



A deep look at a highly mobile soil mercury pool, using Hg stable isotope analysis, XANES and EXAFS

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While mercury (Hg) is recognized as a dangerous global pollutant, its toxicity and mobility strongly depend on its speciation, requiring one to look beyond mere concentrations to perform risk assessments at Hg-contaminated sites. We took an integrated approach to understand species transformations at a former wood preservation site in SW-Germany, where highly soluble aqueous HgCl_2 had entered loamy, low organic matter soil. Firstly, Hg concentrations and speciation were analyzed in two soil cores. Secondly, to identify species transformation processes, Hg stable isotope analysis was conducted on sequentially extracted and total Hg pools of the soil cores. Changes in Hg stable isotope signatures during Hg species transformations have been reported in laboratory studies to be representative of different transformation processes [1]. Hg speciation was assessed qualitatively using sequential extractions (SE) and pyrolytic thermo-desorption (PTD) [2]. Selected samples were then analyzed quantitatively using X-ray Absorption Near Edge and Fine Structure Spectroscopy (XANES, EXAFS).

Maximum concentrations of $802 \mu\text{g g}^{-1}$ Hg were found at 2.5 m depth in core K2, whereas the secondarily contaminated core K3 contained only up to $100 \mu\text{g g}^{-1}$ Hg. The speciation of all measured samples was distinctly different from the original contamination source ($\text{Hg}^{(II)}$ -chloride). Samples contained at least 34% and up to 91% (in K3) of refractory Hg phases according to SE, confirmed as β -HgS by XANES. XANES also revealed significant amounts of reduced $\text{Hg}^{(0)}$ in the most contaminated samples, in agreement with the PTD results. Surprisingly, XANES revealed the presence of a $\text{Hg}^{(I)}$ phase, likely calomel (Hg_2Cl_2), which is rarely found in environmental samples. Hg isotope ratios measured using CV-MC-ICP-MS [3] exhibited clearly resolvable variations between the extracted pools. Bulk core samples showed $\delta^{202}\text{Hg}_{\text{NIST-3133}}$ values as low as -0.43‰ ($\pm 0.09\text{‰}$ 2SD), similar to average literature values of industrial Hg sources. Water extracts were enriched in heavy isotopes (up to $+0.18\text{‰}$) similar to groundwater from nearby wells. Our findings agree well with laboratory studies reporting a corresponding enrichment of light isotopes in precipitated HgS and in $\text{Hg}^{(0)}$ reduced via abiotic dark processes [1].

The studied field system displays an unusual assembly of Hg species, which partially underwent reduction and precipitation. Despite oxidizing conditions in the soil, significant formation of $\text{Hg}^{(0)}$ and $\text{Hg}^{(I)}$ has altered the Hg pools' isotopic signatures, painting a complex picture of soil Hg transformations, and influencing the mobility of Hg towards the groundwater.

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[2] Bollen A, Wenke A, Biester H (2008) Mercury speciation analyses in HgCl_2 -contaminated soils and groundwater—implications for risk assessment and remediation strategies. *Water Res.* 42:91–100.

[3] Wiederhold JG, Skyllberg U, Drott A, Jiskra M, Jonsson S, Björn E, Bourdon B, Kretzschmar R (2015) Mercury isotope signatures in contaminated sediments as a tracer for local industrial pollution sources. *Environ. Sci. Technol.* 49:177–185.