# Hg isotope analysis and sequential extractions of industrially contaminated soils in Valais, CH

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The partitioning of mercury (Hg) into different pools within soils and sediments controls its fate and behaviour, but characterising these pools is a challenge. We examined industrially contaminated soils and sediments from Visp, Switzerland, by combining stable Hg isotope analysis and sequential extractions. Previous work suggested that the samples (up to 150 mg kg$^{-1}$ Hg) contained no elemental and only minor sulfide-bound Hg pools, and were dominated by Hg(II) species presumably bound to organic matter (OM) and/or mineral surfaces. We employed an extraction sequence of (1) water (for labile mercury), (2) NaOH or $Na_4P_2O_7$ (for organically bound Hg), (3) $NH_2OH$-HCl (for Mn and Fe (oxyhydr)oxides), and (4) aqua regia (residual pools). Hg isotope ratios were measured using CV-MC-ICP-MS.

The proportions of the total Hg pool extracted by water (≤1.5%), NaOH (≤36%), $Na_4P_2O_7$ (≤18%), and $NH_2OH$-HCl (≤1.0%) were relatively small. Although both NaOH and $Na_4P_2O_7$ primarily dissolve OM and the Hg bound to it, differences between the two extractions indicate that they also attack other Hg pools. Hg associated with sulfide and/or Fe and Mn (oxyhydr)oxide colloids, were likely important in some samples and were extracted more efficiently by $Na_4P_2O_7$ than NaOH. The Hg that was not removed by the first three steps in the extraction procedure may be bound to recalcitrant OM or crystalline minerals. A series of consecutive $H_2O$ extractions showed that labile Hg species are released slowly.

Surprisingly and in contrast to previous findings [1-3], Hg isotope signatures in sequential extracts and bulk digests were mostly indistinguishable (2SD ≤ 0.14‰). However, $NH_2OH$-HCl extractions produced heavy MDF and negative MIF values (max. difference from bulk: $\delta^{202}$Hg=+0.87‰, $\Delta^{199}$Hg=-0.15‰), presumably an extraction artifact caused by reduction of Hg(II) by Fe(II) followed by volatile Hg(0) loss.

Our results provide insight into the action of sequential extractions and develop the application of Hg isotopes to understanding Hg partitioning in environmental media.

[1] Wiederhold *et al.* (2013), *ES&T* **47**, 6137-6145.
[2] Yin *et al.* (2013), *Chem. Geol.* **336**, 80-86.
[3] Wiederhold *et al.* (2015), *ES&T* **49**, 177-185.