

## Oral Presentations: Session 1

### [OP 1.1]

#### Use of Selective Extractions to Assess the Bioavailability of Inorganic Mercury in Sediments and Soils

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A novel sequence of selective extractions was developed for Hg in solid media. Mercury is separated into fractions which 'make sense' biogeochemically, rather than striving for compound-specific identification, which is impossible by wet extraction methods. Experiments elucidated the effects of extraction time, solids:liquid ratio, and alternate solvents (1N HCl, 1N HN<sub>2</sub>OH) in natural samples, reference materials, and pure compounds. Compounds tested included cinnabar (red HgS), metacinnabar (black HgS), freshly precipitated HgS, HgCl<sub>2</sub>, Hg<sup>0</sup>, Hg-humate, Hg/Au amalgam, and HgO. Based on these findings, a 5-step sequence of extractions was established to provide the best separation of the compounds into distinct biogeochemically meaningful categories (Table).

Method blanks and detection limits of 0.1-5 ng/g were obtained for the various analytical fractions, depending largely upon the reagent concentrations used. Precision was in the range of 2-8% for the major fractions in a given sample, but increased to 2-40% for fractions making up less than 5% of the total. Recovery of total Hg by the sum of species in reference materials showed that the overall accuracy of the method on homogeneous samples is in the range of 90-105% of the true values.

Although limited to a few high-level samples, EXAFS analysis confirmed the ability of the selective extraction scheme to separate HgS from non-HgS. Methylation potential, determined by anoxic incubation of aliquots of the samples with biological sediments showed that inorganic Hg extracted in the 1N KOH fraction is most strongly correlated with the methylation potential. In all natural and sediment incubation samples, most of the Hg present was found either in the 1N KOH (organic) or aqua regia (HgS) fractions.

Fraction	Solvent	Description (major species)
1-a	deionized water	volatile water soluble Hg (low Hg <sup>0</sup> )
1-b	deionized water	freshwater leachable Hg (HgCl <sub>2</sub> , HgO)
2	0.1M CH <sub>3</sub> COOH + 0.01M HCl	'stomach acid' soluble Hg (HgO, HgAu)
3	1M KOH	organic (humic) associated Hg (org-Hg)
4	12 M HNO <sub>3</sub>	remainder of non-cinnabar Hg (high Hg <sup>0</sup> )
5	Aqua Regia	cinnabar, metacinnabar (HgS)

### [OP 1.2]

#### Metal Speciation in Natural Waters – Measurements and Modelling

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No speciation technique can measure all individual species, so reliance has to be placed on measuring single or sets of species and using calculations to estimate the remaining species. The new technique of diffusive gradients in thin-films (DGT) is no exception, but it does have several advantages over other procedures. In DGT, metals are transported across a defined diffusion layer of hydrogel before binding to a chelating resin layer. Only labile species that can dissociate as they pass through the diffusive layer are measured. Another discriminator is the pore size of the diffusive gel layer which can be varied by changing the gel composition. In this way, DGT can be used to distinguish between small and large species, which we have ascribed to inorganic and organic species present in natural waters. This operational definition is based on their mobility, calibrated by simple inorganic solutions, or by fulvic or humic acids. Only labile species are

measured, which is appropriate for speciation calculations based on equilibrium models. The measured total labile inorganic species can therefore be used as an input parameter, along with major ions and cations in a speciation program, allowing a calculation of the concentration for all species. The free ion activities of metal ions measured using DGT with an appropriate speciation calculation are compared with independent measurements using adsorptive cathodic stripping voltammetry. The implications of these results are then discussed. DGT can measure a suite of up to 10 trace metals simultaneously and it can be deployed in situ in natural waters. Moreover, it is simple, robust, easy to use and can be used in diverse matrixes without any special precautions. It therefore provides a breakthrough in the routine quantification of labile species and free ion activities for both regulatory monitoring and studies of biological uptake.