	Experiment title: Influence of the rhizosphere on the speciation of lead in a smelter contaminated site.	Experiment number: 30-02-1
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Report:

Materials and methods

Five soil samples with Pb concentration ranging from 1500 to 3000 mg Pb / kg soil and a sample of pyromorphite ($Pb_5(PO_4)_3OH$), which serve as a model compound for Pb chemical form in soil samples, were studied during this project.

EXAFS data were recorded at the Pb L_{III}-edge (13.055 keV) at cryogenic temperature (20K), with a monochromator equipped with two Si(111) crystals. Due to their low Pb concentration, EXAFS data of the five soil samples were collected in fluorescence mode using a germanium 30-element solid state detector. Since these soil samples contain large amount of Fe (5 wt%), a Cr filter was used to damp the fluorescence of this element. No filter was used to attenuate the Rayleigh scattering of the beam. Between 6 and 8 scans were recorded for each sample. Due to its large Pb concentration, the pyromorphite sample was dilute in cellulose to reach the optimal Pb concentration for EXAFS experiment in transmission mode. Only two scans were necessary to reach a good signal/noise ratio for this sample.

Quality of the raw EXAFS spectra of soil samples

The signal to noise ratio of the data recorded with the Si(111) crystals is good but the spectra are not usable after k = 8 $^{-1}$ because of the presence of defects which can be evidence on a zoom on the EXAFS oscillations of the raw fluorescence spectrum (sum of 6 scans) of one of the five soil samples (Figure 1A). These defects induce artifacts on the corresponding EXAFS spectra as can be seen on the EXAFS spectrum obtained from the raw data presented in Figure 1A (Figure 1B).

Some of the defects can be related to glitches which are visible on I_0 (Figure 1A). These glitches occur at the same energy in all the spectra of the soil samples (Figure 2) and are not related to impurities absorption edges. Other defects are not related to artifacts in I_0 and might have many origin which are not yet understood (heterogeneity of the samples, diffraction peaks in the sample, non-linearity between I_0 and I_F combined with a noisy I_0). These defects appear at various positions among the spectra of the soil samples (Figure 2).

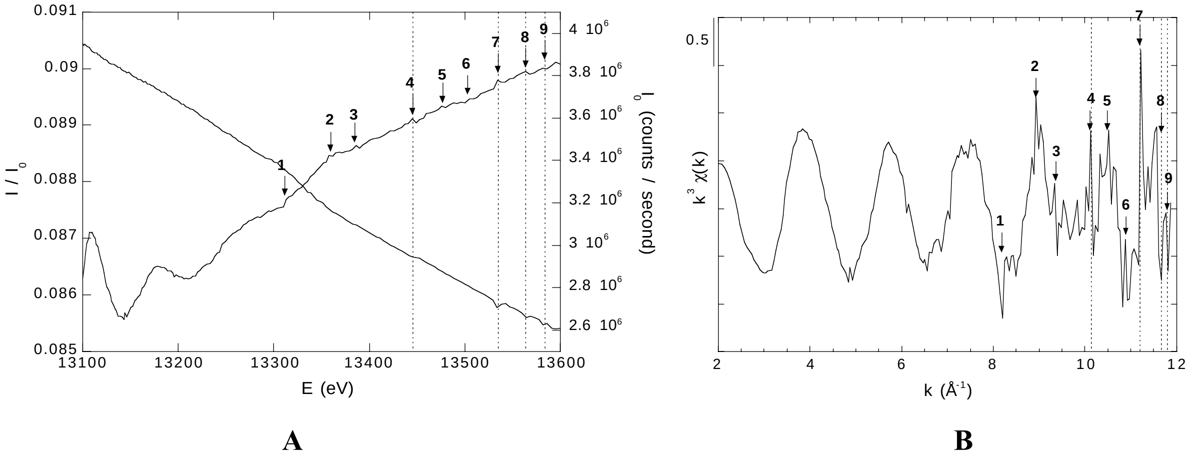

Figure 1 . A - EXAFS region of the Pb-L_{III} edge raw spectrum of the rhizospheric soil after 1 week Pea growth with double solid phosphate adding (I_0 is also plotted for comparison). B — EXAFS spectrum corresponding to the raw spectrum presented in Figure 1A. Arrows indicate defects which are labelled from 1 to 9. Dotted lines indicate glitches which are visible on I_0 on Figure 1A.

