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Cd localization and speciation in a contaminated sediment and in the Zn and Cd hyperaccumulating plant *Arabidopsis halleri*

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Abstract

The purpose of this work was to characterise the chemical speciation of Cd in a Zn- and Cd-contaminated dredged sediment subjected to a phytoremediation treatment with the hyperaccumulator plant *Arabidopsis halleri*. The investigations were performed using analytical chemistry, scanning electron microscopy and synchrotron techniques including X-ray microfluorescence and X-ray absorption spectroscopy (EXAFS and XANES). The paper focuses on the initial state of the sediment before the beginning of the phytoremediation treatment.

Introduction

In the Northern part of France, the maintenance of waterways by regular dredging generates large volumes of metal-polluted sediments. These materials are usually deposited on landfill sites (180 sites in the Nord-Pas de Calais region). Phytoremediation could be a way to treat these polluted sediments. However, to our knowledge, there are few investigations into phytoextraction using hyperaccumulating plants on contaminated sediments. This study is part of a larger project investigating the modifications of cadmium speciation in a contaminated sediment planted with the Zn and Cd hyperaccumulator *Arabidopsis halleri*. The goal of this study was the characterisation of the contaminated sediment in its initial state.

Metals are generally present in a variety of different chemical species and phases (co-precipitates, adsorbed species, etc.) in soils and sediments, including micro- and nanoparticles. Laterally resolved synchrotron techniques with micrometer-scale resolution offer the opportunity to study these heterogeneous and complex systems in detail. Here, we used electron microscopy coupled with energy dispersive X-ray microanalysis (SEM-EDS) and synchrotron-based techniques including micro X-ray fluorescence (XRF), micro- and bulk X-ray absorption spectroscopy (Cd L_{III}-edge μ XANES, S K-edge XANES and Cd K-edge EXAFS) to study the localization and the chemical form(s) of cadmium in the sediment.

Materials and methods

Sampling area and characteristics of the sediment

The sampling area is located in the North of France, about 30 km south of Lille. This region is among the oldest and largest industrial areas in Europe. Past and present contamination by non-ferrous metal processing has released huge amounts of ore particles and slags into the environment (Thiry *et al.*, 2002). Five hundred kg of sediment were collected by dredging the Scarpe River in an area known to be heavily polluted with Cd (around 140 ppm). The sediment was mixed and left to drain, protected from rainfall, for 7

months in order to reduce its water content. Thereafter, the sediment was mechanically homogenized several times. Macroscopic characterization of the bulk sediment included the determination of major and trace element concentrations, granulometry and physico-chemical parameters.

Physical methods

Samples of the sediment were freeze-dried, ground and pressed as pellets for EXAFS measurements. Cd K-edge EXAFS spectra of powder samples were recorded on the beamline FAME (ESRF, Grenoble, France) and compared to sample spectra of model compounds, including Cd-substituted and Cd-sorbed minerals and Cd-complexed organic compounds. Data processing further included linear combination fits and FEFF simulations using the structure of greenockite (CdS) and cernyite ($\text{Cu}_2(\text{Cd}_{0.37}\text{Zn}_{0.33}\text{Fe}_{0.29})\text{SnS}_4$) (Szymanski, 1978).

Some samples of the freeze-dried sediment were embedded in epoxy resin, cut to 30 m-thick thin sections, micro-polished and mounted on glass slides. These sections were examined by environmental SEM-EDS and by μ XRF, Cd L_{III}-edge μ XANES and S K-edge μ XANES spectroscopy on the beamline LUCIA (SLS, Villigen, Switzerland) with a spot of $3 \times 3 \mu\text{m}$.

Results and Discussion

EXAFS analyses on bulk sediment

Linear combination fits of the bulk sediment spectrum showed that greenockite provided the closest reference spectrum, but the two spectra showed some differences. Adding a second component did not improve the fit, suggesting that our database of Cd reference compounds did not contain the species present in the sediment. The sediment spectrum was then treated by FEFF simulations. The first shell was correctly simulated with 3.9 S at 2.52 Å. The second shell was not correctly simulated with Cd only (Figure 1a-b). The fit was improved by adding Zn in the 2nd shell (not shown). The best fit was obtained with a mixture of Zn, Cd and Fe (7.2 Zn, 2.6 Cd and 1.4 Fe at 2.51 Å, 3.88 Å, 4.18 Å and 3.69 Å, respectively, Figure 1c-d). This suggests that Cd was present in form of a mixed Cd,Zn,Fe-sulfide. This is not surprising

since pyrite and sphalerite have been identified before in similar sediments (Isaure *et al.*, 2001).

