Environ Monit Assess (2018) 190: 158
https://doi.org/10.1007/s10661-018-6551-4

Sediment matrix characterization as a tool for evaluating the environmental impact of heavy metals in metal mining, smelting, and ore processing areas

**Silvia Ružičková · Dagmar Remeteiová ·
Vladislava Mičková · Vojtech Dirner**

Received: 7 November 2017 / Accepted: 12 February 2018 / Published online: 21 February 2018

Abstract In this work, the matrix characterization (mineralogy, total and local chemical composition, and total organic (TOC) and inorganic carbon (TIC) contents) of different types of sediments from mining- and metallurgy-influenced areas and the assessment of the impact of the matrix on the association of potentially hazardous metals with the mineral phases of these samples, which affect their mobility in the environment, are presented. For these purposes, sediment samples with different origins and from different locations in the environment were analyzed. Anthropogenic sediments from metal-rich post-flotation tailings (Lintich, Slovakia) represent waste from ore processing, natural river sediments from the Hornád River (Košice, Slovakia) represent areas influenced predominantly by the metallurgical industry, and lake sediments from a water reservoir Ružín (inflow from the Hornád and Hnilec Rivers, Slovakia) represent the impact of the metallurgical and/or mining industries. The total metal contents were determined by X-ray fluorescence (XRF) analysis, the local chemical and morphological microanalysis by scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), and the TOC and TIC contents by infrared (IR) spectrometry. The mobility/bioavailability of Cu, Pb, and Zn in/from sediments at the studied areas was assessed by ethylenediaminetetraacetic acid (EDTA) and acetic acid (AA) extraction and is discussed in the context of the matrix composition. The contents of selected potentially hazardous elements in the extracts were determined by the high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS).

Keywords Matrix characterization · Anthropogenic and natural sediments · Ore processing, environment, heavy metals

Introduction

The need for environmental protection has arisen from the characteristics of modern life and society. Despite their positive effects, global industrialization and urbanization have also had negative impacts on the environment as a consequence of rapid increases in heavy metal pollution (Maranhão et al. 2011; Sun et al. 2010). In terms of pollution prevention and environmental protection, it is important to know not only the state of its basic components but also the characteristics of the undesirable products of anthropogenic activities significantly influencing this state (Rao et al. 2010). Heavy metal pollution is a serious problem due to their toxicity, bioavailability, and non-biodegradability in the environment (Morillo et al. 2008). Metals are present in the environment as a result of natural processes related to

---

S. Ružičková (✉) · D. Remeteiová · V. Mičková
Faculty of Materials, Metallurgy and Recycling, Institute of Recycling Technologies, Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic
e-mail: silvia.ruzickova@tuke.sk

V. Dirner
Faculty of Mining and Geology, VŠB – Technical University of Ostrava, 17. listopadu, 708 33 Ostrava-Poruba, Czech Republic

minerals in solid materials and of anthropogenic activities involving dust particle emissions (Maranhão et al. 2011) from vehicles or coal combustion, industrial waste, and the dry and wet deposition of other pollutants (Sun et al. 2010).

Mining activities are a major source of environmental contamination by potentially hazardous substances; the mobility of such substances in the surrounding environment is a complex function of various factors, e.g., hydrology, geology, geochemistry, mining, and ore processing (Salvarredy-Aranguren et al. 2008). Metal mining, smelting, and processing generate different types of waste that can contaminate the surrounding natural environment with heavy metals in excess of natural background concentrations (Anju and Banerjee 2010; Anju and Banerjee 2011). Tailings spills, dump failures, seepage, or direct discharge into waterways can result in serious and long-term environmental problems (Franks et al. 2011) because of the high content of potentially hazardous elements; the mobility of these elements may pose an environmental hazard to surrounding ecosystems (Favas et al. 2011). Conventional tailings dams are the most common form of mineral processing waste disposal utilized by the mining industry (Franks et al. 2011). Tailings dams isolate the waste material from the surrounding environment through storage and containment. Tailings are typically piped into dams as a wet slurry, and the height of the dam wall progressively increases as the volume of waste material increases. The chemical stability of a tailings impoundment depends on the decomposition of minerals over time and the propensity for the release of elements and organic compounds from the waste material. The residues/wastes from mining and metallurgical operations also contain toxic heavy metals, which can be dispersed in the surrounding environment by wind and/or water after their disposal (Navarro et al. 2008).

