Standard Project

Experimental Report template

Proposal title: **Contamination of crops by Pb-rich atmospheric fallouts: Mechanisms and implications for human health**		**Proposal number:** 20110141 (30-02-1023)
Beamline: FAME, ESRF	**Date(s) of experiment:** from: 20-25 octobre 2011	**Date of report:** August 2012
Shifts: 12	**Local contact(s): RANIERI Vincent**	*Date of submission:*

Objective & expected results (less than 10 lines):

The consumption of crops exposed to atmospheric contaminants may represent a risk for human health. To evaluate this risk, it is essential to determine the status of the particles and of lead present on/in the leaves. The purpose of this experiment was to investigate the speciation of lead by Pb LIII-edge EXAFS spectroscopy in two model crops (lettuse and rye grass) exposed to the atmospheric fallouts of a lead battery recycling plant located in the peri urban area of Toulouse. The same plants were also subjected to a root exposure to the same particles, by growing them in a mixture of soil amended with the particles. Other investigations were conducted in parallel on the plants, including measurement of metals accumulation, localizaiton of Pb and other metals by SEM-EDX and ToF SIMS, localization and speciation of minerals by micro RAMAN spectrometry, and quantification of metals accumulations in localized spots by LA-ICP-MS.
Expected results included new insights on the fate of deposited particles on plant leaves, on their possible incorporation in leaf tissues and on the changes in speciation induced by this incorporation. The comparison of plant leaves after foliar and root exposure should provide insights on the mechanisms of Pb sequestration and detoxification, and provide some clues on the toxicity for the consumers. These results should help to improve the current models for risk assessment in the case of atmospheric vs soil contamination.

Results and the conclusions of the study (main part):

Plants were brought to the ESRF, harvested and washed based on human (lettuce) or animal (rye-grass) ingestion scenario: A two-step washing method with deionized water was performed for lettuce shoots, and ryegrass was not washed in order to reproduce the scenario of consumption by cattle. Plant leaves were then flash frozen, ground in liquid nitrogen and conditionned as frozen hydrated pellets.
First, a series of Pb reference compounds spectra were recorded including Pb minerals, Pb sorbed species, and Pb organic complexes in solution. The atmospheric fallouts emitted by the smelter and collected in the smelter courtyard were also studied, in pristine state and after ageing.
All spectra were recorded at 10°K using the He cryostat available on FAME. EXAFS spectra were recorded in transmission or fluorescence depending on Pb content. For the fluorescence mode, the 30-element Canberra detector was used. A total of 2 to 12 spectra of 40 minutes each was averaged, depending on the signal to noise ratio. The individual spectra of the 30 elements of the detector were inspected individually, and the noisiest were discarded. The important noise on some detectors light be due to the presence of ice crystals in the ground plant tissues (contrary to the aqueous solutions, no glycerol is added to the samples). In a more recent experiment, we used a mechanical cryogrinder, so the plant powders were finer, and the quality of the spectra was clearly improved.

The comparison of the reference compound spectra allowed us to estimate the sensitivity of XANES and EXAFS for the types of compounds possibly present in the plant samples.
Both the XANES and EXAFS spectra were treated by linear combination fits of reference compounds spectra with a maximum of 3 components (Figure 1). For the XANES part, no E0 shift of slope correction was allowed. The spectrum for the pristine particles were included in the library of reference compounds for the fit of the aged particles, and both the pristine and aged particles were used as reference compounds for the fit of the plant spectra. Principal component analysis was not used because the set of spectra was too limited.
The pristine and aged particles contained a mixture of αPbO and PbSO4, with a higher proportion of the latter species in the aged particles.
The plant samples contained a mixture of Pb minerals emitted by the smelter (αPbO and PbSO4) and of secondary compounds including Pb-organic acids and Pb-cell wall complexes. Pb phosphate was identified in the leaves of rye

grass after root exposure. The leaves of lettuce after root exposure could not be receorded because of a too low signal. The washed plants did not contain less primary minerals than the unwashed ones, whish suggests that the particles are tightly bound ot the leaves. This is consistent with microscopic observations, which showed that Pb-containing particles were located underneath the cuticle and/or trapped in an organic layer, possibly the cuticular wax. The presence of Pb bound to thiol compounds such as cystein, glutathione or phytochelatin was ruled out.

Our results suggest that Pb speciation strongly depent on the type of exposure (foliar vs root exposure). The alteration of the primary particles induced the formation of Pb-COOH/OH species, which suggests an accumulation of Pb in the cell walls of the plant. Pb-cell wall complexes were identified as the main Pb chemical form in another plant species (Tian et al., 2010). Pb phosphate species might be present either in the vacuoles which are rich in phytate, or in the cell wall as well. This species is highly insoluble and constitutes an efficient detoxification process for the plant, and may be weakly available for the consumers (Cotter Howells et al., 1991, 1999). At the opposite, PbO and $PbSO_4$ may be a source of Pb^{2+} for the plant and for the consumers.

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

During the first 24h, the connection to the server for piloting the beamline was lost unexpectedly due to a conflict of IP numbers between BM30A and BM30B (not the fault of BM30B). Once this problem was fixed, the beamline was very reliable and the experiment went smoothly. The Pb content in the fresh plant samples was very low, so we had to average a large number of spectra.

References

Cotter Howells, J. D., Champness, P. E., and Charnock, J. M. (1999). Mineralogy of Pb-P grains in the roots of Agrostis capillaris L. by ATEM and EXAFS. *Mineralogical Magazine* **63**, 777-789.
Cotter-Howells, J., and Thornton, I. (1991). Sources and pathways of environmental lead to children in a Derbyshire mining village. *Environmental Geochemistry and Health* **13**, 127-135.
Tian, S., Lu, L., Yang, X., Webb, S., Du, Y., and Brown, P. (2010). Spatial imaging and speciation of lead in the accumulator plant Sedum alfredii by microscopically focused synchrotron X-ray investigation. *Environ. Sci. & Technol.* **44**, 5920-5926.

Publication(s):
-in preparation: Schreck, E., Uzu, G., Sarret, G., Sobanska, S., Nowak J.., Magnin V., Ranieri V., Dumat, C., Influence of transfer way on lead speciation and concentration in leaves of plants exposed to particulate matters from a smelter