



	Experiment title: Determination of the soil solid-phase chemical forms of Cd that are phytoavailable	Experiment number: 30-02-657
Beamline: BM30B	Date of experiment: from: 23/06/2004 to: 26/06/2004	Date of report: 16/12/2005
Shifts: 9	Local contact(s): Vivian NASSIF, Olivier PROUX	<i>Received at ESRF:</i>
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Report:

Aims of the experiment and scientific background

Many soils exist worldwide that are polluted with cadmium (Cd). Once in the soil, Cd disrupts the biological processes upon which the maintenance of soil fertility depends. Although non-essential to plants, Cd can also be accumulated in quantities that have chronic adverse health effects on the animal or human population consuming the contaminated vegetation. In addition, the concentration of Cd in agriculture produce may form the basis of non-tariff trade barriers to the global trade of food commodities. Therefore, a worldwide health, and economic, need exists to identify the chemical forms of soil Cd that are phytoavailable.

For over 50 years the chemical form of an element in soil that is phytoavailable (*L* value) has generally been regarded as the surface-adsorbed element that is exchangeable with the soil solution at dynamic equilibrium (McAuliffe et al. 1947). Although not an unreasonable assumption, this hypothesis has not been experimentally verified. Therefore, with the development of third generation synchrotron facilities, it is now possible to experimentally confirm this hypothesis for Cd, commonly found at low concentrations in soils, with the use of extended X-ray absorption near-edge structure (XANES) and X-ray absorption fine structure (EXAFS) spectroscopy.

Due to beamtime constraints, the aim of this experiment was restricted to the use of XANES and EXAFS spectroscopy to characterise the solid-phase speciation of Cd in one polluted soil (five were initially proposed to be examined). It was envisaged to compare these data with previous results on the quantity of phytoavailable Cd in this soil (Gerard et al. 2000; Collins et al. 2003) and would experimentally verify, or otherwise, the hypothesis that the chemical form of phytoavailable soil Cd is surface-adsorbed metal. It was also envisaged that further XANES/EXAFS spectroscopy analyses of this soil would be made after the pH of the soil had been varied. In conjunction with our previous experiments (Collins et al. 2003), these data should identify other chemical forms of soil Cd that are potentially phytoavailable after plant-induced variations of pH.

Experimental method

The soil (total Cd ~20 mg Cd/kg) was sampled from the Nord - Pas de Calais region in northern France and has been described elsewhere (Gerard et al. 2000; Collins et al. 2003). The soil was separated according to particle size before XANES/EXAFS analyses (26.6 - 27.6 keV). This simple non-destructive fractionation process should increase the quality of the spectra by: 1) concentrating Cd in certain size fractions and; 2) separating the different chemical forms of Cd. The soil was also fractionated after its pH had been decreased. In addition, as the aim of the experiment was to determine the quantity of adsorbed Cd, small quantities of Cd was sorbed onto all particle size fractions. In this fashion, the Cd XANES/EXAFS spectra of the particle size fractions could be compared before and after the sorption experiments. The Cd concentrations of these various fractions were analysed by ICP-MS. The XANES/EXAFS spectra of reference standards were analysed in conjunction with the soil fractions and consisted of the pure mineral forms of Cd that represent the aerosol forms deposited on this soil (e.g. sulfide, oxide) as well as possible reaction intermediates (e.g. CdCaCO₃, as the soil has been limed) and inner-sphere organic complexes (e.g. Cd-acetate). X-ray diffraction analyses of the small soil particle size fractions (0.2 – 2 and 2 – 25 µm) revealed that these fractions were primarily amorphous. Nevertheless, laboratory prepared Fe-(hydr)oxides samples to which Cd had been adsorbed were prepared. All samples and references were analysed as (5 mm diameter pellets) and the XANES/EXAFS spectra were recorded in fluorescence mode (transmission for the reference samples) using a 30 element solid-state Ge detector.