An environmental concern over sulfide mining is the contamination of surface and groundwater by the deposition of waste from the mining (rocks) and processing (flotation tailings) of ores (Heikkinen et al. 2009). After the disposal of sulfide mining waste, exposure to atmospheric oxygen and water leads to the oxidation of sulfide and the production of acidic drainage waters with varying pH and sulfate and heavy metal contents depending on the sulfide minerals present and the neutralization capacity of the tailings. Acidic water in the mine environment dissolves ore and rock minerals, which results in a significant increase in the contents of major elements (Fe, Al, Mg, Ca) and heavy metals (Zn, Cu, Ni, etc.) in the water (Lintnerová et al. 1999). The trace-level heavy metals dissolved in water sorb predominantly to suspended Fe hydroxides or oxyhydroxides, as well as to clay minerals and organic material, what is promoted by the pH increases that occur after mixing the acidic mine water with the neutral water of natural recipient (Lee et al. 2008). The mining and processing of sulfide ore deposits are often a source of high levels of toxic elements, which can be released to natural water systems. The mobility of the elements released from these deposits depends on their occurrence, abundance, reactivity, and hydrology (Nordstrom 2011).

Natural bottom sediment can be described as "material that is transported by water and settles down from the water column" (Cappuyns 2012). Natural sediments are typically mixtures of several components, including different mineral forms and organic materials, and are often contaminated by anthropogenic activities (Šestinová et al. 2015). Sediments are a sink for heavy metals, but when environmental conditions (pH, redox potential, etc.) change, the sediment may become a source of metals to the water column (Morillo et al. 2008). The mobility of metals in sediment is directly influenced by the solubility of organic matter (Peng et al. 2009; Schneider et al. 2014). The complexation of metal ions with soluble organic compounds and decreasing pH increase metal mobility (Peng et al. 2009). The redox potential indirectly alters the metal distribution between soluble and insoluble sediment phases, mainly by changing the pH.

The behavior of heavy metals in the environment depends on their chemical form and the type of the binding or associations with different phases of the environmental matrix (Rao et al. 2010). The total content of heavy metals is not sufficient for assessing the environmental impact of polluted sediments because the metals can be present in different chemical forms (easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, ions in crystal mineral lattices, etc.) that differ in their mobilization capacity and bioavailability (Morillo et al. 2008).

Selective extraction/leaching methods are often used to simulate different environmental conditions (i.e., acidic, alkaline, oxidizing/reducing) in contact with the solid phase (soil, sediment, waste) and to evaluate the chemical behavior (mobility, solubility, bioavailability, and toxicity) of heavy metals in the environment (Favas et al. 2011). Single extractions are a relatively fast, inexpensive, and simple technique for trace element mobility monitoring in contaminated soils and sediments (Cappuyns and Swennen 2008; Cappuyns 2012). Depending on the aim of the extraction, water, diluted salt solutions (buffered or unbuffered), organic chelating reagents, weak organic, and very strong inorganic acids are used (Anju and Banerjee 2011; Cappuyns and Swennen 2008; Cappuyns 2012; Rao et al. 2008). Single extraction reagents can also release elements from particular phases to which they are bound or associated (Rao et al. 2008). The fraction bound by covalent forces (sorbed) requires for the displacement the hydrogen ion. Organic chelating reagents, such as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA), are commonly used for extractions because of their strong chelation ability for different heavy metals. The content of elements isolated by these reagents reflects the potentially bioavailable/mobile fraction in sediments (Jamshidi-Zanjani et al. 2015). Weak organic acids such as acetic acid (AA) may be used to identify the heavy metals associated with acid-soluble phases, such as carbonates (Mahanta and Bhattacharyya 2011; Cappuyns 2012) or crystalline hydroxides (Cappuyns 2012). The EDTA and AA-extractable/mobilizable (MF)/potentially available fractions are known for their high availability to plants (Chaudhary et al. 2016; Abollino et al. 2011; Cappuyns and Swennen 2008; Cappuyns 2012). The AA-extractable phase contains the highly mobile and bioavailable fraction of metals, which may be released into solution upon slight changes in the pH of sediments, whereas EDTA extracts metals from non-silicate sediment phases such as organic-bound fractions (Chaudhary et al. 2016). Extraction with a 0.43-mol dm^{-3} EDTA solution enables evaluation of the metal fraction remobilized after acidification of environment to the pH of the extractant (Cappuyns 2012).

This paper presents part of an extensive experimental study focused on the rapid evaluation of heavy metal mobility in industrially (mainly mining and metallurgy) influenced areas. Fractionation analysis was used to determine the basic chemical properties of environmental samples, characterize their basic structural (matrix) components, and assess the impact of the matrix on the association of potentially hazardous elements with the mineral phases of these samples, which underlies the mobility of these elements in the environment—the aim of this contribution. The different sediment samples were analyzed in two experimental stages: (1) complex characterization of the sediment matrix and (2) evaluation of Cu, Pb, and Zn mobility/bioavailability via EDTA and AA extractions.

Materials and methods

Description of the sediment sampling sites

Mining dumps in the surrounding area of Banská Štiavnica (Central Slovakia, Europe) contain fine-grained materials from the flotation processing of sulfide ore (Feketeová et al. 2015). The studied tailing impoundment in Lintich originated from hydrotechnic operations such as an artificial water reservoir, and the current register confirms the environmental loads at this location. Lintich, although inactive for 40 years, still contains high concentrations of heavy metals. The surface of the impoundment is predominantly covered by secondary minerals (gypsum) (Lintnerová et al. 1999).

