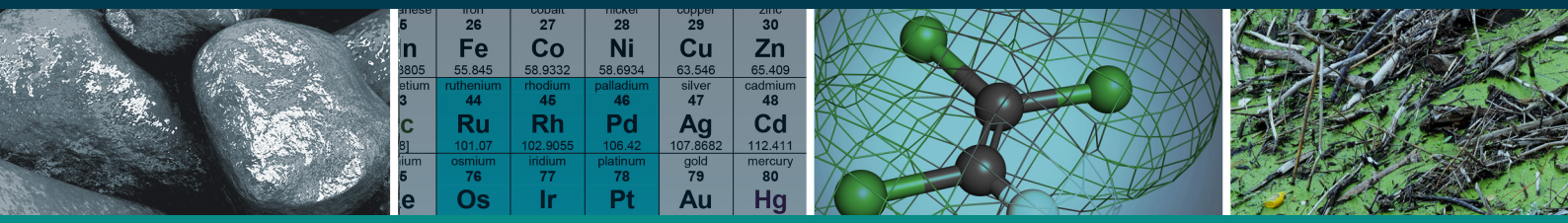
מכון ויצמן למדע
WEIZMANN INSTITUTE OF SCIENCE



COST Action TD 1407

Workshop on Environmental Concentrations, Cycling & Modeling of Technology Critical Elements

January 18-19, 2017

The David Lopatie Conference Center

Weizmann Institute of Science

ABSTRACT BOOK

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NOTICE

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Wednesday, 18 January

8:30 Registration

9:00 Opening
Prof. Gilad Haran, Dean of the faculty of Chemistry, Weizmann Institute of Science, Israel

9:10 **Antonio Cobelo-Garcia,** chair of COST Action TD 1407
Introduction to COST Action TD 1407

SESSION 1
SOURCES OF TCE'S
chair: **Montserrat Filella,** University Geneva, Switzerland

9:20 **Keynote 1**
Philip Nuss, European Commission, Joint Reseacrh Centre, Italy
Towards better monitoring of critical raw materials in Europe

9:50 **Eckhard Helmers,** University of Applied Science Trier, Germany
Platinum as a precious and critical element ? Lessons learnt from Life Cycle Assessment

10:10 **Erika Machacek,** Geological Survey of Denmark and Greenland
Tracing Rare Earth Element uses in the Danish economy

10:30 Coffee Break

11:00 **Athanasios Karamalidis,** Carnegie Mellon University, USA
Selective adsorption and solid phase extraction of rare earth elements from aqueous Media

11:30 **Yoshiko Fujita,** Idaho National Laboratory, USA
Potential impacts of rare earth element recycling in wastewaters on biological wastewater treatment

11:50 Poster flash presentation (1 min short introduction, 1 slide)

12:10 Lunch Break and Poster Session

SESSION 2
ANALYTICAL METHODS FOR TCE'S
chair: **Jörg Schäfer,** University Bordeaux, France

13:30 **Keynote 2**
Ilia Rodushkin, Luleå University of Technology, ALS Laboratory Group, Swede
Determination of technology critical elements by ICP-SFMS

14:00 **Karel Folens,** Ghent University, Belgium
Characterization of nanoparticulate platinum in road dust leachate

14:20 **Florian Weigl,** Technical University Munich, Germany
An analytical platform for species selective preconcentration, size determination and quantification of rhodium nanoparticles

14:40	**Beata Godlewska-Zylkiewicz,** University of Bialystok, Poland Determination of Platinum Group Metals in environmental matrices; methods for PGE separation
15:00	Coffee Break
15:30	**Joanna Szpunar,** LCABIE, Pau, France Single particle (SP)-ICP MS characterization of the uptake and metabolism of platinum and palladium Nanoparticles by plants
15:50	**Josep Galceran,** University of Leida, Spain Indium speciation and availability in aquatic solutions probed with electroanalytical techniques
16:10	**Franz Lehmann,** Helmholtz Centre for Environmenatl Research - UFZ, Germany A new method for Ge speciation using HPLC-ICP-MS
18:30	Dinner

Thursday, 19 January

SESSION 3

TCE'S IN THE ENVIRONMENT I

chair: **Birgit Daus,** Helmholtz Centre for Environmental Research, Germany

9:00	**Keynote 3: Michael Bau,** Jacobs University, Germany Tracing anthropogenic rare earth elements in the environment
9:30	**Ester Torres,** Spanish National Research Council, Spain Acid mine drainage: a possible source of rare earth elements and yttrium
9:50	**Carlos Ruiz,** University of Huelva, Spain Mobility of rare earth elements (REE) from unwanted by-products of the fertilizer industry
10:10	**Aya Schneider-Mor,** Geological Survey of Israel Environmental changes in the southern Tethys productivity belt: a multi-proxy study of the phosphorite deposition
10:30	Coffee Break
11:00	**Montserrat Filella,** University of Geneva, Switzerland Environmental concentrations of TCEs: are they really increasing?
11:20	**Kirsty Crocket,** Scottish Association of Marine Science, UK Source, cycling and circulation effects on seawater rare earth elements in the NE Atlantic
11:40	**Sebastien Rauch,** Chalmers University of Technology, Sweden A peat-based record of atmospheric iridium and osmium accumulation
12:00	**Remi Marsac,** University of Rennes, France Cerium(III/IV) aquatic geochemistry: what can be learnt from actinide analogues?
12:20	Lunch Break and Poster Session

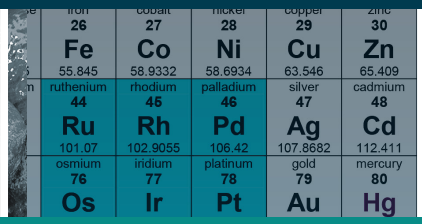
SESSION 4

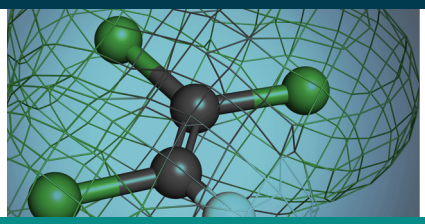
TCE'S IN THE ENVIRONMENT II

chair: **Michael Bau,** Jacobs University Bremen, Germany

13.40	**Loic Martin,** Institute de Physique du Globe de Paris, France Complexation study of thallium with natural organic matter using donnan membrane technique
14:00	**Andreas Voegelin,** EAWAG, Switzerland Thallium sorption on illite and its importance in soils
14:20	**Gijs Du Laing,** Ghent University, Belgium Presence and mobility of Nb, Ta, Tl and In in sediments and soils of the Scheldt estuary and around smelters in the Campine region (Belgium)

14:40	**Sarah Jane White,** Princeton University, USA Deposition of rare earth elements and indium from the atmosphere to a bog in the Northeastern United States
15:00	Coffee Break
15:20	**Melina Abdou,** University of Bordeaux, France Recent platinum contamination of a major European estuarine system: a bivalve biomonitoring study
15:40	**Sonja Zimmermann,** University of Duisburg-Essen, Germany Biological availability, uptake and bioaccumulation of Pt, Pd and Rh by freshwater animals
16:00	**Clara Almecija,** Instituto de Investigaciones Marinas, Spain Sedimentary behaviour of natural and traffic-borne platinum in the salt marshes
16:20	Closing Discussion





POSTER SESSION

Maria Wiesinger
Short term scientific mission (STSM) report on: technology critical elements in our environment - project

Nevenka Mikac, Rudjer Boskovic Institute, Croatia
Sources and distribution of rare earth elements in the Zrmanja river estuary, Adriatic sea, Croatia

Dana Alina Magdas, National Institute for Research and Development, Romania
Chemometric discrimination of Romanian vegetables based on their elemental fingerprint

Nadya Teutsch, Geological Survey of Israel
Leaching and phytoavailability of trace elements in soils amended with coal fly ash (FA) treated biosolids

Ana Romero-Freire, University De Lorraine, France
(Bio)Accumulation of REE in a natural area: from rocks to plants

Elzbieta Zambrycka-Szelewa, University of Bialystok, Poland
Determination of ruthenium in environmental samples using imprinted polymeric sorbents by ETAAS

Teba Gil-Diaz, University of Bordeaux, France
Tellurium (Te) reactivity in estuarine gradients and implications for accidental radionuclide release scenarios

Gila Merschel, Jacobs University Bremen, Germany
Technology critical metals in the shells of freshwater bivalve "Corbicula fluminea": bioavalability and anthopogenic gadolinium and other anthopogenic rare earth elements in German rivers

Nicoleta Vedeanu, University of Medicine and Pharmacy, Cluj-Napoca, Romania
Macro-, micro- and trace elements distribution in different growing stages

Nathalie Korf, Technical University of Berlin, Germany
Adapted round robin test: Analytical methods for multielement analysis of anthropogenic ores

Nathalia Ospina Alvarez, University of Potsdam, Germany
Solid phase extraction of chromiun, thallium and arsenic using SGX C18 modified with APDC as sorbent

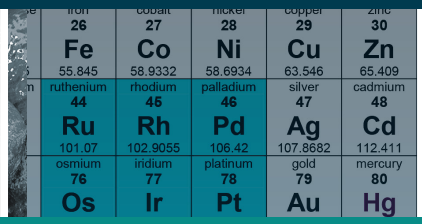
Kerstin Ringering, University of Bremen, Germany
Towards understanding the mobility of indium and gallium in groundwater systems: constraining the role of sorption in sand column experiments

Madeleine Laitz, Imperial College London, UK
Toxicological and Environmental Analysis of Rare Earth Elements and Indium

Patricia Neira, Instituto de Investigacións Mariñas, Spain
Time-Series (1991-2014) Trends of Technology-Critical Elements Accumulation in Mussels from an Urban Coastal Area (Vigo Ria, NW Iberian Peninsula)

Antonio Cobelo-García, IIM-CSIC, Vigo, Spain
Dissolved Rare Earth Elements in Estuarine and Coastal Waters of the Gulf of Cádiz (South Spain)

Pedro Brito, Portuguese Institute of Sea and Atmosphere, Lisbon, Portugal
Sources and distribution of yttrium and rare earths in Tagus Estuary sediments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Co
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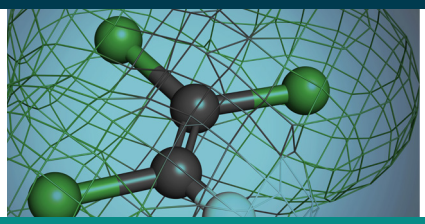

ABSTRACTS

Towards better monitoring of critical raw materials in Europe

P. Nuss
European Commission, Joint Research Centre

The characterization of elemental cycles has a rich history in biogeochemistry. Famous examples include the global carbon cycle, or the cycles of the 'grand nutrients' nitrogen, phosphorus, and sulfur. Knowledge of natural cycles has evolved over many decades as new sinks and sources have been discovered and missing flows between reservoirs have been quantified. More recently, efforts to better understand the cycles of elements in the man-made environment ('anthroposphere') have increased. Tools such as material-flow analysis (MFA) can help understanding how elements are transported and accumulated in man-made technological systems.

However, to date both biogeochemical cycles and MFA studies suffer from narrow system boundaries, failing to fully illustrate relative anthropogenic and natural flow magnitude, natural reservoirs that are not in mass balance, and the degree to which human activity has perturbed the natural cycling of elements. As a result, only a handful of global elemental cycles, inclusive of natural and anthropogenic stocks and flows, have been constructed quantitatively, but no cycles of this kind exist at the level of the EU. This happens despite the fact that a combination of both natural and anthropogenic cycles can help to quantify the link between societal flows and stocks of metal and their natural cycling. They also show, in very general terms, what could be done to isolate the societal cycle further from the natural cycle – a decoupling at the elemental level.

