ESRF	**Experiment title:** Effect of the plant *Anthyllis vulneraria* on Zn and Cd speciation in a mine tailing in a context of phytostabilisation.	**Experiment number**: EV-7
Beamline: BM08 Gilda	**Date of experiment**: from: 17/04/2013 to: 23/04/2013	**Date of report**: 30/08/2013
Shifts: 18	**Local contact(s)**: Angela Trapananti	*Received at ESRF:*

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Objective and expected results

The legume plant *Anthyllis vulneraria* has been revealed as a pionner plant to revegetalize metal-contaminated mining sites (Frérot et al. 2006). An experimental site has been set up for 10 years to evaluate the impact of the plant on metal speciation in the soil. The aim of this experiment was to determine the speciation of Cd and Zn in the contaminated bare soil (with no plant) and in *A. vulneraria* rhizosphere after 10 years of experiment. We intended to identify the mechanisms occurring in the rhizosphere, and particularly the possible mechanisms of dissolution/re-precipitation and complexation with organic compound around the roots. In this purpose Zn and Cd K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy was performed on different bulk and fractionated soils with or without plant samples.

Experimental

Soil samples were collected on the experimental site: the bare soil (*i.e.* without plant) and the rhizospheric soil (Anthyllis soil) around *A. vulneraria* roots. Both soils were collected at the surface (0-7 cm). In addition to bulk samples, grain-sized fractionation was performed : (i) coarse fraction, *i.e.* 2000-200 µm, (ii) 200-50 µm fraction, (iii) 50-2 µm fraction and (iv) the finest fraction *i.e.* < 2 µm. Part of soil samples was also used for densimetric characterization. The soil was divided in "heavy" and 'light" fraction according to the density using a sodium polyntungstate liquor (d=2.9). Bulk and fractions samples were ground and prepared as pressed pellets. The beam was monochromatized with Si(311) crystals. Zn K-edge (9659 eV) EXAFS signal was collected in transmission mode whilst Cd K-edge (26711 ev) measurements were done in fluorescence mode using a 13-element germanium detector. Measurements were done at ambient temperature, and calibration was done with Zn and Cd metallic foils. EXAFS signal was extracted using Athena software.

Results and conclusions of the study

Cd K-edge EXAFS measurements:

Figure 1 displays Cd EXAFS spectra collected on several soil samples and on Cd model compounds. Firstly, spectra recorded on bulk bare soils are similar to spectra recorded on bulk rhizospheric soil (Anthyllis soil – Figures 1 and 2) indicating that plants have no or weak impact on the bulk Cd speciation of the soil. The comparison with Cd model compounds shows that Cd in soil occurs as $CdCO_3$ but not only (Figure 2A). This observation suggests that there is a mix of Cd species, and data treatment using linear combination fitting and shell fitting is in progress to identify the other species.

Secondly, soil fractions show that Cd speciation slightly differs in coarse and fine fractions for both bare and rhizospheric soils (Figure 2B), and that the coarse ones are approximatly similar to the bulk ones. We also observe that spectrum recorded on soil near the roots looks similar to spectrum recorded on coarse and bulk fraction, suggesting that if the plant has an impact on Cd speciation, the effect is strictly localized to the vicinity of the roots. Spectra recorded on densimetric fractions show that there is no difference of Cd speciation in heavy fraction between bare soil and rhizospheric soil. Maybe spectra for light fractions slightly differs between the vegetalized and non vegetalized soil, suggesting that the plant could modify this fraction, but this impact is weak.