The water reservoir Ružín is situated in the Hornád basin (Eastern Slovakia, Europe). This region is known for its historical mining and metallurgical activities, which have influenced the quality of bottom sediments in the reservoir. Within the basin of the Hornád and Hnilec Rivers, which flow into the Ružín reservoir, are several old, abandoned, and flooded mining dumps created during the mining, treatment, and metallurgical processing of Cu, Fe, and Hg ores containing impurities of toxic elements. The main minerals in the deposits from these activities are pyrite and chalcopyrite. The neutralization of acid mine drainage upon contact with surface water causes the precipitation of Fe and Al oxyhydroxides (Šestinová 2012; Šestinová et al. 2015).

The Košice residential city agglomeration in East Slovakia is an important center with historic and current industrial activities. In the past, this agglomeration was known for mining and magnesite processing. The most important producer of solid waste materials with varying contents of potentially toxic elements is the large ferrous metallurgical plant US Steel Košice. The Hornád River, after flowing out of the Ružín reservoir, flows through Košice.

Sampling

The sampling and analysis of sediments were carried out in accordance with the following current standards in the given area: STN EN ISO 5667-1: Water quality. Sampling. Part 1: Guidance on the design of sampling programmes and sampling techniques. STN EN ISO 5667-12: Water quality. Sampling. Part 12: Guidance on sampling of bottom sediments. STN EN ISO 5667-15: Water quality. Sampling. Part 15: Guidance on the preservation and handling of sludge and sediment samples.

Samples of lake sediments collected from the Ružín water reservoir represent areas influenced by the inflow of the Hornád (RHO) and Hnilec (RHN) Rivers to the reservoir (Fig. 1). Sampling of these sediments was realized using a tube core barrel sampler triggered by gravity. The length of a core was approx. 30 cm. A composite sample for each sampling site was prepared by mixing four individual samples.

Samples of river sediments were collected on two sides of the Hornád River: "Ťahanovce" (HT), near the inflow of the Hornád River to Košice, and "Nad Jazerom" (HNJ), near the outflow of the Hornád River from Košice (Fig. 2). The river sediment samples were collected by a plastic scoop at a depth of approx. 15 cm. A composite sample was prepared by mixing four individual samples.

Samples of anthropogenic sediments were collected from the front of the black landings on the dam of the tailing in Lintich (LD) and from a strand of tailing lagoon (LL) (Fig. 3). The samples were collected at depth of approx. 20 cm. After collection, all final sediment samples were dried and homogenized by grinding in an agate mill.

Sediment matrix characterization

The sediment matrix was investigated in terms of the phase composition, total organic (TOC) and inorganic carbon (TIC) contents, total contents of matrix elements (Al, Ba, Ca, Fe, K, Mg, Na, Si, S, and P) and selected environmentally significant heavy metals (As, Cd, Cu, Cr, Ni, Pb, and Zn), and contents of elements in the selected particles. X-ray diffraction (XRD) analysis was applied to investigate the mineralogical (phase) composition of the studied samples (powder diffractometer, Bruker D8 Avance, USA). SEM with X-ray microanalysis (SEM with energy-dispersive spectroscopy (SEM-EDS)) using a Philips XL scanning electron microscope with an EDAX energy-dispersive X-ray spectrometer provided information about the elemental composition of a particular location on a particle surface. The TOC and TIC contents were determined by infrared (IR)

Fig. 1 Sampling sites—the water reservoir Ružín

Fig. 2 Sampling sites—the Hornád River

analysis (multi N/C 3100 instrument, Analytik Jena, Germany, with thermocatalytic oxidation and membrane-conductometric nondispersive infrared (MC-NDIR) detection for TOC analysis). The total