The European Commission has recently amplified efforts to assemble data on anthropogenic material stocks and flows in the EU economy to more effectively manage its resource base. Proper monitoring of the raw materials situation in Europe and globally is crucial to increase sustainability efforts (e.g., through greater circularity of material flows) and quantify the availability, or "elemental criticality," of raw materials used in Europe. The European Commission's Joint Research Centre (JRC) provides strong scientific and technical transdisciplinary support to the EU Raw Materials Initiative and Innovation Partnership on Raw Materials. This presentation will provide a concise overview of currently ongoing efforts by the JCR to enhance the monitoring of raw materials in Europe including the development of anthropogenic cycles of technology-criticality elements. It will discuss the recently initiated Raw Materials Information System (RMIS), which aims at providing a single platform with information and knowledge on non-energy and non-food raw materials by life-cycle stage. The Raw Materials Scoreboard provides overarching indicators and integrates, in one place, knowledge from governments, academia, and business on the provision and use of raw materials in Europe and beyond. The revised EU criticality methodology aims at improved capturing of the economic importance and potential supply disruptions of raw materials. Together these tools and platforms allow a more integrated assessment of raw materials, inform EU policy making, and manage resource use more wisely. The presentation concludes with ideas on how existing anthropogenic cycles of the elements and natural cycles (anticipated within the COST action) could be increasingly combined to derive more complete material cycles for the EU and globally.

Platinum as a precious and critical element – Lessons learnt from Life Cycle Assessment

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Birkenfeld, Germany

Platinum-group metals (PGMs) enable many industrial processes, however the automotive sector is the largest user of PGMs. Because of its technical relevance and scarcity, PGM were assigned to the group of critical raw materials. Since the 1980s, particularly platinum (Pt) has received high attention in analytical and environmental science because initially it was the most important catalytically active component in three way catalysts of petrol cars, an efficient emission after treatment technology, first introduced in the USA in the 1970s, followed by European countries in the 1980s [1,2]. Pt pollution was early described due to autocatalyst emissions [3], but without danger of geochemical enrichment [4]. PGM production, on the other hand, has a highly adverse environmental impact. Accordingly, the human toxicity impact by catalyst production has been compared with the positive impact of autocatalysts on air quality by a Life Cycle Assessment (LCA) approach [1].

Today, Pt is again important in automobile technology because of a possible key role in future sustainable mobility: It is an essential component in the cell stacks of fuel cell (FC) electric vehicles. However, as autocatalysts include a few g Pt only, a current automobile FC contains 30 – 80 g Pt [5]. Besides the cost problem, this is associated with a huge adverse environmental impact. A comprehensive sustainability assessment of electric vehicles needs LCA, because the vehicle's production can dominate throughout the lifecycle, even in case of a battery electric vehicle (BEV) [6]. Full LCA modelling of Pt production using Ecoinvent database is presented and discussed here exhibiting that the above Pt content of a fuel cell causes impacts in the order of a full life cycle impact of a BEV.

References

[1] Nazmul, K.M. (2015): Does a catalytic converter cause more loss of lives than it saves? A human health life cycle assessment study. Master thesis, Chalmers University of Technology, Gothenburg, Sweden. Report no. 2015:13, 139 pp

[2] Helmers, E. (1997): Platinum Emission Rate of Automobiles with Catalytic Converters - Comparison and Assessment of Results from Various Approaches. ESPR - Environ. Sci. & Pollut. Res. 4 (2), pp 100 – 103

[3] Helmers, E., Mergel, N. (1998): Platinum and rhodium in a polluted environment: studying the emissions of automobile catalysts with emphasis on the application of CSV rhodium analysis. Fresenius J. Anal. Chem. 362:522–528

[4] Helmers, E., Kümmerer, K. (1999): Anthropogenic Platinum Fluxes: Quantification of Sources and Sinks, and Outlook. ESPR - Environ. Sci. & Pollut. Res. 6 (1), pp 29 – 36

[5] Pollet, B.G., Staffell, I., Shang, J.L., Molkov, V. (2014): Fuel-cell (hydrogen) electric hybrid vehicles. In: Alternative Fuels and Advanced vehicle technologies (Ed. Folkson, R.). Woodhead Publishing Limited, pp 685 – 735

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Tracing rare earth element uses in the Danish economy

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Centre for Minerals and Materials, Geological Survey of Denmark and Greenland (GEUS),
Øster Voldgade 10, 1350 Copenhagen,

Following the price peak of rare earth elements (REE) in 2011, the discourse on rare earth elements (REE) has expanded substantially [1]. Notions of criticality, value-added by industrial activity, and supply security have drawn upon REE as flagship minerals to illustrate their significance for specific functions in end-use products, and in particular, of their role as material constituents or components [2] [3]. Estimates on their uses have been product-specific for the global or national scale [4] [5] [6]. However, little is known about the significance of REE use for national economic activity.

This paper partially addresses this knowledge gap and traces REE use in Denmark, an economy which is internationally renowned for advancements in energy technology, construction, maritime transport, bio-technology and pharmaceutics. Empirical data has been collected from relevant firms associated with nine intermediate industrial sectors known for potential REE use [7] [8]: batteries, automobile catalysts, process catalysts, ceramics, glass additives and polishing, magnets, metallurgy and alloys, phosphors, and other, future uses.

Findings show that REE use in the form of oxides is limited in the Danish economy, and tied to advanced material research and development in high-tech engineering. REE are otherwise, knowingly, or unknowingly, sourced as part of material components and semi-finished products for further assembly, or distributive sales. In neither of these cases are notions of criticality or concerns regarding supply prevalent among these small volume users or component distributors. This illustrates that the notion of criticality is relative and tied to a firm's positioning in the value chain.

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[1] Chakhmouradian, A. R. and Wall, F. (2012) Rare Earth Elements: Minerals, Mines, Magnets (and More). Elements 8 (5), 333-340.

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[3] Massari, S., Ruberti, M. (2013): Rare earth elements as critical raw materials: Focus on international markets and future strategies. Res. Pol. 38 (1), 36-43.

[4] Du, X. and Graedel, T. E. (2011) Global in-use stocks of the rare earth elements: a first estimate. Environ. Sci. Technol., 45 (9), 4096-4101.

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[6] Habib, K., Schibye, P. K., Vestbø, A. P., Dall, O. and Wenzel, H. (2014) Material Flow Analysis of NdFeB Magnets for Denmark: A Comprehensive Waste Flow Sampling and Analysis Approach. Environ. Sci. Technol. 48 (20), 12229-12237.

[7] Castilloux, R. (2014) Rare Earth Market Outlook: Supply, Demand and Pricing from 2014-2020. Adamas Intelligence.

[8] Roskill (2011). Rare Earths & Yttrium: Market Outlook to 2015.14th edition. London: Roskill Information Services Ltd.

Selective Adsorption and Solid Phase Extraction of Rare Earth Elements from Aqueous Media

Athanasios K. Karamalidis[1]*, Jonathan C. Callura[1], Kedar Perkins[2], David A. Dzombak[1], Newell R. Washburn[2], Clinton W. Noack[1]

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The rare earth elements (REE) are commonly defined to include the naturally occurring lanthanides (Lanthanum (La) to Lutetium (Lu), excluding Promethium (Pm)) as well as the lighter, but chemically similar elements Yttrium (Y) and Scandium (Sc). Prized for their unique properties, the REE are widely applied in both consumer and industrial technologies from electronics displays and batteries to high-strength lasers and magnets[1]. However, global supplies of these materials are undiversified (with up to 95% of global demand being met by Chinese production), primarily because mineable ores are limited in number and geography [2] . Mining, which is expensive and laborious with a significant environmental burden, is currently the economically preferable method of extracting and harvesting REE. Previous research has shown that fluids generated through various industrial processes (e.g. geothermal energy production) may be enriched with REE and represent a heretofore potentially untapped source of these critical materials.

This work describes the development and application of functionalized sorbents capable of selectively extracting REE from dilute aqueous feedstocks. A suite of ligands and adsorbent supports were tested under various reaction conditions, and their capacity, selectivity, and uptake kinetics were compared directly. A range of the developed materials were tested in real and simulated brines to demonstrate the high selectivity and capacity, with REE uptake yields of up to 99.4% for lanthanides in synthetic brines. The synthesized materials demonstrated robustness and retained their adsorptive capacity after exposure to elevated temperatures (100°C) and acid/base solutions. A bench-scale column system was developed and packed with functionalized supports to simulate a potential fluid treatment scheme. Influent characteristics – such as temperature, ionic strength, and REE concentration – were varied to replicate the range of conditions that might be encountered in a full-scale treatment process. Mathematical modeling software was implemented to make projections based on experimental results.

References:

[1] Bauer, D.; Diamond, D.; Li, J.; Sandalow, D.; Telleen, P.; Wanner, B. US Department of Energy Critical Materials Strategy; 2010.

[2] U.S. Geological Survey Mineral commodity summaries 2015; 2015; p 196 p.

Potential impacts of rare earth recycling wastewaters on biological wastewater treatment

Yoshiko Fujita

Idaho National Laboratory

Increasing demand for rare earth elements (REE) is expected to lead to new development and expansion in industries processing and or recycling REE, and these new technologies will likely generate new waste streams. These wastes may contain residual REE as well as other components added or carried through processing. For some industrial operators, sending aqueous waste streams to a municipal wastewater treatment plant may be a cost effective disposal option. However, wastewaters that adversely affect the performance of biological wastewater treatment at the plant will not be acceptable. Currently, data on the effects of REE on biotic systems in general, whether natural or engineered ecosystems such as wastewater treatment modules, are scant. The objective of our research is to assess the effects of wastewaters that might be generated by new REE recycling processes on biological wastewater treatment, using both model pure strains and mixed microbial communities. The presentation will discuss our studies with both aerobic and anaerobic microbial cultures, with the rare earths europium and yttrium. These REE were targeted because they are major components of fluorescent light phosphor powders; fluorescent lamps have potential for near-term commercial recovery of REEs due to their high content of Y, Eu and terbium (Tb), the large volumes of lamps already in use, and the existence of end-of-life recycling services. In addition to these metals, the effects of organic compounds used in extraction and separation of rare earths on microbial activity have been examined. Results to date indicate that responses to REE vary among microbial species, and in some cases the tested organic waste components have greater impacts than the metals themselves.

Determination of technology-critical elements by ICP-SFMS

Ilia Rodushkin[1,2]

[1] Division of Geosciences, Luleå University of Technology, S-971 87 Luleå, Sweden
[2] ALS Laboratory Group, ALS Scandinavia AB, Aurorum 10, S-977 75 Luleå, Sweden

State of the art inductively coupled plasma mass spectrometry (ICP-MS) instrumentation possesses the prerequisite sensitivity to carry out multi-elemental trace analyses at sub-ng L^{-1} to sub-pg L^{-1} levels in solution making the technique ideally suitable for determination of technologically-critical elements. However, constraints mainly imposed by spectral interferences as well as various sources of contamination ultimately limit the detection capabilities and accuracy of results obtained. Here we review ICP-SFMS (also known as HR-ICP-MS) figures of merit for multi-elemental trace analyses in environmental and clinical matrices.

