Mercury speciation at a former wood preservation site

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Speciation of Mercury (Hg), a toxic global pollutant, strongly controls its mobility and bioavailability in natural systems. Hence, it must be studied for risk assessment at contaminated sites. Sequential extractions (SE) and pyrolytic thermo-desorption (PTD) are readily available and cost-effective destructive approaches used to identify different Hg pools in contaminated soils. PTD identifies Hg species based on their temperature of volatilization by pyrolysis in small temperature increments; SE divides the total pool of mercury into operationally defined sub-pools using a series of extractants. Complementary to the above, XAFS spectroscopy is a non-destructive technique that can provide quantitative information about mixed Hg phases. However, the high detection limit and criterion for information content imposed by Nyquist Theorem pose challenges for successful use for XAFS in natural mixed-species systems. Our work has 1) overcome typical challenges of Hg XAFS studies by using meaningful geochemical constraints provided by PTD and SE, and 2) provided robust analyses regarding co-existence of four Hg species.

At a former industrial site in SW-Germany where highly soluble aqueous $Hg^{(II)}Cl_2$ was used for wood preservation, two soil cores were analyzed for Hg concentrations and speciation. Hg speciation was first assessed using a 4-step SE procedure and PTD. Six samples, selected for high Hg concentrations from 100 to 800 μg g^{-1}, were then analyzed using Hg XANES and EXAFS spectroscopy. XAFS experiments were conducted at -200 °C in fluorescence mode at beamline 13-ID-E of the Advanced Photon Source in Argonne National Laboratory (USA).

The speciation of Hg for all samples was distinctly different from the original contamination source ($Hg^{(II)}$-chloride). Based on SE, samples contained at least 34% and up to 91% of very stable, aqua-regia-extractable Hg. We interpret this pool as β-HgS, which was found in similar percentages by XANES linear combination fitting. XANES also revealed significant amounts of reduced $Hg^{(0)}$ in the most contaminated samples, agreeing with the PTD results. Surprisingly, XANES revealed the presence of a $Hg^{(I)}$ phase, likely calomel ($Hg^{(I)}_2Cl_2$), which is rarely found in environmental samples and was not detected using SE or PTD whose release peaks of calomel overlap with those of $Hg^{(0)}$ and several $Hg^{(II)}$phases (e.g. $HgCl_2$, $Hg(NO_3)_2$). EXAFS modeling confirmed the presence of $Hg^{(0)}$, $Hg^{(I)}$ (as Hg_2Cl_2), and β-HgS in the samples. In addition, EXAFS also revealed encapsulation of Hg by Fe-(oxyhydr)oxides.

In summary, integrating complementary approaches (SE, PTD and XAFS) provided a nuanced picture of the soil cores' Hg speciation, ranging from mobility of the species (SE) to their speciation (all methods). Hg XANES and EXAFS broadly agreed with SE and PTD results, and added new insights regarding the oxidation states and exact species of Hg in the soil and its interaction with soil matrix constituents such as iron oxides at environmentally relevant concentrations <1 mg g^{-1}.It is important to point out that complications of using Hg XAFS for field sites, namely complex soil matrix, multitude of Hg species, and short EXAFS data range which are typical for Hg in natural systems, were overcome by using geochemical information obtained from PTD and SE to provide meaningful constraints for EXAFS modeling with high confidence.