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- fill in a separate form for each project or series of measurements.
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- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

![ESRF logo] **ESRF**	**Experiment title:** Hg colloid formation and Hg speciation changes in a periodically flooded riparian soil	**Experiment number**: 01-01-834
Beamline: BM26A	**Date of experiment**: from: 02.12.2010 to: 07.12.2010	**Date of report**: 28.02.2011
Shifts: 15	**Local contact(s)**: Sergey Nikitenko	*Received at ESRF:*

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Report: Hg speciation in colloids formed during flooding of a riparian soil

Introduction

Our goal was to identify speciation changes of colloidal Hg in the pore water of a contaminated floodplain soil during soil flooding and reduction. In a previous laboratory microcosm study, we observed that within a few days of soil flooding, Cu was mobilized into the soil solution as metallic Cu nanoparticles associated with suspended bacteria, followed by their transformation into Cu_xS colloids during subsequent sulfate reduction [1]. Further work indicated that the dynamics of colloidal Hg closely followed the trends in colloidal Cu concentrations. We therefore hypothesized that colloidal Hg formation was also due to initial Hg(II) reduction to Hg(0) followed by conversion into HgS during sulfate reduction, and that Hg in the soil matrix followed the same transformation sequence. In this experiment, we therefore aimed at determining the speciation of colloidal and soil Hg by X-ray absorption spectroscopy (XAS).

Materials and methods

Soil flooding was simulated in a microcosm setup as described previously [1-3]. Briefly, contaminated topsoil material containing 1 mg/kg Hg was collected from a riparian floodplain at the Mulde River close to Muldenstein (Germany). The dried soil material was flooded in microcosms for up to 30 days. The microcosms were equipped with open pore suction cups (pore size 12-16 μm), that allowed to collect soil pore water including suspended colloids. Soil pore water was sampled directly into a glovebox (pO_2 < 1 ppm) for further analysis. Colloidal Hg concentrations were determined as the difference of total and dissolved (passing a 0.025 μm filter membrane) concentrations. Colloids were collected on cellulose nitrate filter membranes, which were washed, dried and cut into pieces, stacked and mounted on aluminum sample holders for XAS analysis. Mercury concentrations on filters ranged between 0.3 – 16 mg/kg. Two additional samples were prepared using a pre-enrichment step, which yielded concentrations of 17 mg/kg on a cellulose nitrate filter and 500 mg/kg on a polycarbonate filter.

Analyses by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at the Hg L3-edge were performed at beamline BM26A (DUBBLE). Colloid spectra were collected in fluorescence mode up to 12 Å^{-1} in *k*-space in a closed-cycle He cryostat at 30 K (to prevent sample oxidation and beam damage and to reduce thermal disorder in Hg coordination geometry, i.e., to enhance the signal amplitude and thereby signal-to-noise ratio). References such as cinnabar (α-HgS), metacinnabar (β-HgS) and freshly precipitated disordered HgS (HgS$_{prim}$) were measured at 30 K in transmission mode. Elemental Hg(0) was slowly cooled to below its melting point (-39°C) using a -20°C and a -80°C freezer to assure the formation of crystalline metallic Hg before analysis at 30 K in fluorescence mode. The beam size was set to 7 mm x 0.5 mm, since defocussing minimizes artifacts related to sample heterogeneity in fluorescence measurements.

