



## 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.



	<b>Experiment title: EXAFS study on the binding of Cd<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> to O, N and S functional groups in natural soil and stream organic matter at low metal concentrations</b>	<b>Experiment number:</b> ME-602
<b>Beamline:</b> ID 26	<b>Date of experiment:</b> from: 09/07/03 to: 15/07/03	<b>Date of report:</b> 25/03/04
<b>Shifts:</b> 18	<b>Local contact(s):</b> Olga Safonova	<i>Received at ESRF:</i>

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**Report:**

**Materials and methods:** Samples from different types of organic soils and natural organic matter (NOM) from streams with Cu and Cd concentrations of 450 to 25 000  $\mu\text{g g}^{-1}$  were prepared by addition of solutions of Cu and Cd salts to freeze-dried samples. The suspensions were allowed to evaporate to pastes with an approximate ionic strength of 10 mM NaNO<sub>3</sub> and pH was adjusted (4.6-6.6). The first 6 shifts were used to collect data at the Cu K-edge (8979 eV) and the last 12 shifts were used to collect data at the Cd K-edge (26711 eV), both in fluorescence mode. The two edge-energies were calibrated with Cu-foil and Ag-foils (25514 eV), respectively. At the Cu K-edge a 3 $\mu\text{m}$  Ni filter, and at the Cd K-edge a 3 $\mu\text{m}$  Ag filter, was placed between the sample and the Si-photodiode detector to reduce the scattering radiation. Samples were positioned at 45° to the incident beam. EXAFS data were collected at ambient atmospheric pressure and temperature. In all NOM samples the concentration of reduced S (thiol+organic sulphides and disulphides) was quantified using XANES, and in some cases by X-ray photoelectron spectroscopy (XPS).

**Results:** The Cu data are not reported here since we had problems with radiation damage in most of our samples. Changes in the pre-edge and edge region suggested that added Cu<sup>2+</sup> was reduced to Cu<sup>+</sup>. It is obvious that with the high-flux at ID26 precautions such as cryogenic cooling need to be undertaken.

After a problem with the second mirror had been resolved (it took 32 hours to reach reasonable calibration at the Cd K-edge), Cd data could be collected. Even if the quality of data was not the best (c.f. Fig. 1b), we collected information that made it possible to determine the binding environment of Cd in 4 carboxyl- and thiol cation-exchange resins (used as model compounds) and in 15 organic soil and NOM samples.

In the carboxyl resin Cd was coordinated by 4.8 O in the first atomic shell and 2.0 C in the second shell. The Cd-O bond length was 2.27 Å, consistent with 6-coordination. In the thiol resin at pH 8.8, Cd was coordinated by 3.1 Cd at 2.46 Å and 1.3 O at 2.28 Å. The bond length is indicative of a mixture of Cd in a trigonal, planar structure with S and 6-coordinated, hydrated Cd. In the second shell 2-3 C was encountered at 3.32 Å. When pH was decreased to 7.1 and 4.1 less S and more O was found in the first coordination shell of Cd in the thiol resins. Thus, Cd became more hydrated and less strongly bound to S. An increase in the Cd-S bond length to 2.52 Å suggests that Cd was 4-coordinated by S in the first shell at pH 7.1 and 4.1. The Cd-C bond length was maintained at 3.26-3.27 Å. At pH 8.8 80% of Cd was inner-sphere-associated with S and 20% was hydrated and at pH 4.1 60-70% of Cd was coordinated by S and 30-40% was hydrated.

