



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- 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.



Experiment title: The importance of free, low and high molecular weight amino acids and thiols for the complexation of the class B metals Cd and Pb in soils and humic streams

Experiment number:
EC-320

Beamline:

Date of experiment:

from: 02-juil-08

to: 08-juil-08

Date of report:

10-oct-08

Shifts:

Local contact(s): Pieter Glatzel

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

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Report: Materials and methods: Natural organic matter (NOM) from a humic stream was upconcentrated and separated into size fractions < 1 000 Da, 1 000 – 10 000 Da and 10 000 Da – 0.22 μm by use of ultra-filtration (Millipor pellicon II Tangential Flow Filtration) and freeze-out technique. The concentration of free amino acids was analyzed in the original humic stream sample, by HPLC coupled to fluorescence detection. The concentration of oxygen and sulfur functional groups associated to NOM were determined by acid-base titration and S XANES spectroscopy. Two organic soils for which the structures of Cu, MeHg, Hg, Cd and Zn bonded to NOM have been determined in previous studies were also included in the study. Freeze-dried samples were added Cd and Pb (as nitrate solutions) yielding metal concentrations in the approximate range 400 – 20 000 $\mu\text{g g}^{-1}$. The pH-range was 3 – 9 with most samples in the range 5 – 7. For Cd conventional EXAFS data were collected as total fluorescence yield at the Cd K-edge (26711 eV). For Pb both conventional EXAFS and high energy resolution fluorescence detection (HERFD) data were collected in the XANES region at the Pb L_{III}-edge (13035 eV). Data were also collected for Cd and Pb model compounds like oxides, sulfides, amino acids and thiols. HERFD spectra of Pb(II) model compounds were compared to FEFF 8.4 multiple scattering calculations and density of state (DOS) simulations to determine the origins of the spectral features.

Results and discussion:

Cadmium

The upgrade of ID26 made it possible to collect data with a much improved signal to noise ratio as compared to our experiment conducted in 2003 (experiment ME-602). This will make it possible to extract more information on Cd-NOM structures by including third shell and multiple scattering contributions. Preliminary comparisons of the three size fractions of NOM from the humic stream, suggest that reduced sulphur groups (thiols) are highly involved in the complexation of Cd in the smallest size fraction (< 1 000 Da). In the largest size fraction (10 000 Da – 0.22 μm) O/N functional groups are the predominant complexing ligands. This is illustrated by the shift of the major FT peak in Figure 1 to higher R (distance between Cd and nearest atom), making it similar to Cd – S associations in cysteine. The intermediate size fraction (1 000 – 10 000 Da) showed a mixed ligation of thiol – S and O/N ligands.

Lead

The complexation of lead to NOM is much more difficult to study than Cd. The reason for this is that Pb show variable and unusually high coordination numbers with O/N ligands. Furthermore, the Pb – O distances show an extremely high incoherence (different distances for each Pb – O bond within a structure). This limits the possibilities for structural determinations using conventional EXAFS. Another limitation of conventional EXAFS is that only data up to 10 k (\AA^{-1}) can be used for structural information owing to an interference with the K-edge of Br at 13 474 eV (Figure 2). In addition to conventional EXAFS (Figure 3), we therefore explored the possibilities of using HERFD XANES (Figure 4). As a first step structures of model compounds PbO, PbNO₃, Pb acetate (PbAc), and PbS were examined.

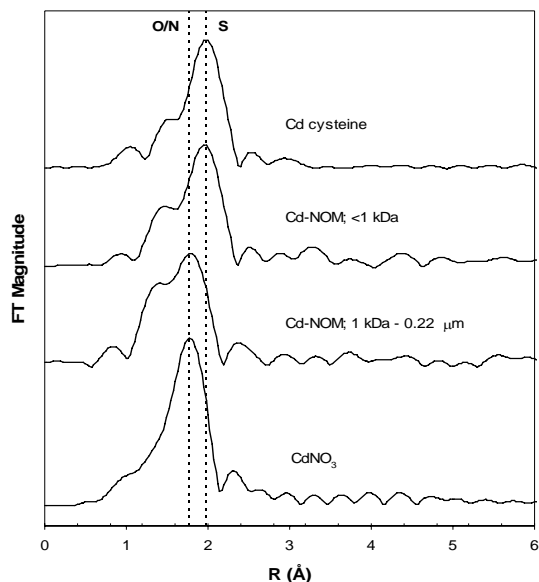


Figure 1. Fourier transformed Cd K-edge EXAFS data for the smallest and largest NOM size fractions in comparison to two model compounds. pH 5 and 1000 $\mu\text{g Cd g}^{-1}$.