Characterization of nanoparticulate platinum in road dust leachate

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[1]Ghent University, Department of Applied Analytical and Physical Chemistry, Coupure Links 653, 9000 Gent, Belgium,
[2] Swedish University of Agricultural Sciences, Department of Soil and Environment, Almas Allé 8, 750 07 Uppsala
[3] Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, 9000 Gent, Belgium
[4] Chalmers Institute of Technology, Department of Civil and Environmental Engineering, Sven Hultinsgata 8, 412 96 Göteborg, Sweden

Catalytic converters were introduced in the exhaust system of passenger vehicles from 1970 on. Platinum Group Elements (PGEs) possess the unique catalytic properties for oxidation of CO and hydrocarbons and reduce NOx. During the entire use, mechanic abrasion and chemical processes at the catalyst surface are responsible for the emission of platinum (Pt), palladium (Pd) and rhodium (Rh) through exhaust gasses, leading to the dispersion of these elements in airborne particles, road dust, roadside soil and eventually aquatic sediments.[1] Although originally it was believed that PGEs were purely metallic and non-bioavailable, research to date has shown that these elements can to some extent be soluble and bioavailable.[2]

This study focused on the leaching of platinum from collected road dust and certified reference material BCR-723 under different environmentally relevant conditions. Road dust samples were collected throughout different locations in Ghent (Belgium) and Gothenburg (Sweden) and sieved to 80 µm. Nanoparticulate Pt was extracted by ultrasonic energy from the road dust using natural stormwater runoff collected at large municipal collection point. ICP-MS was used to determine the Pt concentration in solution, revealing an extraction efficiency of 2.7% for the BCR-723 tunnel dust and 0.7% for collected road dust samples. This supported the presence of a small quantity of Pt that is available upon contact with stormwater, besides a larger, more inert fraction of Pt.

Single particle ICP-MS was applied as new analytical tool in determining particle size information of elemental nanoparticules in the stormwater extracts.[3] Nanoparticuate Pt was thus detected, where the Pt mass per particle corresponded to a size of 10.4 ± 2.4 nm for Ghent and differed ($p = 0.028$) from road dust of Gothenburg having average size of Pt of 15.6 ± 4.1 nm, possibly due to specific differences related to the sampling site. Both groups were in overall agreement with the reference BCR-723.

References:

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[2] Gómez, B., Palacios, M., Gómez, M., Sanchez, J., Morrison, G., Rauch, S., McLeod, C., Ma, R., Caroli, S., Alimonti, A., Petrucci, F., Bocca, B., Schramel, P., Zischka, M., Petterson, C., Wass, U. (2002): Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities.
[3] Laborda, F., Bolea, E., Jiménez-Lamana, J. (2013): Single particle

An analytical platform for species selective preconcentration, size determination and quantification of rhodium nanoparticles

F. Weigl*

Technical University of Munich, Chemical Department, Lichtenbergstraße 4, D-85748 Garching

Platinum group metals (PGMs) are particularly known for their extraordinary catalytic properties making them of substantial interest not only for existing industrial applications but also for the development of new technologies. The concentration of these technology-critical elements has increased in surface soil layers, especially close to busy roads [1]. In order to investigate not only the spread of PGMs in total, but also to characterize the PGM-species (e.g. dissolved, nanoparticular) in the environment further, an appropriate species selective platform is needed. An analytical platform for routine analysis of PGM nanoparticles (NPs) should provide a high level of efficiency in terms of selectivity, sensitivity, robustness, easy handling and time consumption.

The complex matrix of environmental samples is a significant issue for highly sensitive determination techniques. Therefore, a selective enrichment method is needed, to eliminate matrix influences and at the same time enrich the analytes. After species selective preconcentration a variety of determination techniques may be used for quantification and characterization of NPs like electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma mass spectrometry (ICP-MS) and single particle ICP-MS (sp-ICP-MS).

In this work, an analytical platform coupling cloud point extraction (CPE) with ET-AAS and (sp-ICP-MS) is described for size determination and quantitative analysis of rhodium nanoparticles (RhNPs) in environmentally relevant concentrations (ngL^{-1} range).

Samples for CPE were prepared using highly selective thiourea as a chelating agent for dissolved Rh. The addition of a nonionic surfactant allows the formation of micelles after heating above the so called cloud point. Non-polar molecules are able to enter the micelles and are therefore co-extracted, while polar substances and ions will remain in the aqueous phase [2]. The polarity of the very stable Rh-thiourea complex is designed for phase transition into the aqueous phase, while the RhNPs enter the non-polar surfactant rich phase. The two phases are easily separated by centrifugation and subsequent decantation of the aqueous phase – RhNPs remain in the surfactant rich phase.

An enrichment factor of 80 and a low limit of detection (6 ng/L) is achieved using ET-AAS. Using sp-ICP-MS, an enrichment factor of 8, an limit of detection of 0.8 ng/L and a minimum detectable particle size of 7 nm (at the presence of 1 µg/L Rh(III)) is achieved. Environmentally relevant salts and natural organic matter show very low or no influence on the extraction efficiency of RhNPs in the ng/L range.

References:

[1] Sievers, H., Schuster, M., (2015): Long-Term Monitoring of Palladium and Platinum Contents in Road Dust of the City of Munich, Germany., Platinum Metals in the Environment: Springer 187-198

[2] Hartmann, G., Schuster, M., (2013): Species selective preconcentration and quantification of gold nanoparticles using cloud point extraction and electrothermal atomic absorption spectrometry., Anal Chim Acta 761, 27-33

Determination of platinum group metals in environmental matrices – methods for PGE separation

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Platinum group elements (PGE) belong to the group of critical elements, as they possess both high supply risk as well as high impact of the supply. The growing world consumption of PGE is connected with wide application of precious metals in various branches of industry (as catalysts of numerous technological processes), in production of car's catalytic converters, in medicine and jewelry. The emission of noble metals from anthropogenic sources causes the increase of their concentration in environmentally relevant matrices, especially in roadside dust, sludge and soils.

Direct determination of PGEs in environmental samples by spectrometric methods (FAAS, ETAAS, ICP-OES, ICP-MS) is often not possible due to insufficient sensitivity of these techniques and their susceptibility to spectral and matrix interferences. In order to obtain accurate results efficient procedures of matrix separation must be applied. A solid phase extraction technique based on novel sorbents has been widely recognized as an universal separation/preconcentration method for numerous applications.

Development of an ion imprinting technology offered a new prospects for enhance of efficiency and selectivity of separation process. Ion imprinted polymers (IIP) possess specific recognition sites which are formed during synthesis process carried out in the presence of a template molecules. The potential of the IIP prepared using different template molecules (various complexes of Pt(IV), Pd(II), Ru(III) and Rh(III)), functional and cross-linking monomers was tested for separation of PGE from environmental matrices. The influence of polymerization reagents on selectivity, adsorption capacity of the IIP towards imprinted ions and their stability was evaluated. Examples of procedures elaborated for separation of noble metals prior their determination by ETAAS in environmental, industrial and waste samples will be presented.

The potential of metal sorption by certain types of biomass provides the basis for the development of a new approach to remove heavy metals when they are present at low concentration. Due to good sorption performance and high selectivity, microorganisms, such as fungi, yeast, bacteria, could be used for the recovery of these metals from real effluents and waste materials as well as in analytical application for the separation and preconcentration of metals from interfering matrix before their determination by spectrometric techniques. The employment of biosorption processes for removal/recovery of Pt, Pd and Rh from wastes and the procedures of their determination in environmental samples using biosorption process and different detection techniques will be presented and discussed. The accuracy of results was confirmed by analysis of certified reference materials.

Content of PGE in road dust collected in Bialystok between 2000-2010 was determined by evaluated methods.

Single Particle (SP)-ICP MS Characterization of the Uptake and Metabolism of Platinum and Palladium Nanoparticles by Plants

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Recently, the use of platinum and palladium nanoparticles (NPs) in different fields of nanoscience and nanotechnology has significantly increased, leading to their release into the environment and impact on plants, which provides a potential pathway for human exposure. Despite their potential toxicity, the biogeochemical behavior of Pt and Pd-NPs is poorly understood and there is a lack of information about their uptake and metabolism by plants.

A method based on an enzymatic digestion followed by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) analysis was developed in order to extract intact nanoparticles from the plant tissues. SP-ICP-MS technique gives an opportunity for the simultaneous determination of the nanoparticles size, nanoparticles number concentration and together with the presence of dissolved platinum and palladium in the samples. In order to extract the largest number of nanoparticles, the enzymatic digestion method was optimized. The analytical performance of the proposed method in terms of limit of detection, reproducibility and recovery was also evaluated. Total amount of platinum and palladium in plant samples was determined after mineralization by off-line ICP MS. The data obtained indicate a possibility of uptake of intact Pt- and Pd-NPs by plants root system and their transport to shoots and leaves. NPs with higher sizes than the nominal one were observed as well, suggesting the occurrence of an aggregation process. The presence of dissolved forms of metals was not detected.

Indium speciation and availability in aquatic solutions probed with electroanalytical techniques

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Indium is a critical element, widely used in electronic devices and other applications. From them, it can eventually leak towards the environment. Despite its large use, there are many unresolved aspects of the behaviour of Indium, particularly regarding its speciation and availability, all of which demand dedicated work [1].

Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) is a relatively new electroanalytical technique designed for the determination of the concentration of free metal ions in target solutions such as seawater, river water, dispersion of nanoparticles, wine or soil extracts [2]. The implementation of AGNES with mercury electrodes requires amalgamating elements such as Zn, Cd, Pb, Sn or In. When Indium is tackled with AGNES, due to some irreversibility on the Hg electrode, it is not possible to compute directly the potential associated to a given preconcentration factor or gain. A new strategy, based on taking into account the charge and the volume of the Hg drop, has been developed to calibrate [In^{3+}] with AGNES.

Speciation results in the system Indium+Nitrilotriacetic acid with AGNES agree with

computations using database NIST 46.6, unless the total ligand concentration is larger than the metal one (in which case the stability constants of Biver et al.3 are more suitable). Similarly, the stability constants in NIST 46.6 in the system Indium+Oxalate are not as accurate as those of Vasca et al.[4] A new approach, called Accumulation under Diffusion Limited Conditions (ADLC), can be applied to compute the lability degree of complexes. The lability degree is strongly linked to the availability of this element as it describes the contribution of the complexes to the overall uptake flux. The use of highly labile complexes (such as those of oxalate) allows for a dramatic reduction of the deposition times at huge gains. For instance, in the system oxalate+In at pH 3, equilibrium for a gain larger than 300000 was attained in just 25 seconds retrieving free Indium concentrations below nanomolar. In precipitated solutions at pH 5.5 (where the free Indium concentration is fixed despite the addition of the helping oxalate), free Indium concentrations in the picomolar range were determined.

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A new Method for Ge Speciation using HPLC-ICP-MS

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Germanium belongs to the so called technology-critical elements (TCEs) [1]. It is used for fibre optic systems, infrared optics, semiconductor detectors, monochromators, as polymerization catalyst, and substrate for wafers [1]. The increasing use of TCEs and thus the demand for a higher availability in the coming years require a better understanding of the chemical behavior. Therefore, elemental speciation is of importance for the investigation of the environmental behavior and might also play an important role in technical processes. One example is germanium speciation in the technical process of bioleaching and subsequent metal recovery processes [2]. In contrast to environmental samples, such samples contain higher concentrations of germanium as well as many by-elements and may also contain high salt contents. The present study demonstrates the separation of inorganic germanate ($Ge(OH)_4$) and the methylated species monomethyl (MMGe) and dimethyl germanium (DMGe) and its use for the investigation of bioleaching processes of germanium.

For the separation of the three Ge species in aqueous solution anion exchange chromatography (Hamilton PRP-X100 column (150 mm x 2.1 mm, 10 µm)) was used and coupled to an ICP-MS (Agilent 7700, m/z = 72) for element-specific detection. Tartrate had to be added as complexing agent into the samples to enable the chromatographic separation.

Addition of 80 mM tartrate resulted in a baseline separation of $Ge(OH)_4$, MMGe and DMGe. DMGe elutes first, followed by MMGe and $Ge(OH)_4$. Sulfate, which is a component of the bioleaching samples, might compete for the functional groups at the stationary phase and thus might affect the separation. Therefore, the influence of sulfate on the separation was investigated. Furthermore, the retention behavior of sulfate at the anion exchange column was studied by HPLC coupled to a triple quad ICP-MS (Agilent 8800) to analyze the sulfur as SO^+ (m/z = 48). Increasing the sulfate concentration in the sample causes a change of the Ge(OH)4 peak shape and a shorter retention time of MMGe. The addition of 1 mM tartrate to the mobile phase compensates for this influence at least to a sulfate concentration of 150 mM (14 g L^{-1}). Application of the Ge species analysis to bioleaching solutions will be presented.