Results

Cadmium XANES and EXAFS spectra could not be obtained for the whole soil due to a combination of the low concentration of Cd and high concentrations of interfering elements (e.g. Fe and Pb). Elemental filters did not sufficiently eliminate these problems. However, analyses of the separated particle size fractions revealed that spectra could be obtained for samples whose Cd concentrations were as low as 7.4 mg Cd/kg (Table 1), thereby showing that this simple method can eliminate certain elemental interferences and allows XANES/EXAFS analyses of elements that exist at relatively low concentrations in soils.

Table 1: Cadmium concentrations in the separated soil particle size fractions before and after the sorption of Cd. Values in bold represent samples where Cd XANES and EXAFS spectra could be obtained.

Soil particle size (µm)	Cd concentration (mg/kg)		
	Original Soil	Acidified Soil	After Cd Sorption
0.2-2	54.4	51.3	86.5
2-25	16.3	37.6	63.5
25-50	6.9	6.8	38.9
50-200	7.4	10.1	45.6
>200	19.6	17.6	58.6
Total	20.0		

The Cd EXAFS spectra for the soil particle size fractions are shown in Figure 1. It can be observed that the spectra for the two smaller and two larger size fractions shared many similarities, indicating that the Cd in the two respective fractions probably exists in similar chemical environments at relatively constant proportions. The Cd EXAFS spectra of the (0.2-2 and 2-25 µm) soil particle size fractions after Cd sorption were also extremely similar (Figure 2) indicating that the sorbed Cd exists in a comparable chemical environment to the native Cd. This was not observed to be the case for the larger soil particle size fractions (data not shown).

Furthermore, acidification of the soil did not change the EXAFS spectra of the two smaller soil particle size fractions, indicating that the changes observed in Cd bioavailability (and hence chemical speciation) upon acidification occurs in the coarser particle size fractions.

The results of this experiment indicate that Cd EXAFS data can be obtained in separated soil particle size fractions at Cd concentrations as low as 7.4 mg Cd/kg. However, this is also dependent on the concentration of interfering elements in particle size fraction that can saturate the detector. Modelling of the EXAFS spectra is ongoing but preliminary results tend to suggest that the native Cd in the smaller particle size fractions exists primarily as inner-sphere complexed cations. These results will, therefore, assist in relating the isotopically exchangeable pool of Cd to a defined chemical (and bioavailable) state.

Figure 1: Cadmium EXAFS spectra for the soil particle size fractions (μm).