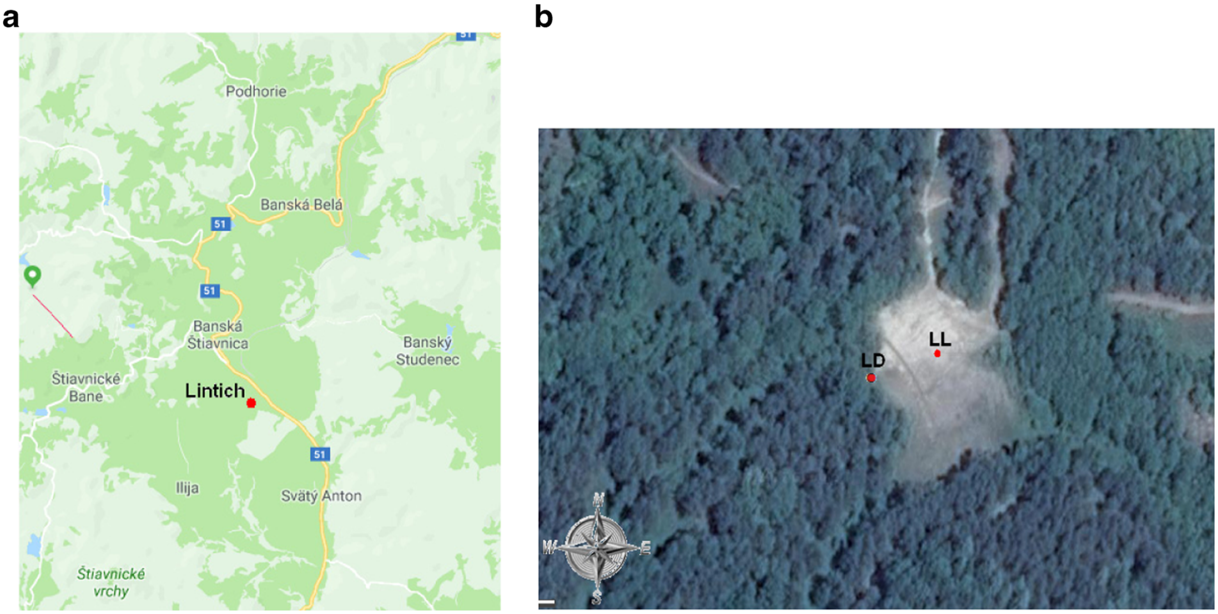

Fig. 3 Lintich. **a** Localization. **b** Sampling sites

element contents were determined by energy-dispersive X-ray fluorescence (*ED-XRF*) analysis using a SPECTRO XEPOS 3 instrument (Spectro, Germany).

Single extraction procedures

The MFs of Cu, Pb, and Zn in the sediment samples (LL, LD, RHO, RHN, and HNJ) were isolated by applying the following extraction reagents with different extraction abilities and conditions:

- Extraction with EDTA or Na_2EDTA (disodium salt): a mixture of 5 g of dry sediment and 50 cm^3 of 0.05 mol dm^{-3} EDTA (buffered, pH = 7) was shaken for 1 h in a polyethylene vessel at room temperature (Ure et al. 1995).
- Extraction with AA: a mixture of 1 g of dry sediment and 40 cm^3 of 0.43 mol dm^{-3} CH_3COOH (unbuffered, pH = 3) was shaken for 16 h in a polyethylene vessel at room temperature (Ure et al. 1995).

After completion of the extractions, the contents of the extraction vessels were filtered through filter paper with narrow pores (blue ribbon) and a diameter = 18.5 cm. All vessels were cleaned by washing in 4 mol dm^{-3} nitric acid, followed by extraction reagent, and rinsing with distilled water (Ure et al. 1995). The contents of Cu, Pb, and Zn in each extract were determined by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) using a contrAA 700 spectrometer (Analytik Jena, Germany).

Results and discussion

Samples of the studied sediments were analyzed to identify the total contents of the main elements and selected trace metals (ED-XRF), the morphology and composition of selected elements on particle surfaces (SEM-EDS), the phase composition of the matrix (XRD), and the TOC and TIC contents. The results of these assays provide us with information about the chemical composition of the sample matrix.

Single extractions were performed to isolate the MFs of Cu, Pb, and Zn from the sediment samples and to compare the obtained results with the results of the chemical composition analysis.

Composition of the sediment matrix

The total weight percentages of major/minor elements and organic and inorganic carbon are shown in Table 1, and the total contents of the selected heavy metals (environmentally significant) expressed as milligrams of metal per kilogram of dry sediment are given in Table 2. The total element contents provide information on the element concentrations in the sediments. The main elements (content > 1%) in all samples were Si, Al, Fe, K, Ca, and Mg. Ba, S, and P (Table 1), and Mn (0.1%), Ti (0.16–0.44%), and Na (0.7%), could be classified as minor elements. The concentrations of selected heavy metals ranged from 0.5 (Sb, HT) to 3510 (Zn, LD) mg kg^{-1} and significantly varied depending on the sample type.

Sediment samples from the Ružín water reservoir were characterized by the lowest content of Si and the highest contents of Al and Fe, slightly differing from the contents in the other samples. The highest contents of P and Ti were also found in the samples from the Ružín water reservoir. The major and minor element contents in the Hornád River sediments were approximately the same in both sampling areas. Slightly higher contents of Al and Fe were found in the "Nad Jazerom" area. The matrix composition of the anthropogenic sediment samples from the Lintich tailing was not significantly different from that of the natural sediment samples except for a higher sulfur content, which is typical of this type of waste material, but due to continuous oxidation, part of this sulfur content most likely corresponds to sulfates. Slightly higher contents of Fe and Al, at the expense of lower Si content, were found in the sediment from the lagoon area (LL) than in the sediment from the dam area (LD). Lake sediment samples were also characterized by higher TOC and TIC contents, which indicate higher contents of organic and carbonate materials in these samples. The TOC content was measurable in only one (area Hornád−Nad Jazerom) of the river and anthropogenic sediment samples. The greatest differences in heavy metal contents relative to the sample type were found for Zn, Cu, and Pb; the contents of these metals in the anthropogenic sediments and the contents of Zn and Cu in the lake sediments were at the same level as the minor elements (> 0.01%). The highest levels of Ni, As, Cr, and Sn were found in the lake sediments. Due to the high Si and Al contents in the samples, the predominant materials in all samples can be assumed to be quartz and aluminosilicates containing Fe, K, Ca, Mg, or Na. Other