Results

Colloidal mercury concentrations in the pore water rapidly increased after the onset of soil flooding, peaked after 3 days at 33 µg/L and subsequently decreased with the onset of sulfate reduction, in parallel to colloidal Cu, but dominated total Hg in solution over the entire incubation time (data not shown). Interpretable Hg L3-edge XAS spectra could only be measured on samples from the initial phase between 1.5 and 5 days after soil flooding where colloidal Hg was highest. Also the soil samples were too dilute (1 mg/kg Hg) for XAS analysis. Enriched colloid samples did not yield better signal-to-noise ratios compared to non-enriched samples (Figure 1), possibly because of the simultaneous enrichment of colloidal Cu, which may have attenuated Hg fluorescence. All measured colloid spectra were similar, indicating the same type of Hg species (Figure 1). The colloid spectra differed from the reference spectra of cinnabar (α-HgS), metacinnabar (β-HgS), freshly precipitated disordered HgS (HgS$_{prim}$), and elemental Hg(0), indicating the formation of another Hg species. The well-defined EXAFS oscillations of the colloid spectra suggested that the Hg was contained in a highly crystalline structure. Considering that the colloidal Hg peak was paralleled by the formation of metallic Cu particles, we performed a shell-fit of the EXAFS spectrum of the 3-day colloids based on a model assuming that traces of Hg(0) substituted Cu in Cu metal nanoparticles (Figure 2). The close match of this fit (Figure 2) and the reasonable fit results for atomic distances and coordination numbers (not shown) strongly supported the notion that during initial soil flooding, reduction of Hg(II) to Hg(0) resulted in the incorporation of Hg(0) into metallic Cu nanoparticles (i.e., formation of an amalgam). Unfortunately, colloidal Hg concentrations at later stages of soil flooding were too low for XAS analysis, but it is reasonable to assume that during sulfate reduction, colloidal Hg(0) transformed into Hg-sulfide, in analogy to colloidal Cu(0). TEM-EDX analysis indicated the incorporation of Hg into sulfide colloids, some of which contained small amounts of Hg. However, these results did not allow us determining whether the Hg was incorporated into a mixed metal-sulfide or whether domains of pure HgS formed within metal sulfide nanoparticles.

Conclusions

In this work, we were able to determine the speciation of trace amounts of colloidal Hg in the pore water of a contaminated soil by Hg L3-edge XAS. Our results suggest concomitant reduction of Hg and Cu and the incorporation of Hg into metallic Cu nanoparticles, which may act as effective carriers for Hg release into adjacent surface waters or groundwater. On the other hand, our finding that Hg may be captured in metallic Cu particles suggests that the co-occurrence of Cu with Hg in contaminated wetland soils may impede the formation of volatile elemental Hg(0), which is generally thought to play an important role for gaseous Hg release from contaminated wetland soils.