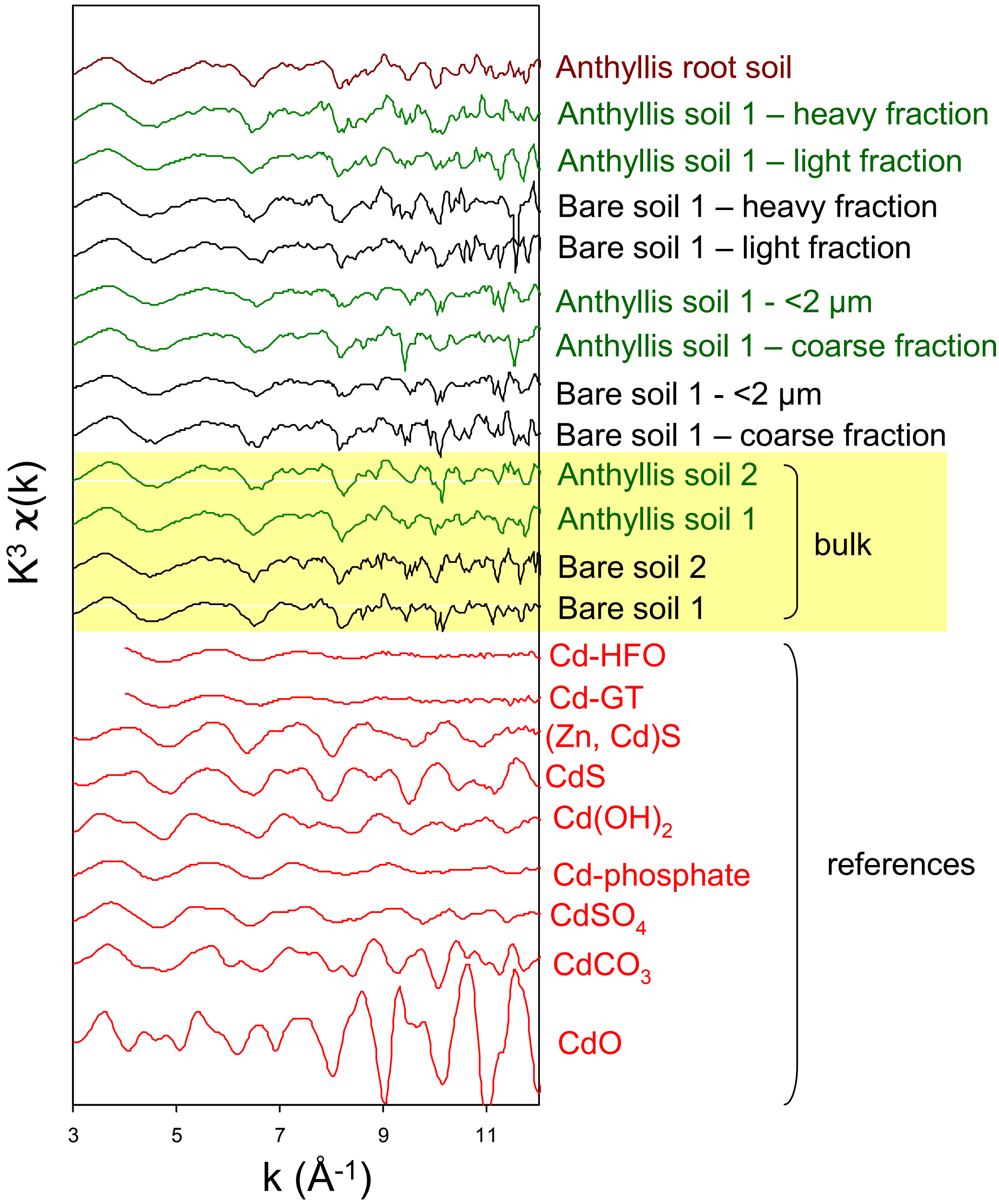

Figure 1: Cd K-edge EXAFS spectra for soil samples and for Cd mineral compounds.

