ESRF	**Experiment title:** Zinc speciation in mining and smelting contaminated overbank sediments	**Experiment number**: 26-01-774
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Names and affiliations of applicants (* indicates experimentalists):

An VAN DAMME *, Rudy SWENNEN *

Geology, K.U.Leuven, Celestijnenlaan 200E, 3001 Heverlee, Belgium

Report:

Introduction

In mining and industrial areas, soils and sediments are often polluted with heavy metals. The chemical risk posed by their presence depends on their mobility and bioavailability and can be assessed by determining their speciation. This experiment focuses on the solid-phase speciation of zinc in mining and smelting contaminated overbank sediments of the Geul river (E-Belgium, S-Netherlands) (Swennen *et al.*, 1994; Cappuyns *et al.*, 2006). In this region, large-scale Pb-Zn mining and smelting took place during the 19th century and the beginning of the 20th century. The most important ore minerals were smithsonite, willemite, hemimorphite, sphalerite and galena.

The aim of the experiment is to investigate the change of speciation of zinc through time in a vertical profile in overbank sediments of the Geul river. Overbank sediments are deposited on the river plain by flood water. Nearly horizontal layers of these sediments accumulate over long time periods. Consequently, the geochemical signal within a vertical profile represents a signal through time.

Materials and methods

A vertical profile in overbank sediments adjacent to the Geul River was sampled a few kilometres downstream of the former mine of Plombières, where sphalerite and galenite were mined from 1845 to 1884. The sampling location is also situated downstream of the former mine of La Calamine, where a mixture of smithsonite, willemite and hemimorphite was mined from 1806 to 1884. The maximal Zn concentration measured in these samples is

11.000 mg/kg, indicating a severe contamination. For Pb, concentrations up to 6.000 mg/kg were measured. Cd and As are minor contaminants.

Zn K-edge (9.659 eV) EXAFS data were collected from 1,3 cm diameter pressed pellets of overbank sediment samples. Most samples were measured in fluorescence mode using a 9-element Ge-detecor. Three scans of 55 minutes each were averaged for every sample. Samples containing more than 10.000 mg/kg Zn were measured in transmission mode (1 scan). The spectra are normalized following standard methods. Also a number of Zn reference compound spectra were collected for data treatment by linear combination fitting.

Results and discussion

Figure 1 shows part of the EXAFS spectra for the overbank sediment samples and references. The high amplitude of the EXAFS signal indicates that well ordered coordination shells (i.e. minerals) are present. Spectra of different Zn-minerals (references) were compared with the spectra of overbank sediments, but the sample spectra could not be fitted with only one component. Most probably, Zn is distributed over a number of species. More data and references are required to be treated by principal component analysis and target transformation to identify Zn species, and by linear combination fitting to determine their proportions in the samples. Also, additional scans of a number of samples and references analysed in this experiment are required to reduce background noise by averaging more spectra.

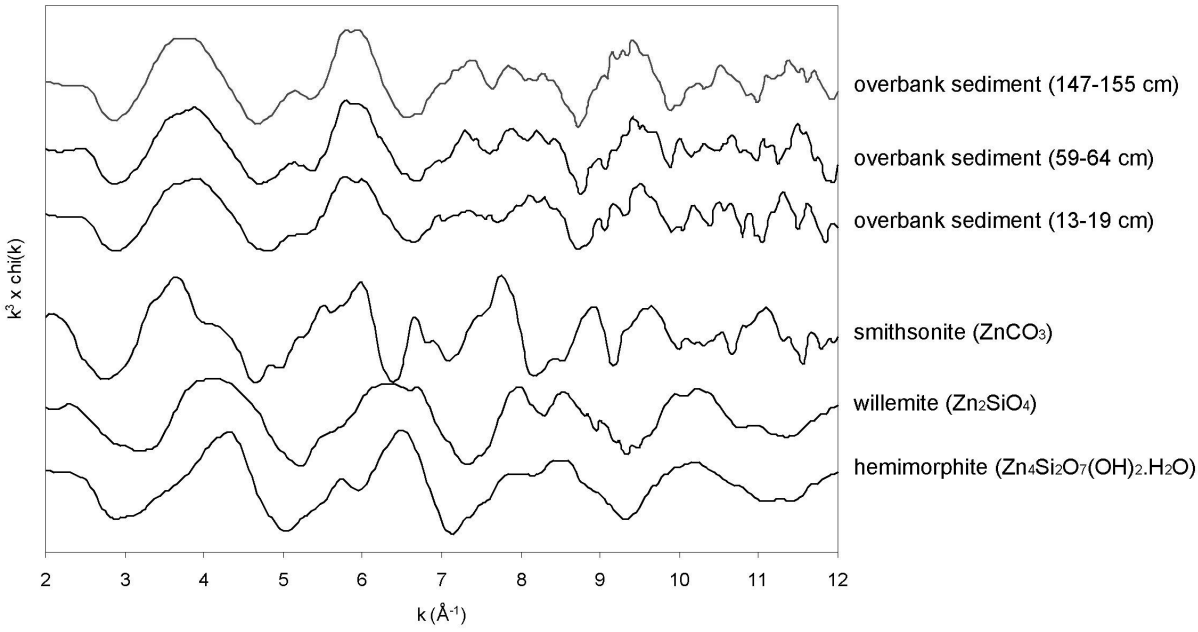

Figure 1: EXAFS spectra (selection): overbank sediment samples taken at the indicated depth in the vertical profile in overbank sediments near Plombières (E-Belgium); Zn-minerals (references) most probably present in the samples

Outlook

Following this experiment, Zn K-edge EXAFS analyses will be done for additional samples of the Geul floodplain at DUBBLE (experiment code 26-01-786). The aim is to extend the dataset with contaminated samples from other locations in the Geul river catchment (different Zn speciation expected) and with additional reference spectra. These data are necessary for the analysis of the current dataset and more conclusions will be presented in the next experiment report.

The data collected in this experiment will be complemented with micrometer scale analyses (micro X-ray fluorescence, micro X-ray diffraction and Zn K-edge μ-XANES) realised at ID22 (experiment code EC223).

References

Cappuyns, V., Swennen, R., Van Damme, A. & Niclaes, M. (2006). Environmental impact of the former Pb-Zn mining and smelting in East Belgium. Journal of Geochemical Exploration, 88: 6-9.

Swennen, R., Van Keer, I. & De Vos, W. (1994). Heavy metal contamination in overbank sediments of the Geul river (East Belgium): its relation to former Pb-Zn mining activities. Environmental Geology, 24: 12-21.