Interpretation of the EXAFS spectra of soil samples

The EXAFS spectra of the five soil samples studied during this project are presented in Figure 2.

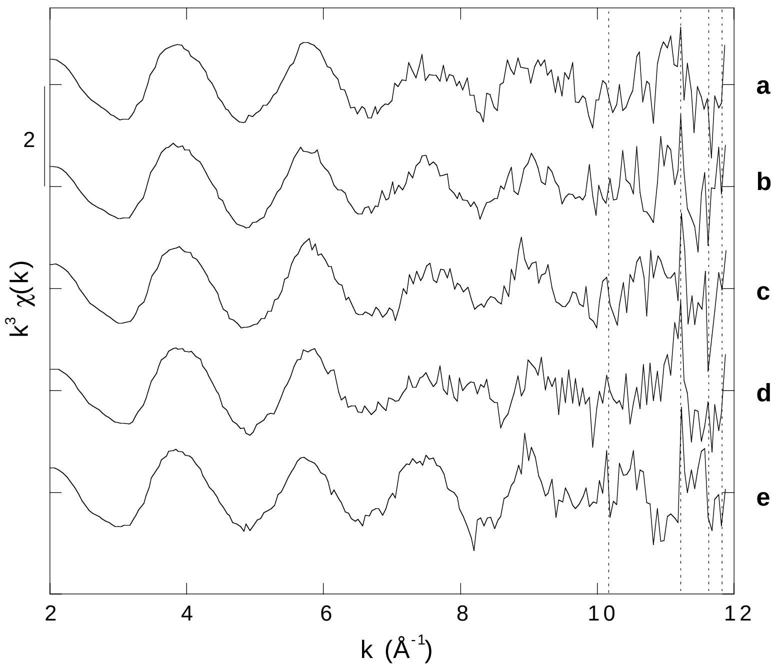

Figure 2 . Pb-L_{III} edge EXAFS spectra of a — reference soil, b — rhizospheric soil after 1 week Pea growth with soluble phosphat adding, c —rhizospheric soil after 1 week Tomato growth with soluble phosphate adding, d —rhizospheric soil after 1 week Pea growth with double soluble phosphate adding and e - rhizospheric soil after 1 week Pea growth with double solid phosphate adding. Dotted lines indicate glitches which are visible on I_0 on Figure 1A.

Comparison of the spectra in the 2-8 $^{-1}$ k-range does not indicate major changes among the samples studied, although some slight differences can be observed in the amplitude and position of the third EXAFS oscillation. Unfortunately, the 8-10 $^{-1}$ k-space region, which might have contained diagnostic information about Pb - 2[nd] neighbors in the samples studied, was not usable. Consequently, it is difficult to relate these slight differences to changes in Pb speciation or to instrumental and/or numerical artifacts.

Conclusions

EXAFS data recorded in transmission mode on the pyromorphite reference sample did not show the artifacts encountered during EXAFS experiments in fluorescence mode on dilute soil samples. For these latter samples, systematic bias in the data above $k = 8$ $^{-1}$ precluded a reliable interpretation of the data in terms of change in Pb speciation among the samples.

Some of the artifacts, especially the glitches, observed on our data should not be topical since the Si(111) set of crystals used during this project was replaced by a new set of Si(220) crystals. Attention should be put on the quality of EXAFS data recorded with this new set of crystals at the Pb L_{III}-edge energy on dilute samples.

Concerning other artifacts, their origin needs to be found to help improvements on BM30B FAME beamline and on samples quality.