

Study of the chemical state of zinc in individual river sediment particles using micro-XANES

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River ecosystems are very vulnerable to water and sedimentary pollution. The Tisza, Szamos and Túr rivers located in eastern Hungary are frequently polluted mainly due to mining activities in the catchment area. At the beginning of 2000, two major mining accidents occurred in the Romanian part of the catchment area due to tailings dam failure releasing huge amounts of cyanide and heavy metals to the rivers. The pollution contained aluminium and copper along with zinc and lead, yielding an average zinc concentration of 3000 µg/g in the contaminated sediment layer. In our previous study [1] it was shown that the heavy metals were concentrated in microscopic volumes, and were mostly associated with pyrite type particles. For this reason it is worth to investigate the chemical environment of heavy metals such as zinc in individual particles. In order to obtain speciation information from a microscopic volume, only the non-destructive X-ray absorption spectrometry is feasible.

Surface sediment as well as particles suspended in water were collected at six sites in March 2000 and five sites in April 2001 and April 2002, from the northeast-Hungarian section of the Tisza, Szamos and Túr rivers. The particulate samples were prepared on Nuclepore filters for micro-XANES.

The experiments were performed at the micro-fluorescence beamline L at HASYLAB. The white beam of a bending magnet was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of 1×1 mm² down to a spot size of 15 µm diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the K absorption edge of zinc (9659 eV) by stepping the Si(111) monochromator. The fluorescence yield was detected at an angle of 90° to the incoming beam using an energy-dispersive Si(Li) detector. Surface sediment and water suspended particles taken from the upper section of the Tisza catchment area of 20-40 µm diameter were selected for XANES measurements. The typical zinc content of the particles was 0.1-3 wt%. Minerals and compounds generally present in soil, sediment and gold mine tailings were selected as standards. The used step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). The measuring time for each point varied from 2 s to 60 s depending on the zinc concentration.

The evaluation of the XANES spectra was performed by linear combination of standard spectra. Using a combination of principal component analysis and target test [2], five compounds were found to be present in the measured particles; zinc silicates (willemite and hemimorphite), basic zinc carbonate, zinc sulfide and (Fe,Zn) oxyhydroxide. The presence of similar compounds in contaminated soil and dredged sediment was reported in the literature [3, 4]. Figure 1 contains two examples of the fitting of the XANES spectra of individual particles recorded at the Zn K edge, showing reasonable agreement between the experimental and the fitted spectra.

The micro-XANES results clearly show the different origin and age of the pollution observed at the three rivers. In the most polluted Tisza sample collected in 2000, zinc was found mostly in the sulfide form, while in the Túr and Szamos samples collected in 2001, the (Fe,Zn) oxyhydroxide and basic carbonate forms were dominant. As a summary, Figure 2 shows the ratios of zinc sulfide and (Fe,Zn) oxyhydroxide forms. In particles suspended in water, less soluble forms of zinc were detected than in sediment particles.

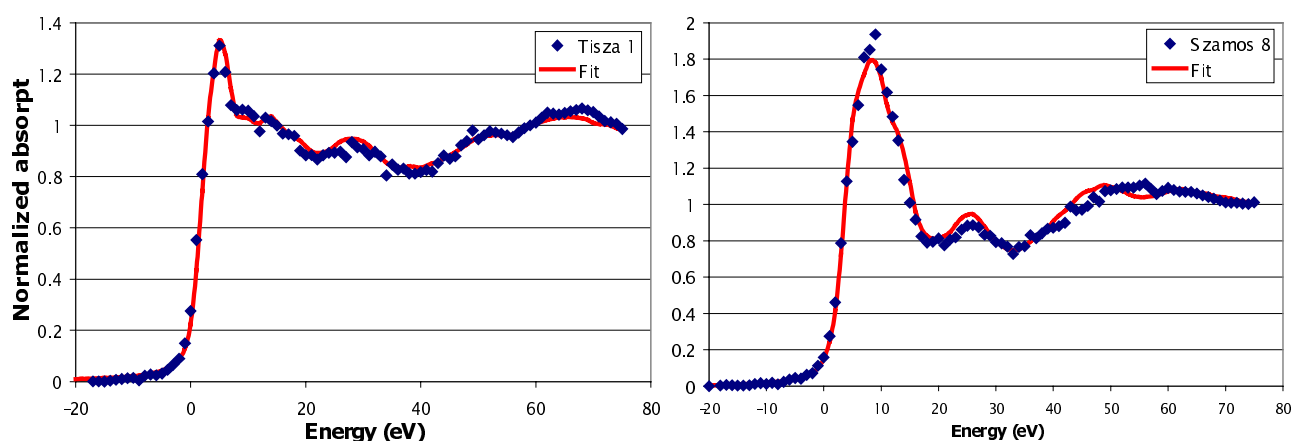


Figure 1: Typical fit of Zn XANES spectra of two individual water suspended particles. Particle “Tisza 1” contains 83 % of Zn as ZnS, while particle “Szamos 8” 80 % as (Fe,Zn) oxyhydroxide.

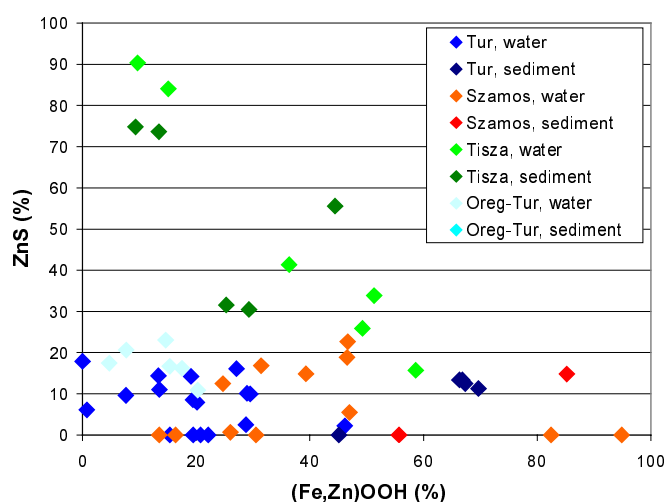


Figure 2: Distribution of the two major zinc compounds [zinc sulfide and (Fe,Zn) oxyhydroxide] over the measured sediment and water suspended particles originating from different rivers

Combining the information obtained using micro-XANES with other bulk and microanalytical methods, the estimation of the environmental mobility of heavy metals connected to microparticles becomes possible.

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