ESRF	**Experiment title:** Phytoremediation of a Cd-contaminated sediment	**Experiment number**: 32-02-884
Beamline: BM30B	**Date of experiment**: From 06/07/2008 to 08/07/2008 and from 29/08/2008 to 02/09/2008	**Date of report**: Feb 2010
Shifts: 18	**Local contact(s)**: Isabelle Alliot	*Received at ESRF:*

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Report:

Aims of the experiment and scientific background

The maintenance of waterways generates large amounts of dredged sediments, which are often rich in metal contaminants and present a risk to the local environment. Phytoextraction is a phytoremediation strategy proposed for the cleanup of metal-polluted soils and sediments. It consists in growing metal-hyperaccumulating plants to extract metals from the soil. The nature and the extent of the modifications in metals speciation in the matrix induced by phytoextraction treatment are largely unknown. Biogeochemical processes taking place in the rhizosphere may strongly modify the chemical form of metals remaining in the substrate and participate to their stabilization, as shown for Zn with graminaceous plants (Panfili et al., 2005). This combined effect (extraction of metals from the soil and stabilization of those remaining in the soil) would enhance the interest of this treatment and reduce its duration.

In this project, we have studied the impact of the plant *A. halleri* on Cd speciation in a metal-contaminated sediment. This plant is a Zn and Cd hyperaccumulator. Plants originating from a contaminated site and a non contaminated site were compared.

Experimental method

We have studied the sediment in its initial state and after six months of culture with *A. halleri* of the two origins, and after 6 monts without plants (control). We have also recorded the spectra for the size fractions of the initial sediment, and Cd reference compounds including Cd-organic and amino-acids complexes in solution, Cd phosphates and other Cd minerals. All samples were ground and pressed as pellets, inserted in a He cryostat, and Cd K-edge EXAFS spectra were recorded in fluorescence mode using a 30-element Canberra detector. 4 to 10 scans of 40 min each were recorded, and averaged. EXAFS Data treatment included linear combination fits and FEFF simulations using the structure of greenockite (CdS) and cernyite ($Cu_2(Cd_{0.37}Zn_{0.33}Fe_{0.29})SnS_4$) (Szymanski, 1978).

Results

The spectrum for the initial sediment presented some similarities with CdS, but the high frequency was not so pronounced. The closest reference was a mixted sulphide (Zn, Cd)S. The best linear combination was obtained with 100% of this latter reference, and adding a second component did not improve the simulation.

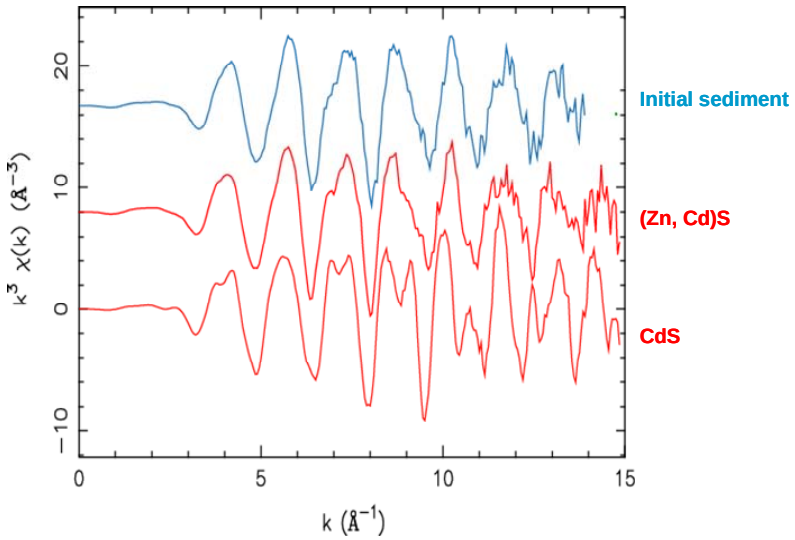

Figure 1: Cd K-edge EXAFS spectrum for the initial sediment and for two metal sulphide reference compounds.

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 (Fig. 2a-b). The fit was improved by adding Zn in the 2nd shell (not shown). Finally, the best fit was obtained with a mixture of Zn, Cd and Fe (1.4 Fe, 7.2 Zn and 2.6 Cd at 3.69, 3.88Å and 4.18Å, respectively, Fig.1c-d). This suggests that Cd is present in a mixed Cd,Zn,Fe sulphide with Zn as major cation. Pyrite and sphalerite have been identified in the sediment (Isaure et al., 2001). Thus, Cd and Fe are likely present as Zn substituents in sphalerite.
We have also analyzed the spectra for the sediment after size fractionation (not shown here).