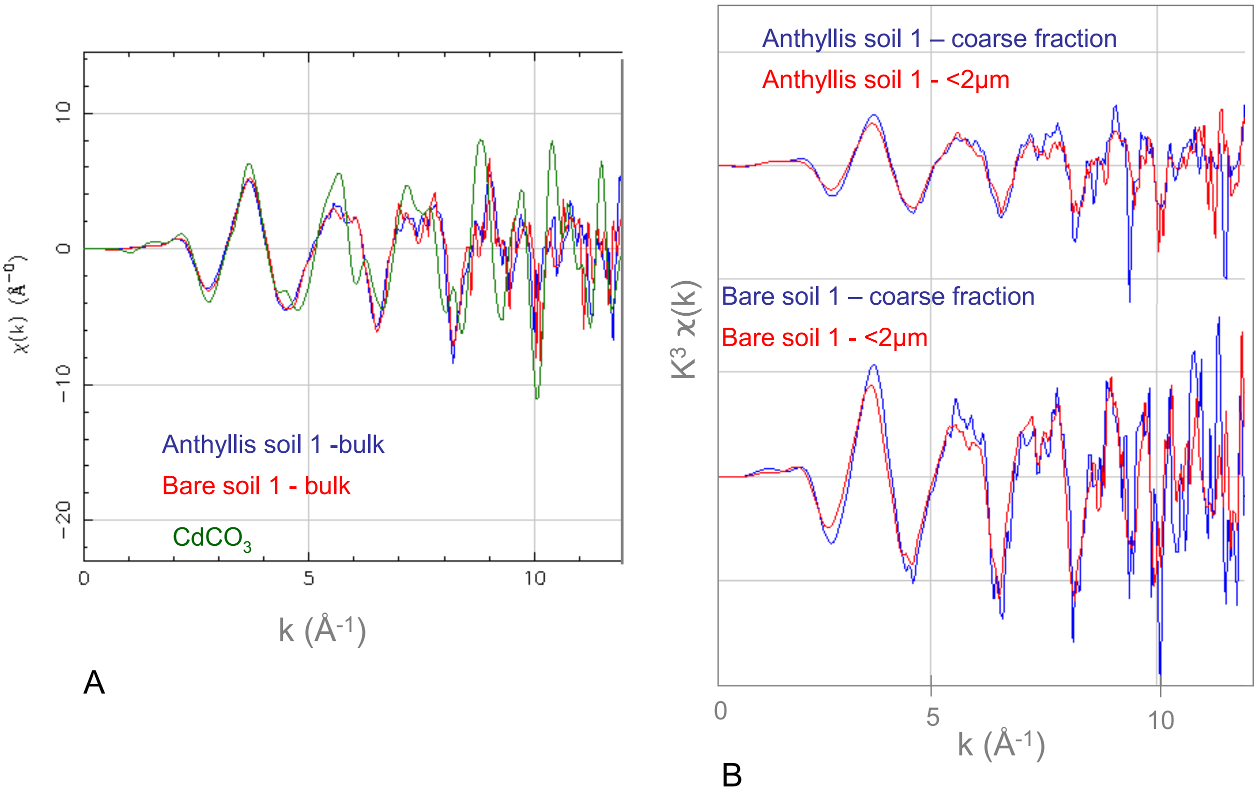

Figure 2: Zoom of Cd K-edge EXAFS spectra for soil samples.

Zn K-edge EXAFS measurements:

Figure 3 displays Zn EXAFS spectra collected on several soil samples and on Zn model compounds. As observed for Cd, spectra recorded on bulk bare soil are similar to spectra recorded on bulk rhizospheric soil and on soil collected near the roots (Figure 4). This results suggest that there is no or very low impact of *Anthyllis* culture on the bulk Zn speciation in soil. The comparison with Zn model compounds shows that Zn in soil mainly occurs as $ZnCO_3$ (Figure 4). Data treatment is still in progress, but this result suggests that other Zn species are minor. Interestingly, Zn speciation differs between fine fraction and other granulometric fractions (Figure 4), for both bare soil and rhizospheric soil.

Spectra recorded on densimetric fractions show that there is no difference of Zn speciation in heavy and light fractions of bare soil. Spectra recorded on heavy fraction of rhizospheric soil is similar than the one recorded on bare soil. We did not analyze the light fraction of rhizospheric soil.