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Tracing anthropogenic rare earth elements in the environment

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The rare earth elements (REE) are comprised of La and the fourteen 4f-elements from cerium (Ce) to lutetium (Lu), while the REY (rare earths and yttrium) also include Y which is the geochemical twin to holmium (Ho). Since the early days of geochemistry in the 1920s and 1930s, scientists like V.M. Goldschmidt have made use of the REY as geochemical proxies to learn about processes and the physico-chemical environments in which they operate(d). However, it took until the turn of the century for the REY to move into the spotlight of geopolitics and media attention. Their use in numerous high-technology products and processes, and particular their importance for renewable energy (e.g., wind turbines), petroleum refining (FCC catalysts) and medical diagnostics (MRT contrast agents), for example, created strongly increasing demand to which the single supplier (China) responded with price hikes and export restrictions. As such, the REY are prime examples of technology critical elements. However, their increasing use is accompanied by the release of increasing amounts of these formerly exotic trace elements into the environment. This is somewhat disturbing, as only little is known about their behavior in the Earth's surface system, their bioavailability or their (eco)toxicity.

The first report of the presence of anthropogenic REY in surface waters dates back to 1996 when anthropogenic gadolinium (Gd) had been found in river waters in Germany. Since then, anthropogenic Gd has been reported from rivers in all continents except Africa and Antarctica. The anthropogenic Gd is related to MRT contrast agents which, after they are excreted from a patient's body, are transported with sewage water to waste water treatment plants (WWTPs), where they cannot be removed. Hence, they enter rivers and lakes with the clear water effluent from these WWTPs.

Anthropogenic lanthanum (La) and samarium (Sm) have recently been observed in the Rhine River in Germany. This anthropogenic REY contamination is related to an industrial point source (a production plant for FCC catalysts).

In the presentation, the anthropogenic Gd cycle in urban areas (e.g., its presence in tap water and popular soda drinks) and the fate of anthropogenic Gd that enters coastal seawater will be discussed. Moreover, the bioavailability of anthropogenic Gd will be compared with that of anthropogenic La and Sm.

Acid Mine Drainage: a possible source of Rare Earth Elements and

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Rare Earth Elements and Yttrium (REY) are raw materials of increasing importance for modern technological developments. Most of production is concentrated in China, and finding alternative sources of REY has become a need for the rest of countries. Acid Mine Drainage (AMD) is commonly considered an environmental pollution that is expected to flow out from coal and sulfide mines for hundreds of years. However, AMD may contain REY in concentration various orders of magnitude higher than the rest of waters. AMD passive remediation systems neutralize AMD based on its reaction with calcite-based permeable substrates followed by decantation ponds. The treatment leads to a sequential precipitation of Fe(III) and As as schwertmannite and Al and Cu as hydrobasaluminite. Observations from both stream and passive remediation systems demonstrate that schwertmannite does not allocate REY, which in turn are retained in basaluminite (Kd between 100 and 150 kg/L). A preliminary survey from the Iberian Pyrite Belt AMD treatments shows that the REY rates in the residues range between 0.03 and 8% REY2O3. Although REY rates in the treatment residue may be competitive, the annual reserves for an entire region such as the Iberian Pyrite Belt are low and only comparable to the more modest producing countries. However, AMD remediation systems may provide a new and almost inexhaustible natural source of REY that is sustainable and beneficial for the environment.

Mobility of Rare Earth Elements (REE) from unwanted byproducts of the fertilizer industry

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Europe is facing that its mineral richness has been actively mined over many centuries so accessible mineral deposits are mostly exhausted. Although raw materials are essential for the European Union (EU) economy, their availability is increasingly under pressure. This is especially significant for rare earth elements (REE) which at least 85% of the annual global supply in the last decades was provided by China [1]. The lack of primary deposits has encouraged EU members to seek alternative secondary deposits. One promising possibility is stockpiled industrial wastes such as phosphogypsum (PG) which can host significant concentrations of REE. During the acid attack of phosphate rock to obtain phosphoric acid, around 70-85% of REE originally contained in phosphate ends up in PG [2]. Before addressing the recovery of these elements enclosed in PG, a detailed study on REE mobility should be performed, focusing especially on the chemical and mineralogical controls on REE release. There is a controversy as to which minerals host REE in PG; some authors [2, 3] have reported the presence of REE in the gypsum lattice by inner adsorption or included in the mineral structure, while others [4] conclude that REE may be hosted by separate phases. In order to address the source and mobility of REE in PG, samples from a fertilizer plant were leached with different acids (i.e. HCl, HNO_3 and H_2SO_4), quelants (i.e. DTPA) and water. The higher leaching was obtained with 3M HNO_3 (80%) followed by 1M HCl (65%), 0.5M H_2SO_4, (50%), 0.5M DTPA solution (20%) and water (<1%). Raw and leached samples were examined by scanning electron microscope (SEM) which evidenced the dissolution of accessory fluoride under acid leaching. This mineral is supposed to host REE in PG while the different leaching efficiency among acids may be due to the different complexation capacity of anions (i.e. $NO_3^- > Cl^- > SO_4^{2-}$).

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Environmental changes in the southern Tethys productivity belt: a multi-proxy study of the phosphorite deposition

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The Santonian to Maastrichtian age (85-65 Ma) phosphates in Israel are part of an extremely large Cretaceous to Eocene phosphorite deposition belt that stretches from Turkey to Morocco. Previous studies suggested that phosphorite deposits occur in two different facies: pristine phosphorite deposits that are attributed to high productivity and sedimentation rates in suboxic or anoxic conditions, and reworked phosphorites (the economic facies) deposited under oxidized conditions at low sedimentation rates in high-energy events accompanied by bioturbation. Although many studies have been made on the deposition conditions of the Middle East phosphorites and their enclosing rocks, several aspects of the environmental conditions of the phosphogenesis remain unclear and can be explored with organic nitrogen isotopes ($\delta^{15}N^{org}$), organic carbon isotopes ($\delta^{13}C^{org}$), redox sensitive trace elements (RSTE), and rare earth elements (REE) content. In this study we used the combined geochemical records to reconstruct the paleo-deposition condition prevailed during the phosphogenesis processes.

Preliminary work was performed on nine sections from the Zin syncline in the Negev. The sections were collected from different phosphate fields spread from north to south in the Zin Syncline. The sections present alternation of the layers between pristine and reworked facies. Our results show that pristine phosphorites are enriched in redox trace elements (RSTE) compared to reworked phosphorites, with the exception of elements that are known to be associated with carbonate-fluorapatites (such as U). The organic carbon content varies between 0.1% to 15%, represents low organic phosphate fields to bitumen phosphate fields. However, no correlation was found between RSTE content to TOC concentration. The δ^{15}Norg show more depleted values in the pristine phosphorites compared to the rework phosphorites suggesting presence of nitrogen fixers during the phosphogenesis processes.

Environmental concentrations of TCEs: are they really increasing?

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It is generally assumed that the increased use of metals and other chemical elements, characteristic of the Holocene, necessarily leads to an increase in their concentrations in the different environmental compartments. It is well-known, for instance, that increases in elements' anthropic uses are reflected in the so-called environmental archives (e.g., ice, peat bogs, lake sediments). This is the case of some extensively studied elements such as lead and mercury. It should be mentioned however that, even in the case of such elements, source apportionment is often far from straightforward, particularly when far from a direct source and/or when the level of natural or indirect sources (e.g., coal combustion) is high. The follow-up and understanding of changes in surface water concentrations are even more difficult. First, the detection of concentration trends in waters requires the existence of long temporal series of reliable concentration data; this represents already a formidable obstacle because such series are extremely scarce. Secondly, element concentrations in lake waters are not only the result of direct inputs (e.g., water treatment plants and atmospheric deposition) but also of runoff contributions (of geological or anthropogenic origin) and reflect internal processes in soils and waters.

Whether the concentration of technology-critical elements -particularly the less studied ones- are really increasing in environmental compartments will be discussed in this communication on the basis of (i) a comprehensive literature review, (ii) original data furnished by researchers in the field; (iii) our own results on concentration trends in Lake Geneva waters.

Source, cycling and circulation effects on seawater rare earth elements in the NE Atlantic

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Seawater rare earth element (REE) data are increasingly applied to reconstruct water mass histories by exploiting relative changes in the distinctive normalised concentration pattern. The mechanisms by which water masses gain their REE patterns, however, have yet to be fully explained. To address this, we collected water samples during the 2015 Extended Ellett Line (EEL) cruise, an oceanographic transect between Iceland and Scotland, and measured dissolved REE concentrations. The proximity of the two geologically distinct landmasses and the importance of deep water mass circulation in this climatically sensitive gateway region make it an ideal location to investigate sources of REE to seawater and the effects of vertical cycling and lateral advection on their distribution. To constrain the source inputs of REE to the ocean, we also present a salinity transect of dissolved REE concentrations along a Scottish sea loch (Loch Etive) that receives river waters from relatively pristine environments characterized by a mix of mountainous and organic rich (peat bog) terranes.

The samples were filtred through 0.4 µm membranes, and the river and sea loch samples were further size fractionated by ultrafiltration (<30 kDa and <5 kDa) to differentiate the role of smaller fulvic acids in REE transport compared to larger humic acids. Sample REE concentrations were determined on 20 ml by preconcentration (x40) using a SeaFAST instrument (ESI, USA) and measured by ICP-MS (ThermoScientific Xseries 2) using a 6-point external calibration. External reproducibility was monitored by repeat measurement of GEOTRACES intercalibration BATS 2000 m seawater and the NRC coastal water NASS-6.

The seawater samples show an obvious concentration gradient from seafloor sediments to the overlying water column, highlighting release of light (L)REE and mid (M)REE from a sedimentary source, most likely Fe-rich phases from pore waters. The mid-depth water column has REE compositions closest to typical open ocean seawater and is dominated by lateral advection. The intense spring bloom in the NE Atlantic coincides with the timing of the EEL (May/June), and thus affords the opportunity to consider the influence of biogeochemical cycling on water column REE concentrations. While the surface ocean shows depleted heavy (H)REE concentrations, the EEL dissolved oxygen minimum corresponds to positive HREE deviations, indicating maximum rates of organic matter remineralisation and associated HREE release. We tentatively suggest that these HREE patterns demonstrate bacterial cycling. The sea loch samples demonstrate features typical of estuarine mixing, e.g. decreasing La/Lu ratio with increasing salinity. However, we also observe conservative mixing of the ultrafiltered REE fraction across the salinity gradient in Loch Etive, with greater export to higher salinities of HREE than LREE. Further analyses are required to identify the carrier phase that appears to be resistant to estuarine electrostatic flocculation.

