

Pollution particles in river Túr (Hungary): characterization using synchrotron radiation

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River Túr is a small tributary of river Tisza, originating in northwestern Romania. Although the Tisza river was affected by water pollution due to two major mining accidents occurred in the Romanian part of the catchment area at the beginning of 2000, the concentration of heavy metals in sediments and suspended particulate matter (SPM) decreased to the mineral background level one year after the pollution event [1]. In the tributaries Szamos and Túr, however, no significant decrease of the heavy metal concentrations were observed in the recent years. Permanent pollution of inorganic microcontaminants (like heavy metals) originates from industrial, agricultural activities and municipal sewage discharges. A major part of permanent pollution originates from the upstream countries of the catchment area. According to the EPCEM Project Report [2], the most polluted tributaries are the Rivers Túr, Szamos, Sajó, Maros and the Lónyai Canal. The high zinc level in River Túr was in particular also noticed by the local water authority. The aim of the present research was to identify and characterize the pollution related particles in the water and sediment of River Túr. The use of non-destructive microanalytical techniques based on scanning electron microscope and synchrotron radiation makes a complex characterization possible.

Surface sediment and SPM samples were collected at five sites in April 2001, April 2002 and March 2003, from the northeast-Hungarian section of the Tisza, Szamos and Túr rivers. The particulate samples were prepared on Nuclepore filters for micro-XRF and micro-XANES. The experiments were performed at the micro-fluorescence beamline L at HASYLAB. An 80 μm diameter white beam of a bending magnet was used for micro-XRF measurements. The beam size was determined using tungsten cross-slits. The fluorescence yield was detected at an angle of 90° to the incoming beam using an energy-dispersive HPGe detector. In order to suppress the low-energy X-ray photons, a 25 μm thick aluminum absorber was placed in front of the detector collimator. X-ray spectra were collected from selected individual particles, the trace composition was determined using a reverse Monte Carlo method [3]. The micro-XANES measurements were carried out using monochromatic excitation using a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of $1 \times 1 \text{ mm}^2$ 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 Mn and Zn (6539 and 9659 eV) by stepping the Si(111) monochromator. 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 concentration.

In the SPM samples collected from river Túr, strange fibres were observed by electron microscope, these particles were aluminosilicates enriched with zinc and manganese. This particle type was observed in samples collected in 2001, 2002 and 2003. Several particles of this type were further studied by μ -XRF and μ -XANES. Fig. 1 shows a secondary electron image of a typical fibre, and a comparison of measured and simulated μ -XRF spectra obtained using white excitation. The zinc content of the particle exceeded 1 wt%, and 150 ppm cadmium was also detected. This highly toxic and bioavailable heavy metal was also concentrated in this particle type. Zn and Mn K-edge XANES spectra collected from bulk sediment and reference compound samples are shown in Fig 2, compared to μ -XANES spectra of the fibre-shaped pollution particles. In the case of zinc (Fig. 2, left) there is no striking difference between the chemical environment of Zn in bulk sediment and the single particles characteristic for the pollution. Linear combination of standard spectra showed that 55 % of Zn was connected to carbonates and 45 % to silicates. Among silicates, in the bulk sample only Zn containing phyllosilicates were detected, but the fibre particles contained 20 % of zinc as willemite.

