

FA Forel Earth and Environmental Sciences Faculty of Sciences Mercury (Hg) is a global concern for water pollution. Both in sediment and water column, fate of mercury may be influenced by the presence of primary producers [1]. Aquatic primary producers are key organisms for ecosystems because they represent a source of oxygen and food at the basis of trophic chains. Assessing Hg bioaccumulation in those organisms is essential for notably predicting its probable impact on higher trophic levels. We studied the accumulation of Hg (inorganic Hg – IHg and methyl Hg - MeHg) in *Elodea nuttallii*, a rooted submerged freshwater macrophyte and in *Chlamydomonas reinhardtii*, a phytoplanktonic species. Both have been shown to play important role in Hg bioaccumulation and biomagnification in freshwater systems food web [2]. We exposed the organisms to IHg or MeHg spiked artificial water in the laboratory and measured accumulated Hg both in kinetics experiments (from 10 min to 8 hours) and wide range of increasing concentrations (10<sup>-11</sup> to 10<sup>-7</sup> M Hg). In addition, subcellular localization of accumulated Hg was investigated in *E. nuttallii*, notably inthe cell wall and in the cell sap. Accumulation of Hg from the water is quite rapid in *E. nuttallii*, mainly in the cell wall when exposed to MeHg, or in both cell wall and cell sap when exposed to IHg. This study shows that there is a difference in bioaccumulation kinetics (i.e. assimilation and elimination) between both Hg forms in *E. nuttallii* and we aim at comparing this result to kinetics experiments with *C. reinhardtii*. References: [1] Regier, N. et al. (2012). "Effect of *Elodea nuttallii* Roots on Bacterial Communities and MMHg Proportion in a Hg Polluted Sediment". Plos one 7(9): e45565. [2] Bravo, AG *et al.* (2013). "Extremely elevated methyl mercury levels in water, sediment and organisms in a Romanian reservoir affected by release of mercury from a chlor-alkali plant". Water research (in press).

#### TH100

**Mercury levels in target organs of cetaceans stranded in the Southwest coast of Spain.**

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#### TH101

**Estimation of mercury bioaccessibility in contaminated agricultural environment**

F. Zoz, University of Udine / Department of Agricultural and Environmental Sciences; M. Contin, University of Udine; A. Emili, Department of Mathematics and Geoscience; A. Acquavita; A. Khakbaz, M. De Nobili, University of Udine The existence of mining activity in Idrija (Slovenia) has been demonstrated to be the primary source of mercury (Hg) in the Gulf of Trieste (northern Adriatic sea) through the Isonzo river inputs. Due to erosion of the mining region, particulate material strongly enriched in Hg was transported downstream and deposited on the riverside soils by the flooding of the Isonzo river. As a consequence the soils of the area are characterized by a diffuse Hg contamination with concentrations reaching up 80 µg g<sup>-1</sup>, o.d.w. This work was carried out in order to evaluate the application of a bioaccessibility parameter within the calculation of a site-specific risk assessment of these contaminated soils. To evaluate the Hg bioaccessibility, the PBET (Physiologically Based Extraction Test) procedure, considering the risk associated to direct oral intake of contaminated soil was applied. Two separate extractions simulating both the stomach and small intestine secretions were sequentially performed. Hg concentration in soil (average 9.41 ± 6.40 µg g<sup>-1</sup>) show a clear trend moving downcore, reaching the maximum value of 20.77 µg g<sup>-1</sup> in the upper layer. However, the element seems to be accumulated also in the deepest horizon probably due to ingression of contaminated groundwaters. By applying the Bloom et al (2003) selective sequential extraction procedure emerged that Hg is almost entirely in form of cinnabar (HgS)

(72.9+94.1%), whereas the presence of the bioavailable form is negligible. Total bioaccessible Hg, estimated by PBET, ranged from 0.029 to 0.389%, thus confirming the prevalence of HgS form. Moreover, all bioaccessible Hg is present in the stomach phase (acid condition), whereas at the small intestine level (basic condition) no Hg dissolution from the solid phase was observed. In addition to the lab tests, it was evaluated the output

obtained with a dedicated software, RiskNet, for the calculation of health risk due to the accidental ingestion of soil contaminated with Hg. The simulation demonstrated that the health risk is close to, or well above, the limit of acceptability. These results confirm that when an evaluation risk analyses is conducted, it is necessary to take into account the whole site-specific geochemistry of the soil.