A peat-based record of atmospheric iridium and osmium accumulation

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The study presented here provides evidence for the anthropogenic overprint of the natural biogeochemical cycles of Ir and Os using a ca. 7000-record of atmospheric Ir and Os accumulation at a remote site in NW Spain. The record was constructed using samples obtained from peat cores taken at the Penido Vello bog, an ombrotrophic peat bog receiving minerals only through atmospheric deposition. The samples were prepared by NiS fire assay and analysed by isotope dilution ICP-MS at the Woods Hole Oceanographic Institution. Ir and Os accumulation rates were then inferred from measured concentrations and estimated peat accumulation rates. The obtained record demonstrates that important changes in Ir and Os accumulation occurred starting with early metal mining (ca. 4700 before present). Highest accumulation rates were found in most recent samples (ca. 6000-4700 before present). Iridium accumulation increased from 0.06 ± 0.01 ng m^{-2} yr^{-1} in pre-anthropogenic samples to 8.5 ± 4.8 ng m^{-2} yr^{-1} in most recent samples (ca. 1989-1999). Osmium accumulation increased from 0.10 ± 0.06 ng m^{-2} yr^{-1} to 20 ± 8 ng m^{-2} yr^{-1} for the same samples. Changes in Os/Ir concentration ratio and Os isotopic composition support that changes in accumulation rates are due to a combination of sources. While automobile exhaust catalysts have been identified as a major source of platinum group elements in urban and road side environments, the peat bog record obtained from a remote site suggests that other sources contribute to the global biogeochemical cycle of these elements.

Cerium(III/IV) aquatic geochemistry: what can be learnt from actinide analogues?

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Cerium (Ce) is the most abundant rare earth element (REE) in the Earth's crust and is used for many applications (technical, medical, catalytic, etc, [1]). By contrast with its REE neighbors that are most stable under the +III oxidation state, Ce can be found as Ce(III) or Ce(IV) under environmentally relevant condition, which has drastic consequence on Ce aqueous chemistry, solubility and sorption to natural particles and colloids, mobility and bioavailability. Geochemical speciation modeling might be a helpful tool to understand Ce speciation. Unfortunately, huge gaps in Ce aqueous thermodynamic databases (especially for Ce(IV) hydrolysis and solubility) prevent us from using accurately such approach. f-elements (REE (5f) and actinides (An) (6f)) show rather consistent chemistry under the same oxidation state, and are often considered as chemical analogues. Many studies where dedicated to An(IV) (An = Th, U, Np, Pu) hydrolysis and solubility because they are key elements in the field of nuclear waste disposal. In particular, Pu might be a relevant actinide analogue for Ce aqueous chemistry. Indeed, effective ionic radii of Ce^{4+} and Pu^{4+} are comparable and we found that solubility product of $CeO_{2(cr)}$ is highly consistent with that of $AnO_{2(cr)}$ [2].

In this study, we estimated Ce(III/IV) aqueous (including redox) speciation on the basis of REE(III), An(IV) and Pu(III/IV) behavior. Moreover, using a recently developed approach to predict sorption and redox speciation of Pu at mineral surfaces [3], it was possible to predict available laboratory data of Ce sorption to manganese oxide, which is known as efficient sorbent and oxidant for Ce(III) [4]. Although preliminary, these results are very promising and might help to predict Ce speciation in naturally relevant conditions.

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Complexation study of thallium with natural organic matter using Donnan Membrane Technique

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Thallium (Tl) is a potential contaminant at the vicinity of mining sites and is as polluting as Hg, Pb, Cd. Tl is both lithophilic and calcophilic element and found in S-bearing minerals and K-bearing minerals such as feldspars or micas. Tl has natural sources by weathering and anthropogenic sources with mining activities (sulfide ores and S-rich coal ores). Speciation of Tl is poorly-known mainly due to its low concentration in aquatic environments.

Review of Tl geochemistry clearly shows a lack of quantitative information about interactions with natural organic matter(NOM). Organic ligands could play a part in Tl bioavailability, chemical reactivity (adsorption or photo oxidation inhibition or catalysis) and hence geochemical transfers.

Based on equilibrium between two solutions that are separated by a selectively permeable membrane, the so-called “Donnan membrane technique” (DMT) provides a measure of free ion concentrations [1]. Analyte measurements are performed by HR-ICP-MS Element 2 (Thermo Scientific). Experimental setup allows the Donnan equilibrium to be reached after 72 hours for Tl. Experiments performed with purified natural organic matter and modelled data using NICA-Donnan model within Ecosat, allow determining complexation constants.

Two range of NOM has been tested, 50 and 200 $mg.L^{-1}$. First experimental results showed only 5± 6% of Tl^{+} is complexed to low NOM concentration. At higher concentration, 16± 10% of Tl+ is complexed. It appears that Tl has low interaction with NOM and those results are confirmed by modeling. Even though further investigation are needed (e.g. to have complexation constants in various conditions), we bring new data and interpretations to an active debate on Tl geochemical behavior. To conclude, this work brings a new vision on risk assessment for mining activities and fate of Tl in environmental systems.

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Thallium sorption on illite and its importance in soils

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Thallium (Tl) is a highly toxic trace metal. In the environment, Tl occurs as monovalent Tl^{I} and trivalent Tl^{III}. Tl^{I} exhibits both chalcophilic and lithophilic character. Because Tl^{+} has a similar ionic radius as K^{+}, it can substitute K^{+} in a wide range of K-bearing minerals. In soils and sediments, Tl^{I} uptake by the clay mineral illite has long been considered to be a key retention mechanism. Direct evidence for Tl uptake by illite in soils was provided by a recent spectroscopic study on geogenically Tl-rich soils [1]. To date, however, data on Tl sorption by illite and its effect on Tl solubility in soils are lacking.

We currently investigate the sorption of Tl^{I} by pure illite (Illite du Puy) in batch experiments. First results confirm that Tl^{I} uptake by illite is highly specific and exhibits similar trends as known for Cs^{+} [2,3]: Limited pH dependence, marked sorption competition with Na^{+}, and slow sorption/desorption kinetics. The new sorption data for Tl^{+} on illite will be quantitatively described in the framework of a generalized model of K^{+}, Rb^{+}, Cs^{+} and NH_4^{+} uptake by argillaceous rocks [4].

To gain direct insight into the effect of Tl sorption by illite in soils, we examine the solubility and extractability of Tl in geogenically Tl-rich soils from the Swiss Jura mountains [1] covering a wide range in Tl contents. Results from extracts targeting soluble (10 mM $CaCl_2$) and exchangeable cations (1 M NH_4-acetate) are in line with Tl uptake by illite as solubility-controlling process. Additional time-resolved extracts reveal slow Tl release kinetics, probably from high-affinity sorption sites.

In continuing work, further insight into Tl uptake by illite and Tl speciation in soils will be obtained using synchrotron-based X-ray absorption spectroscopy. By combining macroscopic sorption experiments and soil extractions with spectroscopic data on Tl speciation, this project will contribute to an improved quantitative and mechanistic understanding of the solubility, mobility and bioavailability of Tl in soils.

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Presence and mobility of Nb, Ta, Tl and In in sediments and soils of the Scheldt estuary and around smelters in the Campine region (Belgium)

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This study monitored, on the one hand, the dispersion of selected TCEs in the Scheldt estuary and near industrial sites in Flanders, and on the other hand determined the mobility and availability of the elements through leaching. Water (n = 30) and intertidal sediment (n = 90) samples were collected along the Belgian part of the Scheldt estuary. In total, 10 locations were considered and sampled in triplicate. The sediment samples were taken at the depth of 0-5 cm, 5-15 cm and 15-80 cm. In addition, soil samples (n = 30) in the vicinity of 2 smelters were taken. To study the mobility of the elements, pore water samples of the soils and sediments were collected using Rhizon samplers. Water samples were filtered through cellulose microfilters of 0.45 µm pore size. Soil and sediment samples were dried, grinded and sieved over 1 mm, before 0.5 g was weighted and digested with Aqua Regia. All solutions were consecutively analyzed for niobium, tantalum, indium and thallium concentrations by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

The presence of niobium, tantalum, indium and thallium was demonstrated in the studied terrestrial environment. We observed significant concentrations for niobium and tantalum in the soil and sediments of the Scheldt estuary (soil Nb: 245 ± 11 µg kg^{-1}; sediment Nb: 569 ± 59 µg kg^{-1}; soil Ta: 45 ± 25 µg kg^{-1}; sediment Ta: 39 ± 10 µg kg^{-1}). The low variability of Nb concentrations between the different locations indicates a homogenous distribution in the top soil and sediments. Indium (sediment: 38 ± 1 µg kg^{-1}; soil: 69 ± 74 µg kg^{-1}), on the other hand, is characterised by enrichment in the soil near the smelters, clearly indicating the smelters to be point sources. This anthropologic proliferation of indium, mainly through atmospheric deposition, was demonstrated earlier by Tessier et al. [1]. The high soil concentrations of thallium (963± 32 µg kg^{-1}), meanwhile, could imply a potential risk. Rhizon extracts however revealed that the element is little available and less than 0.1 % was leached after 3 days.

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Deposition of rare earth elements and indium from the atmosphere to a bog in the Northeastern United States

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The industrial production of the rare earth elements (REE) and indium is increasing dramatically due to new uses in rapidly growing electronics, clean energy, and defense applications. Little is known, however, about the natural or industrial cycling of these elements or their environmental behavior, despite the fact that industrial emissions to the environment appear to already exceed natural sources.

The history of metal deposition from the atmosphere is often reflected in the vertical profiles of the metals in ombrotrophic bogs, which by definition do not receive surface or subsurface runoff. Previous analysis of a peat core obtained using a novel freeze corer at Thoreau's Bog in Concord, MA shows that the rate of indium deposition to the bog increased beginning in the early 1900s, peaked in the early 1970s, and then decreased dramatically to pre-1900 values by the present time. This profile is counter to the pattern of indium's industrial use, but coincides well with the estimated history of particulate emissions from smelting and from coal combustion in North

America. Analysis of the rare earth elements in the same peat core has shown similar profiles to indium, suggesting a similar source of the rare earth elements to the atmosphere in the northeastern US.

This study suggests that humans have had a significant impact on the environmental cycling of indium and the rare earth elements, at least in part because of releases from metal smelting and coal burning.

Recent platinum contamination of a major European estuarine system: a bivalve biomonitoring study

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Technology-Critical Elements (TCEs) emissions into all Earth compartments are growing due to their increasing demand and the number of new applications. Environmental studies on Platinum (Pt) and other TCEs, clearly show the presence of such elements considered as emerging contaminants. However, data on field studies reporting Pt levels and potential biota contamination in estuarine/marine systems are still scarce. Stripping voltammetry was used for accurate determinations of Pt in historical records of wild oysters from the Gironde Estuary mouth (collected from 1981 to 2013). The chronicled samples displayed Pt concentration variations with Pt concentrations between 0.80 ± 0.01 pmol.g^{-1} and 3.10 ± 0.14 pmol.g^{-1}. These variations reflect the evolution of Pt pressure in this ecosystem over three decades. The rise of a recent Pt source attributed to the extensive increase of Pt demand for car catalytic converters (~70% of total Pt demand in the EU) points towards the increasing importance of this emerging source to the aquatic system [1]. These results suggest that anthropogenic vehicle-derived Pt emissions may profoundly affect the Pt budget of the watershed inducing enhanced Pt uptake by biota. Considering the paucity of data on the distribution of Pt in aquatic environmental matrices, and especially in marine systems, monitoring programs on Pt should be conducted in the future [2]. Wild oysters have proven to be sensitive bio-monitors of Pt contamination over the time. In order to confirm the biomonitoring potential of bivalves, preliminary results of historical records in wild mussels from the Toulon Bay, France will be presented. Furthermore, this study showed that oysters may bioconcentrate Pt (Bioconcentration Factor, BCF ~ 10^3) and potentially transfer this metal contamination to the higher food chain. Ecotoxicological impacts of such rapid, profound change in the Pt use and emission into the environment are yet still widely unknown and need further investigations on environmental Pt cycles, transfer processes and possible adverse effects to biota. To this purpose, preliminary results of an exposure study of Pt on marine bivalves will also be presented and discussed in terms of uptake rate and bioconcentration potential.