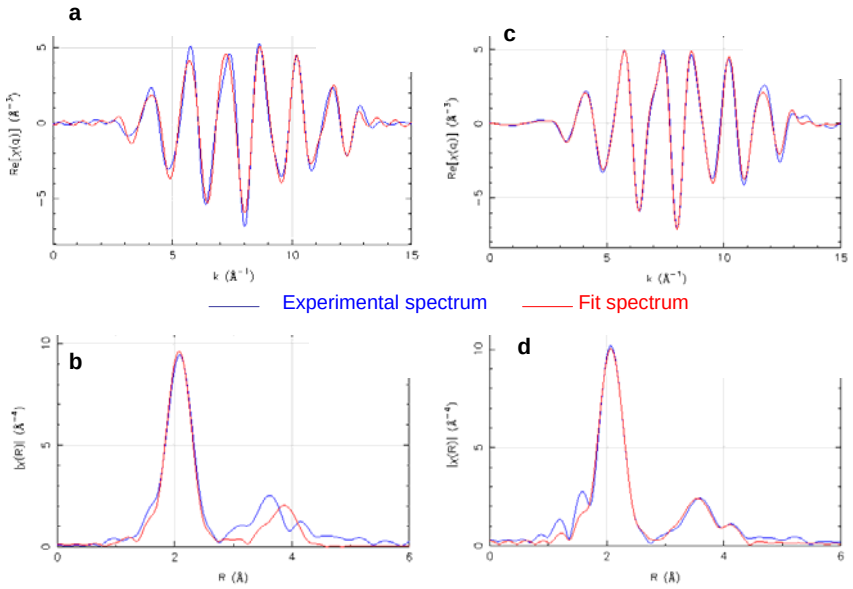

Figure 2: (a,b) Cd K-edge EXAFS spectrum for the initial sediment and its and Fourier transform (blue line) and FEFF simulation with a S first shell and a Cd second shell (a-red line). (c,d) Same spectrum simulated with a S first shell and a Cd, Zn, Fe second shell.

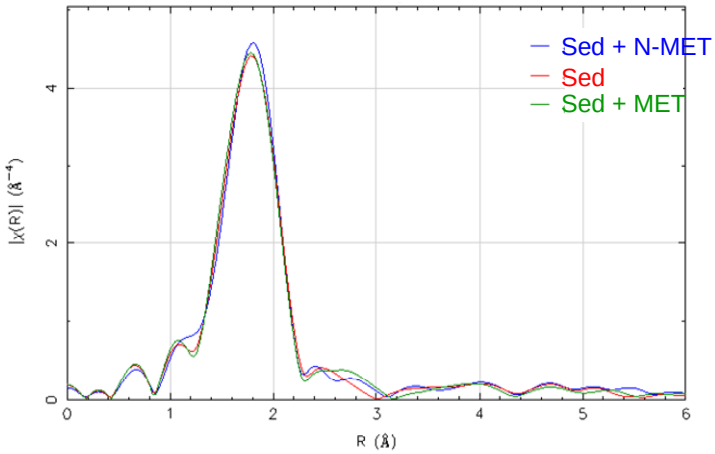

Figure 3: Fourier transformed spectra for the sediment after 6 month of culture with A. halleri from a metallicolous origin (MET), non metallicolous origin (N-MET), and for the control without plant (Sed).

The speciation of Cd was completely modified after 6 months in pot, but plants were not the key factor since no significant difference was observed between the control and planted sediment (Fig. 3). In all three cases, Cd was present as a mixture of Cd-organic complexes and weakly crystallized Cd phosphate. The aeration of the sediment and the alterning dry and wet conditions (because of regular watering) may have favoured microbial and abiotic processes of sulphide oxidation. Cd was weakly exchangeable as shown by chemical extractions and DGT measurements.

References

Panfili, F.; Manceau, A.; Sarret, G.; Spadini, L.; Kirpichtchikova, T.; Bert, V.; Laboudigue, A.; Marcus, M.; Ahamdach, N.; Libert, M. The effect of phytostabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy and principal components analysis. Geochim. Cosmochim. Acta 2005, 69, 2265-2284.

Isaure M.P., Laboudigue A., Manceau A., Sarret G., Tiffreau C., Trocellier P., Lamble G., Hazemann J. L., Chateigner D., 2002, Quantitative Zn speciation in a contaminated dredged sediment by µ-PIXE, µ-SXRF, EXAFS spectroscopy and principal component analysis, *Geochim. Cosmochim. Acta*, 66, 1549-1567.

Scientific production

Communications

Huguet S., Sarret G., Bert V., Isaure M.P. and Laboudigue A., Phytoextraction: A suitable green treatment of contaminated sediments? International Symposium on Sediment Management (I2SM), 9-11 July 2008, Lille, France.

Huguet S., Bert V., Laboudigue A., Isaure MP., Sarret G., Cd localization and speciation in a contaminated sediment and in the Zn, Cd hyperaccumulating plant Arabidopsis halleri, 9*th International Conference on the Biogeochemistry of Trace Elements (ICOBTE*), 15-19 July 2007, Beijing, China.

Thesis

Huguet S., PhD Thesis « Culture d'*Arabidopsis halleri* sur sédiment de curage fortement contaminé : étude du devenir du Cd dans le sédiment et évaluation des mécanismes d'accumulation de Cd dans la plante », Lille, 18 dec 2009**.**

Two articles in preparation.