



Mercury concentrations, redox state, and isotope ratios in consecutive water extracts of Hg(II)-chloride contaminated soils

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Mercury (Hg) leaching from contaminated soils into groundwater or surface waters represents a serious environmental problem at industrial legacy sites, whereby Hg mobility strongly depends on its chemical form. For example, the water solubility of potentially relevant Hg compounds ranges over several orders of magnitude ($\text{HgCl}_2 > \text{HgO} > \text{Hg}_2\text{Cl}_2 > \text{Hg}^{(0)} > \text{HgS}$). Water leaching experiments may provide important information on Hg mobility and help assess its fate at contaminated sites. However, single extraction steps are often not sufficient to extract the entire water-soluble Hg pool. Performing multiple consecutive water extracts on the same sample allows investigating the relative importance of kinetic and thermodynamic controls on Hg mobilization. Moreover, differences between the Hg isotope composition of water extracts and the bulk soil may offer novel insights into the transformation dynamics of Hg species as well as the evolution of Hg isotope signatures at contaminated sites [1].

Here, we present results of consecutive water extractions performed on three soil samples and one artificially-contaminated aquifer material from former industrial sites in Germany contaminated with highly soluble HgCl_2 using three extraction solutions (oxygenated water, oxygen-depleted water, 2 mM CaCl_2). Batch extractions were conducted with up to nine consecutive steps over timescales of up to three months. Aliquots of selected extracts were purged with argon to remove $\text{Hg}^{(0)}$ and to quantify the $\text{Hg}^{(0)}/\text{Hg}^{(\text{II})}$ ratio by comparison with unpurged extracts. Hg concentrations were measured by CV-AAS/AFS and Hg isotope ratios were determined using CV-MC-ICP-MS. Pyrolytic thermodesorption analysis was used on selected samples to investigate changes in the solid phase speciation.

Total Hg concentrations in extracts decreased after the first step (range: 17 to 1270 $\mu\text{g L}^{-1}$) but remained surprisingly high until the ninth step (range: 3 to 263 $\mu\text{g L}^{-1}$) illustrating continuous slow Hg release from the contaminated soils in contact with water. The fraction of total soil Hg mobilized at the end of the experiments ranged from 5.6% to 30%. The extracts exhibited large $\delta^{202}\text{Hg}$ variations from -0.75‰ to $+0.94\text{‰}$ relative to bulk soil indicating preferential mobilization of either light or heavy Hg isotopes for different samples and extraction conditions. Lower Hg concentrations in the purged extracts provided evidence for the presence of $\text{Hg}^{(0)}$ approaching its solubility in some extracts, particularly under oxygen-depleted conditions with up to 85% of total

dissolved Hg, which is produced by reduction from Hg^(II) in our HgCl₂-contaminated samples. The isotopic mass balance between purged and unpurged extracts revealed an important control of the Hg⁽⁰⁾/Hg^(II) ratio on $\delta^{202}\text{Hg}$ extract values of some samples with Hg⁽⁰⁾ being about 2‰ lighter than Hg^(II), consistent with theoretical predictions for equilibrium isotope fractionation. Our results demonstrate that consecutive water extracts can leach large amounts of Hg from contaminated soils accompanied by significant Hg isotope fractionation during the mobilization from solid to solution phase, which is at least partly controlled by equilibrium isotope effects between Hg redox states in solution.

[1] Brocza FM, Biester H, Richard J-H, Kraemer SM, Wiederhold, JG (2019) Mercury isotope fractionation in the subsurface of a Hg(II) chloride-contaminated industrial legacy site. *Environ. Sci. Technol.* 53, 7296-7305.