



	<b>Experiment title:</b> Mercury speciation in natural organic matter at ratios of reduced sulfur to mercury relevant to nature	<b>Experiment number:</b> EV-3
<b>Beamline:</b>	<b>Date of experiment:</b> from: 17/07/2013 to: 23/07/2013	<b>Date of report:</b> 25/02/2014
<b>Shifts:</b> 18	<b>Local contact(s):</b> Pieter Glatzel	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr Alain Manceau* Pr Kathryn Nagy*		

## Report:

### Context

The objectives of this proposal were to investigate mercury(II) coordination environment in natural organic matter (NOM) using HERFD for the first time.

### Samples investigated

Three types of samples were measured:

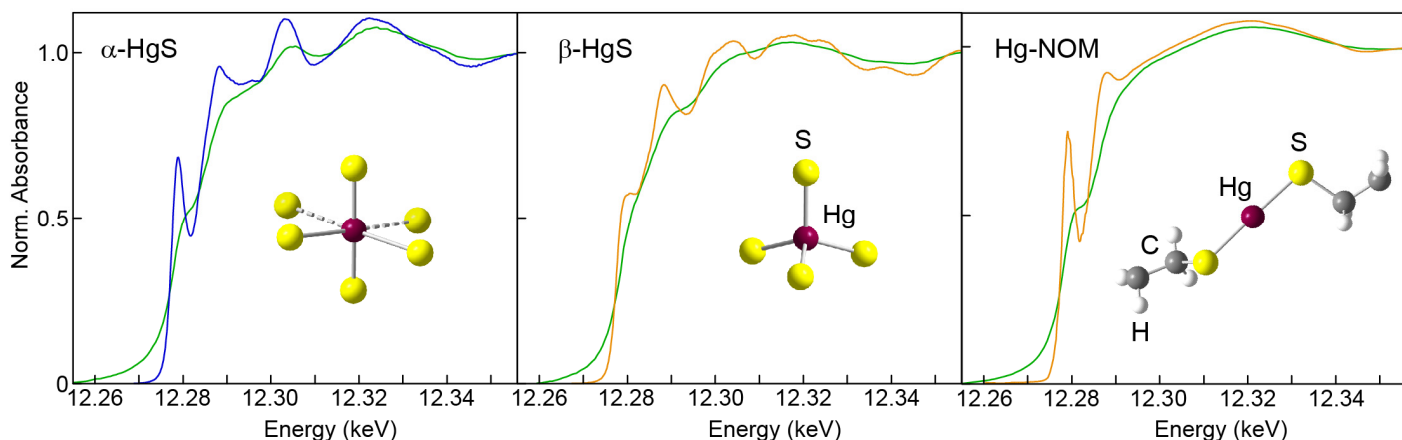
- Organic and inorganic Hg reference compounds with different types of ligands (S, O, Cl, I) and Hg coordinations (2, 3 and 4).
- Natural organic matter (NOM) standards from the International Humic Substances Society with exogenous Hg at added Hg concentration as low as 20 ppm, and also protein-rich fractions extracted in our laboratory by chromatographic separation methods.
- The organo-clay fractions (0.1-2.0  $\mu\text{m}$ ) of a topsoil and subsoil from a drained riparian floodplain contaminated by the discharge of dissolved mercury in a well-aerated surface stream. The two samples contained 48 ppm and 80.7 ppm dry weight (DW) Hg, respectively. The higher Hg concentration at depth results from higher historical Hg releases and the subsequent burial of older deposits with relatively cleaner alluvial sediments.

The HERFD spectra were collected at 10K and in continuous scanning mode to reduce beam damage.

