

Tracing Hg transformations in contaminated soil using Hg isotopes

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Mercury (Hg) undergoes biogeochemical transformations whose products differ drastically in their bioavailability, mobility and toxicity. Knowing Hg speciation in natural systems is thus key to understanding its risk. The 7 stable isotopes of Hg vary in their abundances in environmental samples. Mass-dependent and mass-independent isotope fractionation have also been shown to take place during biogeochemical reactions in nature and the laboratory. This allows for a new application: to identify and potentially quantify Hg transformation pathways and processes.

Hg stable isotope ratios have been measured by CV-MC-ICP-MS [1] on vadose zone soil samples at a former industrial site in SW-Germany [2] to better understand the transformations of the pollutant HgCl₂ in the system. Despite oxidizing conditions in the bulk soil, HgCl₂ is partly reduced to metallic Hg⁽⁰⁾. On two soil cores, total soil digests and sequentially extracted Hg pools were analyzed for Hg concentrations, Hg isotope ratios and speciation based on pyrolytic thermo-desorption.

Digests of the most contaminated soil samples (up to 800 mg kg⁻¹ Hg) showed $\delta^{202}\text{Hg}$ values within the expected source signature of industrial Hg of around $-0.43 \pm 0.09\text{‰}$ (2SD, relative to NIST-3133). Among the sequentially extracted Hg pools within the samples, Hg isotope ratios varied significantly. Contaminated groundwater from a close-by well was strongly enriched in heavy isotopes ($+0.75\text{‰}$), contrasting with the light bulk soil signatures. Among the most Hg-rich soil samples, which contained a mixture of metallic Hg⁽⁰⁾ and Hg^(II) phases, it was the H₂O-extractable and most mobile fraction which was heaviest, exhibiting $\delta^{202}\text{Hg}$ values of up to $+0.18\text{‰}$. A series of sequential water extracts revealed slow dissolution kinetics of mobile Hg pools from the soil, continuously releasing isotopically heavy Hg into solution.

The identified Hg pools showed significant Hg isotope fractionation among themselves, and also between different sampling depths of the soil cores. Our results demonstrate the potential of Hg isotopes to be useful tracers of Hg transformations in contaminated soil systems.

[1] Wiederhold *et al.* (2015) *ES&T* **49**, 177-185.

[2] Bollen *et al.* (2008) *Water Res.* **42**, 91-100.