Comparison of sediment pollution in the rivers of the Hungarian Upper Tisza Region using non-destructive analytical techniques

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Abstract

The rivers in the Hungarian Upper Tisza Region 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 the failure of a tailings dam releasing huge amounts of cyanide and heavy metals to the rivers. Surface sediment as well as water samples were collected at six sites in the years 2000–2003, from the northeast-Hungarian section of the Tisza, Szamos and Túr rivers. The sediment pollution of the rivers was compared based on measurements of bulk material and selected single particles, in order to relate the observed compositions and chemical states of metals to the possible sources and weathering of pollution. Non-destructive X-ray analytical methods were applied in order to obtain different kinds of information from the same samples or particles. In order to identify the pollution sources, their magnitude and fate, complementary analyses were carried out. Heterogeneous particulate samples were analyzed from a large geographical territory and a 4-years time period. Individual particles were analyzed only from the "hot" samples that showed elevated concentrations of heavy metals. Particles that were classified as

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anthropogenic were finally analyzed to identify trace concentrations and chemical states of heavy metals.

Although the Tisza river was affected by water pollution due to the two major mining accidents at the beginning of 2000, the concentration of heavy metals in sediments decreased to the mineral background level one year after the pollution event. In the tributaries Szamos and Túr, however, no significant decrease of the heavy metal concentrations was observed in the recent years, indicating a continuous pollution. Among the water suspended particles collected from river Túr, fibers of unknown origin were observed by electron microscopy; these particles were aluminosilicates enriched in Zn and Mn. Cd was also concentrated in this particle type. Zn in the sulfide form was observed by microbeam X-ray absorption near-edge structure (XANES) analysis only in the samples collected from river Tisza in 2000, while this metal was connected to carbonates and silicates in the other samples. The dissolved Zn content of the river water and the chemical state of Zn in the fibers collected from river Túr indicate that the heavy metal pollution arrived to the Hungarian section originally mostly in the dissolved phase. The accidental heavy metal pollution of River Tisza, however, was in the form of microscopic metal sulfide particles.

Keywords: sediment, water, transboundary pollution, XRF, EPMA, XANES, TXRF

1. Introduction

Countries downstream of international watercourses often suffer from upstream water and sediment pollution. The watercourse belonging to the fluvial territory of a state is subject to the sovereignty of the riparian state. If the pollution source is under the sovereignty of a state different from the state where the pollution is sustained, the source definition might be difficult. Many conventions regulate the monitoring of such waters but the standard monitoring techniques often result in ambiguous information in case of heterogeneous pollution like the case of sediments.

An important mining and industrial area is located in the catchment area of the Tisza river that suffered several major accidents in year 2000. The two major tailings dam failures that occurred in January and March 2000 in NW Romania, contaminated the Sasar–Lapuş–Someş (Szamos) and Novaț–Vaser–Vişeu river systems, respectively. Since then, different stakeholders, the authorities and the research sector have carried out thousands of analyses to monitor the water quality. Sediment analysis, however, was only carried out almost exclusively on the Tisza river, but only occasionally or not at all on the small tributaries as the Szamos and Túr. These rivers are low-gradient and high-sinuosity with some flood-defense embankment in the urban sections.

Immediately after the pollution event, international missions organized by EU and UN were carried out [1, 2]. Later several articles discussed the results in international scientific journals [3, 4, 5], among them a very comprehensive study [3] that was carried out after the accidents on the Lapuş and Szamos rivers. The latter article contains most information on the sediments taken after the accidents in 2000; however, the exact dates are not specified. Close to the tailings the authors found that Cd and Zn were associated with the exchangeable phase (73 and 47%, respectively) while Pb was found to be predominantly associated with Fe and Mn oxides (71%), but Pb concentrations in the residual phase were relatively high in the upper Tisza. It has been observed that during the sampling time, Cu was more evenly distributed between the four phases than the other four elements determined.

The aim of the present study is to compare the sediment pollution of the rivers in the Hungarian Upper Tisza Region based on samples collected during a four-year survey. Measurements of bulk material and selected single particles were carried out in order to relate the observed compositions and chemical states of metals to the possible sources and age of pollution. Non-destructive analytical methods were applied in order to obtain different types of information from the same samples or particles.

2. Materials and Methods

2.1. Samples and sample preparation

Surface sediment and water sampling from the main riverbed of Tisza was carried out in March 2000 (after the Baia Borşa accident). From 2001, the sampling was extended to the tributaries Szamos and Túr. Additional sediment collection campaigns were carried out in April 2001, April and August 2002, as well as March 2003 from the Northeast-Hungarian section of the Tisza, Szamos and Túr rivers. Sampling sites for the extended campaigns were selected as Szamosbecs and Olcsvaapáti (Szamos, 45 and 5 river-km, respectively); Kishódos and Sonkád (Túr, 24 and 7 river-km, respectively); Túristvándi (Öreg-Túr); as well as Szatmárcseke and Tivadar (Tisza, 720 and 705 river-km, respectively). A map indicating the sampling sites is shown in Figure 1. Sediment samples were collected from 0-2 cm depth using 100 mL plastic containers just below the water surface. Water samples were collected at the same sites, but around 2 m inwards the rivers from the upper 50 cm of the water column by means of 500 mL glass containers. Two parallel sediment, as well as two parallel water samples were collected at each sampling site during each campaign, resulting in 32 sediment and 34 water samples in total. The sediment samples were stored deep-frozen prior to preparation for analysis. The water samples were filtered through 47 mm diameter 0.4 µm pore size Nuclepore (Whatman, Florham Park, NJ, USA) polycarbonate membrane filters, resulting in suspended particulate matter and filtered water samples.

For bulk X-ray fluorescence (XRF) and X-ray absorption near-edge structure (XANES) analysis, the sediment material was dried at room temperature and ground to microscopic particles (0.5 µm < *d* < 20 µm) using an agate mortar. Then, 20 mm diameter pellets were pressed containing 0.45 g of dried sediment material and 0.05 g of boric acid as a binding material. For single-particle analysis, around 5 mg sediment material was suspended in 20 mL n-hexane solution containing 2 % rubber cement (Thalens, The Netherlands), then filtered through a 0.4 µm pore size Nuclepore membrane filter, and dried for 5 min at room temperature. The particle concentration in the suspension was optimized to disperse single particles on the filters with sufficient spacing for single-particle analysis. Rubber cement was found to be an ideal fixing material containing trace elements at very low concentration in a low-Z element matrix and providing elastic fixing [6]. In order to break large particle agglomerations into individual particles, the suspension was subjected to ultrasonic vibration during 20 min (T660/H ultrasonic bath, ELMA, Germany). Dried sediment samples were prepared on adhesive carbon disks for low-*Z* electron probe X-ray microanalysis (EPMA) of single particles. The particulate matter filtered from water samples was treated with n-hexane solution of rubber cement for fixing all particles in the 0.4–200 µm diameter range to the substrate. Some sediment samples were prepared on Formvar film [7]. 10 mg of sediment material was suspended in 15 mL of chloroform solution containing 1.5 % Formvar (Polaron, Watford, UK). 500 µl suspension was dropped to a degreased glass slide, centrifuged at 3000 1/min for 15 s and dried at room temperature for 5 min. The resulting particle-containing film was transferred to the Al sample holder after floating it in distilled water. The remaining water filtrates were further used for dissolved metal analysis by total reflection X-ray fluorescence (TXRF).

2.2. Bulk elemental analysis using XRF

The tube-excited XRF measurements were performed using a Seifert diffraction tube with W anode and Ag secondary target, operating at 60 kV tube voltage and 30 mA current. The X-ray spectra were collected by a Canberra Si(Li) detector with an energy resolution of 170 eV for Mn-Kα X-rays. The typical measuring time was 1000 s. The characteristic X-ray spectra obtained from the samples have been evaluated by non-linear least-squares fitting, using the

AXIL code [8]. For quantitative analysis, the sensitivity curve of the measurement system was determined by measuring a series of Micromatter (Seattle, USA) standard thin foils. In order to test the precision and accuracy of the method for pressed pellets, a standard river sediment sample (IMEP-14, IRMM, Geel, Belgium) was measured under the same conditions. The composition of the matrix was estimated from the low-Z EPMA results (see below), as the average major composition of particles classified in the most abundant group. Assuming that the major composition of the river sediments is similar and using the estimated matrix composition (46 wt% O, 2.3 wt% Mg, 14 wt% Al and 24.8 wt% Si) for the standard as well, the relative difference between the certified and measured concentrations of heavy metals was found to be within 15 %.

2.3. EPMA measurements on individual particles

The analyses of water-suspended particles collected on the Nuclepore filter were performed using a Philips 505 scanning electron microscope (SEM) equipped with a Link energy-dispersive X-ray (EDX) detector. The detector has a 7.62 μm thick Be window, and its energy resolution is 150 eV at 5.9 keV. The EPMA measurements were carried out at an accelerating voltage of 20 kV, and a beam current of 1 nA. The single particles were measured automatically, controlled by in-house developed computer software, only scanning the electron beam over the whole projected area of the particles.

Measurements of sediment particles prepared on carbon disks were carried out on a JEOL 733 (Tokyo, Japan) electron probe micro-analyzer equipped with an Oxford (Bucks, UK) ultrathin-window EDX detector, which allows the measurement of C and O as well. The resolution of the detector is 133 eV for Mn-Kα X-rays. The spectra were recorded by a Canberra S100 multichannel analyzer. The localization and selection of individual particles for X-ray analysis were based on the backscattered electron (BSE) signal, because of its strong atomic number dependence: particles usually have BSE signals above a pre-selected threshold level. An accelerating voltage of 10 kV and a beam current of 1 nA was chosen for all the measurements. In order to obtain a statistically significant number of counts in the X-ray spectra, a typical measuring time of 20 s was used. Morphological parameters such as diameter and shape factor were calculated by the image processing routine of the measuring program.