In NOM samples from soils (pH 4.5 – 7.1), S was only encountered in the first atomic shell at the lowest concentrations of Cd (450 – 1000 ppm). A bond length of 2.43 – 2.58 may imply a mixture of 3-, 4- and 5-coordination. Given an uncertainty in bond length of approximately 0.03 Å and a range of 2.47 – 2.62 for Cd coordinated by 4 S in well-defined organic molecules (mainly proteins), we suggest that Cd was 4-coordinated by S at the lowest loadings of Cd in both soil and aquatic NOM. The involvement of S was further supported by a longer Cd-C bond of 3.17 – 3.24 Å, as compared to Cd bond lengths of 2.80 – 3.19 Å in samples with only O in the first shell. In the sample with highest contribution from S, was 25% of Cd associated with S in an inner-sphere complexation and 75% was bound to O in the first atomic shell. Even if only 1 C was found in the second shell, data quality was not good enough to distinguish hydrated Cd from complexation by oxygen functional groups of NOM in this sample. In samples with less contribution from S, approximately 6 O was found in the first shell at a distance of 2.24-2.27 Å, strongly suggesting a 6-coordination. In some NOM samples from soils 2-3 C was found in the second shell, indicating inner-sphere complexation with carboxyl and / or phenol groups. In NOM samples from aquatic environments 2.1 – 8.0 C was found in the second shell, indicative of a predominant contribution from inner-sphere complexation by oxygen functional groups.

We can conclude from our results that sulfur groups undoubtedly are involved in an inner-sphere complexation of Cd in NOM from soils, and likely from streams, at ambient concentrations of Cd (in most cases much lower than our smallest loading of 450 ppm). The sum of CN for O and S in the first shell indicates that even at 450 – 1000 ppm some Cd was coordinated by 4 S (or 3 S and 1O), suggesting that there are reduced S groups available for such a coordination geometry even at quite high concentrations. Our results have implications for the transport and bioavailability of Cd in soils, sediments and streams.

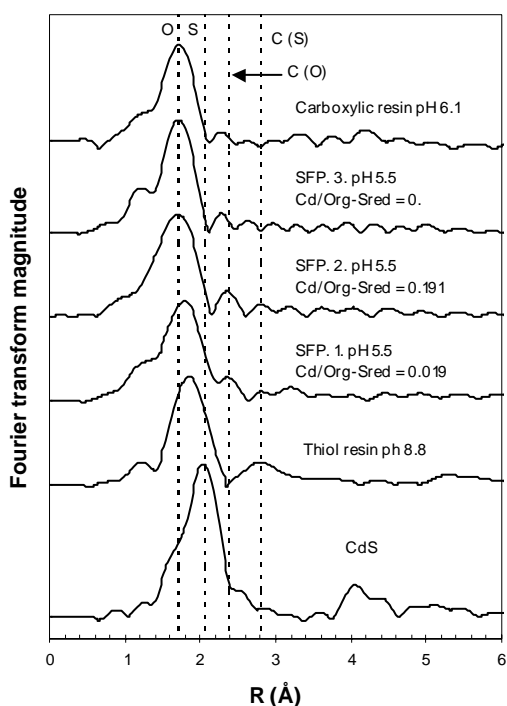


Figure 1a. Fourier transformed EXAFS data. For models and three soils.

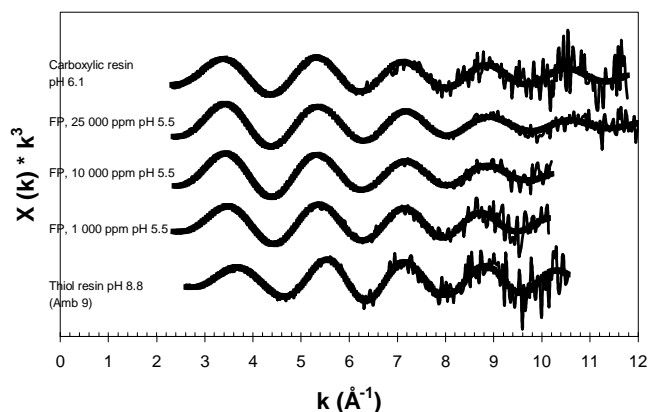


Figure 1b. EXAFS data for model compounds and a peat Soil sample with increasing concentrations of Cd.

