



	<b>Experiment title:</b> Zinc speciation in mining and smelting contaminated overbank and river sediments using EXAFS spectroscopy	<b>Experiment number:</b> 26-01-786
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## Report:

### Introduction

Mining and smelting of metal ores often result in increased metal concentrations in soils and sediments. This may cause toxic effects on humans, plants and micro-organisms. The environmental risk associated with the presence of metals underlines the need to understand how the metals are present at the molecular level. Knowing the chemical form of metals (i.e. their speciation) is essential to gain more insight in the bioavailability and mobility.

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). In this region, large-scale Pb-Zn mining and smelting took place during the 19<sup>th</sup> century and the beginning of the 20<sup>th</sup> century. The most important ore minerals were smithsonite, willemite, hemimorphite, sphalerite and galena. The aim of the experiment is to investigate the speciation of zinc at different depths (i.e. with different deposition date) in vertical profiles in overbank sediments of the Geul river and in riverbed sediments.

## Materials and methods

Vertical profiles in overbank sediments adjacent to the Geul River were sampled a few kilometres downstream of the former mines of La Calamine and Plombières. The maximal Zn concentration measured in these samples is 70.000 mg/kg, indicating a severe contamination. Zn K-edge (9659 eV) EXAFS data were collected from 1,3 cm diameter pressed pellets of overbank sediment samples. Samples were measured in fluorescence mode using a 9-element Ge-detector or in transmission mode, depending on Zn concentration. Several scans of 55 minutes each were averaged for every sample. The spectra of this session and session 26-01-774 were treated together as one dataset. Normalisation was done following standard methods. The  $k^3$ -weighted EXAFS spectra were analysed by combining principal component analysis (PCA) with linear combination fitting (LCF) of reference spectra to experimental data. For this purpose, a database with 45 Zn reference compounds was created with spectra measured during these sessions at DUBBLE and with spectra provided by A. Manceau, F. Panfili, G. Sarret, A. Scheinost and A. Voegelin.

## Results

PCA showed that the set of 28 EXAFS spectra can be described with 3 independent components. The nature of Zn species was determined by target transformation. Six species were positively identified: high-Zn kerolite ( $\text{Si}_4(\text{Mg}_{0.6}\text{Zn}_{2.4})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ), smithsonite ( $\text{ZnCO}_3$ ), Zn-sorbed ferrihydrite, Zn sorbed on humic acid, Zn sorbed on fulvic acid and Zn-reacted hydroxylapatite (phosphate). Since the last four references have similar spectra, it was not possible to differentiate them. Therefore the generic term “tetrahedrally coordinated sorbed Zn” was used for this pool of species. Zn-containing kerolite is used as a proxy for Zn in a trioctahedral local environment in phyllosilicates.

The nature and proportions of Zn species contained in each analysed sample were determined by LCF of the experimental data to the identified Zn species (figure 1). Additional references were considered in the fit as long as this resulted in a decrease in NSS by at least 10 %.

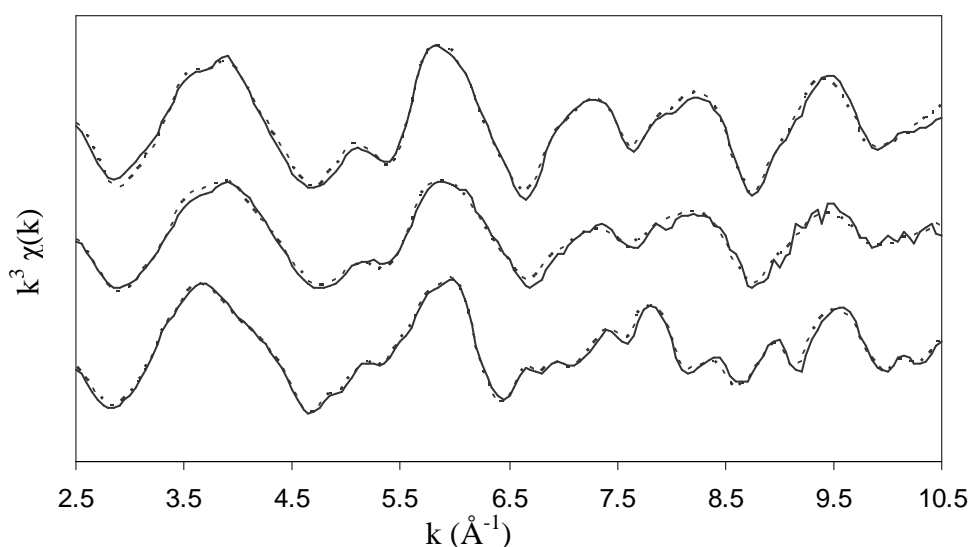


Figure 1: Zn K-edge EXAFS spectra of selected samples (plain lines) and best linear combination fits (dashed lines)

Zn-containing phyllosilicate was identified in all samples in proportions ranging from 32 to 117 %. This is a common species in soils and sediments and was detected in a number of EXAFS studies (Manceau *et al.*, 2000; Isaure *et al.*, 2005; Panfili *et al.*, 2005; Kirpichtchikova *et al.*, 2006; Jacquat *et al.*, 2008). This species results from the coprecipitation of dissolved zinc and silica upon weathering of primary (mining- and smelting-related) Zn minerals. The proportion of smithsonite in the samples ranged from 0 to 61 %. Smithsonite is not commonly detected in EXAFS studies. However, the sampling locations are situated downstream of the former mine of La Calamine, where smithsonite was mined. Smithsonite particles have been transported by the river and deposited on the floodplain. This mineral was also identified by X-ray diffraction in sample concentrates (125-250  $\mu\text{m}$ , dense fraction). The pool of tetrahedrally coordinated sorbed Zn represents 0 to 35 % of the total Zn.

Willemite, hemimorphite and sphalerite were detected by X-ray diffraction in concentrates of these samples, but their presence was not detected in this EXAFS study. Including the spectra in the LCF procedure did not improve the fit. This means that their contribution to the total amount of Zn is below 10 % (estimated detection limit).

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