Table 1 Total contents of matrix elements in the sediment samples

Sample	Content/weight %										
	Si	Al	Fe	K	Ca	Mg	Ba	S	P	TIC	TOC
RHO	24.40	8.36	4.49	2.41	2.23	1.18	0.099	0.230	0.185	5.3	0.5
RHN	23.51	8.74	5.06	2.28	0.76	0.89	0.050	0.430	0.158	7.3	1.4
HT	32.77	4.82	2.82	1.44	2.64	1.05	0.109	0.064	0.062	< 0.05	< 0.05
HNJ	32.54	5.72	3.18	1.54	2.25	1.31	0.128	0.068	0.065	< 0.05	1.4
LD	33.75	4.71	2.96	3.07	1.41	0.77	0.222	0.733	0.041	< 0.05	< 0.05
LL	30.48	6.04	3.63	3.17	2.35	1.08	0.197	0.425	0.044	< 0.05	< 0.05

mineral or amorphous forms, such as barite, other sulfates, and phases with P, Mn, and Ti, can be considered.

The results from the total content determinations and for the phase composition of the sample matrix were evaluated by XRD analysis, which enables determination of the most abundant mineral (crystalline) forms. Selected diffractograms and the identified phases are shown in Fig. 4.

The diffraction patterns indicated that the compositions of natural sediments (Fig. 4a, b) were approximately similar, except that sanidine (sodium-potassium aluminosilicate) was not confirmed in the river sediment sample. The most abundant component in both natural samples was quartz, namely, α-SiO_2, but in the river sediment sample, the abundance of quartz was higher than that in the lake sediment sample, in accordance with the total Si contents in these samples. The presence of other minerals (aluminosilicates) decreased in the following order: muscovite, clinochlore, and albite. The lowest percentage of sodium aluminosilicates was consistent with the lowest total Na content in the samples. The mineral composition of the matrix of the anthropogenic sediment samples (Fig. 4c) was different from that of the natural sediments. The proportion of quartz in the anthropogenic sediments was dominant and slightly lower than that in the river sediment sample. Unlike the natural sediments, in the LL and LD samples, sanidine and albite were not detected, but the presence of orthoclase (potassium silicate) was confirmed, in accordance with the highest potassium content in the anthropogenic sediments.

Due to its detection mechanism and properties, XRD cannot be used to identify mineral forms at lower concentrations or amorphous structures; therefore, samples were subjected to SEM and SEM-EDS local microanalysis. The pictures obtained by electron microscopy are shown in Fig. 5 (lake sediments), Fig. 6 (river sediments), and Figs. 7 and 8 (anthropogenic sediment). The results of the local microanalysis of the sites (points/areas) indicated in the pictures, as well as of other sediment types, are listed in Table 3 (natural sediments) and Table 4 (anthropogenic sediment).

Both the natural and anthropogenic sediments were variable in shape and size, with a tendency to form clusters of particles; this tendency was clearer in the natural sediments.

Table 2 Total contents of selected heavy metals in the sediment samples

Sample	Content/mg kg^{-1}							
	Zn	Cu	Pb	Ni	As	Cr	Sb	Sn
RHO	501	266	57.8	79.0	85.1	230	1.9	11.9
RHN	418	435	84.7	42.0	59.4	312	0.9	10.7
HT	121.2	56.0	23.9	32.0	19.3	101	< 0.5	5.8
HNJ	120.4	56.0	30.2	27.0	17.9	107	0.5	7.1
LD	3510	179	999	4.0	14.3	92.0	15.7	2.3
LL	2890	659	2390	5.0	18.9	217	11.9	3.2