The characteristic X-ray spectra obtained from the particles have been evaluated using the AXIL code [8]. Semi-quantitative calculation of the particle composition including light elements, such as C, N and O, was performed by a recently developed reverse Monte Carlo method [9], for the particles collected on carbon disks. Using the procedure, the concentrations of the detected elements in standard particles down to 0.3 µm can be calculated with good agreement between the concentrations expected from the chemical formulae and the calculated concentrations (within 3–8 % relative).

Based on the data set obtained, the particles were further classified using hierarchical cluster analysis (HCA). The calculations were performed using the statistical software package IDAS [10]. The classification of the particles prepared on carbon film was based on all calculated concentrations. The particles collected on Nuclepore filters were classified using the normalized X-ray intensities, as it was shown that the groups obtained are the same whether the HCA is based on the intensity or the concentration data obtained by conventional EPMA [11]. The average concentrations (or intensities) and particle diameters were calculated for each particle group. For comparison of the samples collected at different sites, all particles in the entire sample set were classified into groups using the non-hierarchical clustering algorithm (NHCA) of Forgy [12]. For the particles collected on Nuclepore filters the average intensities of each group were converted to concentration values using the MULTI software [13], based on the sum of the X-ray spectra of all particles classified to that group. The calculations were performed using a standardless peak-to-background method [14].

2.4. Synchrotron-based X-ray methods

The experiments were performed at the micro-fluorescence beamline L of the DORIS III synchrotron ring, which is operated by the Hamburg Synchrotron Radiation Laboratory HASYLAB at the German Electron Synchrotron DESY (Hamburg, Germany). A 70-µm diameter white beam from a bending magnet was used for micro-XRF measurements. The low-energy X-ray photons of the exciting radiation were suppressed using a 4-mm thick Al absorber. 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 fluorescence photons, a 25-µm thick Al absorber was placed in front of the detector collimator. X-ray spectra were collected from selected individual particles; the trace composition was determined using the fundamental parameter method [15], and refined by Monte Carlo simulations [16, 17, 18]. The used experimental setup allowed the quantification of trace lanthanide elements using their K lines.

The micro-XANES measurements were carried out using a setup modified for monochromatic excitation. The white beam was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems, E Greenbush, NY, USA) was employed for focusing a beam of 1×1 mm^2 down to a spot size in the micrometer range (20 μm at 10 keV, 30 μm at 6.5 keV) . 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. The X-ray fluorescence photons were detetected by a Silicon drift chamber with 50 mm^2 active area (Radiant Vortex). Surface sediment and water-suspended particles taken from the rivers of the Upper Tisza region of 20-40 μm diameter were selected for XANES measurements. The typical content of the elements of interest in the particles was 0.05-3 wt%. 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 of the element of interest. The bulk XANES spectra of pressed pellets were recorded using a defocused beam of 200×200 μm^2. Minerals and compounds generally present in soil, sediment and gold mine tailings were selected as standards. Zinc minerals franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), hemimorphite and smithsonite ($ZnCO_3$) obtained from the mineral collection of the Eötvös Loránd University (Budapest, Hungary), as well as *pro analysis* grade chemicals were prepared. Pressed pellets containing 1.0 wt% of the element of interest diluted with boric acid, as well as particulate standard samples were measured. The fluorescence XANES spectra of the diluted standard pellets were corrected for self-absorption using the method reported by Iida and Noma [19], resulting in identical spectra for bulk and particulate standards. No self-absorption correction was necessary for the bulk and micro-XANES spectra of sediment particles.

Elemental maps were collected from a few selected particles at the 1B2 beamline of the Pohang Accelerator Laboratory (Pohang, South Korea). The white beam of a bending magnet was focused using Kirkpatrick-Baez mirrors, resulting in a beam of 1.5×2.3 μm^2. Due to the 45° geometry, the spot size on the sample was 1.5×3.5 μm^2. The mirrors act as high-energy filters with a cut-off at a photon energy of around 20 keV. The tank including the mirrors was filled with high-purity He gas. The sediment particles mounted on Formvar film were positioned on a sample stage allowing a remote controlled X-Y movement of the sample with a reproducibility of better than 0.5 μm. The sediment particles to be analyzed were carefully selected by means of optical microscopy. The experiment was carried out by scanning the particles over the beam while recording the fluorescent intensities with a Si(Li) energy dispersive detector. The horizontal and vertical step size was set to be equal to the beam size, 3.5 and 1.5 µm respectively. A 20 s sampletime was used for each pixel. Elemental maps were constructed using the recorded fluorescent intensities representing the elemental distribution over the particles.

2.5. Water analysis by means of TXRF

Trace analysis of water samples was carried out by total reflection X-ray fluorescence (TXRF) spectrometry. Some 5–20 µl of river water was pipetted onto the pre-cleaned sample reflectors that were dried, and the solid film residue was placed into the TXRF setup. The TXRF spectra were measured by a novel Peltier-cooled Si drift detector (SDD) of 10 mm^2 area (V5, KETEK, München, Germany). The X-ray generator (Mo-anode) was operated at 50 kV high voltage and 20 mA current. The energy resolution of the SDD detector was 160 eV at 5.9 keV. The spectra were evaluated by the AXIL software package.

The TXRF spectrometer was calibrated using solutions of commercially available mono and multielemental standards. Single element stock solutions (1000 mg/L, Spectrascan) and ICP multielemental standard (1000 mg/L, Spectrascan) were diluted using Milli-Q water (REWA HQ-5). Only 5 µL of solutions were pipetted on the quartz reflectors and dried in laminar air flow. The detection limit (DL) of Mn, Cu, Zn, Pb was determined from blanks and analysis of 100 mg/L single-element and ICP multielemental standard solutions, using 1000 s counting time. DLs of 4.6, 5.4, 5.1 and 10.9 µg/L for Mn, Cu, Zn and Pb, respectively, were reached by the system. The dissolved metal concentrations were determined from filtered river water samples by adding 50 µg/L Co standard as internal standard.

3. Results

In order to identify the pollution sources, their magnitude and fate, complementary analyses were carried out. When heterogeneous particulate samples have to be analyzed from a large geographical territory and the monitoring aims to encompass longer time periods, an analysis strategy has to be set up to reduce the number of samples to an acceptable laboratory load. Further the selection rule for samples to undergo individual particle analysis was the following. Normal and polluted samples were classified based on the bulk concentration of S, Fe, Cu, Zn and Pb. Further those samples were selected that showed elevated concentrations of these elements. Among these samples some typical particles that were classified as anthropogenic were finally analyzed to identify the chemical state of heavy metals by micro-X-ray absorption methods.

3.1. Elemental composition of bulk sediments

The concentrations of 18 elements were determined in all sediment samples collected from the Tisza, Szamos and Túr rivers using bulk XRF. The analysis results are summarized in Table 1. Concentrations above the intervention level in soils according to the Hungarian Standard are accentuated in boldface numbers. In the first row of the table, concentration values are given for unpolluted sediment layers collected from the Tisza river before the heavy metal pollution event in 2000. Samples collected from the Upper Tisza shortly after the Baia Borşa tailings dam failure (10 March 2000), contained one order of magnitude higher Cu, Zn and Pb concentrations than the background level for river and lake sediments in Hungary [20, 21]. Even the Fe concentration is higher for these samples, about double the values obtained for other samples, while S concentrations were at the percentage level indicating the presence of pyrite, which was confirmed by powder X-ray diffraction and single particle analysis as reported earlier [22]. The relatively high concentration (4.7–6 %) of this mineral is an indication of mine tailings origin, since samples collected close to the mine tailings in Maramureş County, Romania, contained metals almost exclusively in the sulfide form [3]. The results for surface sediment samples collected at the upper section of the Tisza river at least one year after the massive pollution event in 2000, showed that the heavy metal concentrations had decreased to the normal crustal mineral background level. These results indicate that no further significant heavy metal pollution affected the studied river section until March 2003. Surface sediments collected from the Szamos and Túr rivers in 2001, however, contained heavy metals at concentrations above the intervention level. The difference of the concentration ratios of the polluting elements indicates that the pollution source was different for the three rivers. In the surface sediment of Szamos, elevated Cu, Zn and Pb concentrations were observed simultaneously. These concentrations were in the same range as observed by Macklin et al. [23] in samples collected at the Romanian section of the Szamos (in Romanian: Someş) river close to the Hungarian border, in July 2000. In the Túr sediment, only the concentration of Zn exceeded the intervention level, accompanied by elevated Mn content. No significant decrease of the heavy metal concentrations was observed in the surface sediment of Szamos and Túr in 2002 and 2003, indicating the continuous nature of the pollution in these tributaries.

3.2. Major elemental composition of single particles

After identifying the contaminated surface sediment samples with bulk XRF analysis, microanalytical techniques were used, enabling the determination of the composition at the single particle level. Using these methods, individual particles carrying the pollution-originating heavy metals could be identified. EPMA has the advantage that compositional and morphological information can be obtained simultaneously. In our previous study [22] dealing with samples collected from the Tisza riverbank after the Baia Borşa pollution event, the presence of pyrite in the polluted sediment was confirmed using single-particle EPMA. By selecting exclusively the heavy metal containing particles using the BSE contrast, different heavy metal containing – mostly sulfide – particles could be identified with a diameter below 2 µm.

Thin-window EPMA allows to detect C and O, providing information about the stoichiometry of heavier elements. Using this method sulfide and sulfate can be easily distinguished that is important for identifying contamination particles in river sediment. Around 300 particles in each of the sediment samples collected in 2001, prepared on carbon adhesive tapes, were measured using thin-window EPMA. A contaminated sample from the 2000 sampling campaign at the Tisza river was also measured, and classified together with the more recent samples by NHCA. Table 2a shows the average elemental concentrations and the average diameter obtained for the eight particle classes. The variation of their relative abundance over the whole sample set is tabulated in Table 2b. The particle classes are listed in the tables in the order of decreasing overall abundance. The results show that most of the particles were natural constituents of sediment (aluminosilicates, quartz, calcium carbonate). In the most polluted sample collected at the Tisza River immediately after the major pollution event (March 2000), pyrite particles were observed, at an abundance level of 5 %. In the Tisza samples collected in 2001, the abundance of the pollution particles was negligible, showing the cleaning effect of the river. In the Túr samples collected in 2001, Zn containing particles were observed with elevated Mn and Fe content. In the sample collected from the Szamos River, however, pollution-related individual particles could not be identified; the distribution of the contaminant heavy metals is presumably more homogeneous among the particles.

