure for Ge (IV) determination, which allows the analysis of natural water samples with complicated matrices. The proposed procedure is based on the adsorptive stripping voltammetric method of germanium determination using a renewable mercury film silver based electrode (Hg(Ag)FE) as a working electrode [1]. The composition of the supporting electrolyte, accumulation potential and time on the germanium voltammetric signal were verified. In the optimized conditions the detection limit for Ge(IV) determination was about 0.1 nM for a deposition time of 30 s. The influence of interfering substances present in the matrices of natural water samples on the Ge(IV) signal was precisely examined and the satisfying minimization of these interferences was proposed. Analytical results of analysis of natural water samples collected from eastern areas of Poland showed that the proposed procedure of trace germanium(IV) determination is suitable for direct environmental water analysis.

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Monitoring ecological impacts of metallic pollution in urban rivers using field-bioaccumulation study of a filter-feeding bivalve

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Urban rivers are among the most threatened ecosystem worldwide primarily due to the extensive water pollution caused by various human activities. Traditional river monitoring assesses water pollution based on the measurement of contaminant concentrations of the ambient environment or the presence/absence of the pollution sensitive or tolerant species. The long-term impacts of bioaccumulative metals and other contaminants on the river ecosystem could be underestimated and thus leading to serious mismanagement. Urban rivers in Taiwan, as similar to other parts of monsoonal Asia, are severely impacted by water pollution due to agricultural and industrial development. These rivers are also strongly influenced by monsoon climate, the seasonal spates could complicate the bioaccumulation impacts via increasing surface runoff and flow. Yet, limited bioaccumulation studies have been conducted in the urban rivers of monsoon region. In this study, we investigated the metal bioaccumulation of a filter-feeding bivalve *Corbicula fluminea* in two urban rivers (Danshuei River and Datun River) in northern Taiwan by field bioaccumulation study. Metallic concentrations of water, sediment in the studied rivers and the experimental *C. fluminea* tissues were measured with ICP-MS and IP-OES. Our results suggest that *C. fluminea* is a good indicator for metallic pollution in urban rivers from monsoonal Asia due to its differential accumulation capacities of different metals. Our findings confirm the high potential of *C. fluminea* for biomonitoring and ecological impacts for metal bioaccumulation of the urban rivers.

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