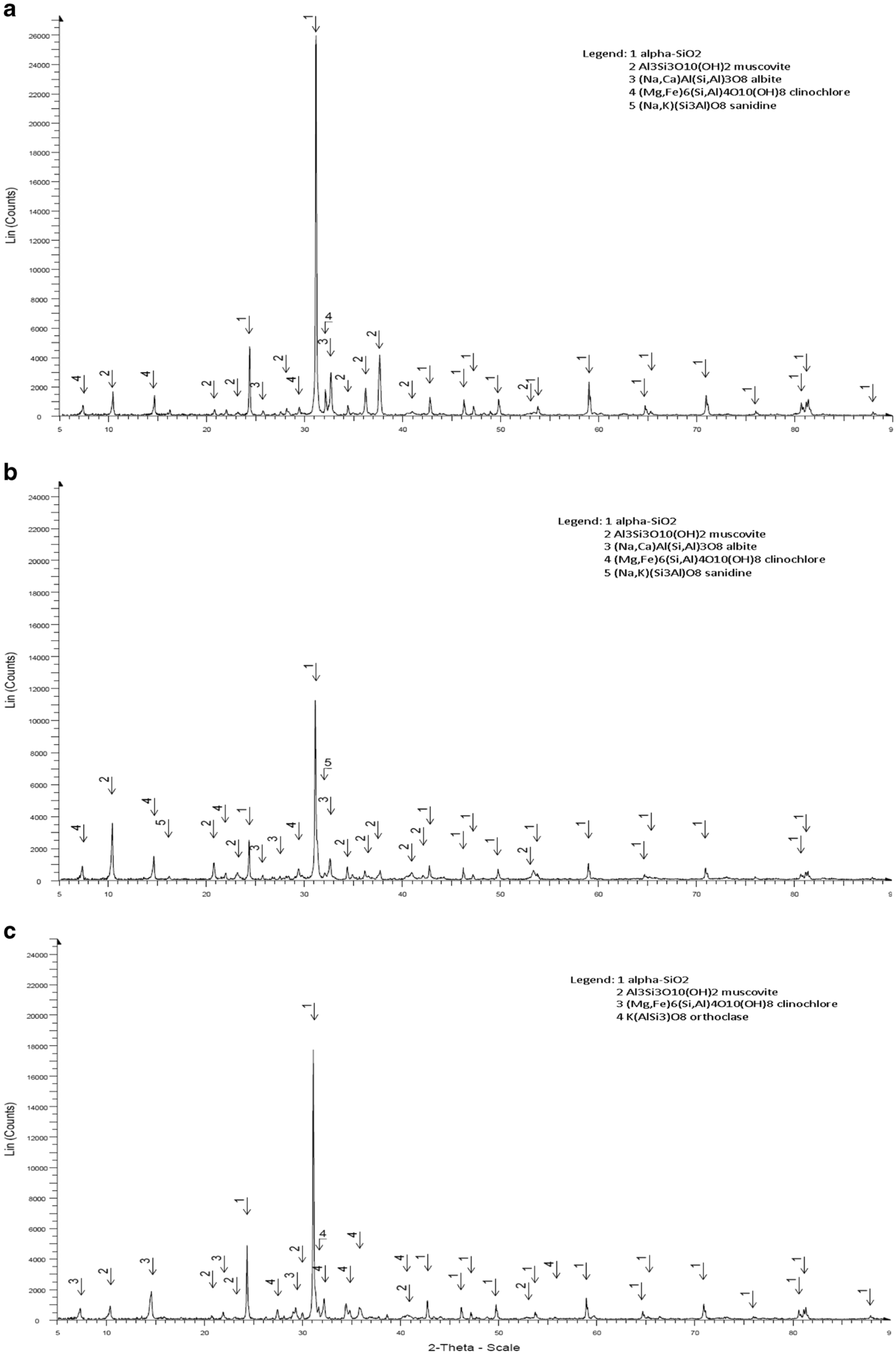

Fig. 4 XRD spectra of sediment samples. **a** River—Hornád River–Nad Jazerom. **b** Lake—Ružín reservoir–Hornád. **c** Anthropogenic—Lintich tailing–lagoon

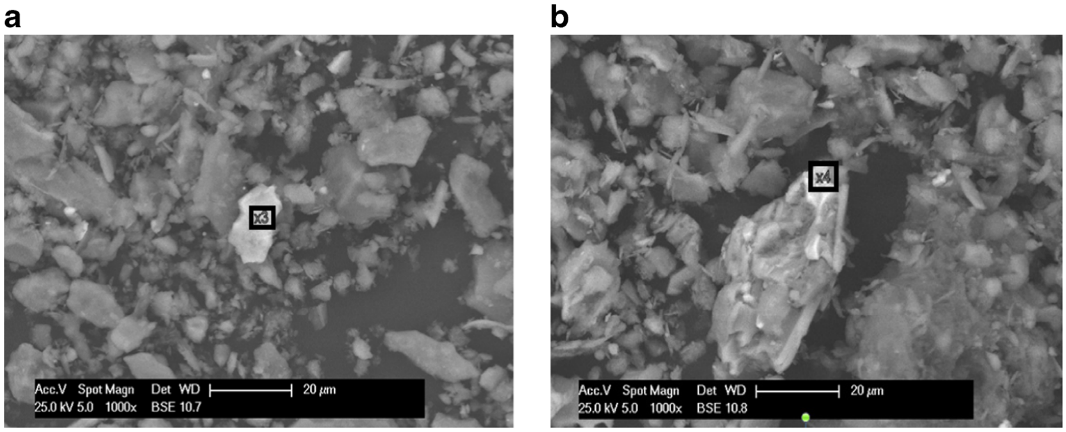

Fig. 5 SEM images of the natural lake sediment samples. **a** Ružín–Hornád. **b** Ružín–Hnilec