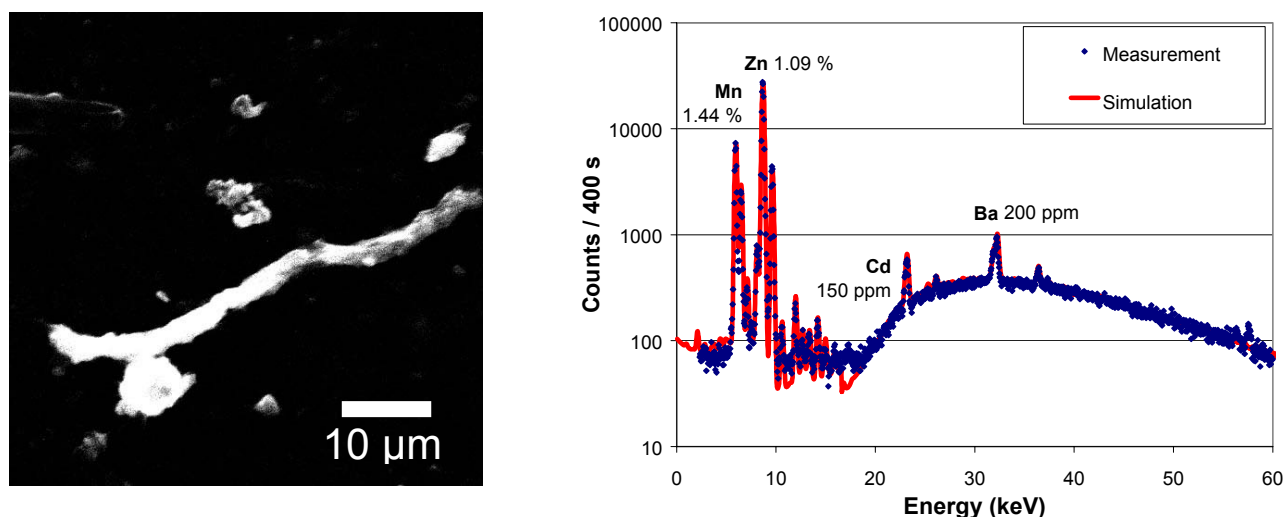


Figure 1: Secondary electron image (left) and white-beam μ -XRF spectra (measured and simulated, right) of a pollution particle identified in river Túr .

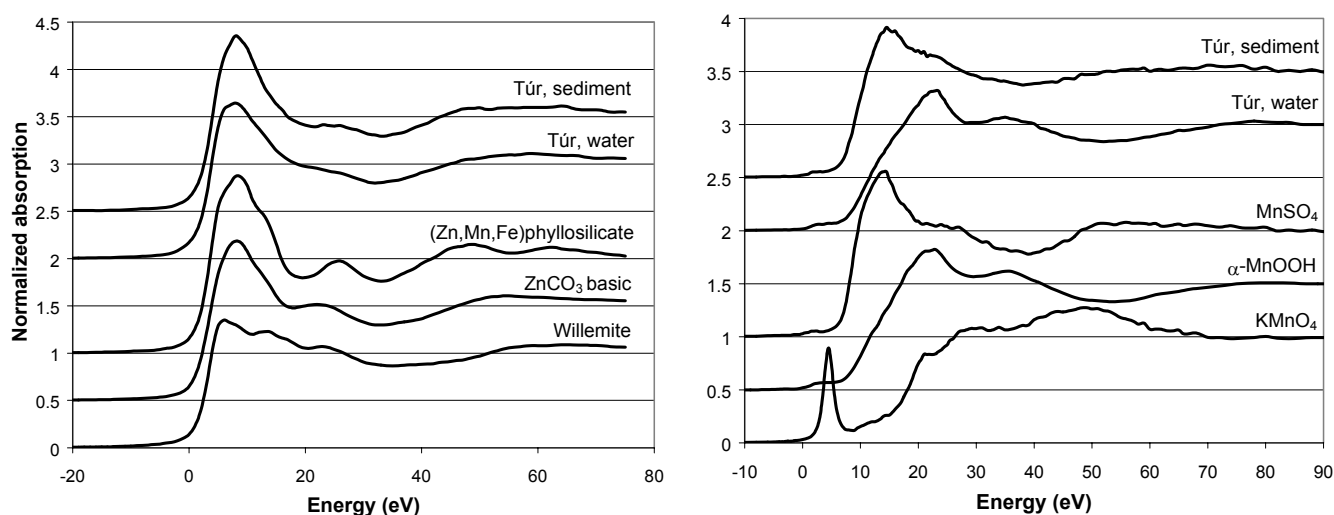


Figure 2: (μ -)XANES spectra of bulk sediment and pollution particles from River Túr compared to reference compounds, Zn K-edge (left) and Mn K-edge (right)

The chemical form of Mn was also studied in bulk sediment samples and water suspended particles collected from the Túr river (Fig. 2, right). Mn was found in Mn(III) oxyhydroxide form in all water suspended particles, while in the bulk sediment collected from the same place only Mn(II) compounds were present. Mn(III) oxyhydroxide can remove heavy metals from the water solution by complexation processes. Therefore the heavy metal pollution of River Túr arrived to the Hungarian section originally mostly in the dissolved phase, while the accidental heavy metal pollution of River Tisza was in the form of microscopic metal sulfide particles [4].

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