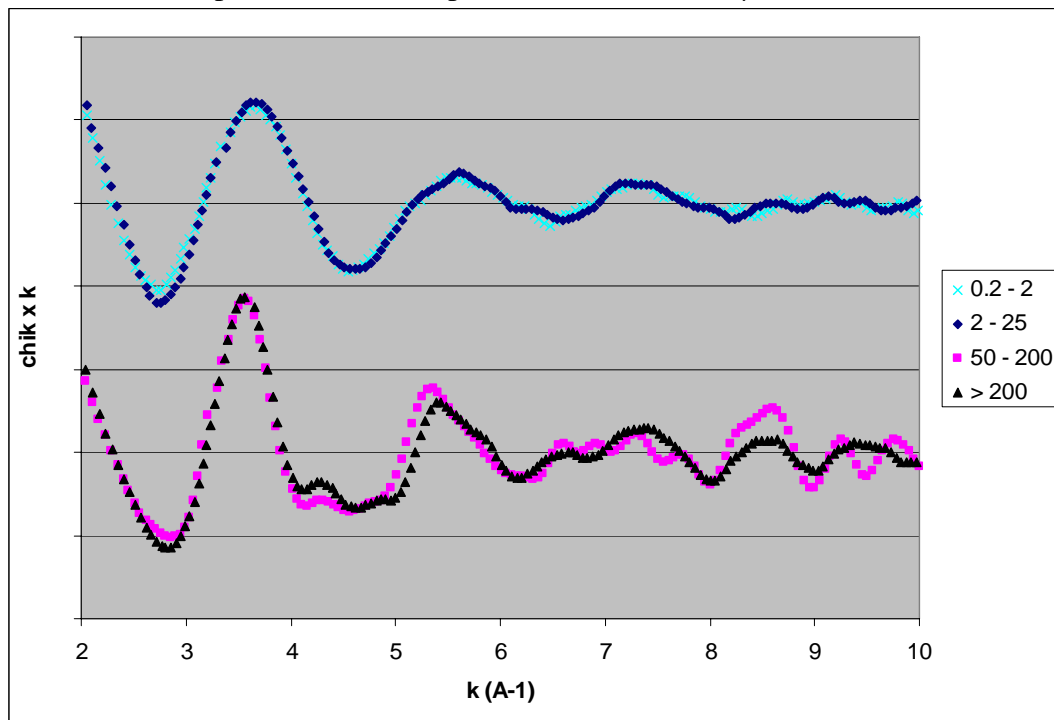
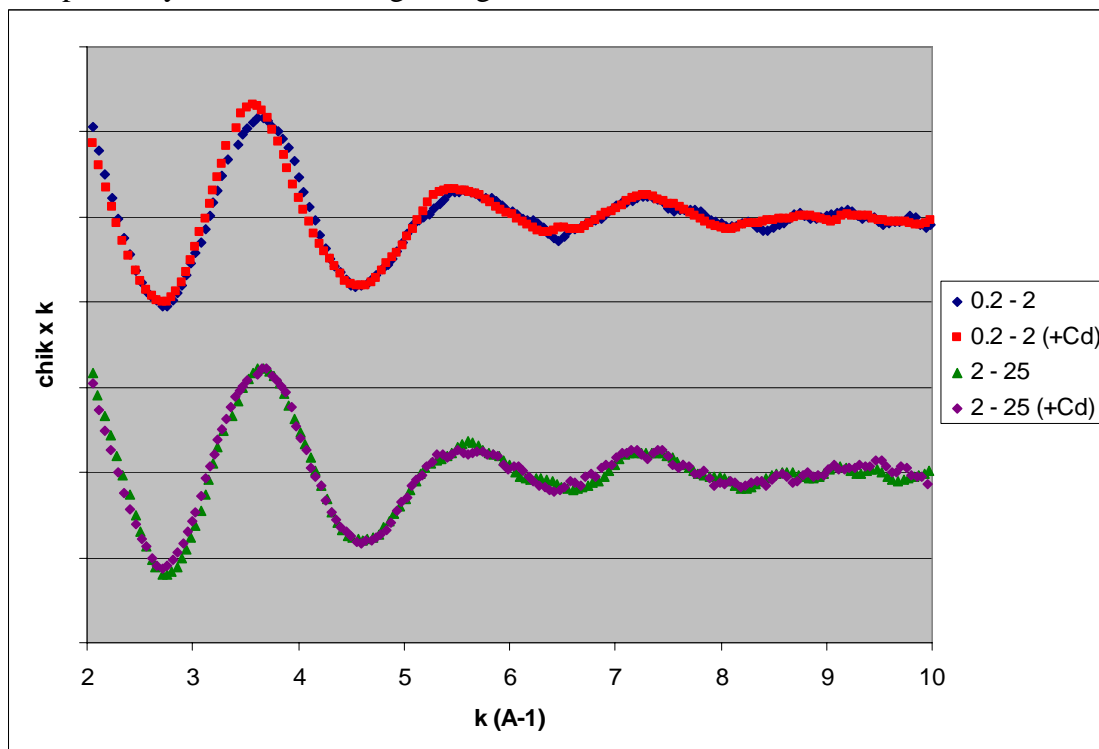


Figure 2: Comparison of the Cd EXAFS spectra for the (0.2-2 and 2-25 μm) soil particle size fractions after the addition, respectively, of 32 and 47 mg Cd/kg.



References

- Collins RN, et al. (2003) *Soil Sci. Soc. Am. J.* 67, 112-121
 Gerard E, et al. (2000) *J. Environ. Qual.* 29, 1117-1123
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