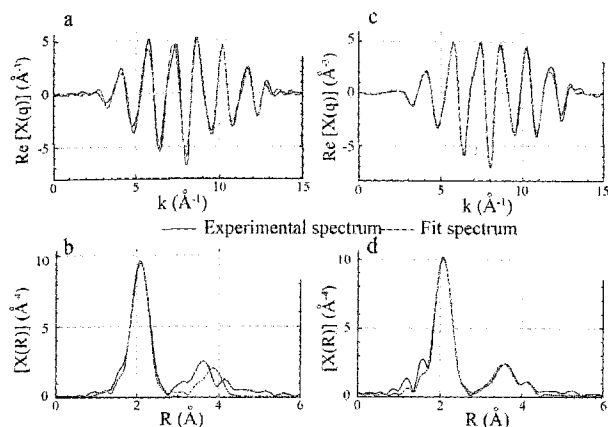


Figure 1. (a, b) Cd K-edge EXAFS spectrum for the bulk sediment and its Fourier transform (blue line) and FEFF simulation with a S first shell and a Cd second shell (a-red line). (c, d) Same spectrum simulated with a S first shell and a Cd, Zn, Fe second shell.

SEM-EDS and μ XANES analyses on bulk sediment

SEM-EDS was used to study geochemical associations of Cd in Cd-rich regions of the sediment samples. The bright grains on the backscattered electron image shown in Figure 2a contain associations of Cd, Fe, Zn and S (Figure 2c-f), which is consistent with the EXAFS results.

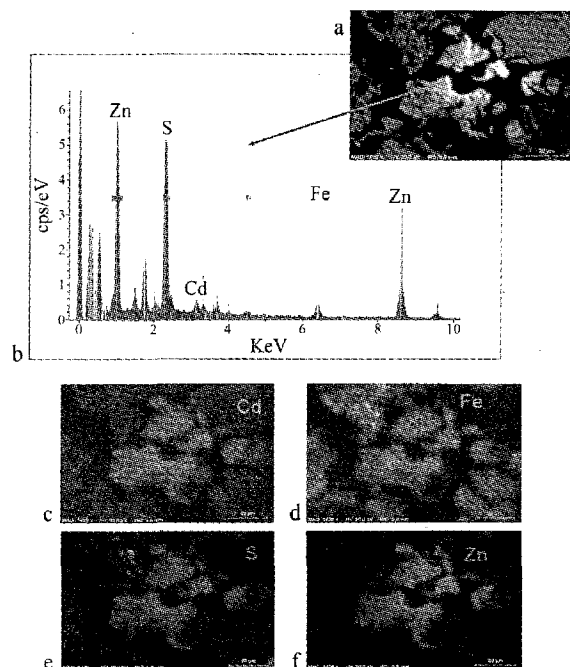


Figure 2. (a) backscattered electron SEM image and (b) EDS spectrum of a Cd-rich spot of the sediment thin section. (c-f) Elemental maps for Cd, Fe, S and Zn of this region.

The comparison of μ XANES spectra recorded on Cd-rich regions with reference spectra shown in Figure 3a suggests the occurrence of CdS. This conclusion should still be refined by comparing the μ XANES spectra with a mixed sulfide reference. Sulfur was not only present in reduced forms. Indeed, also oxidized S species were found in Cd-poor and S-rich regions, (Figure 3b).

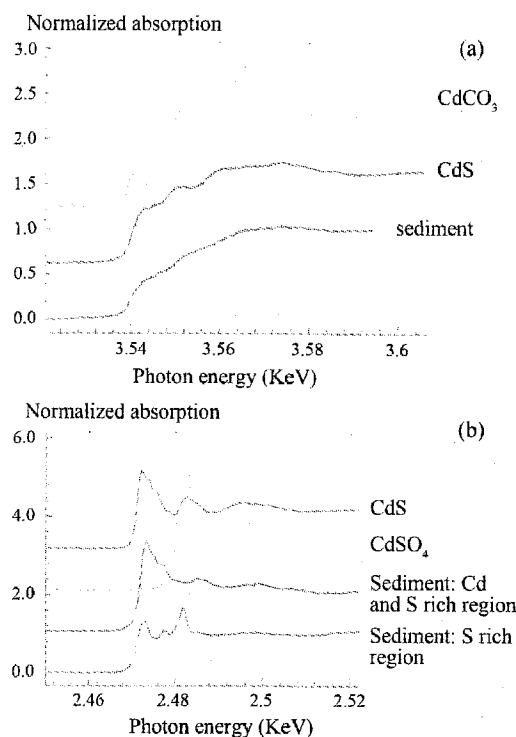


Figure 3. (a) Cd L_{III}-edge μ XANES spectra of a Cd-rich region of sediment and reference compounds and (b) S K-edge μ XANES spectra recorded on two sediment samples (one Cd and S rich region and one S rich region)

Conclusion & Perspectives

The electron microscopy and X-ray absorption results obtained at the Cd and S edges were consistent with the presence of a mixed sulfide (Cd, Zn, Fe)S as the major Cd species. Further microanalyses (in progress) should provide more information on minor phases.

In subsequent experiments, we will grow hyperaccumulator plants on the sediment and study the impact of the plants on Cd speciation in the substrate. In particular, we will look into metal sulfide oxidation and Cd redistribution between the various phases.

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