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Biological availability, uptake and bioaccumulation of Pt, Pd and Rh by freshwater animals

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The uptake and bioaccumulation of Pt, Pd and Rh by different freshwater animals (i.e. the Zebra mussel, *Dreissena polymorpha*, the European eel, *Anguilla Anguilla*, the Barbel, *Barbus barbus*, and the fish parasites *Paratenuisentis ambiuus* and *Pomphorhynchus laevis*) were investigated in laboratory studies using soluble metal species as well as ground catalyst materials and road dusts (reviewed in [1]). The exposure studies were performed under different experimental conditions to demonstrate the effect of different confounding factors on the biological availability and bioaccumulation, with respect to:

Test organisms:

All test organisms demonstrated a clear PGE uptake after exposure to soluble as well as particle bound PGE sources. However, the degree of bioaccumulation differed between the test organisms. Highest bioaccumulation was found for parasites, living in the fish intestine. Among the different fish tissues, kidney showed the highest and muscle the lowest PGE accumulation.

Metal source:

Soluble PGE species demonstrated the highest biological availability to zebra mussels followed by PGE from ground catalyst materials and then by PGE from road dust. The period to reach the accumulation plateau was significantly shorter for soluble PGE than for particle bound PGE.

Water type:

Humic water increased the bioaccumulation of Pt, Pd and Rh from catalyst material and road dust in zebra mussels as compared with tap water. In contrast, using soluble PGE species humic water decreased the Pt and Pd bioaccumulation and increased the Rh bioaccumulation.

Unfortunately, exposure concentrations of laboratory tests are generally far above real field situations due to analytical limits in the determination of Pt, Pd and Rh in biological samples. However, the available laboratory results deliver valuable information to understand the basics of PGE uptake and bioaccumulation by aquatic organisms.

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Sedimentary behaviour of natural and traffic-borne platinum in the salt marshes

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Platinum, due to its siderophile affinity [1], is one of the least abundant elements in the earth crust, showing and average concentration of 510 pg g^{-1} [2]. However, its use in several human activities, mainly automobile catalytic converters, is leading to its enrichment in surface soils and sediments.

This study was carried out to characterize the behaviour of Pt released in sediments of natural coastal environments, still poorly studied, paying close attention to ascertain the role of vegetation on the Pt sedimentary biogeochemistry and to assess the transference of Pt into the biological compartments. Several sediment cores were sampled in salt marshes (in unvegetated and vegetated areas) of the Tagus Estuary (W Iberian Peninsula) under different traffic pressure. Platinum concentrations were analyzed in solid sediment, interstitial water and roots, leaves and stems of a typical saltmarsh plant, Sarcocornia fruticosa. Furthermore, other interpretative parameters (e.g. redox potential, dissolved oxygen, pH, total reduced sulfur species, salinity and dissolved Fe and Mn in interstitial waters) were also determined.

Although surface enrichment of Pt exists in all sediments (> 2 ng g^{-1}), the highest concentration was found in the area subject to highest traffic density (> 40 ng g^{-1}). However, this surface Pt- enrichment in sediments was not reflected in the interstitial waters (from 0.14 to 0.70 ng L^{-1}), pointing out that the catalytic-converters-derived Pt remains almost inert in the sediment (typically less than 1% of traffic-emitted Pt is dissolved [3]), while the natural Pt is involved in a dissolution/precipitation cycle.

Platinum concentration in roots (0.9±0.6 ng g^{-1}) reflects the Pt concentration in surrounding interstitial waters in each moment, indicating a reversible transfer. Results also suggests that different Pt species (with different bioavailability) may exist in the rhizosphere and also a low translocation of Pt from the roots to aerial parts (0.04 ± 0.05 ng g^{-1}).

Therefore, while the traffic- borne Pt remains mostly inert in the first centimetres of sediments, the geochemical behaviour of natural Pt in sediments is affected by vegetation due to the control of the redox conditions by roots (O_2 release and organic matter degradation), determining the chemical species in the solid and dissolved phases. The low Pt bioaccumulation by plants decreases the ability of Pt to be incorporated into the food chain.

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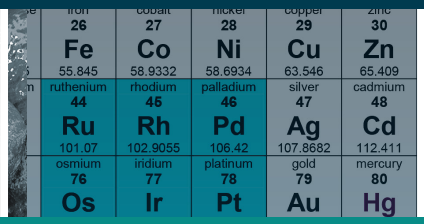

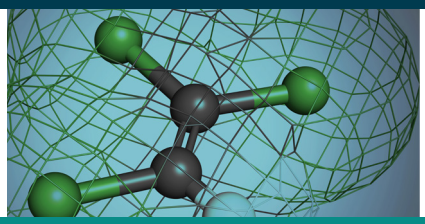

POSTER ABSTRACTS

Short Term Scientific Mission (STSM): Technology Critical Elements in soil

M. Wiesinger

As part of a project to investigate the mobility of Technology Critical Elements (TCEs) in soils, 19 soil samples covering 3 soil types were collected from Austria and Israel. The soils were air-dried, ground and sieved, and the portion in the size range 250 µm was subjected to a fractionation scheme involving sequential extraction with acid soluble fraction, reducible fraction, oxidizable fraction and residual fraction. At each stage, the mixture was centrifuged and the supernatants were analyzed for a range of elements (65 elements) by using inductively coupled plasma mass spectrometry. The results from the first experiments with a single sample from Haifa Israel are reported.

Sources and distribution of rare earth elements in the Zrmanja river estuary, Adriatic sea, Croatia

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Distribution of rare earth elements in sediments of the Zrmanja River estuary and surrounding soils was investigated. Analysis of REE was performed by HR ICPMS after a total MW digestion of samples [1]. Study was prompted by the fact that Zrmanja River estuary represents a small semi-closed system incised in a karst landscape characterized by prevailing red soil (*terra rossa*) cover, numerous bauxite pits and vicinity of the former alumina plant, which represents a source of materials enriched in rare earths. Both sediment and soil samples displayed significant variation in terms of REE concentrations as well as their normalized patterns, with overall highest REE levels measured in bauxite soils (ΣREE 333-593 mg kg^{-1}); up to an order of magnitude higher than in other samples. In estuarine sediments ΣREE ranged from 29.7 mg kg^{-1} to 180 mg kg^{-1}, and displayed an increase along the salinity gradient. However, sediment REE normalized patterns and associated fractionation parameters (ΣLREE/ΣHREE) showed similarity to those observed for soil samples, confirming significant influence of the local lithology on the REE sediment content. Moreover, highest levels of rare earths in sediments of the Zrmanja River were observed in the vicinity of the former alumina plant, indicating transfer of particles from the immediate vicinity of the former factory to the surrounding environment and its influence on the geochemistry of the estuarine sediments.

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Chemometric discrimination of Romanian vegetables based on their elemental fingerprint

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In this work, a number of 200 vegetables samples were investigated from their isotopic and elemental content point of view, in order to identify the most suitable markers, that are able to differentiate organic from conventional vegetables, or which might differentiate greenhouse grown vegetables from those grown in the field. These classifications were established using chemometric tools applied upon isotopic and multielemental experimental data [1].

For the identification of suitable markers that could differentiate greenhouse grown vegetables from those produced in the field, LDA test was applied and the classification criterion was the growing condition of vegetables. The parameters obtained as being the best predictors for this criterion were: Ni, Mo, Cd, Pb, and $\delta^{13}C$. By taking into account these variables, an initial classification of 100% for the original samples was obtained whereas a percent of 93.3% was obtained in cross-validation. For the differentiation of organic vegetables from those grown under conventional practices, LDA data processing was applied using all experimental data obtained for entire investigated vegetables set. The two groups were initially correct classified in a percent of 84.4% followed by a similar cross-validation percent. In order to a better distinguishing of the two product types (organic vs. conventional), a splitting of the samples into two groups was made, accordingly vegetables types: subterranean and above-ground plants. In this case, a differentiation of organic samples in a percent of 100% for subterranean vegetables was obtained while, for aboveground plants a separation of 92.9% was archived. It was observed that the best differentiation percent between organic and conventional vegetables was obtained when statistical treatment was applied inside the same plant categories (i.e. salads, potatoes, cabbages). For cabbages samples, the initial and cross validation was made based on P, Cr, Tl and Eu, and were validated 100% percent in both cases.

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Leaching and phytoavailability of trace elements in soils amended with coal fly ash (FA) treated biosolids

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Two Israeli waste streams generating secondary materials can be combined to an agricultural product suitable for beneficial use: (1) raw sewage sludge (RSS) from treatment of primarily municipal wastewater, and (2) coal combustion fly ash (FA) from electricity production. The RSS contains highly significant elements for plants growth (e.g., P, K and N) and essential microelements (Fe, Mn, Zn, Cu, Mo). Blending of RSS, FA and lime in specific proportions and under specific conditions produces the agricultural additive N-Viro Soil (NVS), which has been found to be of beneficial agricultural use. The FA addition creates a texture that can be spread efficiently in the field. Utilization of NVS has raised concerns regarding release of toxic elements from the FA. The overall aim of this study is to examine the effects of FA in NVS on contaminants' uptake by plants and leaching to water resources.

The study included a greenhouse lettuce experiment in mini-lysimeters and leachability assessment was evaluated using two US-EPA Methods: (1) 1313 - liquid-solid partitioning as a function of eluate pH, and (2) 1314 - Liquid-Solid Partitioning (LSP) as a function of liquid-to-solid ratio using an upflow percolation column. For both field and lab experiments, the same materials were used comprising of two soils (sand and clay) amended with two levels of NVS: maximum permitted load (500 kg N/ha; MP) and elevated load (five times MP). The chosen FA represents a worst-case scenario for FA produced in Israel, as it is characterized by high concentrations of contaminants during standard leaching with water (EN 12457-2). Materials and leachates were analyzed for the major and trace elements: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Ti, Ag, As, B, Ba, Be, Cd, Co, Cu, Cr, Hg, Mn, Mo, N, Pb, Sb, Se, Th, Tl, U, Zn and V.

The NVS being a mixture of RSS, FA and lime is reflected in its chemical composition. In alkaline pH range, the high leachability from FA dominates NVS characteristics. Arsenic (toxic for humans) was leached from NVS in concentrations greater than national drinking water (DWI) and treated wastewater for irrigation (IWI) standards at most test conditions (pH range; L/S ratios and leachates collected during lettuce growth). Elevated leaching concentrations were observed for other oxyanions (i.e., Mo, Sb, Se) and B (toxic for plants) above applicable reference thresholds only under certain pH and L/S conditions. The primary source of all these elements is the FA. An additional layer of soil in the column test (US-EPA 1314) reduces considerably leaching of elements of concern (e.g., As and B). All other metals, including Cd and Pb, were leached in low levels under the DWI and IWI standards, and many even under detection limits. There is a good comparability between mini-lysimeter study and the column testing (US-EPA 1314). All lettuce produced in this study were safe for human consumption.

(Bio)Accumulation of REE in a natural area: from rocks to plants

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Rare earth elements (REEs) are naturally present in the environment, forming a chemically uniform group [1]. They use has increased exponentially during last decades [2]. Consequently, the exploitation of areas with abundance REE in rocks is a main activity worldwide. Physicochemistry weathering of these rocks leads to soil formation, and thus will also participate in sediment and freshwater composition. Few studies have dealt with the distribution of REE in natural areas [3]. Our studied site is located in a high REE concentration area in Canada and the most special feature is that the main deposit presents an intrusion with ferrocarbonatites, which difference this area from those seen elsewhere [4]. The area has been previously investigated but never exploited [4], this gives a specific value to study the natural transfer evolution from the rock material to other environmental compartments.

For this research a total of 7 sampling points were selected according to their parent material and the existence of a watercourse. three where directly sampling in the upper part of the ferrocarbonatite rock, two above pyroxene material, one above tonalite material, and, a control point, was sampling in a limit of the tonalite and basalt material. At each point, has been collected different aliquots of soil, sediment, surface water and suspended material in water. For the REE bioaccumulation, two vegetal species were selected: a terrestrial specie (Equisetaceae sp.) and aquatic specie (Typha sp.).