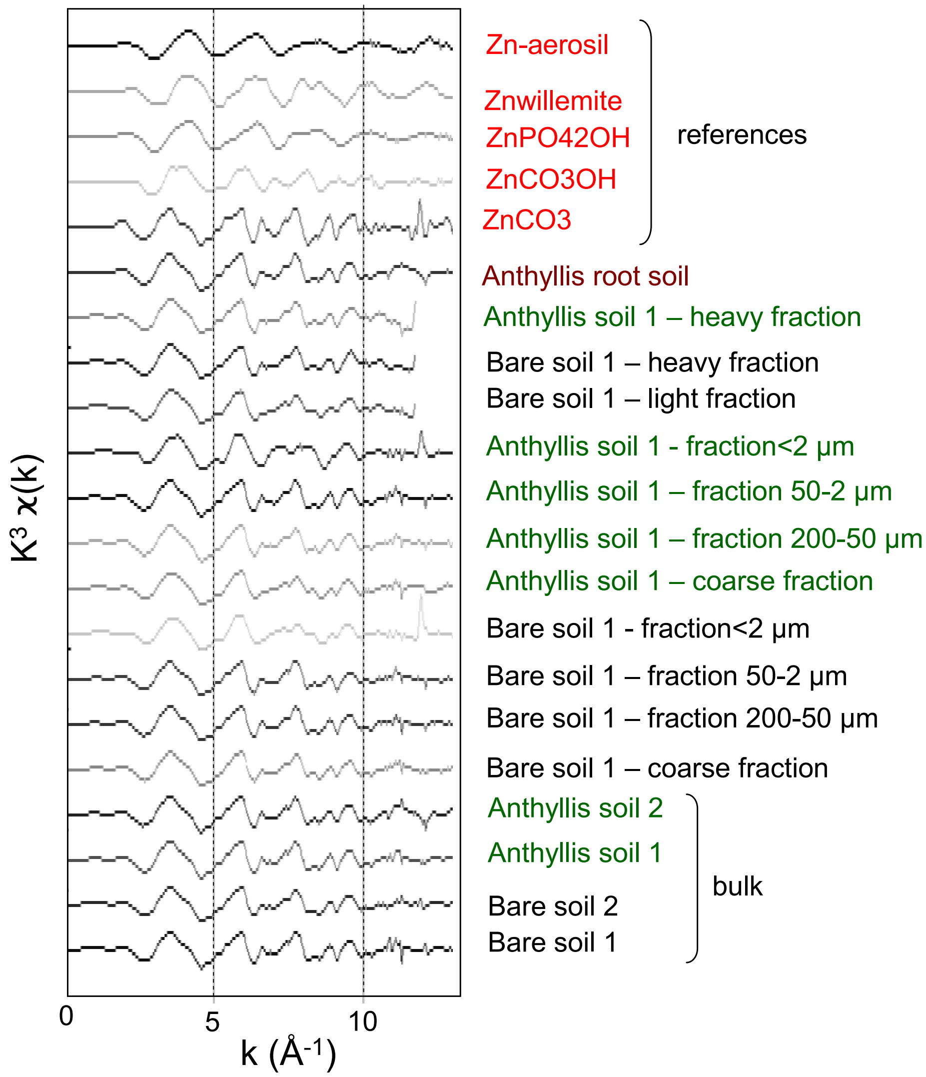

Figure 3: Zn K-edge EXAFS spectra for soil samples and for references compounds.

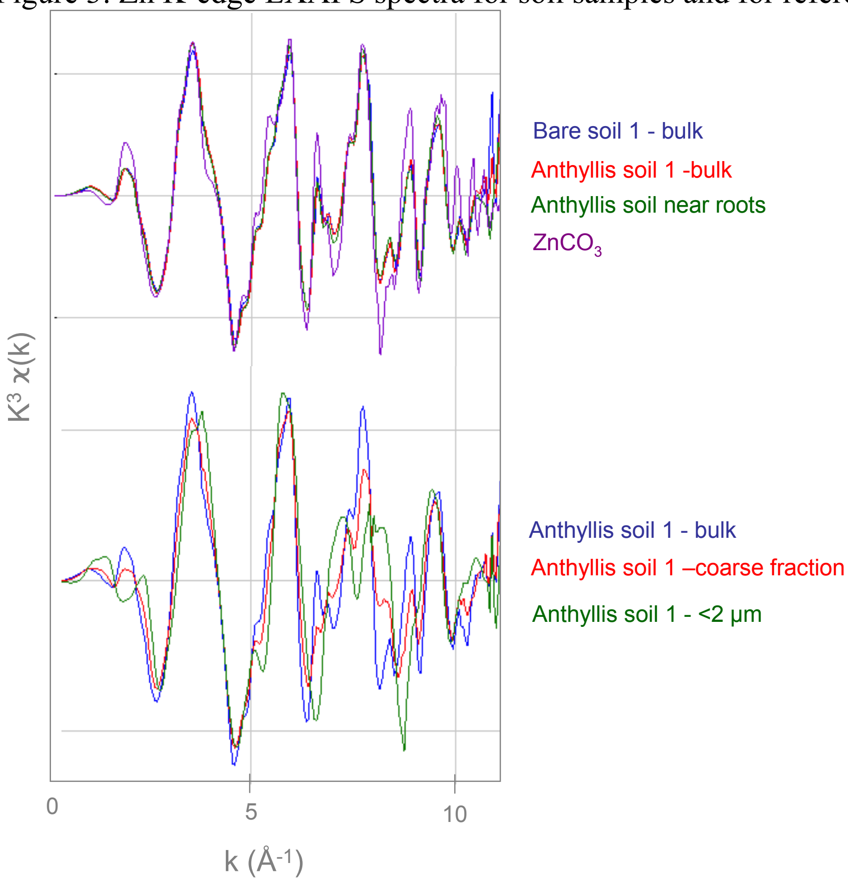

Figure 4: Zoom of Zn K-edge EXAFS spectra for soil samples.

To sum up, there is no a real impact of *Anthyllis* growth on bulk Cd and Zn speciation in soils after 10 years of phytostabilization. The plants could slightly change the metal speciation in the light fraction, thus possibly suggesting the addition of contaminated organic matters, but this results need to be confirmed. We also highlighted a slight difference of Cd and Zn speciation in soil (rhizospheric and bare soil) depending on particules size. Data treatment is still in progress. An experiment has been scheduled in parallel to study thin sections of soil and rhizosphere by µXRD and µXAS in order to focus on the root/soil interface.

Justification and comments about the use of beam time (5 lines max) :

One shift was dedicated to the beamline set up at Cd K-edge, and we spent 8 shifts for Cd measurements. Then, the beamline was aligned for Zn K-edge measurements (one shift), and we used 8 shifts for Zn measurements. The beamline worked very well and no technical issues occurred.

References :

Frérot H, Lefèbvre C, Gruber W, Collin C, Dos Santos A, and Escarré J (2006) Specific interactions between local metallicolous plants improve the phytostabilization of mine soils. *Plant and Soil*, 282, 53-65.