In order to obtain information on the fate of the particulate pollution, water-suspended particles were measured and compared to surface sediment particles. Several hundred individual water-suspended particles collected in 2000 and 2001, prepared on Nuclepore filters, were measured using EPMA, employing an X-ray detector with Be window, which is not transparent for the low-energy X-rays from C and O. Their classification by NHCA was based on the normalized X-ray intensities. The average intensities of each particle group were converted to elemental concentrations that are listed in Table 3a. Concentrations of C and O were calculated from stoichiometry, assuming that Ca is present as $CaCO_3$, and the other metals as oxides in the particles. Average diameters and overall abundance of the eight particle classes are also included in the table. The variation of their relative abundance over the whole sample set is tabulated in Table 3b. Particle classes obtained for the water-suspended particles were similar to sediment particles discussed above. However, the average diameter of the pollution-related particles was smaller and their abundance was higher than in the sediment collected from the same site. The abundance of pyrite particles in the most polluted water sample collected at the Tisza River immediately after the major pollution event (March 2000) exceeded 7 %, with an average diameter of 1.8 µm. In the Szamos River, special pollution-related water-suspended particle types could not be identified, similarly to sediment particles. Water-suspended particulate samples collected from river Túr, however, contained particles with elevated Zn concentration at an abundance level of 20–30 %, with an average diameter of 2.4 µm. Because of the high abundance of these particles that can be related to the pollution, special attention was paid to them, including visualization and application of different non-destructive microanalytical techniques for their detailed characterization.

In the water-suspended particulate samples collected from river Túr, typical fibers were observed by electron microscope; these particles were aluminosilicates enriched with Zn and Mn. Most of the Zn containing particles included in Table 3 were fragments of these fibers that were on average 5–10 µm wide and several hundred µm long. This particle type was observed in samples collected in 2001, 2002 and 2003. Figure 2 shows a secondary electron image of a typical fiber-like particle; the corresponding measured and simulated EPMA spectrum together with the major elemental composition calculated by the reverse Monte Carlo method are shown in Figure 3. The particles contained around 19 wt.% Mn and 15 wt.% Zn. Several particles of this type were measured, and no significant difference in composition was observed within the same sample, but the Zn content of the particles is slightly lower in the samples collected in 2003 than in the samples collected in 2001.

3.3. Trace elemental composition of single particles

Since EPMA is sensitive for lighter elements ($Z < 25$), and it is not very sensitive for heavy elements, particles with pollution related elements can be efficiently identified at the single particle level if they are present as major components. For example, EPMA could not distinguish natural and anthropogenic particles collected from river Szamos, since their Pb concentration was below the detection limit of the technique. In order to differentiate particles based on trace components, like Cd, As, Sn, Ba, Zr, synchrotron-induced micro-

XRF analysis was applied. Altogether 81 particles of 20–80 µm diameter selected from the most contaminated samples taken from three rivers (Tisza 2000, Szamos and Túr 2001) were measured, and classified using HCA based on the minor and trace concentrations relative to Fe. Sediment and water-suspended particles were classified together. The micro-XRF measurements were carried out at HASYLAB beamline L, using a 70×70 μm^2 white beam. The method was advantageous compared to focused monochromatic beam excitation in the sense that heavy metals and lanthanide elements could be determined using K lines. The relatively large beam size, however, just allowed the analysis of particles and particle agglomerates in the sedimentation size range. The average minor and trace composition and abundance of the resulting eight classes are listed in Table 4. At the top of the table the abundance of the different classes in the different rivers is listed in order to indicate the differences in the composition of particles collected from the three rivers. The composition of the two most abundant clusters was very close to the elemental composition of the corresponding contaminated bulk sediment samples. Because of the relatively large diameter of the particles analyzed, particles classified to the first two groups were agglomerations of heavy metal containing particles and “normal” uncontaminated sediment particles reflecting the mineral background of the studied area. Particles in the first cluster contained more Zn and less Pb than particles in the second one; therefore sediment particles collected from river Túr were not classified to Cluster 2, only to Cluster 1. Lead was a more characteristic contamination element for rivers Tisza and Szamos. Cluster 3 contained only water-suspended particles from river Túr, the fiber-shaped particles that were also observed with the electron microscope. The concentration ratio of Mn, Fe and Zn was similar to that measured by EPMA. It was found that the pollution-related particles in river Túr contained on average 800 µg/g Cd. This highly toxic and bioavailable heavy metal was concentrated in this particle type. The determination of this metal was not possible using EPMA and tube-excited bulk XRF. Measured and simulated micro-XRF spectra of a typical fiber-like particle classified to Cluster 3 are plotted in Figure 4, showing good agreement. Cluster 4 contained mostly Pb-rich particles originating from river Túr, water-suspended particles as well. Particles in Clusters 5 and 6 contained Ba in relatively high concentration (0.24 and 0.52 wt.%, respectively). The Ba-containing particles are most likely of natural origin, since no significant difference was observed in the Ba concentration of the polluted and unpolluted bulk sediment samples measured by XRF (see Table 1). An extremely high Pb concentration was characteristic for particles in Cluster 7 (0.79 wt.%), which contained Cd at elevated concentration level (340 µg/g). For Clusters 3 and 7, Cd was mostly associated with Zn containing particles in river Túr, and with Pb-rich particles in rivers Szamos and Tisza. Cluster 8 contained exclusively particles originating from river Szamos. Elevated lanthanide (La, Ce and Nd) and Sr concentrations were characteristic for this cluster. No pollution-related heavy metals were associated with this cluster. Although the number of analyzed particles was not statistically sufficient for complete description of the variability of particles in the contaminated samples, individual particle analysis by micro-XRF provided an insight to the trace composition of particle types characteristic for the pollution.

3.4. Distribution of elements in selected particles

Selected water-suspended particles collected from the Tisza river after the mine pollution accident (2000), as well as from the Túr river in 2001, were analyzed for better identification of heterogeneities on the single particle level. Elemental maps of particles were obtained at the Pohang Accelerator Laboratory using a 1.5 µm vertical and 3.5 µm horizontal step size. As a typical example for the pollution of river Túr, elemental maps of Ti, Mn, Fe, Cu, Zn and Pb collected from the fiber-like particles are shown in Figure 5. There was a striking difference between the spatial distribution of Cu, Zn and Pb in the particles originating from the Tisza and Túr rivers. In the former sample, the different metals were concentrated in different areas of less than 2 µm in large particles, or in separate small particles. In the latter case, however, the distribution of the elements of interest was almost homogeneous over the particles independent on their size, indicating that the pollution can be connected to one specific particle type, where each particle contains all of the toxic elements.

3.5. Speciation of metals in bulk sediments and individual particles

In addition to the concentration of the dissolved heavy metal ions in the water phase that is monitored by the authorities, the speciation of the metals in the particulate phase is also important, because the weathering of the particles can change the bioavailability of the metals of interest. As Zn was a typical pollutant element present in sediments and water-suspended particles of all the three rivers, our study was focused on the non-destructive speciation of this metal. Additionally, because the pollution particles identified in river Túr contained Mn as a matrix element, the chemical state of Mn was investigated in the Túr samples by bulk and micro-XANES. In order to prove that the chemical state of selected metals in individual particles is characteristic over the surface sediment, XANES spectra were also collected from bulk sediment samples and compared to single particle results.

3.5.1. Chemical state of Zn by XANES

Five bulk surface sediment samples and several individual surface sediment and water-suspended particles collected from the three rivers were analyzed by bulk and micro-XANES at the K absorption edge of Zn. An extended spectral data set on bulk and particulate standard compounds and minerals possibly present in environmental microparticles was collected. Minerals franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), hemimorphite and smithsonite ($ZnCO_3$) were obtained from the mineral collection of the Eötvös Loránd University (Budapest, Hungary). The compounds ZnO, $ZnSO_4.H_2O$, $ZnSO_4.7H_2O$, ZnS and $ZnCO_3.2Zn(OH)_2.H_2O$ were prepared from *pro analysis* grade chemicals (Merck, Darmstadt, Germany and Reanal, Budapest, Hungary). (Zn,Mn,Fe)-phyllosilicate particles were found as weathered Zn minerals from the franklinite–willemite–zincite mineral formation. The composition of the particles was verified using EPMA, and the XANES spectra of these particles were similar to those obtained for Zn containing phyllosilicates in the literature [24].