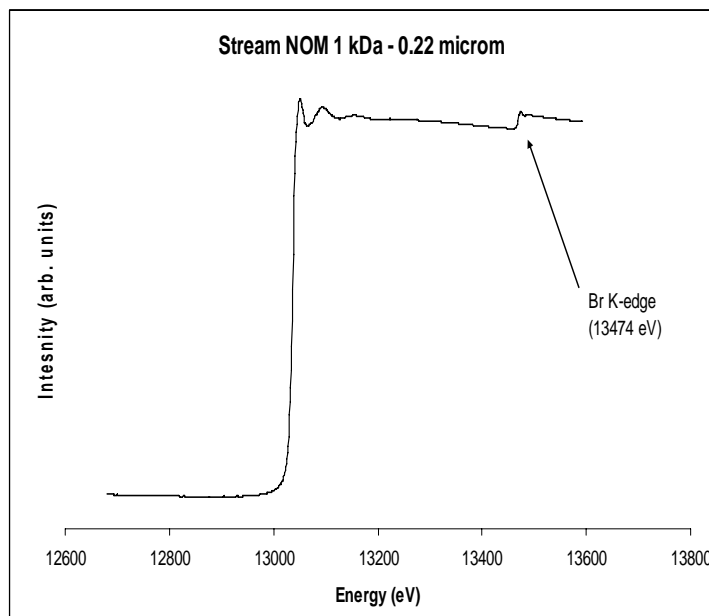


Figure 2. Interference of Pb L_{III} -edge EXAFS by the Br K-edge at 13 474 eV.

In contrast to Cd, conventional EXAFS did not reveal large differences in Pb bonding to different size fractions of NOM in the humic stream. Given that Pb is expected to bind to a combination of O and possibly N (but not to S) functional groups it may be difficult to detect structural differences among size fraction. There was, however, a marked effect of pH (Figure 3), which seems to be quite similar in all size fractions of NOM. Also the binding environment in the organic soils was highly pH dependent, with distinct features in “ k -space”. In the organic soils traces of iron-hydroxides may contribute to the bonding. Preliminary analysis of Pb model compounds using HERFD XANES reveal differences in peak energies and intensities that can be attributed to S, N and O coordination environments. In the next step HERFD XANES analysis will be applied to our NOM and organic soil samples in order to extract information that could complement the conventional EXAFS analysis.

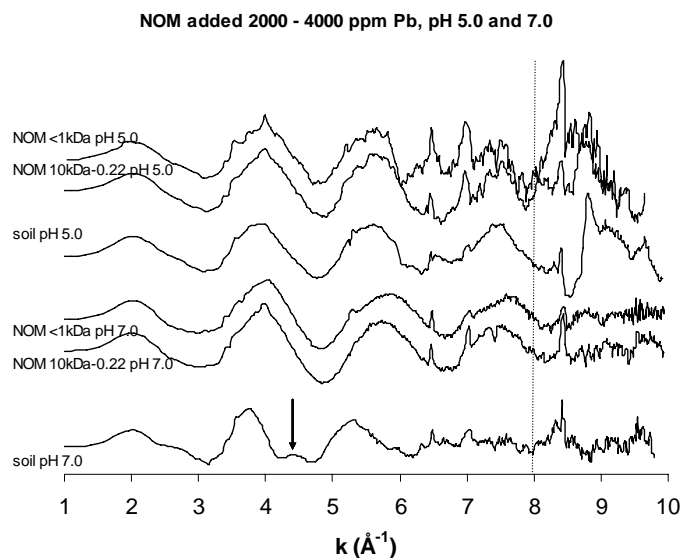


Figure 3. k^3 -weighted EXAFS spectra for two NOM size fractions at pH 5.0 and 7.0 and one of the organic soils at the same pH. Differences observed above 8 \AA are more related to pH than to size fraction, as indicated by the vertical line. The organic soil showed features (arrow) not present in the humic stream NOM sample.

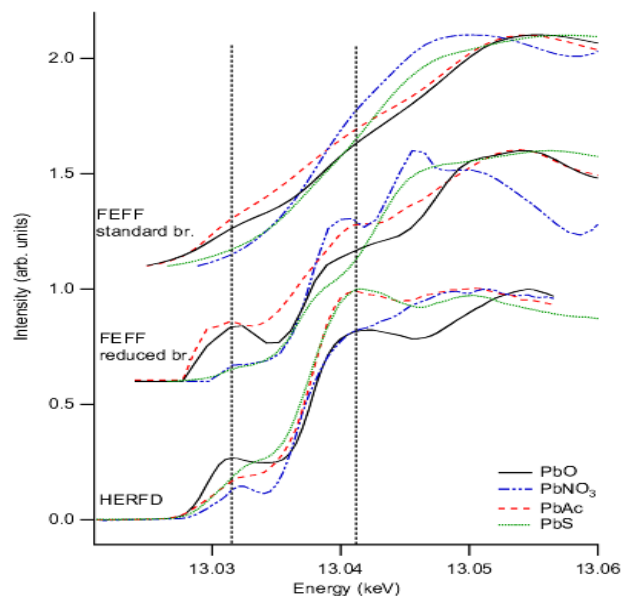


Figure 4. Comparison of PbO, PbNO₃ and Pb acetate spectra, measured and FEFF-calculated spectra, with standard and reduced broadening. The vertical lines serve as a guide for the eye for the pre-edge and post-edge regions.