#### TH102

**Relations between total mercury, methyl-mercury and selenium in five tissues of Sepia officinalis captured in the South Portuguese Coast**  
J.R. Raimundo, IPMA / DIVOA; P. Pereira, Biology department; C. Vale, IPMA Instituto Portugues do Mar e da Atmosfera; J. Canario, University of Lisbon / Instituto Superior Técnico; M. Gaspar, IPMA Mercury (Hg) is one of the priority hazardous pollutants in the world, with no role in biochemical processes. Speciation influences Hg mobility in various environmental compartments, being methylmercury (MeHg) the most toxic form. Methyl-mercury is produced in aquatic environment by bacteria and biomagnifies through the food web as result of slower elimination than uptake. Mercury is uptake mainly through diet with MeHg being the form predominantly stored in muscle tissue. Selenium (Se) is an essential trace element known to have an antagonistic action against the toxicity of mercury forms in aquatic organisms. This element seems to have a blocking mechanism in methylation by the precipitation of HgSe or to contribute to MeHg demethylation. The relation Se-Hg has been mainly searched in fish, and fewer studies have been done with invertebrates. The cuttlefish, *Sepia officinalis*, is a nektobenthic species, with high metabolic rates, short life span (around two years), feeding on a large variety of living prey. This work reports the concentrations of total- and methyl-mercury and total Se in digestive gland, branchial hearts, kidney, mantle and gills of *S. officinalis* caught in the south Portuguese coast (Olhão and Vila Real Sto António). The involvement of Se in the mechanism of MeHg demethylation in each tissue was examined. To the best of our knowledge these are the first data on Hg, MeHg and Se in branchial hearts, kidney and gills of cuttlefish. Digestive gland, branchial hearts and kidney presented higher levels of Hg and Se than mantle and gills. Methylmercury was significantly higher in digestive gland, branchial hearts and mantle. The enhanced levels of Hg in digestive gland and branchial heart reinforce the elevated storage capacity of these two tissues. The percentage of MeHg varied from 6.1 % in gills to 92 % in mantle. Linear and positive MeHg-Hg relations were obtained for the five tissues, being the better relation and higher slope observed for mantle, followed by branchial hearts, digestive gland, kidney and gills. The Se:Hg molar ratios showed a surplus of Se in all tissues. Calculations based on the equimolarity of Se:Hg point that 95 to 99% of Se are not linked to Hg (Se free). The negligible quantity of Se associated with Hg suggests that the mechanism of MeHg demethylation was not triggered in none of the tissues, presumably because the threshold for MeHg toxicity was not achieved.

#### TH103

**Hepatic Bioavailability of Total Mercury (THg) in Cichla sp from Tapajós River Region, Brazilian Amazon**

J.d. Azevedo, Federal University of Sao Paulo / Biological Sciences; J.E. Sarkis, M.A. Hortellani, IPEN - Nuclear and Energy Research Institute / Center for Chemical and Environmental Technology Most of the Hg occurring in the Amazon is of natural origin. However, the intense gold mining activity in the region has increased the levels of this toxic metal, especially in the middle section of the Tapajós River. Specimens of the *Cichla* genus have great economic and ecological significance, as they are the most consumed fish in the Brazilian Amazon region and are at the top of the Amazon food chain. In addition, they are a good indicator of Hg bioaccumulation because the concentrations of Hg in their tissues tend to reflect the accumulation process of successive exposure. A total of 26 adult specimens of *Cichla sp* were obtained by fisheries in the Tapajós River region’s contaminated gold mining area. In the laboratory, morphometric data of each fish was taken, for instance total length, total weight and sex. The liver tissue was removed from each specimen, washed with distilled water, packed in polyethylene identified bags and kept at - 20°C for subsequent total mercury (THg) analysis. Assays were carry out in the total liver and in the cytosol hepatic fraction obtained by ultracentrifugation of the tissue in buffer Tris-HCl 10 mM, pH 7.4. The analyses were performed by flow injection Cold Vapor Atomic Absorption Spectrometry (FIA-CV AAS) with detection (DL) and quantification limits (QL) of 0.527 and 2.585 µg Kg<sup>-1</sup>, respectively. Individuals of *C. sp* had active gonadal maturation, including spawning and post-spawning individuals. The average length and total weight was 395 ± 51 mm and 840 ± 418 g, respectively. High levels of THg were obtained in the total liver ranging from 1.7 mg Kg<sup>-1</sup> to 3.8 mg Kg<sup>-1</sup>. However, only 0.2% of the THg were available to the cytosol hepatic fraction. A significant and positive correlation (r<sub>s</sub> = 0.65) was found between the concentration of the THg in the total tissue and in the hepatic cytosol fraction. These data are a preliminary study with respect to the bioavailability of total mercury (THg) in different compartments of the hepatic tissue of *C. sp* in order to understand some aspects of the detoxification mechanism of this toxic metal in bioindicator species from the Amazon region. In fact, it was possible to observe differences in the transference of this important toxic metal into the cell and its

linkage in the compartments.