The evaluation of the XANES spectra was performed by linear combination of standard spectra. The required minimum number of standard compounds for the linear combination was determined by principal component analysis (PCA), and the measured standard spectra were tested using target transformation (TT), described in detail by Ressler et al. [25]. The error of the evaluation is estimated as 5-7 % (absolute). Four Zn compounds were accepted to be present in the measured particles: willemite, basic zinc carbonate, zinc sulfide and (Zn,Mn,Fe)-phyllosilicate. Figure 6 shows the XANES spectra of the ZnS and the (Zn,Mn,Fe)-phyllosilicate standards and the five bulk samples. The presence of similar compounds in contaminated soil and dredged sediment was reported in the literature [24, 26]. Examples of fits of XANES spectra of individual particles recorded at the Zn-K edge are presented in our previous study [27], showing reasonable agreement between the experimental and the fitted spectra. Table 5 summarizes the speciation results as well as the total Zn concentration for the bulk sediment samples. In the Tisza “background” sample that was collected from the unpolluted sediment layer, the (Zn,Mn,Fe)-phyllosilicate form was dominant, resulting from the weathering of Zn minerals, and around 22 % of Zn was present as basic Zn-carbonate. Only the contaminated Tisza samples contained Zn as ZnS; the ratio of this compound to the total zinc content was between 31 to 60 %. Although the Zn content of the bulk sediment samples collected from Túr and Szamos was in the same range as that of the contaminated Tisza samples, they contained Zn in the basic carbonate and phyllosilicate form. The fraction of the phyllosilicate form in the latter samples was smaller than in the Tisza “background” sample, only 40–45 %. The chemical state of Zn was also investigated in individual sediment and water-suspended particles. The micro-XANES results clearly show the different origin and age of the pollution observed at the three rivers. As it was expected, the highest fraction of ZnS was observed in particles collected from the Tisza river shortly after the Baia Borsa accident. Less than 30 % of Zn was found to be present as ZnS in the other particles. In rivers Túr and Szamos, the particles contained Zn mostly in the phyllosilicate and basic carbonate forms, but the diverse ratios indicate that the surface sediment and particulate matter suspended in water was a heterogeneous mixture of particles. In rivers Túr and Öreg-Túr, surface sediment particles contained more Zn in the phyllosilicate form than water-suspended particles. There is no striking difference between the chemical environment of Zn in bulk sediment of river Túr and the single fiber-shaped particles characteristic for the pollution. Linear combination of standard spectra showed that 55 % of Zn was connected to carbonates and 45 % to silicates. The microscale Zn speciation results point out that the sediment as well as the river suspended particulate is a heterogeneous mixture of particles, which can be most efficiently analyzed at the single particle level. It is at the single particle level where the difference between the pollution-originating and natural sediment becomes apparent.

3.5.2. Chemical state of Mn by XANES

To complement the elemental analysis, the chemical speciation of Mn was studied in bulk sediment samples and fiber-shaped water-suspended particles collected from the Túr river. Standard compounds MnO_2, $KMnO_4$ and $MnSO_4.H_2O$ were prepared from *pro analysis* grade chemicals (Merck, Darmstadt, Germany). For comparison, transmission mode standard spectra of α-MnOOH and Mn_3O_4 recorded by Ressler et al. [25] at SSRL were used. Figure 7 shows the micro-XANES spectra of pollution related water-suspended particles. XANES spectra of multiple samples of the bulk surface sediment collected at the same location and time, with selected standards are presented as well. The spectrum of the water-suspended particle has very similar features (position of absorption edge and shape of the near-edge structures) as those of α-MnOOH. The absorption edge position of the bulk sediment spectrum is very close to that of $MnSO_4$, indicating that Mn was found in Mn(III) oxyhydroxide form in all water-suspended particles. In the bulk sediment collected from the same location, only Mn(II) compounds were identified. Mn(III) oxyhydroxide can remove heavy metals from the water solution by complexation processes. For this reason, the dissolved heavy metal content of the water samples was also investigated.

3.6. Composition of the dissolved phase

One day after the 2000 pollution event, the Hungarian environmental authorities enforced measures to monitor continuously the heavy metal concentration in the water at various sites of the catchment area of the Tisza river. After the pollution event, authorities sampled every two hours at the monitoring sites and, more than five days after the main pollution event, one sample was taken daily from the middle of the stream. The maximum concentration of total (suspended and dissolved) Pb and Zn was 2.9 mg/L, when the pollution wave reached the upper Tisza Region by 12 March 2000. The dissolved concentrations were orders of magnitude lower: 90-100 µg/L. In later days when the pollution peak has traveled downstream, the dissolved heavy metal concentration gradually decreased. In 2001, the Zn values were between 10 and 25 µg/L in the Upper Tisza [2].

Filtered water samples collected from Tisza, Szamos, Túr and Öreg-Túr rivers in 2003 were further analyzed for heavy metal concentrations. The samples from Túristvándi (Öreg-Túr) and Sonkád (Túr) showed elevated Zn concentrations, 115 µg/L and 71.5 µg/L, respectively. Dissolved Zn concentration in samples from Tisza and Szamos rivers, as well as dissolved Cu and Pb concentrations in all analyzed samples, were below the detection limit of the applied TXRF technique (<5.1 µg/L) in compliance with results of Óvári et al. [28].

4. Discussion and conclusions

The elemental and chemical state analysis delivered very important chemical information that enabled exact chemical characterization of pollution source terms with limited sample number for a relatively large geographic area of different tributaries of the river Tisza. For the time period of 2000 to 2003, the type of industrial activity at the pollution sources was very different for each river. For this reason the results for each river are discussed individually.

4.1. River Tisza

The Hungarian upper section (744–685 rkm) of the Tisza river suffered from the tailings dam failure at Baia Borsa (170 km upstream the river entering Hungary) occurring at 10 March 2000. Surface sediment samples collected at Szatmárcseke (720 rkm) and Tivadar (705 rkm) just six days after the pollution event showed the maximum heavy metal (Cu, Zn and Pb) concentrations. This area was the main sedimentation zone of the pollutants, as it was shown by other authors [29]. According to the first report of the Hungarian Environmental Ministry [30], the pollution arrived mainly in the form of suspended particles and to a lesser extent as dissolved metals. Elevated dissolved metal concentrations were observed only during the pollutant plume that left the Upper Tisza Region already two days later. The report mentioned above assumed that the metals characteristic for the pollution source were present in different phases, because the concentration maxima of Cu, Zn and Pb in the suspended particles were not coincident. The maximum of the Pb concentration was delayed by 6 hours, presumably because of the higher density of the Pb-containing particles. Based on the present and our previous results [22, 27] obtained at the single particle level, the assumption of the report can be supported, because the pollutant metals were enriched in small particles around 2 μm in diameter and Cu, Zn and Pb were connected to different particles. The chemical state studies by μ-XANES clearly showed that the pollution arrived mostly in the form of metal sulfide particles confirming the mine tailings origin of the pollution. In addition to ZnS, PbS and CuS, other forms like $CuFeS_2$ were also detected [27]. Since the heavy metal concentrations in the surface sediment were decreased to the natural background level one year after the tailings dam failure, one can conclude that although the pollution event was severe, it was a unique accidental event. Because of the fast exchange of the surface sediment layer in the river, the ecosystem survived the pollution event.

However, as the pollution event was followed by a flood event, a major part of the polluted sediment was transported to floodplain areas and oxbow lakes. In floodplain areas of agricultural activities, oxidized metal sulfides can be taken up by plants. A Hungarian group studied sediment cores of an oxbow lake of Upper Tisza sampled each year from 2001 to 2004 [31]. They could clearly distinguish a sediment layer enriched with Cu, Zn and Pb that was related to the pollution event in 2000. They observed that the thickness of that layer was not growing in the later samples, indicating no migration of heavy metals from the pollution layer. For this reason the heavy metals most probably remained in the sulfide form in a buried pollution-related layer of the oxbow lake sediment.

4.2. River Szamos

The cyanide pollution accident in Baia Mare, Romania, of January 2000 affected the Hungarian section of River Szamos (0–47 rkm) and Tisza (below 685 rkm), leaving the Upper Tisza intact. This transboundary pollution event was widely discussed in the scientific literature, mostly because of the acute effect of cyanide on the river ecosystems [32, 33]. The first report of the Hungarian Environmental Ministry [30] declared that the cyanide containing wastewater itself did not contain significant amounts of heavy metals, but it could remobilize Cu from the sediment phase based on complexation processes. This was the reason for the increasing dissolved Cu content of the river water while the cyanide plume traveled through Hungary.

The results of our extended survey in the time period 2001–2003 show that the concentrations of heavy metals (Cu, Zn and Pb) were still above the intervention level. According to the above-mentioned report [30], a significant amount of heavy metals was already present in the surface sediment before the cyanide pollution event, indicating a continuous metal pollution from the catchment area independent from the cyanide accident in Baia Mare. The single particle investigations in the present study with diverse techniques, however, could not identify characteristic pollution-related particles with heavy metals as major components in this river. Cu, Zn and Pb were detected only as minor and trace elements in single particles. The pollution-related elements were found to be quite homogeneously distributed in the sediment material, even at the single particle level. Zn was found to be connected to phyllosilicates and carbonates in sediment and water-suspended particles that was also observed in sediment samples containing Zn at the mineral background concentration. As there are diverse anthropogenic activities at the catchment area of River Szamos, no single source of the pollution could be identified.

4.3. River Túr

Results of the present study showed that an elevated amount (above 1500 µg/g) of Zn was present in the surface sediment of the smallest tributary studied. The Túr sediment contained five times more Mn than Tisza and Szamos river sediments in 2001–2003. Based on the single-particle EPMA investigations, a very characteristic Zn-rich particle type could be observed that was enriched with Mn. 5–10 µm wide and several hundred µm long fiber-like particles were observed among water-suspended particles collected from Túr. They were aluminosilicates containing around 19 wt.% Mn and 15 wt.% Zn. Some particles were found in the surface sediment as fragments of these fibers. As the Zn pollution could be related to one characteristic particle type, the more sensitive synchrotron-based single-particle methods could be applied in a very effective way. As a highly toxic and bioavailable element, Cd was found to be connected to the fibers, at a concentration level of 800 µg/g. Mn was found in Mn(III) oxyhydroxide form in the fibers, that can remove heavy metals from the water solution by complexation processes. The latter result indicates that a major part of the heavy metal pollution arrives to the Túr river in the water phase, this was supported by TXRF measurement of the dissolved Zn content of the Túr water, being above 70 µg/L. Immediately the river entering Hungary at Kishódos, a high Zn concentration was observed in the surface sediment indicating that the continuous Zn pollution arrives from Romania. Previously published results supported this argument by reporting high dissolved Zn concentrations in the Romanian section of the Túr river [34, 35]. They claimed the intense mining activities at the Turt mine being the most probable cause of the continuous pollution.

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Figure captions

Figure 1 Map of the Northeastern part of the Tisza catchment area showing the sediment sampling sites (KH: Kishódos, OA: Olcsvaapáti, SB: Szamosbecs, SC: Szatmárcseke, SD: Sonkád, TI: Túristvándi and TV: Tivadar). The pollution sources of the mining accidents in 2000 (Baia Mare and Baia Borsa) are also indicated.