First results in rock material show that the concentration of REE is significantly high compared to the average concentration in the continental crust (AC) [5], such as an increase in La >2517% (AC: 18 ppm), >923% for Sn (AC: 3.9 ppm) or >340% for Dy (AC: 3.5 ppm). Our next step will be analyze by ICP-MS the REE concentration in the aliquots and plants and determine the mobilization in the different compartments in order to predict a transport model for REE. Our insights will help to better understand future environmental problems related to REE.

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Determination of ruthenium in environmental samples using imprinted polymeric sorbents by ETAAS

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Platinum group metals (PGM) belong to technology critical elements (TCE) which are economically and strategically important for the development of new technologies and increase the quality of people's lives. Their limited resources and support are forcing us to secure their availability in the coming years.

Ruthenium, which is member of platinum group metals, is present at about 1 ng g^{-1} in the Earth's crust. Due to its unique physical and chemical properties, such as high melting temperature, inertness towards many chemical reagents, extreme hardness, good conductivity, and excellent catalytic properties, the element is widely used in electronics, electrical and electrochemical industries. Above all, ruthenium and its complexes have been recognized as an efficient catalysts for a large number of reactions of commercial and environmental importance and exhibit catalyst characteristics in acidic as well as in alkaline media. Ruthenium is very important in terms of green energy technologies (solar energy, fuel cell, light emitting diode). Thus, the versatile use of ruthenium in different fields justifies the special attention in developing low cost, selective, sensitive and precise analytical methods for its determination at trace level.

For the determination of ruthenium in environmental samples electrothermal atomic absorption spectrometry (ETAAS) has been proposed. However, it was found that the presence of many transition metals, e.g. Ni, Co, and Fe, causes interferences during determination of ruthenium by ETAAS. The elimination of interferences is possible by the separation of analyte from matrix elements.

To develop a method suitable for the determination of ruthenium in environmental samples a new polymeric materials based on imprinting technology were studied. The ruthenium ions were imprinted in polymeric network in the a form of complexes with thiosemicarbazide (TSd), acetaldehyde thiosemicarbazone (AcTSn), benzaldehyde thiosemicarbazone (BnTSn), allyl acetoacetate (AAA) and 2-thiobarbituric acid (TBA). The imprinted polymers were prepared via bulk polymerization in the presence of methanol, ethanol or chloroform as porogen and 2,2-azobisisobutyronitrile as initiator. The prepared imprinted polymeric sorbents were tested using column procedure for the separation of ruthenium from interfering matrix.

Newly developed methods, applying as a sorbent the Ru(III) ion imprinted polymers were successfully used for preconcentration and determination of trace amounts of ruthenium in many environmental samples, such as river water, sewage sludge, grass, road dust and platinum ore by the ETAAS technique.

Tellurium (Te) reactivity in estuarine gradients and implications for accidental radionuclide release scenarios

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Tellurium (Te) is a potentially toxic Technology Critical Element (TCEs) of environmental concern [1,2]. However, few studies deal with Te behaviour in fluvial-estuarine continuums despite its ubiquity in aquatic environments [3, 4]. This is a consequence of Te ultra-trace environmental concentrations (challenge for analytical quantification methods) limiting the comprehension of its rather unknown biogeochemical cycle, crucial in environmental dispersion modeling [5,6]. Tellurium is also a product of nuclear fission emitted during accidental nuclear power plant (NPP) events with short-term radioactive emissions (^{127m}Te half-live of 106 days). The aim of this work is to improve our understanding on the environmental fate and potential dispersion of Te in the Gironde Estuary (France), the largest estuary in southwest Europe subjected to two nuclear power plants (NPP) i.e. upstream and within the salinity gradient area.

Kinetic adsorption experiments have been performed using stable Te isotopes and estuarine Suspended Particulate Matter (SPM) to determine and predict Te reactivity under estuarine salinity and turbidity conditions. Natural solid/liquid partitioning coefficients ($\log^{10}$ Kd Te ≈4.8 l kg^{-1}) suggest that after 24h ≈90% of total Te is in the particulate phase, independently of salinity, for SPM between 100 mg L^{-1} and >1 g L^{-1}, i.e. in the estuarine Maximum Turbidity Zone (MTZ).

These results suggest that the fate of Te radionuclides released into the estuary in case of NPP accidents will depend on particle dynamics and related control factors such as freshwater discharge, residence time, seasonal MTZ position, reactive particulate carrier phases, etc. This means that the particular/punctual environmental conditions during the accidental event will determine the imminent radioactive exposure of organisms (e.g., seafood) and human beings to Te radionuclides and its decay products, i.e. the more volatile iodine (I) radioactive isotopes.

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Technology critical metals in the shells of freshwater bivalve '*Corbicula fluminea*': Bioavailability of anthropogenic gadolinium and other anthropogenic rare earth elements in German rivers

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The rare earth elements (REE) belong to the group of particle-reactive elements and occur in very low concentrations in surface waters. Over the past years, these high-technology critical metals received increasing public attention, due to their great economic importance and demand, their consumption and subsequent release into the environment have risen sharply.

The best-studied example of a REE as an anthropogenic (micro)contaminant is anthropogenic Gd that is derived from Gd-based contrast agents used in magnetic resonance imaging. These compounds have very high stabilities and are not readily removed by commonly applied waste water treatment technologies. Therefore, they are released from waste water treatment plants into surface waters with the clear water effluent. Hence, this anthropogenic Gd can be used as a tracer for the presence of waste water-derived substances such as pharmaceuticals and other xenobiotics in river, lake, ground and tap waters.

Over the past 20 years, anthropogenic Gd has been identified in numerous surface waters in Europe, North and South America, Asia and Australia. Recently, its presence was monitored along a gradient in the Rhine River, Germany [1,2]. In addition to anthropogenic Gd that is diffusely discharged into the Rhine River via waste water treatment plants, the Rhine River is also microcontaminated with anthropogenic La and Sm, discharged from a local industrial point source close to Worms [1,2]. In order to assess the bioavailiability of the anthropogenic Gd as well as the industrially derived La and Sm, we analyzed the shells of the freshwater bivalve Corbicula fluminea, collected at 10 sites along the Rhine River. The geogenic REEs are incorporated into the shells of Corbicula fluminea similar to what is expected for inorganic calcite, indicating that vital effects do not have a crucial impact on their incorporation. There is no discrimination against the incorporation of anthropogenic La and Sm, the aqueous speciation of which are likely dominated by the same inorganic complexes that control the speciation of the geogenic REEs. In contrast, anthropogenic Gd is not incorporated into the shell, as it likely still occurs bound to the very stable organic complex designed for use as contrast agents in magnetic resonance imaging. This shows that while the anthropogenic La and Sm are bioavailable, the anthropogenic Gd is not, corroborating the conservative behavior of anthropogenic Gd which may be used as a pseudo-natural tracer.

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Macro-, micro- and trace elements distribution in different growing stages

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The uptake of elements in plants grown in different soil conditions is usually affected by plant species, plant maturity or agricultural practices. Macro-, micro- and trace elements content were monitored for identifying the optimal harvest period (for maximum nutritional relevance) of Lactuca sativa (lettuce plants). Lettuce plants were cultivated in greenhouse and a sample collection was made every two weeks. Irrigation of the samples was based on water coming from two different sources, slightly differing in terms of elemental concentrations: the first water source was tap water and the second one was spring water. The same commercial soil was used in the study. All the samples consisting in different plant tissues (roots, nervures and leaves) and soil were investigated. The obtained experimental data were processed with different chemometric techniques.

Lactuca sativa plant presents similar behavior from the point of view of the metal concentration in the whole plant for both irrigation waters. The evolution of elemental content during eight weeks of growing was investigated by applying ANOVA test separately on: macro-elements (Na, Mg, K, Ca, P), essential elements (Fe, Cr, Mn, Cu, Zn) potentially toxic elements (Li, Al, V, Co, Ni, As, Cd, Ba, Pb) and technological critical elements TCE (Ga, Nb, Pd, Eu,Tb, Tl, Ho). The conclusion deriving from the study is that for all element groups the maximum elemental concentrations correspond mostly for to second growing week showing this way that the nutritional value of lettuce plants depends by the growing stage. From the point of view of TCE's, elements like Eu, Tl had a maximum accumulation level in the 2nd week, but for Ga and Nd no regular distribution was followed.

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Adapted round robin test: Analytical methods for multi-element analysis of anthropogenic ores

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With advancing developments and innovations in electrical and electronic equipment (EEE), batteries, and mobility every year new elements and materials are used to face an ever increasing demand in more efficient and inventive ways of e.g. telecommunication, entertainment technology, energy supply, and mobility. Due to global reserves some elements can be categorized as critical, i.e. they are economically and ecologically important and may pose a future supply shortage [1]. This calls for a robust knowledge base for resource planning to support an improved resource management of critical raw materials, but data availability is often times scarce or heterogeneous and methods used to produce data are unknown or not standardized. A first crucial step is method development for characterizing waste and secondary raw materials to facilitate a more efficient recycling of base, precious, and special metals and hence to provide secondary raw materials with a better quality as well as in higher amounts. This is a task the Horizon 2020 project ProSUM – Prospecting Secondary raw materials in the Urban mine and Mining waste tackles.

In spite of established reference methods for the characterization of ores and geological samples in general, there are no such analytical methods for the “ores of the Urban Mine”, i.e. complex materials, both highly heterogeneous and complex regarding metal mass fractions. To address this issue case studies are conducted within ProSUM with the aim to assess common analytical methods using example study cases of particularly interesting materials, to identify element-specific, optimised methods for strategic and critical SRM, establish reference methods, develop recommendations for other matrices, and create sensitivity for this significant field. Shredded printed circuit boards (PCB) from desktop PC, battery residues after thermal treatment (battery ashes), and automotive shredder residues (ASR) were selected as particularly interesting materials. An adapted round robin test involving eight research institutions and laboratories is used to accomplish the listed objectives. In a first step, semi-quantitative analysis with X-ray fluorescence gives information on the heterogeneity of the sample material. Subsequently, the best technique to determine the “true value” for each element of the specific sample is detected using multiple spiking and determination of the recovery rate. In the PCB case study all participating labs received a preprocessed subsample and the instruction to analyse as usual for a specified set of elements (Pt, Pd, Au, Ag, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Cu, Al, Fe, Zn, Sb, As, Ga, Ge, Sn, Ta, Co, Cd, Pb). These results are used to ascertain element-specific systematic effects originating in the choice of analytical method. The same has been done with battery ashes with a different set of elements.

First results show that common analytical methods can be used to determine element contents in shredded PCB and battery ashes. The method development for ASR is still ongoing. The comparison of different analytical techniques applied shows a wide range of results. Some elements are measurable with several methods, such as Au, Cu, Fe, Zn, and Sn. Other elements can only be analysed with one set of method, eg. Pt, Ta, rare earth elements. In a next step,

Solid phase extraction of chromiun, thallium and arsenic using SGX C18 modified with APDC as sorbent

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As, Tl and Cr belong to a group of potentially very toxic elements. The cations As(III), Cr(III), and Tl(III) have some similar chemical properties and can react with dithiocarbamates (DTCs). Application of diethylenodithiocarbamate (DDTC) in speciation analysis of Tl(III) is very promising [1], but for use of DTCs molecules in simultaneous separation and pre-concentration of the Me(III) from a water matrix, it is required the use of another compound. The solubility of the complexes of trivalent ions with ammonium pyrrolidinedithiocarbamate (APDC) are much lower than with DDTC. Therefore, APDC was proposed for simultaneously precipitation of Me(III)APDC (Me = As(III), Tl(III) and Cr(III)).

