

**Experiment title:**

Consequence of the bioalteration processes of the organic matter on the speciation and biodisponibility of heavy metals in soils (case of Cd)

**Experiment**

**number:**  
**30-02-611**

**Beamline:**

BM30B  
FAME

**Date of experiment:**

from: July 16<sup>th</sup> to 22<sup>th</sup>, 2003

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**Shifts:**

9

**Local contact(s):**

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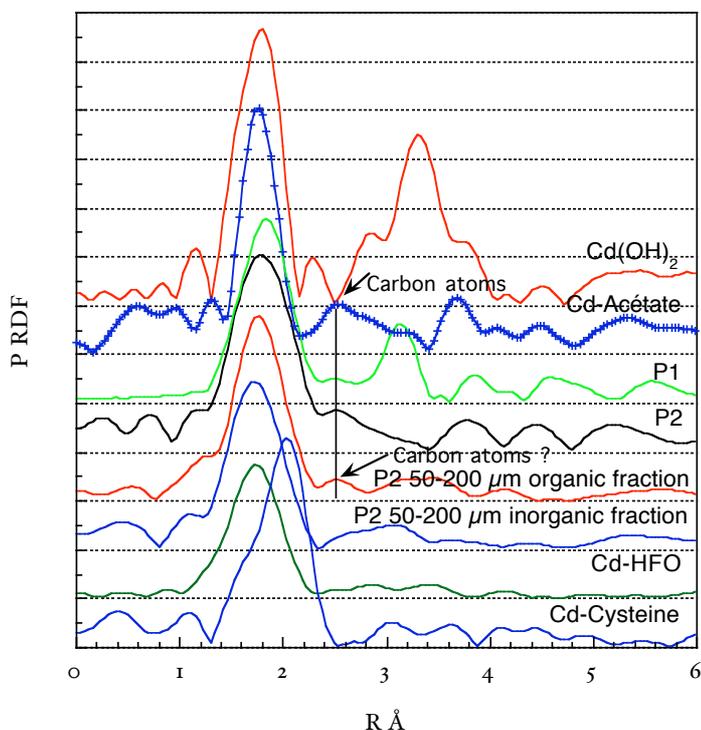
**Report:**

Whether a pollution is diffuse (like in the case of agricultural pollution), or punctual it is essential to anticipate the risk of transfer of metallic pollutants to the living organisms, to the vegetation, and to the solutions of the soils. Fixation phases present in the soils determine the concentration of free ions in solution and therefore the biodisponibility. Among the fixation phases, organic matter and organic phases play a preponderant place in the retention of heavy metals. But organic phases are not static in soils but in transitory regimes in a biological cycle. The hypothesis of this project is that transitory organic compounds appearing during the humification process posses a higher capacity to fix heavy metal than final organic products. The aim of our project is to determine the speciation of cadmium in different fractions of soils from the Aubry region (North of France) to study the role of transitory organic matters and compare with inorganic products.

Cd K-edge XAS experiments have been carried out on the new XAS CRG French beamline (FAME). The Si(220) monochromator was used and the samples were recorded in the fluorescence mode due to the low cadmium concentration in the samples, with a multi-channel fluorescence detector. The configuration of the beamline with the Si220 monochromator and the improvement in the cooling system of the monochromator result in a high stability of the beam and a low signal/noise ratio. The signal/noise ratio was high enough to scan samples with Cd concentration as low as 70 ppm.

The major difficulty of our study is the heterogeneity of the natural samples. Different cadmium fixation sites can exist, organic or inorganic. Therefore we decided to determine the Cadmium speciation on different organic or inorganic granulometric fractions. We used physical separation techniques (granulometric, density, magnetic) in order not to modify the cadmium speciation. This separation has for purpose to record XAS spectra on fractions that present less heterogeneity than the initial raw sample.

Soils have been sampled from areas with different levels of contamination. Soils from these two areas were situated at different distances from old industrial pyrometallurgical plants. Cd concentration in P1 and P2 samples is 80 and 270 ppm respectively. Even if CdS was present in the initial industrial dust, the comparison between P1 and P2 fourier transforms (FT) (figure 1) with FT of reference compounds suggests that the first coordination sphere of Cd is composed by oxygen atoms. Indeed, the Cd-O distance is generally lower than the Cd-S i.e 2.3 instead of 2.5 Å. The modelling has confirmed the presence of 6 oxygen atoms.



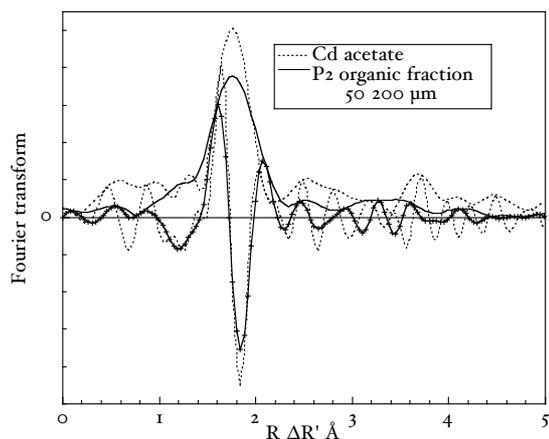
**Figure 1 : Fourier transforms of the EXAFS spectra of natural samples compared with spectra of reference compounds**

In the case of the P2 sample, the comparison between FT of the different fraction reveals the variety of Cd fixation sites. Thus, the physical separation of the different fractions of the soil can be considered as a reliable technique to study natural samples.

The identification of the nature of the Cd atomic sites from the different samples is still under progress. But we can give first interesting results.

In the case of the organic fraction, the position of the first peak and the result of the modelling indicate that oxygen atoms form the first coordination sphere. This point suggests that the thiol functions of the organic matter have no role in the complexation of Cd.

Figure 2 presents the modulus and the imaginary part of the FT of the organic fraction of the P2 sample and the FT of the Cd-acetate.



**Figure 2 : Fourier transforms of the EXAFS spectra of the organic fraction of the P2 sample compared with Cd-acetate.**

Even if the intensity of the FT moduli is different, the two imaginary parts of the FT are in phase in the 1.4-2.6 Å range. Since carbon atoms are present in the second coordination sphere of Cd-acetate, carboxylate groups can complex cadmium in the organic fraction. EXAFS modelling are under progress to confirm or not the presence of carbon

In the case of the inorganic fraction, the height of the peaks of the second coordination sphere is low and the position of the peaks are different from inorganic reference compounds like Cd(OH)<sub>2</sub>, CdO. This result suggests that Cd do not form oxide or hydroxide and is not strongly incorporated in minerals. Cd can be adsorbed at the surface of Fe oxides for example or in the inter-lamellar space of clay particles.