Figure 2 Secondary electron images of fiber-shaped water-suspended particles collected from river Túr

Figure 3 Measured and simulated EPMA spectra, and calculated major elemental composition of a fiber-like particle from river Túr

Figure 4 Measured and simulated white-beam micro-XRF spectra collected from a fiber-like water-suspended particles from River Túr.

Figure 5 Elemental maps obtained by micro-XRF (Cr, Mn, Fe, Cu, Zn, Pb) for a longer fiber-like particle found in the water of River Túr, step size 3.5 µm horizontal and 1.5 µm vertical. The X-ray intensity scale corresponding to the gray levels is indicated on each map.

Figure 6 Zn K-edge XANES spectra of the bulk sediment samples and selected standards. The origin of the energy scale is set to the absorption edge of Zn metal (9659 eV).

Figure 7 Mn K-edge (micro-)XANES spectra of water-suspended particles with the corresponding bulk sediment sample collected from River Túr and selected standards. The origin of the energy scale is set to the absorption edge of Mn metal (6539 eV).

Table 1. Bulk composition of the surface sediment samples measured using XRF. Values exceeding the intervention level for soils according to the Hungarian Standard are indicated in boldface.

River	Sampling site*	Year	Concentration (µg/g)																	
			S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	Y	Ba	Pb
Tisza	TV**	2000	<2500	18000	8300	5100	335	<115	1200	44000	<40.0	75.0	170	<29.0	4.55	115	95	28.5	1700	<56.0
Tisza	SC	2000	21400	16000	6890	3780	329	<120	964	50400	35.9	**592**	**1620**	**56.5**	6.48	96	78	32.1	1920	**1070**
Tisza	TV	2000	30800	17300	8190	3640	241	<103	1050	72200	<48.1	**1250**	**3200**	**148.0**	6.89	114	75	37.0	2100	**2100**
Tisza	SC	2001	<2500	10300	4180	3550	<256	<97	641	25600	<25.2	42.1	126	<19.6	2.54	62	71	19.1	1170	<41.0
Szamos	SB	2001	<2500	11800	11800	3190	284	<121	1530	31200	38.3	**168**	**1260**	**52.5**	4.87	79	106	22.9	1470	*79.9*
Túr	SD	2001	<2500	11100	4690	4500	375	<137	2380	37000	<23.8	51.3	**2070**	<26.2	5.39	90	95	30.2	1480	<52.8
Tisza	SC	2002	<2500	11100	4590	3350	<284	<157	567	24200	<31.1	50.8	117	<9.2	<5.16	56	75	16.2	<1050	20.6
Tisza	TV	2002	<2500	8200	3910	3590	<226	<70	391	19900	<20.2	40.8	84	<6.8	<2.80	42	62	16.2	<970	20.9
Szamos	SB	2002	<2500	12400	13900	5060	284	<142	2070	34900	<41.5	**183**	**885**	16.7	<5.00	87	121	16.2	1860	**190**
Szamos	OA	2002	<2500	13500	19900	4990	343	108	2730	35300	<20.1	**189**	**1110**	28.6	<8.40	83	109	27.7	1100	<35.5
Túr	KH	2002	<2500	11000	4850	4150	282	<73	629	43200	<24.0	72.0	**2500**	<25.6	<8.00	81	87	31.8	1330	<42.5
Túr	SD	2002	<2500	11400	5850	2980	291	<118	1370	27800	<27.2	73.6	**1640**	<7.9	5.25	64	111	16.2	1020	33.0
Öreg-Túr	TI	2002	<2500	9400	6570	2830	232	<139	2470	25700	<24.1	32.2	**1030**	<13.7	4.59	59	94	16.2	2050	23.5
Tisza	SC	2003	<2500	8900	3150	2260	130	<77	499	20100	<20.9	59.8	133	<15.4	<7.19	48	52	19.3	1530	<26.8
Szamos	SB	2003	<2500	10600	9910	5300	274	139	821	22900	18.9	87.2	397	<23.7	<6.79	57	98	29.5	1580	<36.8
Túr	SD	2003	<2500	12600	6400	4200	262	59	3310	39300	21.2	70.2	**2110**	22.5	7.49	88	97	27.2	1730	39.2

* KH: Kishódos, OA: Olcsvaapáti, SB: Szamosbecs, SC: Szatmárcseke, SD: Sonkád, TI: Túristvándi, TV: Tivadar

** Unpolluted sediment layer before the Baia Borsa pollution event

Table 2: Result of NHCA of the surface sediment particles prepared on carbon tape, (a) average composition and average diameter of the major particle classes, (b) variation of the relative abundances over the whole sample set

(a)

Particle	Abun.	Diam.	Concentration (wt%)															
Type*	(%)	(μm)	C	O	Na	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Pb
AlSi	48.2	12.1	9.9	44.6	1.6	1.2	11.0	22.5	0.2	2.6	0.7	0.3	0.3	4.6	0.0	0.0	0.1	0.2
AlSi + Fe	26.7	7.0	7.7	41.1	1.9	2.0	9.0	16.3	1.4	2.0	1.1	0.8	1.3	14.6	0.0	0.2	0.5	0.0
SiO_2	20.0	13.0	8.9	47.7	0.6	0.5	3.5	34.4	0.1	0.9	0.3	0.2	0.2	2.2	0.1	0.1	0.2	0.0
Fe oxide	2.5	8.6	3.8	35.0	0.0	0.2	2.2	7.4	0.0	3.1	1.0	1.7	1.6	40.0	0.9	0.5	0.8	1.2
$CaCO_3$	1.0	12.0	15.9	41.3	0.3	2.1	3.0	7.7	0.0	0.5	21.6	0.1	0.4	3.6	0.2	0.0	0.3	2.3
FeS_2	0.8	7.4	4.3	5.7	0.3	0.0	1.2	1.7	43.1	0.3	0.1	0.0	0.0	36.6	0.0	1.7	0.0	4.6
Ti oxide	0.5	12.7	8.7	40.8	0.6	0.6	3.2	6.0	0.0	0.7	0.4	34.2	0.2	4.5	0.0	0.0	0.0	0.0
Mn, Fe, Zn	0.2	8.7	4.1	33.0	0.0	0.0	1.0	3.8	0.0	0.2	0.2	0.1	29.7	19.8	0.1	0.0	8.1	0.0

(b)

Particle	Relative abundance in sample**					
Type*	TV 2000	TV 2001	SC 2001	SB 2001	SD 2001	TI 2001
AlSi	25.7	49.1	49.1	61.0	58.0	45.6
AlSi + Fe	56.3	16.6	18.7	15.1	28.3	32.7
SiO_2	13.0	23.3	28.0	16.5	11.3	19.7
Fe oxide	0.0	8.5	2.4	2.4	1.7	0.7
$CaCO_3$	0.0	0.7	1.5	3.4	0.0	0.0
FeS_2	5.0	0.3	0.0	0.3	0.0	0.0
Ti oxide	0.0	1.1	0.3	1.3	0.3	0.3
Mn, Fe, Zn	0.0	0.3	0.0	0.0	0.3	1.0

* AlSi: aluminosilicates

** SB: Szamosbecs, SC: Szatmárcseke, SD: Sonkád, TI: Túristvándi, TV: Tivadar

Table 3: Result of NHCA of the water-suspended particles prepared on Nuclepore filter, (a) average composition and average diameter of the major particle classes, (b) variation of the relative abundances over the whole sample set

(a)

Particle	Abun.	Diam.	Concentration (wt%)													
Type*	(%)	(µm)	C†	O†	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Cu	Zn
AlSi	35.4	1.6	0.2	48.6	1.5	11.8	26.0	0.0	0.6	3.4	1.8	0.0	0.0	5.4	0.0	0.6
SiO_2	26.1	1.4	0.2	52.5	0.0	3.4	39.2	0.0	0.0	0.6	1.6	0.0	0.2	1.5	0.0	0.7
AlSi+Fe	18.2	1.8	0.2	46.0	2.1	10.1	18.8	0.0	1.7	1.8	2.1	0.0	4.1	13.0	0.0	0.0
Mn, Zn	7.8	2.4	0.3	39.6	0.0	3.9	8.7	0.0	2.0	0.0	2.5	0.0	23.5	7.1	1.7	10.7
AlSi+Ca	7.5	1.8	3.2	50.7	1.3	3.0	10.1	0.7	1.2	1.0	27.0	0.0	0.0	1.8	0.0	0.0
Fe+AlSi	2.5	1.9	0.2	40.3	0.0	5.9	12.4	0.0	1.1	0.0	1.7	0.0	2.9	34.2	0.0	1.4
FeS_2 +AlSi	1.5	1.8	0.3	26.5	1.8	6.6	13.5	4.5	20.6	0.0	2.2	0.0	0.0	20.7	0.0	3.3
Ti+AlSi	0.9	1.6	0.1	44.6	1.2	6.1	12.6	0.0	1.0	1.2	1.1	27.2	0.0	4.8	0.0	0.0

(b)

Particle	Relative abundance in sample**				
Type*	TV 2000	SC 2001	SB 2001	SD 2001 (a)	SD 2001 (b)
AlSi	50.2	49.6	64.6	16.6	27.7
SiO_2	5.0	29.0	9.2	9.6	13.3
AlSi+Fe	26.2	16.1	20.8	34.9	31.0
Mn, Zn	0.0	0.9	0.8	35.6	21.3
AlSi+Ca	0.3	0.5	0.8	0.0	2.7
Fe+AlSi	9.4	0.9	1.5	2.3	2.3
FeS_2 +AlSi	7.2	0.9	0.0	1.0	0.7
Ti+AlSi	1.9	2.2	2.3	0.0	0.3

* AlSi: aluminosilicates

† Calculated from stoichiometry

** SB: Szamosbecs, SC: Szatmárcseke, SD: Sonkád, TV: Tivadar

Table 4. Summary of the trace element analysis of 81 large (40–100 µm) individual particles by means of white-beam micro-XRF. The concentrations were calculated using the FP method and refined using MC simulations. Eight clusters were obtained using HCA.