### Results

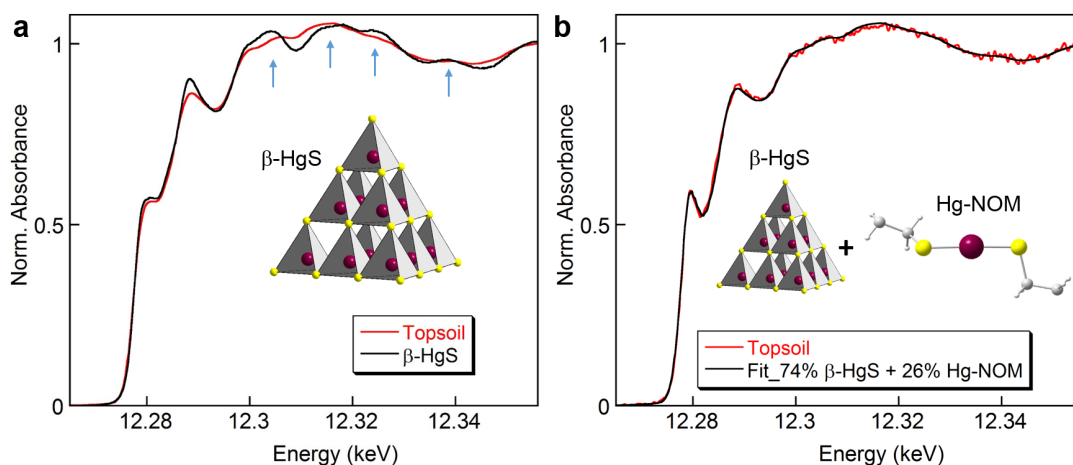
The spectra from the references allowed us to demonstrate the enhanced sensitivity of HERFD to Hg speciation relative to conventional XANES (Figure 1). Most significant is the salient resonance for Hg-NOM at 12279.2 eV ( $2p_{3/2} \rightarrow 5d$  transition), which is missing in conventional XANES. The main reason for this difference is the intrinsic broadening of the  $L_3$ -edge XANES spectra which is as large as 5.5 eV in XANES,

and halved to 2.6-2.7 eV in HERFD mode for quantum reasons. This spectral feature is observed systematically when Hg(II) is coordinated linearly, here to two reduced sulfur ligands, but also to oxygen (HgO, Hg acetate), chloride (HgCl<sub>2</sub>) and iodide (HgI<sub>2</sub>) ligands. The featureless shape of the XANES spectra means that Hg-NOM species cannot be detected by this technique in a mixture with  $\beta$ -HgS in natural materials, such as soil. Using the signature of the 12279.2 eV resonance, the visual detection limit for Hg-NOM mixed with  $\beta$ -HgS by HERFD is estimated to be 15 mol % of the total Hg.



**Fig. 1.** High resolution (HERFD) compared to normal resolution (XANES) L<sub>3</sub>-edge absorption spectra of cinnabar ( $\alpha$ -HgS), metacinnabar ( $\beta$ -HgS), and Hg(II) complexed to natural organic matter (Hg-NOM), with ball-and-stick representation of the coordination environments of Hg. Results from reference compounds show that HERFD has adequate spectral sensitivity to resolve overlapping X-ray contributions from co-occurring Hg species in a multicomponent system.

When compared to those of references, the topsoil spectrum most closely resembles the  $\beta$ -HgS spectrum, and the subsoil even more so (Fig. 2a). The modulations observed above the edge come from the Hg-Hg pairs. The topsoil spectrum was modeled successfully with a linear combination of  $74 \pm 6\%$   $\beta$ -HgS +  $26 \pm 6\%$  Hg complexed to NOM (Fig. 2b). It follows that Hg occurs essentially as  $\beta$ -HgS in the subsurface and as  $\beta$ -HgS and organically-bound Hg-NOM complexes at the soil surface. This is the first time that the second species, which is considered to be the main non-methylated Hg form in organic matter, has been identified in a native soil. A first article is in preparation and will be submitted soon.



**Fig. 2.** Mercury speciation in the topsoil of a native soil contaminated by Hg. (a) Spectrum of the topsoil compared to the  $\beta$ -HgS spectrum. (b) Linear least-squares fit to the topsoil spectrum with  $\beta$ -HgS and Hg-complexed to natural organic matter (NOM).