Local analysis of a light spot (RHO1) on the surface of a particle cluster with a diameter of approximately 80 μm in the lake sediment sample (inflow of the Hornád River to the Ružín reservoir, Fig. 5a) revealed a predominance of Fe, C, and O, which likely corresponds to the carbonate form of Fe. Pure barite (RHO2) and barite particles in the presence of aluminosilicate (RHO3) were also found in this sample. Particles predominantly composed of O, Si, Al, Fe, K, and Mg (RHN1, Fig. 5b) were found in the sediment from the location of the Hnilec River inflow to the Ružín reservoir. These particles are probably clinochlore; particles with similar elemental abundances but lacking Mg (RHN2) may correspond to the association of Fe with muscovite. Particles containing high proportions of Fe and O (RHN3) were also found in this sample, which indicates the presence of Fe oxides. However, electron microanalysis cannot be used to identify the presence of H in a sample, so these particles could also be Fe hydroxides or oxyhydroxides.

Local analysis of a light spot on the surface of a particle with a diameter below 20 μm in the river sediment (HT1, Fig. 6a) revealed a composition of predominately O and Si, with lesser amounts of Fe, Ca, Al, and Mg (clinochlore, albite) and S (sulfates). In this sample, quartz particles (HT2), Fe oxides/hydroxides, and aluminosilicates (HT3) were also found. Despite the better resolution of local SEM-EDS microanalysis than XRD phase analysis, identification of the binding or form of heavy metal associations in the matrix of natural sediment samples was not successful.

The highly abundant Cu, Pb, and Zn forms in the anthropogenic sediments could be predicted based on the results of the local microanalysis of the particles (LD1, LD2, LL1, and LL2). Analysis of a light area of irregular-shaped particles with diameters of approximately 100 μm (LD1, Fig. 7a) showed predominance of Zn, S, and O, which indicates the presence of $ZnSO_4$. Analysis of a smaller particle with a diameter of

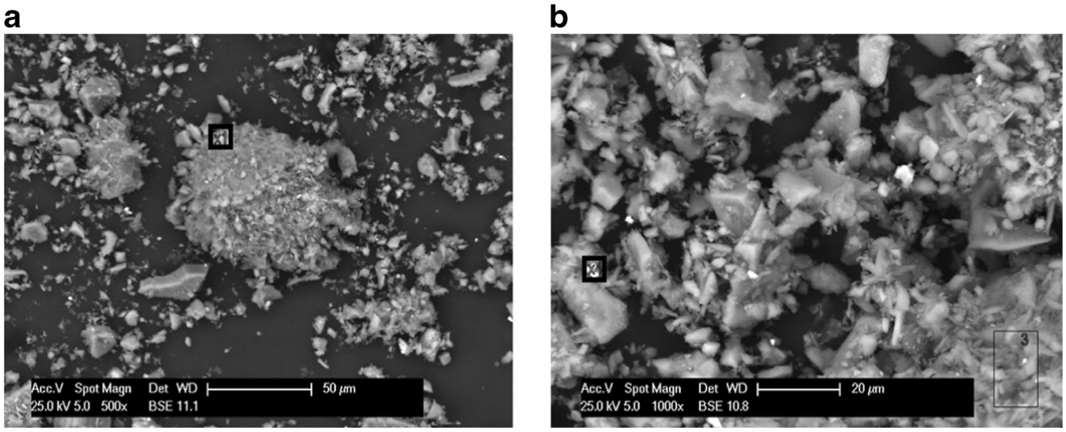

Fig. 6 SEM images of the natural river sediment samples. **a** Hornád–Ťahanovce. **b** Hornád–Nad Jazerom

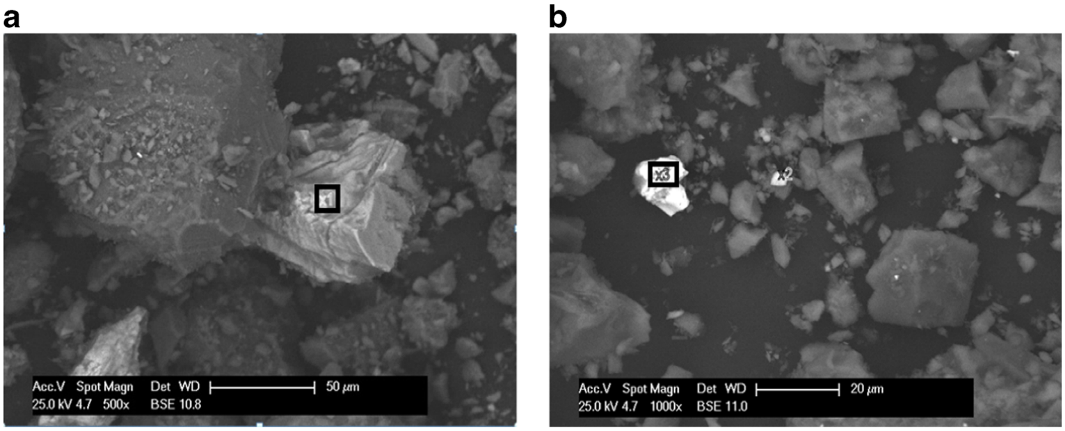

Fig. 7 SEM images of the anthropogenic sediment sample from the dam of the Lintich tailings impoundment at different magnifications. **a** × 500. **b** × 1000