As, Tl and Cr compounds with DTCs can be selectively separated in water samples and soil extracts using solid phase extraction (SPE). SPE have been applied for years, but becomes more and more popular due to the small cost of SPE-chambers and easiness of application. The separation of matrix could be performed in mode off-line as well as on-line SPE

The aim of this study was to develop a method for separation of As(III)/As(V), Cr(III)/Cr(VI) and Tl(I)/Tl(III) in water samples on a SPE column. Octadecyl silica gel (SGX C18) modified with ammonium pyrrolidinedithiocarbamate (APDC) was applied as sorbent.

The method is based on the differences in chelation of metals on different oxidation states and APDC depending on the selected conditions, especially pH. Cr(III), As(III), Tl(I) and Tl(III) can precipitate with APDC in acetic acid solution (pH 5) [2]. Based on literature data, ions As(III), Tl(III) and Cr(III) should be retained on the sorbent as complexes with APDC. The sorbent should be leached using organic solvent, according to hydrophobic properties of the compounds. In turn, ions of As(V), Tl(I) and Cr(VI) are unstable in nitric acid solution and using this acid should lead to leaching of the species of the studied elements.

After SPE, using SGX C18 modified with APDC as sorbent, the content of analyte in the eluent was determined by inductively coupled plasma mass spectrometry (ICP MS). Complex Tl(I)APDC (37% recovery) is much better eluted from the sorbent using 0.1 mol L^{-1} HNO_3 than Tl(III)APDC, which was leached in next step (92% recovery). Both forms of Cr - Cr (III) and Cr (VI) were retained on the SGX C18 column modified with APDC. Cr(III) was retained on the sorbent, but more than 40% passed to the filtrate. The best results were obtained for arsenic without the final elution with EtOH at step 6. At the step 5, As(III) was retained on the column (90%), while only 15% of As(V) was retained.

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Towards understanding the mobility of indium and gallium in groundwater systems: constraining the role of sorption in sand column experiments

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Indium and gallium are metals of very low abundance in the Earth's crust and, correspondingly, the biosphere is only adapted to very small concentrations of these elements. However, in modern semiconductor industries both elements play a central role and are incorporated in devices of mass production such as smart phones and digital cameras. The resulting considerable increase in production and discharge of indium and gallium throughout the last ten years raises questions regarding the fate of both elements in the environment, as both are known to bear potential health hazards. However, the transport behavior of these two metals in soils and groundwater systems remains poorly understood to date.

We studied the mobility of indium and gallium in the groundwater environment via laboratory experiments using quartz sand as an initial porous medium. The experimental strategies focused on the sorption behavior of these two metals and comprised batch, sorption equilibrium, and column experiments with an emphasis on the latter. Trisodium citrate was used as a complexation agent that stabilizes the solution, enabling investigation of the transport of these metals at neutral pH. The effect of natural organic matter on the mobility of indium and gallium was studied by addition of humic acid.

The results suggest that the Freundlich model provides a better fit to the sorption isotherms during batch equilibrium experiments than the Langmuir model. Column experiments of indium indicate that the binding capacity of quartz sand is much lower in the presence of humic acid. Moreover, it could be observed that the binding capacity differs between indium and gallium. For both metals, the presence of humic acid has an effect on the sorption dynamics. For indium, sorption was strongly inhibited, whereas gallium indicated a slightly higher sorption affinity in the presence of humic acid. However, in all cases, it could be shown that binding capacity of gallium to quartz is much weaker than that of indium. The results are consistent with the assumption that indium and gallium form different types of complexes with organic ligands. It was further observed that the complexes of gallium appear to be more stable.

Toxicological and Environmental Analysis of Rare Earth Elements and Indium

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In the search for solutions to the energy crisis, materials have been developed and utilized in novel ways to increase the efficiency and reduce the cost of technologies such as fuel cells, batteries, photovoltaics, LEDs, and advanced electronics. Cerium, a rare earth element (REE), has been incorporated in next generation polymer electrolyte membrane fuel cells to prevent degradation of the membrane electrode assembly. Additionally, common electronics such as iPhones contain the majority of lanthanides. These technologies are evolving at a tremendous rate, and the human health consequences of the increasing demand for REEs and indium are unknown. There is a dearth of research on this topic, and what findings do exist are often in disagreement. Hirano and Suzuki claim that the toxicity of lanthanides decreases with increasing atomic number [1], while Bruce et al. report the opposite trend [2]. It is critical to conduct conclusive toxicological studies in addition to determining the natural and industrial fluxes of these elements to facilitate the sustainable development of modern technologies.

To this end, sediment samples from both an ombrotrophic bog in a remote region of Massachusetts and from a river bordering research facilities in Rochester, NY were analyzed for REEs and indium. While the bog represents background environmental levels of these elements, the river is influenced by such anthropogenic sources as the University of Rochester, Strong Memorial Hospital, Kodak and Xerox research facilities, and is potentially subject to more concentrated waste streams. Particles accumulate unperturbed in the bog via rainfall, whereas the turbulent fluid dynamics of the river would dictate an uneven distribution. Upon sediment digestion and ICP-MS analysis, the levels of REEs and indium in the river sediment were found on whole to be an order of magnitude higher than the bog concentrations.

Additionally, preliminary toxicity studies were conducted in human lung epithelial cells. Both oxide and chloride forms were tested at varying doses and exposure periods, with concurrent decreases in cell proliferation rates observed, indicating toxicity. Cell uptake studies were also conducted and the concentration of neodymium and cerium within the cells quantified by ICP-MS. The mechanism of toxicity is currently unknown, however it is hypothesized to be oxidative stress, with further research required to clarify the consequences of REE exposure within mammalian systems.

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Time-Series (1991-2014) Trends of Technology-Critical Elements Accumulation in Mussels from an Urban Coastal Area (Vigo Ria, NW Iberian Peninsula)

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Current technologies such as electronics, medicine or computer science are evolving rapidly and they need a set of key components for its development, elements that are at very low concentration (<100ppm) but are key for the manufacturing of e.g. batteries, magnets, medical equipment, alloys or everyday products such as lamps, TV, signals or lasers.

The importance of the study of these key elements known as Technology-Critical Elements, TCEs, has increased because of its growing use and release into the environment which can cause changes in their biogeochemical cycles. The TCEs can be bioaccumulated by organisms and their impact needs to be studied more precisely.

In order to shed further light in this area, we present in this study the time-series (1991-2014) trends in concentrations of several TCEs in mussel samples (Mytilus galloprovincialis) collected in an urban beach from the Vigo Ria (NW Iberian Peninsula). The TCEs analyzed were Pt, Y, Ta, Nb, Tl, Au, Ag and the rare earth elements (REEs: Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu). The only element that showed a significant temporal trend linked to human activities was Pt (Neira et al., 2015), an element whose environmental inputs has been linked to its use in catalytic converters in cars. For the other elements, no evident trend was observed except a decreasing trend for Au and Ag. However, REEs show a strong correlation between them and a temporal increase of light-to-heavy ratios (LREEs/HREEs).

The uptake of each element depends on its chemical properties, its concentration in the environment and also the hydrological conditions (e.g. upwelling events, renewal of water) have a major influence. Accordingly, the influence of natural processes on the bioaccumulation of TCEs will be discussed.

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Dissolved Rare Earth Elements in Estuarine and Coastal Waters of the Gulf of Cádiz (South Spain)

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The waters of the Gulf of Cádiz (South Spain) have been historically contaminated by trace metals [1], due to the influence of the Iberian pyrite belt (one of the most important sulfide deposits in the World). This area receives large amounts of trace metals transported by the different rivers running through the belt and discharging into the Gulf of Cádiz. However, there is no information to date on the levels and geochemistry of dissolved rare earth elements (REEs) in this area. To this aim, REEs were analyzed in the outer part of the major estuarine systems (Gudalquivir, Guadiana and Tinto-Odiel) and coastal waters of the gulf. Determination of dissolved REEs was achieved by ICPMS after off-line pre-concentration [2]. Highest total REEs concentrations were found in the systems most influenced by the Iberian pyrite belt, i.e., the Tinto-Odiel estuary (salinity 35.6-36.3; REEs from 92 to 116 ng/L), and the Guadiana estuary (salinity 23.7-30.7; REEs from 67 to 77 ng/L). For the Guadalquivir estuary (salinity 23.4-33.9), REEs were lower and ranged from 40 to 43 ng/L. However, despite the lower total REEs in the Guadalquivir, an evident contamination for Gd was observed with concentrations of 2.3 to 6.2 ng/L and a strong correlation with salinity (r^2=0.994), resulting in an estimated freshwater end-member value of ~ 15 ng/L. This Gd contamination can be explained by the higher urban influence on the Guadalquivir system, receiving discharges from the city of Seville, compared to the Guadiana and the Tinto-Odiel. For the open waters of the Gulf of Cádiz no contamination was observed, indicating an effective dilution of the estuarine waters.

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Sources and distribution of yttrium and rare earths in Tagus Estuary sediments

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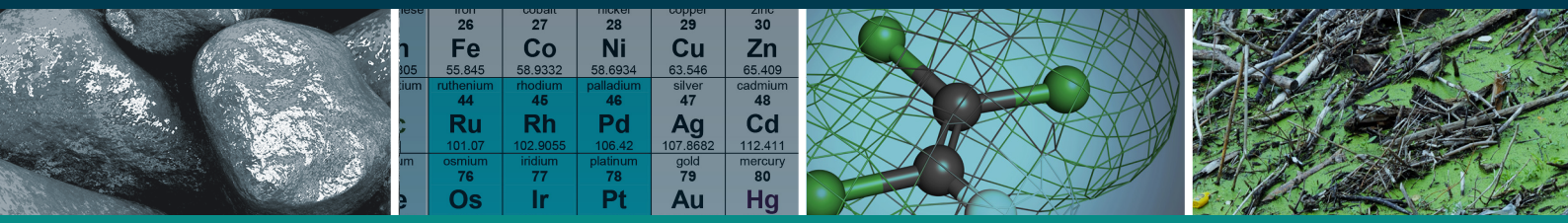
The distribution and sources of yttrium and rare earth elements (YREE) in surface sediments were studied on 78 samples collected in the Tagus Estuary (SW Europe). Biogeochemical cycling YREE have been studied in rivers, estuarine and coastal systems, and reported as geochemical indicators associated with sediment provenance and anthropogenic activities. The Tagus estuary, one of the largest in Europe (c.a. 320 km^2 total area), has an input of freshwater from the main river (Tagus River) and from small tributaries. The estuary has been receiving from decades several agricultural, industrial and domestic effluents located in the large metropolitan area of Lisbon. The objectives of this study were: (1) to characterize the YREE distribution and concentration in the surface sediments, (2) to identify the principal sources and sinks of these elements in the estuary, (3) to evaluate the correlations between YREE and other elements studied (Al, Fe, Mn and Th). To the authors' knowledge, there has been no previous study on distribution and sources of YREE in the Tagus estuary. Total REE (ΣREE) and yttrium concentrations in the sediments ranged from 18 to 210 $mg \cdot kg^{-1}$ and 2.4 to 32 $mg \cdot kg^{-1}$, respectively. All REE and Y exhibited in general significant correlations with fine fraction, Al, Fe and Th suggesting an association with fine-grained particles and oxyhydroxides of Fe and Al. The data showed that the PAAS-normalized ratios within each area of the Tagus estuary were variable and in general lower than the unit.

It is possible to identify different PAAS-normalized REE patterns along the estuary, in particular: (1) a general enrichments of LREE and MREE relative to HREE; (2) a positive anomaly of Eu, predominantly associated with coarse sediments and low REE concentrations; and, (3) a negative anomaly of Ce probably associated with a phosphogypsum source. Preliminary evaluation showed the importance of hydrodynamic conditions and mixing processes along the estuary gradient that contributes to the high variability of YREE concentration in the Tagus estuary sediments.



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