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7	Cluster 8
River	Number of particles in cluster							
Total	33	16	10	8	6	4	2	2
Tisza	15	13	0	0	3	1	1	0
Szamos	5	3	0	2	1	3	1	2
Túr	13	0	10	6	2	0	0	0
Element	Average concentration (µg/g)							
Mn	421	528	63800	2520	171	67	3980	1210
Fe	13800	25200	12800	8110	3530	128	2340	610
Ni	29	72	102	37	4	2	2	0
Cu	173	187	1530	137	59	15	188	12
Zn	1340	670	62000	910	274	7	406	22
As	6	8	42	11	2	75	0	7
Br	4	13	132	22	5	0	92	0
Rb	119	82	43	87	128	73	85	95
Sr	124	36	127	113	65	254	137	7180
Y	22	10	39	23	2	0	170	42
Zr	139	32	13	35	11	5	56	152
Nb	18	10	27	14	3	4	16	1
Cd	15	7	830	36	1	1	344	3
Sn	119	20	14	23	29	6	82	10
Cs	10	7	12	14	26	38	3	5
Ba	534	383	1360	1130	2420	5260	61	212
La	15	11	11	14	5	2	21	286
Ce	42	34	43	39	10	2	46	660
Nd	16	9	23	17	0	1	12	181
Pb	290	465	55	660	56	36	7890	89

Table 5. Result of the XANES speciation of Zn in bulk sediment samples

Sample	Total Zn (µg/g)	Zn compound (%)			
		Zn_2SiO_4	$ZnCO_3$ basic	ZnS	(Mn,Fe,Zn)-phyllosilicate
Tisza 2000 (1)	3200	-	51	31	18
Tisza 2000 (2)	2800	9	16	60	15
Túr 2001	2070	-	55	-	45
Szamos 2001	1260	-	60	-	40
Tisza (background)	120	-	22	-	78

Figure 1

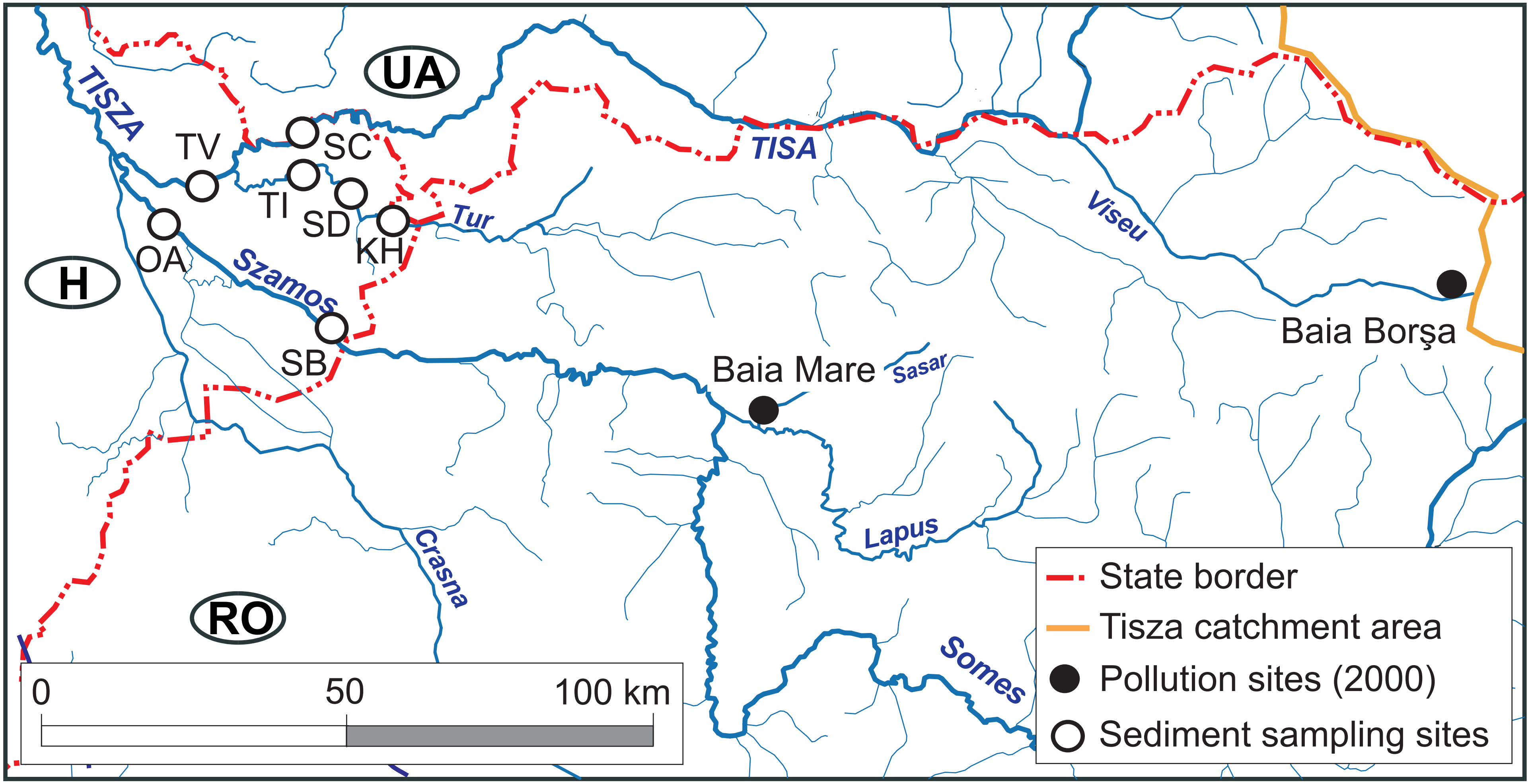

UA
H
RO
TISZA
TISA
Viseu
Tur
Szamos
Crasna
Sasar
Lapus
Somes
TV
SC
TI
SD
KH
OA
SB
Baia Mare
Baia Borşa
State border
Tisza catchment area
Pollution sites (2000)
Sediment sampling sites
0
50
100 km