References

[1] Weber, F.-A.; Voegelin, A.; Kaegi, R.; Kretzschmar, R. *Contaminant mobilization by metallic copper and metal sulphide colloids in flooded soil.* Nature Geosci. **2009**, 2, 267–271.
[2] Weber, F.-A.; Voegelin, A.; Kretzschmar, R. *Multi-metal contaminant dynamics in temporarily flooded soil under sulfate limitation.* Geochim. Cosmochim. Acta **2009**, 73, 5513–5527.
[3] Weber, F.-A.; Hofacker, A.-F.; Voegelin, A.; Kretzschmar, R. *Temperature dependence and coupling of iron and arsenic reduction and release during flooding of a contaminated soil.* Environ. Sci. Technol. **2010**, 44, 116–122.
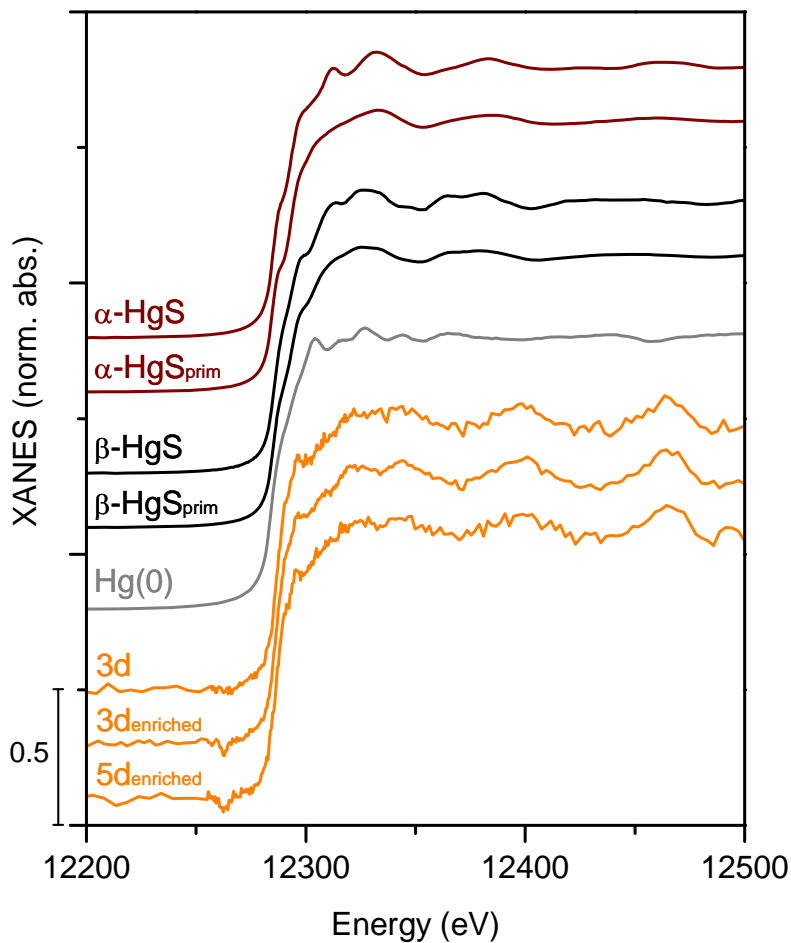
Figure 1:
Hg L3-edge XANES spectra of selected reference materials and of colloids sampled after 3 to 5 days (3d-5d) of flooding. Two enriched colloid samples were prepared by pooling the colloidal material from three individual microcosms.
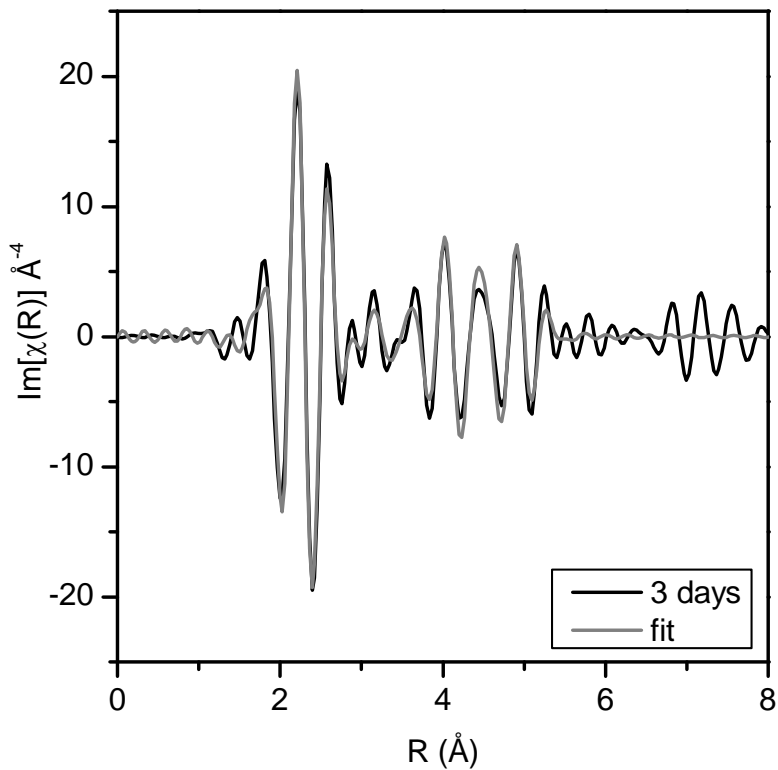

Figure 2:
Imaginary part of the Fourier-transformed EXAFS spectrum of Hg in colloids samples after 3 days of flooding (black line). The shell-fit over the r-range 1-5 Å was calculated with a model that assumed isolated Hg atoms replacing Cu in Cu metal.