#### TH104

**BIOACCUMULATION AND BIOMAGNIFICATION IN AQUATIC ORGANISMS OF THE ALMADEN MINING DISTRICT**  
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The Almadén mining district (Spain) is a singular case of natural mercury concentration in the World. The intensive mining activities during the last two thousand years have caused a dispersion and remobilization of mercury within the area. Water bodies in the area are of special concern, specially the living aquatic organisms. This study is focused on the bioaccumulation of Hg levels on organisms of the Valdeazogues River, the main watercourse traversing the Almadén mining district, and to evaluate the Hg trough the trophic chain. In a preliminary sampling campaign, total Hg ranged from 2.21 to 133.70 mg/kg in biofilm, 0.3-20.6 mg/kg in macro invertebrates or 0.6–861.70 mg/kg in crayfish. These results show an enormous bioaccumulation in the specimens collected and a concerned biomagnification in the trophic chain of Almadén freshwaters.

#### TH105

**Identification of present-day and historical sources of mercury in a complex industrial area**

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Mercury levels were measured in soils and earthworms on behalf of a long-term surveillance program of the emissions from the industrial area of Scarlino (Southern Tuscany, Central Italy), where a municipal solid waste incinerator and two main chemical plants are currently operating. The study aimed at establishing preliminary soil data to be used as baseline for long-term monitoring of mercury contamination of soil and soil biota and to assess eventual contribution of the industrial emissions. Overall total mercury concentration of superficial soils (0-5 cm), collected from 44 sampling sites randomly selected within a circular area up to 1.5 km from the center of the industrial area, was in average 0.29 ± 0.27 µg g<sup>-1</sup>. This value, which remains well below the screening values (1 µg g<sup>-1</sup>) for contaminated soils set by the Italian regulatory framework for residential areas, is approximately 4-5 times higher than the European topsoil baseline (FOREGS) for mercury and highlights a general enrichment of the metal in the area. This is mainly attributable to widespread geochemical anomalies characterizing the Southern Tuscany and to the historical mineral processing and smelting activities that have been carried out in the Scarlino area until the mid-90s. The highest mercury concentrations were found in soils from sampling sites in direct proximity of industrial/artisanal activities, where concentrations up to 1.59 µg g<sup>-1</sup> were reached. Average mercury concentrations (0.25 ± 0.10 µg g<sup>-1</sup>) from agricultural and grazing land soils were also noticeable, although earthworms from the same sites did not show a significant bioaccumulation of the metal (0.11 ± 0.09 µg g<sup>-1</sup>). The generally elevated concentrations and the high variability (overall coefficient of variation = 93%) of mercury soil data from the Scarlino area are questioning the possibility to isolate the influence of a single source of contamination in an environment with a long industrialization history. This is currently prompting further research supported by techniques for monitoring atmospheric depositions (i.e. biomonitoring, passive sampling) to improve estimation of mercury contamination arising from different possible sources in the Scarlino area.

#### TH106

**Historical variations in the isotopic composition of mercury in sediment cores from northern Adriatic coastal environments**

S. Covelli, Dipmento di Matematica e Geoscienze / Dept of Mathematics and Geosciences; C. Baschieri, A. Marchetti, University of Modena and Reggio Emilia / Dept of Chemical and Geological Sciences; A. Acquavita; A. Berni, University of Modena and Reggio Emilia / Dept of Chemical and Geological Sciences; L. Spizzamiglio, University of Trieste / Dept Mathematics and Geosciences The results presented in this study involve the analysis of mercury (Hg) isotopes in two sediment cores from the Northern Adriatic. One core was collected in the Gulf of Trieste, an area contaminated by Hg residues produced by the Idrija Hg mine (Slovenia) during 500 years of activity and transported by the Isonzo River to the sea. The second core was collected in the Marano and Grado Lagoon, where Hg from a chlor-alkali plant was discharged into the Aussa-Corno River system flowing into this coastal environment. In this study, we used the high precision stable Hg isotope analysis of environmental samples made possible by continuous flow cold vapour introduction system coupled with MC-ICP-MS. The main aims of