Figure 2

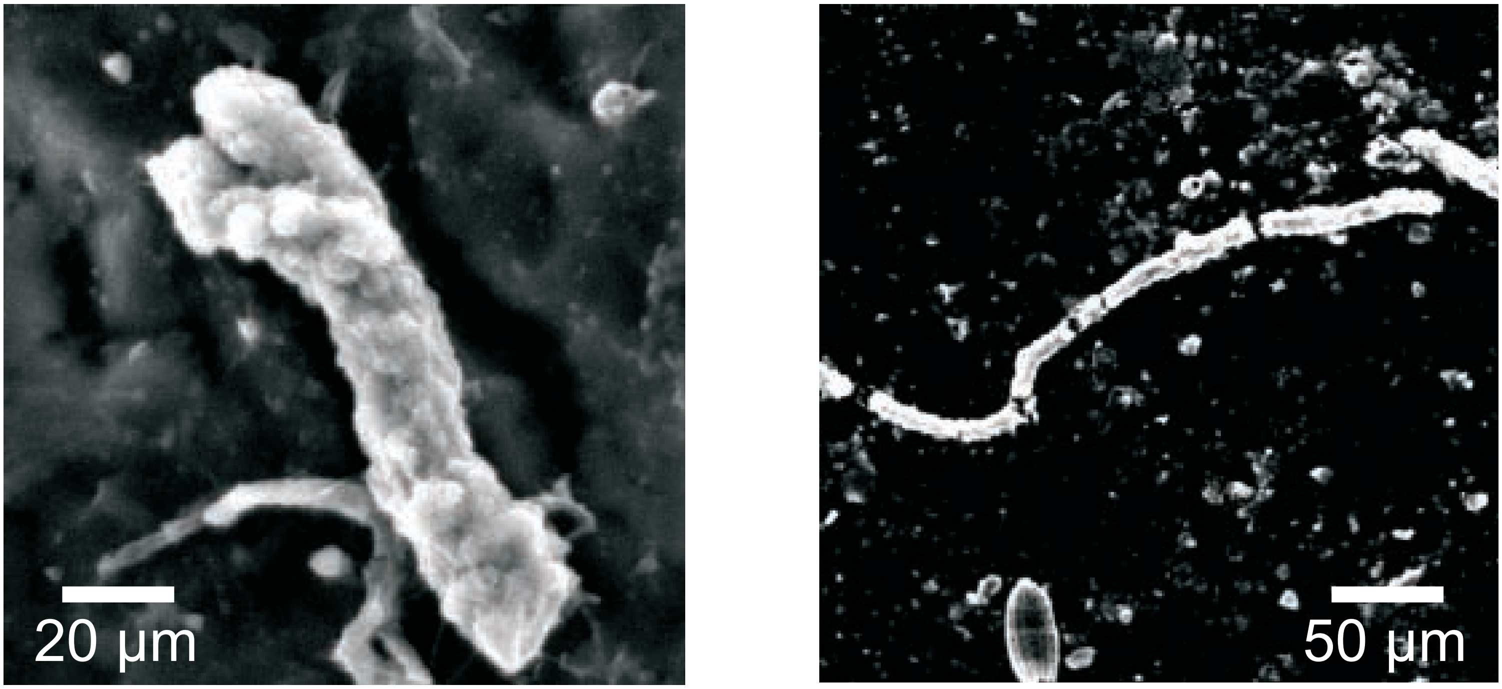
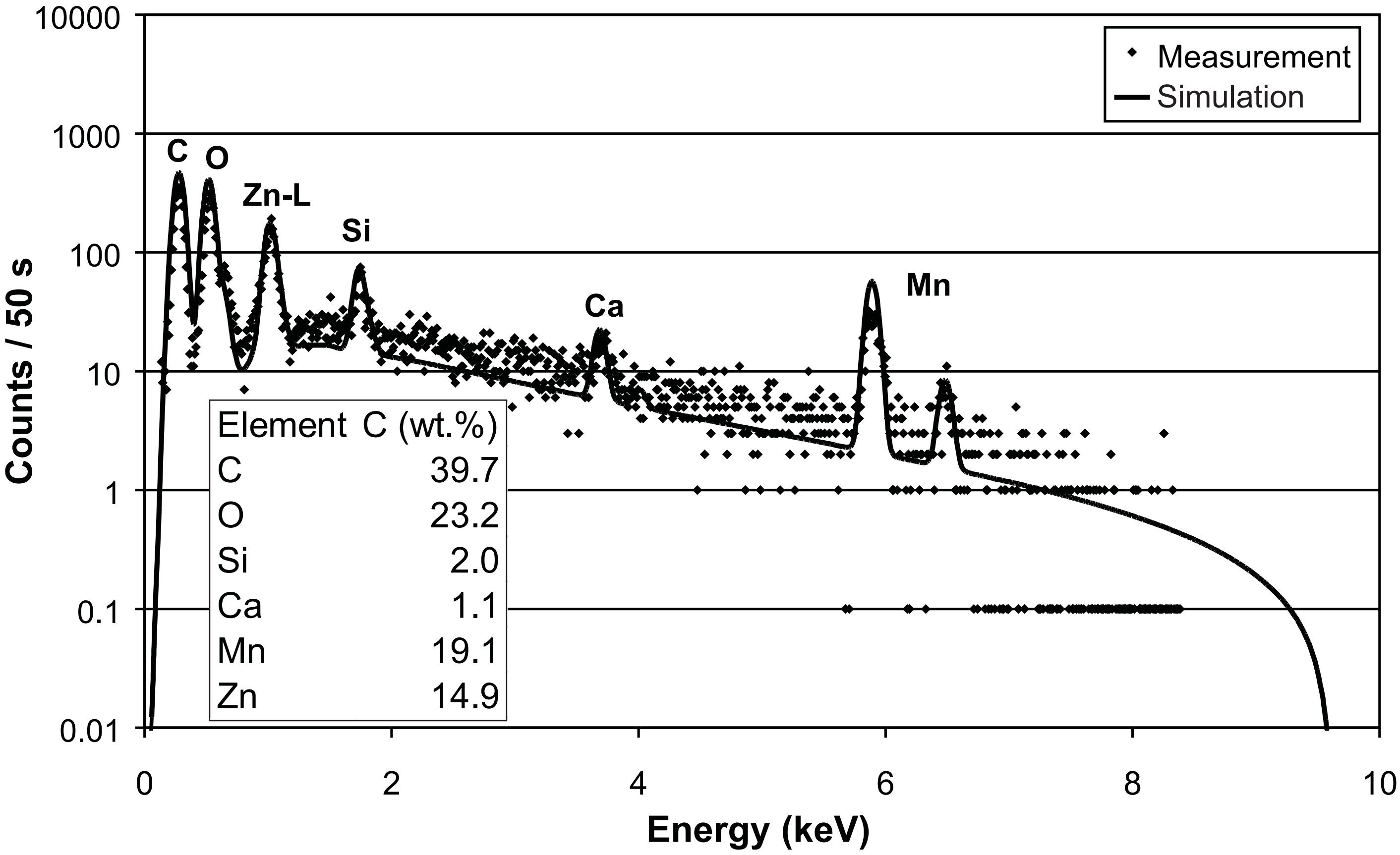
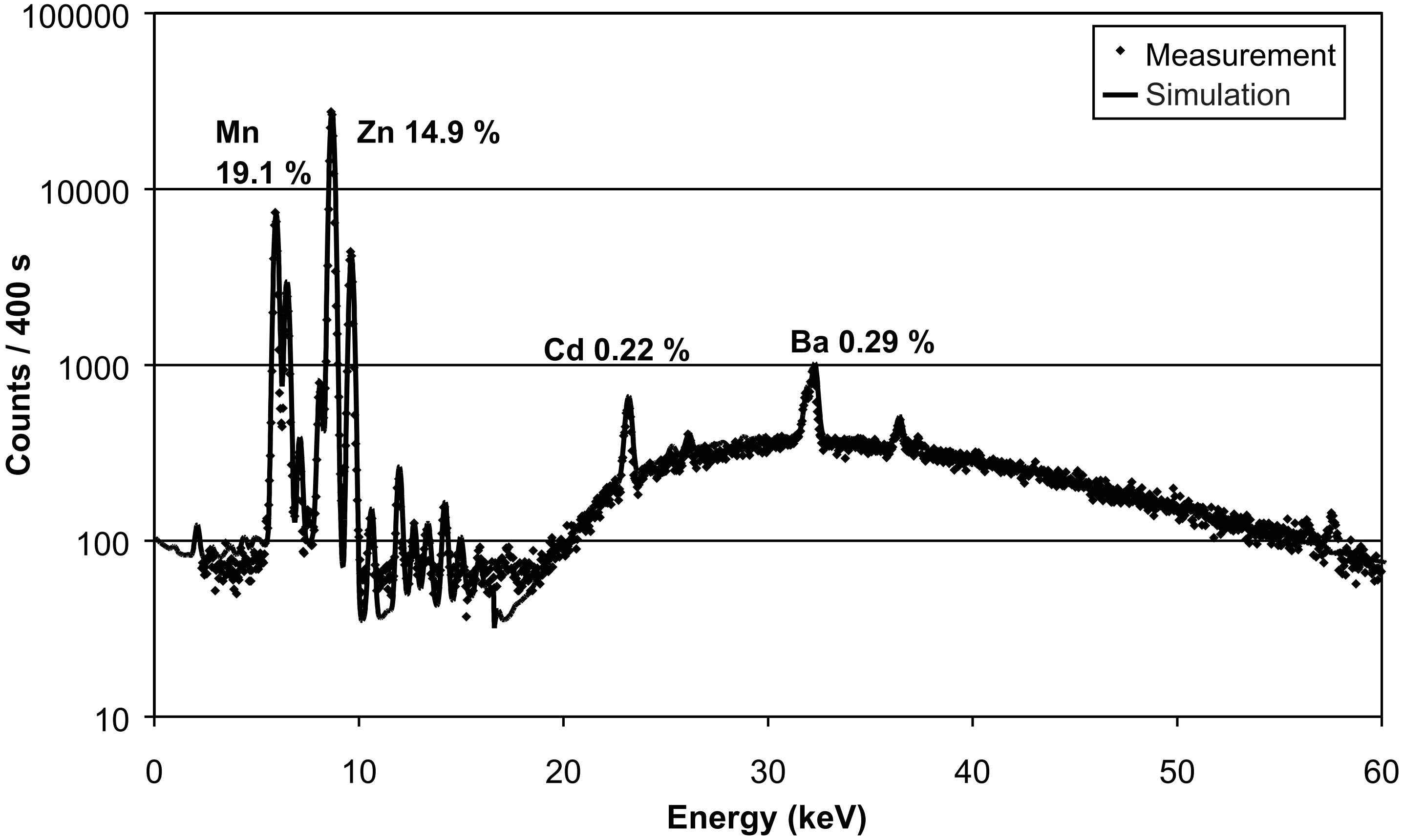


Figure 3



Element	C (wt.%)
C	39.7
O	23.2
Si	2.0
Ca	1.1
Mn	19.1
Zn	14.9

Figure 4


Measurement
Simulation
Mn
19.1 %
Zn 14.9 %
Cd 0.22 %
Ba 0.29 %
100000
10000
1000
100
10
Counts / 400 s
0
10
20
30
40
50
60
Energy (keV)

