	Experiment title: Speciation of Zn, Pb, Cd and As in mining and smelting contaminated overbank sediments using micro-XRF, micro-XRD and micro-XANES	**Experiment number**: EC-223
Beamline: ID22	**Date of experiment**: from: 12 December 2007 to: 17 December 2007	**Date of report**: 28 August 2008
Shifts: 15	**Local contact(s)**: Jean CAUZID, Remi TUCOULOU TACHOUERES	*Received at ESRF:*

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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.

The objectives of this study were: (1) to determine the solid-phase speciation of Zn, Pb and associated trace elements (As, Cd, Cu, Ni, Tl) in contaminated overbank sediments, and (2) to evaluate the effect of weathering over time on metal speciation by investigating samples with different deposition date, varying from 1800 until recently deposited.

Materials and methods

The 3 samples used in this study were collected at different depths in a vertical profile in the overbank sediments of the Geul river (E-Belgium and S-Netherlands), which are severely contaminated with Zn, Pb and Cd due to historical Pb-Zn mining and smelting activities (Swennen *et al.*, 1994). The samples were air-dried, embedded in resin and prepared as

polished thin sections. Microspectroscopic analyses were performed at ID22, including micro X-ray fluorescence (µ-XRF), micro X-ray diffraction (µ-XRD) and micro X-ray absorption spectroscopy (µ-XANES). The spot size on the sample was 4 µm (H) x 2 µm (V).

Results

The distribution and associations of elements ($Z \geq 16$) were obtained from µ-XRF mapping. The energy of the incoming beam was chosen to be 30 keV in order to excite the characteristic X-ray lines of heavy metals up to Cd. Eight regions of 280 x 280 µm² were scanned with continuous motor movement (fast scan) with 4 µm (H) x 2 µm (V) steps and a dwell time of 1 second per pixel. The fluorescence spectra were processed using the software PyMCA. After correction for detector dead times, net peak intensities for the identified elements were determined by taking into account overlapping X-ray peaks and by substracting the background. Elemental distribution images are studied using RGB tri-color maps (example in figure 1) (Manceau *et al.*, 2002).

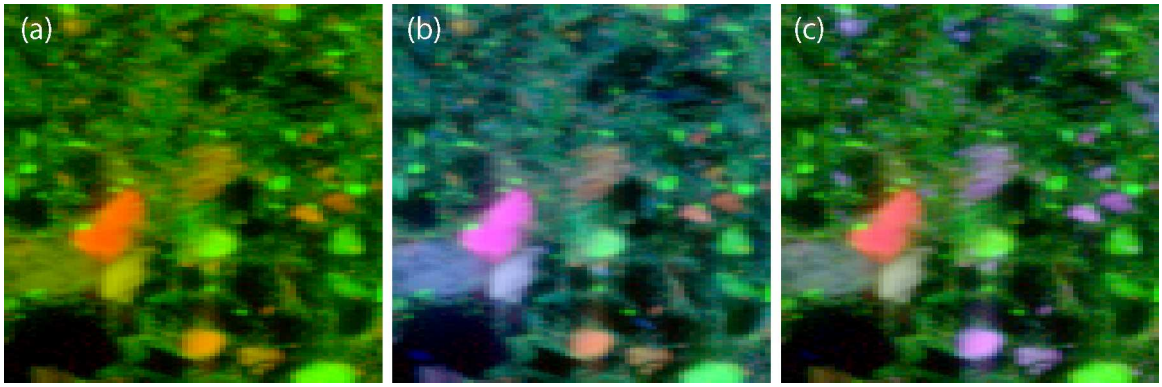

Figure 1: Two-color and tri-color maps of the distribution of Zn, Pb, Fe and Mn in a 280 x 280 µm² region: (a) G (green): Zn, R (red): Pb; (b) G: Zn, R: Pb, B (blue): Fe; (c) G: Zn, R: Pb, B: Mn. The R, G and B channels are logarithmically scaled in order to visualise also areas with low element concentrations. Populations with different ratios of Pb/Fe, Pb/Mn, Zn/Fe, Zn/Mn can be distinguished using scatterplots.

To gain information on mineral phases, regions of interest of variable size were selected on the elemental distribution maps of 280 x 280 µm². In most cases regions with a high fluorescence signal for Zn and/or Pb were chosen. µ-XRD patterns and µ-XRF spectra were simulateously collected for the selected regions with step-by-step scanning at 30 keV using a step size of 4 µm (H) x 2 µm (V) and an exposure time of 2 seconds per point. Transmission XRD images were registered with a CCD camera placed behind the sample. The software Fit2D was used to obtain 1D diffractograms from the µ-XRD images. The sample glass slide caused a large diffuse signal which hampered the visualisation of the diffraction peaks of mineral phases present in the sample (figure 2). Zn and Pb containing phases show only some sharp spots in diffraction patterns and a low signal to noise ratio in the diffractogram. Indications for the presence of hemimorphite and willemite were found. Data treatment is aided by background substraction and principal component analysis (Denecke et al., 2008).

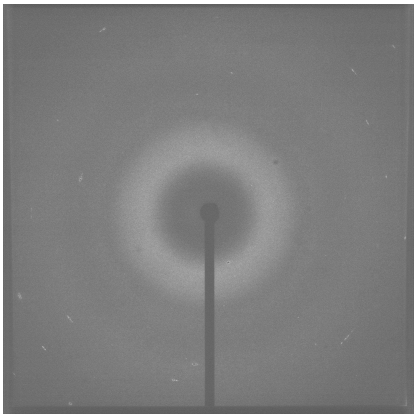
Figure 2: Example of a µ-XRD diffraction pattern (spot containing quartz)

In order to investigate the chemical form of Zn, µ-XANES spectra at the Zn K-edge were collected on 15 Zn-containing points selected on the µ-XRF maps. These data are complementary to the EXAFS data collected at BM26A (cfr. report 26-01-786). Species identified in the samples by bulk-EXAFS or bulk-XRD on concentrates are: Zn-containing kerolite, tetrahedrally coordinated sorbed Zn, smithsonite, willemite and hemimorphite. The XANES spectra are analysed using a linear combination approach (Roberts *et al.*, 2002).

References

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