this research were to determine the isotope signatures of Hg from the two major sources of contamination, to compare them with the same signatures of the regional sedimentary background and to determine if Hg isotope compositions can be used to distinguish between different products deriving from exploitation and processing of Hg-bearing ore. Analysis of the dated core from the Gulf of Trieste showed that Hg concentration increased sharply at the beginning of 1800s, peaked before the first World War (23.32 µg g<sup>-1</sup> in 1913) and then declined to a constant average of ≈ 8 µg g<sup>-1</sup> in recent times (1980s-1990s). δ-values of the <sup>199</sup>Hg/<sup>198</sup>Hg, <sup>200</sup>Hg/<sup>198</sup>Hg, <sup>201</sup>Hg/<sup>198</sup>Hg and <sup>202</sup>Hg/<sup>198</sup>Hg ratios increased upward from the core bottom. Background sediments, where Hg concentration is 0.13 µg g<sup>-1</sup>, have an average δ<sup>202</sup>Hg of -3.93‰ ± 0.92‰ (n=5) which is significantly lower compared to recent contaminated sediments. The isotope signature of Hg deriving from mining activity was not altered by mass-independent fractionation (MIF) related to natural processes. Conversely, it showed mass-dependent fractionation (MDF), due to the transformation processes of Hg-bearing ores (mostly cinnabar but also native Hg in carboniferous schists) to by-products by the retorting processes which caused preferential depletion in the lighter isotopes. The isotope signatures of Hg were quite variable in the contaminated section of sediment cores where δ<sup>202</sup>Hg values ranged between -2.95‰ and 0.88‰. The variability in MDF is due to multiple sources, such as unroasted Hg ores and Hg waste calcines which, with different mixture and isotopic fingerprinting, affected the total isotopic composition of sediments.

#### TH107

**Artificial reservoirs downstream the two largest mercury mining areas in the world: source and/or sink of the metal?**

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Almadén (Spain) and Idrija (Slovenia) were the largest cinnabar (HgS) mines in the world with an approximate production of 10.5 Million of Hg flasks. During time being in operation and, later, after their closure, a great amount of mercury (Hg) was introduced into the environment. Part of this Hg is still stored in the two mining areas and it is currently supplied to the freshwater aquatic environment due to the erosion of soils, Hg tailings and river banks. Whereas the Valdeazogues River directly drains the mining area, the Isonzo/Soca River receives freshwaters from its tributary, the Idrijca River. Both two drainage basins are characterized by artificial reservoirs along their streams with relatively large dams. They are barriers stopping the normal water flow and they can be efficient sedimentary traps. This study focuses on a preliminary comparison of Hg occurrence in the water column and bottom sediments of the two main artificial reservoirs (Castilseras, in Spain and Solkan, in Slovenia) located along the Valdeazogues and Isonzo/Soca rivers. The aim is to understand the effects of physical and biogeochemical factors on the distribution of Hg species. During field works, both reservoirs showed water column stratification more important in the Castilseras reservoir. The average temperature difference between surface and bottom layers was 12.1°C in Castilseras reservoir, while in the Solkan reservoir the same difference was only 5.6°C, except one point where a karst spring flowing at the bottom of the reservoir determined a significant temperature drop (13.3°C). Most of Hg in the water column is in particulate form predominantly associated with very fine suspended particles. Total dissolved Hg (DHg) concentrations in the water column were similar in both reservoirs (

#### TH108

**Mercury environmental quality standards in the European Union**

D.A. Vignati, CNRS / LIEC UMR; S. Polesello, Water Research Institute CNR / Water Research Institute; M.S. Bank, University of Massachusetts / Department of Environmental Conservation Environmental regulatory compliance for Hg pollution has long been assessed in terms of Hg concentrations in the water phase. In such frameworks, Environmental Quality Standards (EQS) are enforced as total Hg concentrations, although methylmercury (MeHg) is the form of highest concern. As a consequence, water quality criteria based on total Hg levels in the water phase may be underprotective against secondary poisoning unless they are adjusted for MeHg levels; a practice that so far is not widespread. Furthermore, monitoring procedures are not necessarily harmonised and even simple filtration before analysis can result in marked differences in Hg levels. To correct for these potential biases, the European Union has introduced, in 2008 and later in 2013, a major shift in Hg monitoring and management by adopting an EQS based on total Hg concentrations in biota as an alternative to the water EQS. The use of a Hg-EQS for biota is scientifically sound