Fig

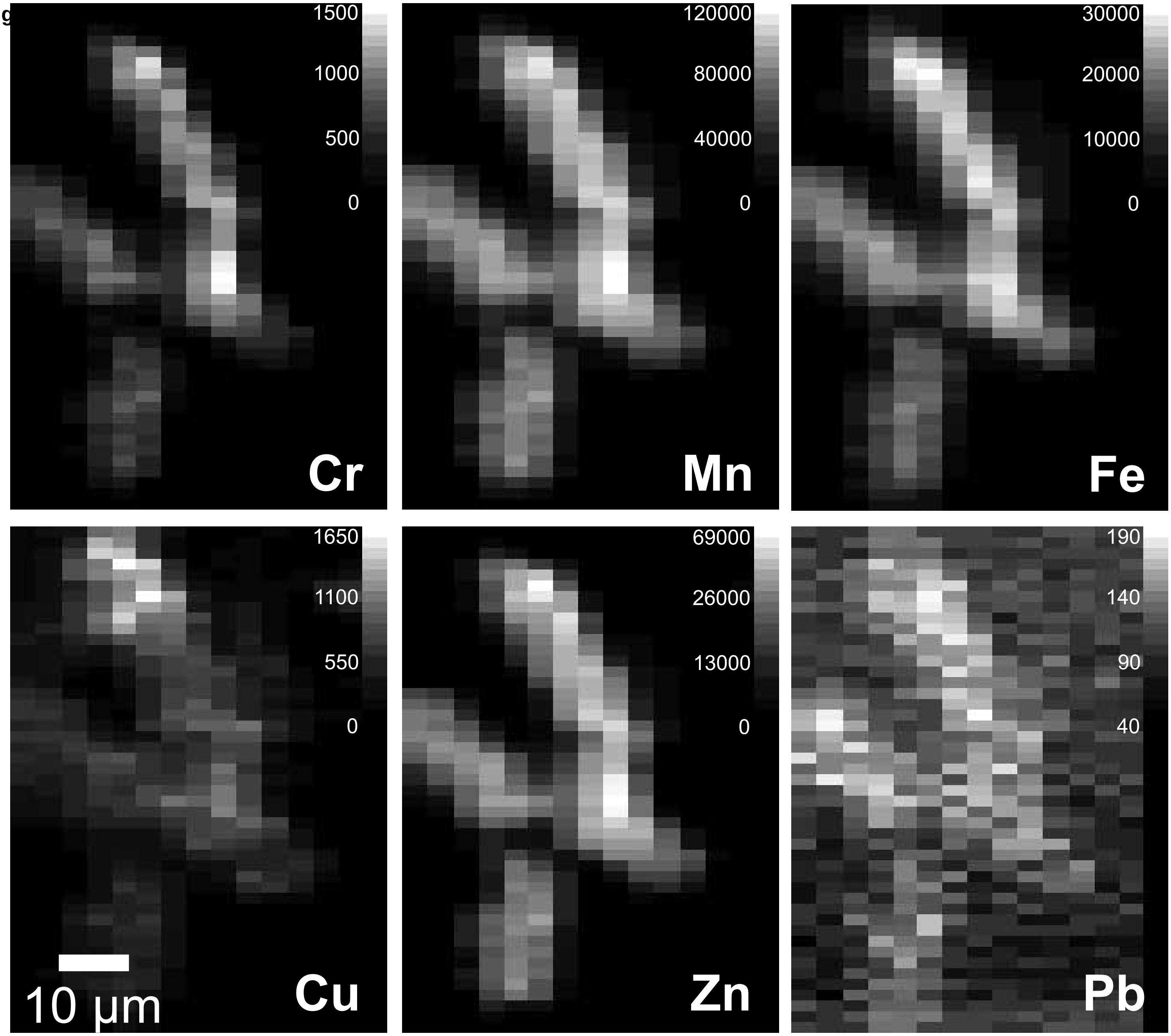
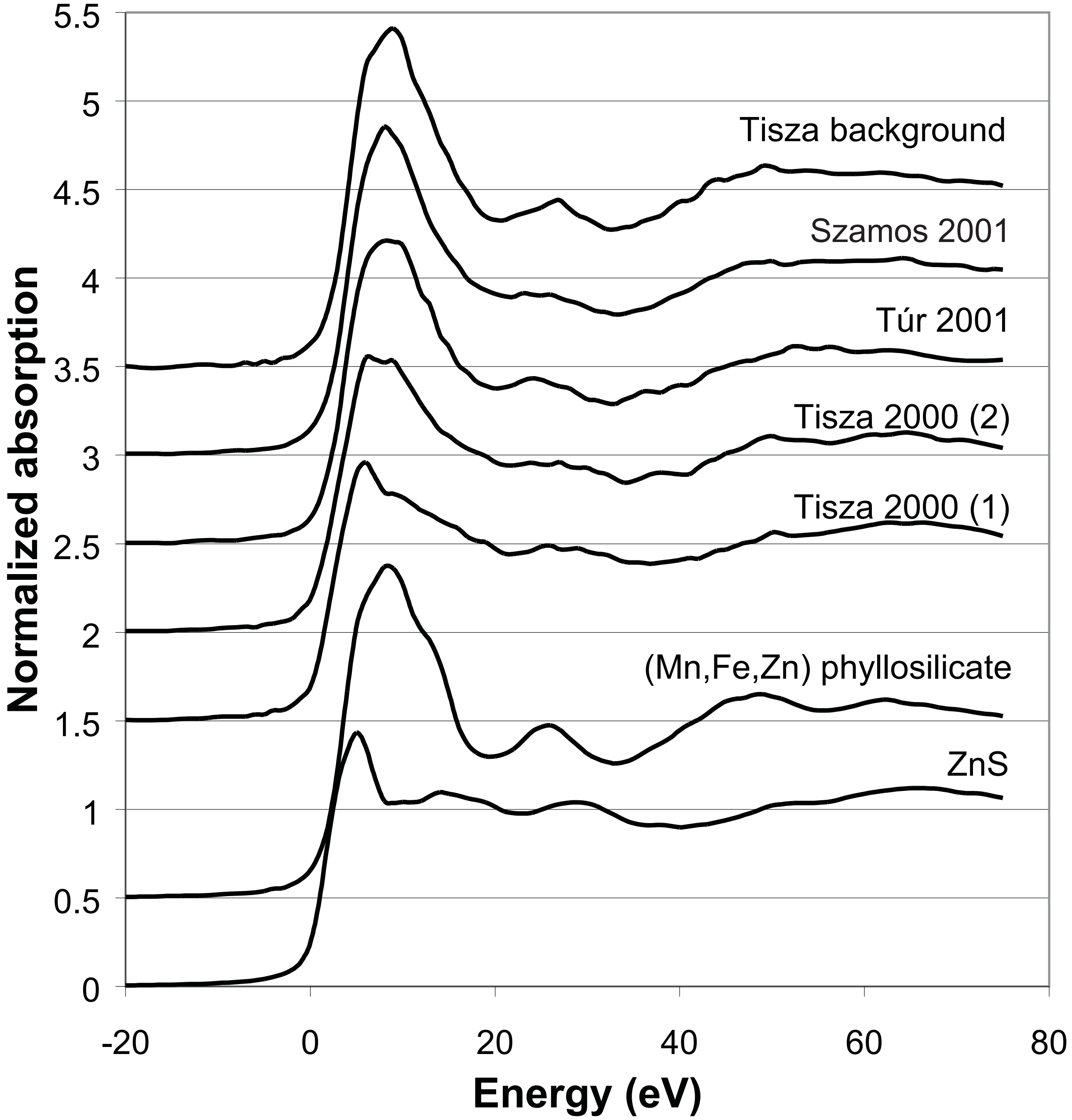
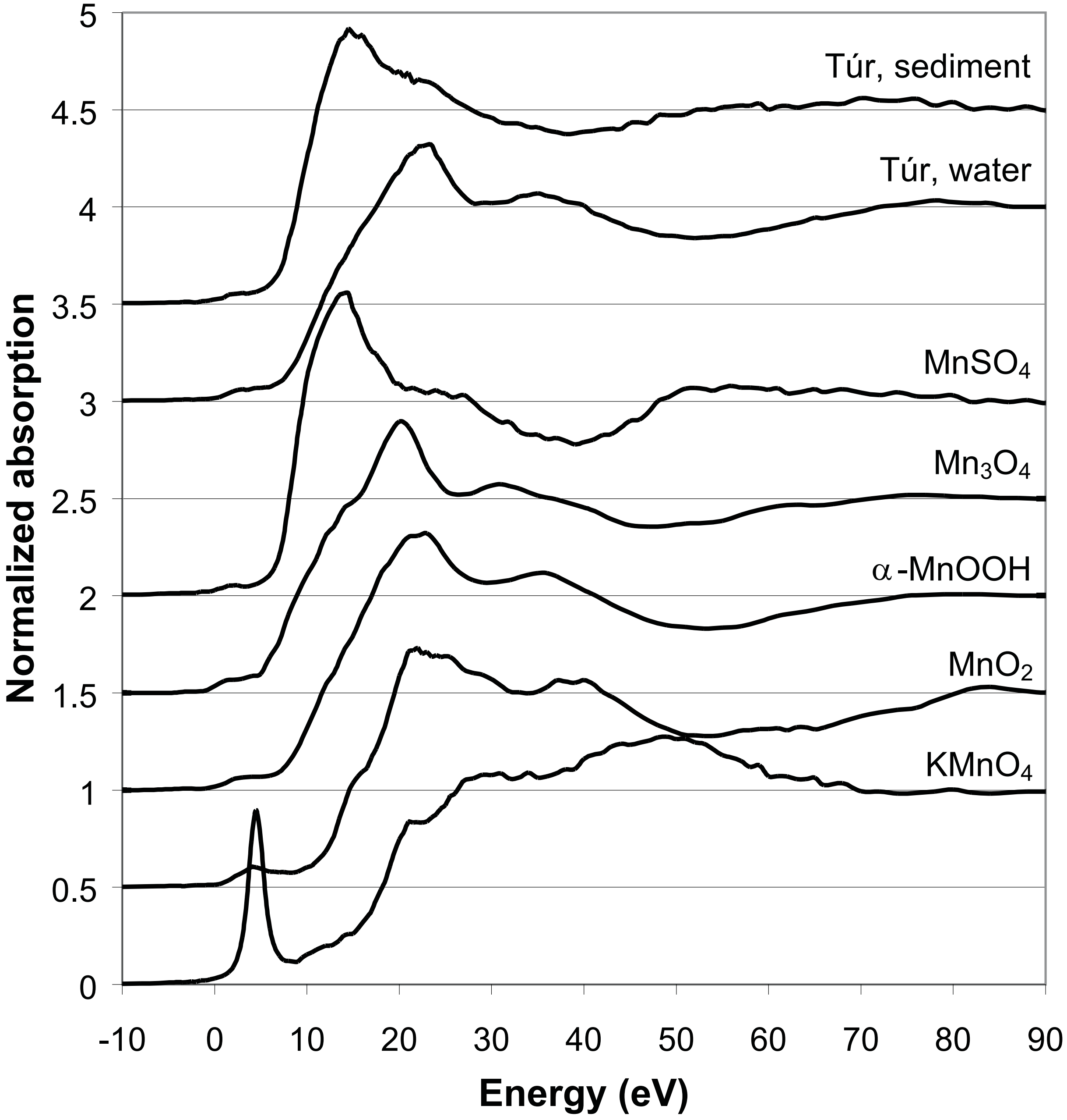

1500
1000
500
0
Cr
120000
80000
40000
0
Mn
30000
20000
10000
0
Fe
1650
1100
550
0
10 µm
Cu
69000
26000
13000
0
Zn
190
140
90
40
Pb

Figure 6



Normalized absorption
Energy (eV)
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-20
0
20
40
60
80
Tisza background
Szamos 2001
Túr 2001
Tisza 2000 (2)
Tisza 2000 (1)
(Mn,Fe,Zn) phyllosilicate
ZnS

Figure 7



Normalized absorption
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-10
0
10
20
30
40
50
60
70
80
90
Energy (eV)
Túr, sediment
Túr, water
$MnSO_4$
Mn_3O_4
α-MnOOH
MnO_2
$KMnO_4$