approximately 10 μm (LD2, Fig. 7b) revealed a Pb content of 75% in the presence of SiO_2. Particles with a significant proportion of barite and SiO_2 (LD3) and of Fe sulfates (LD4) were also found in this sediment sample (area of the tailings dam). Smaller particles containing Cu in the presence of barite and SiO_2 (LL1, Fig. 8a) and particles containing Pb and Zn, in the presence of higher Fe, Si, O, and Al contents (LL2, Fig. 8b), were found in the sediment sample from the area of lagoon. This may indicate the association of these metals with quartz, aluminosilicates, or Fe hydroxides. Fe particles containing Fe sulfates (LL3) or barite and SiO_2 (LL4) were also found in this sample.

The local microanalysis of the sediment samples confirmed the mineral forms detected by XRD analysis and the prediction of other phases, such as carbonates, sulfates, and oxides/hydroxides, and possible bonding of Cu, Pb, and Zn in the form of sulfates and their association with quartz, silicates, and hydroxides.

MFs of elements

The MF of an element represents the concentration of an element (heavy metal) that is easily available to vegetation and releasable under moderate changes in environmental conditions. AA and EDTA are commonly used to isolate this fraction, but their extraction efficiency is dependent on the chemical composition (character) of the material under consideration and on the total content and association of the heavy metals with its phases. In terms of application, AA extraction is significantly more time-consuming (16 h) than EDTA extraction (1 h). The criteria for assessing the impact of sediments on the surrounding ecosystem also include their origin and

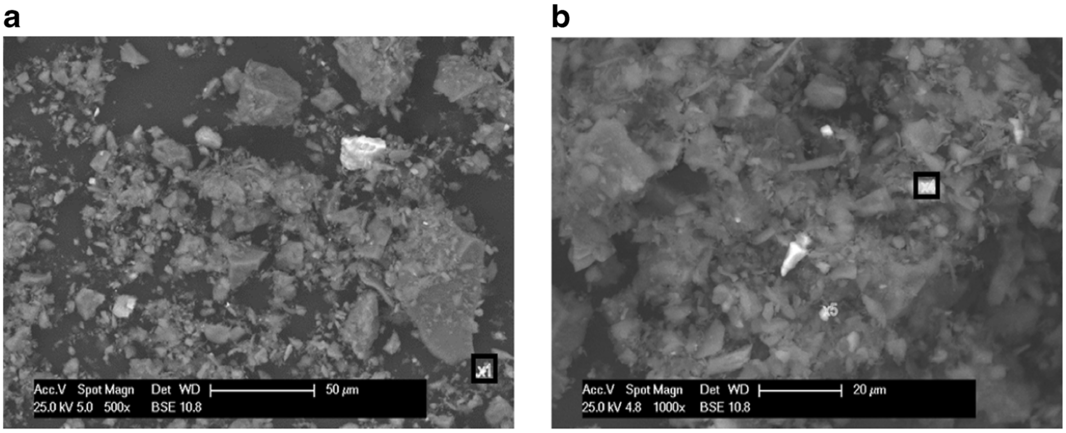

Fig. 8 SEM images of the anthropogenic sediment samples from the lagoon of the Lintich tailings impoundment at different magnifications. **a** × 500. **b** × 1000

Table 3 Chemical composition of the particle surfaces in the individual natural sediment samples

Sample	Content/weight %									
	C	O	Al	Si	K	Ca	Mg	Fe	S	Ba
RHO1 (Fig. 5a)	31	26	6.4	12	1.7	2.2	–	20	–	–
RHO2	–	24	–	–	–	–	–	–	16	59
RHO3	–	23	8.6	12	1.7	–	1.3	–	8.7	45
RHN1 (Fig. 5b)	–	30	12	14	1.0	–	3.5	37	–	–
RHN2	–	47	11	14	2.2	–	–	25	–	–
RHN3	–	29	1.4	1.5	–	–	–	36	–	–
HT1 (Fig. 6a)	–	46	5.8	22	1.4	7.3	5.2	8.7	3.3	–
HT2	–	47	1.6	51	–	–	–	–	–	–
HT3	–	34	5.7	21	1.2	1.0	2.6	31.4	–	–
HNJ1 (Fig. 6b)	–	32	3.8	14	0.5	0.3	–	0.8	10	37
HNJ2	33	29	2.3	4.4	0.5	0.4	0.9	1.5	5.4	22
HNJ3	–	40	11	36	2.2	2.4	1.4	4.7	–	–

status in the environment. The anthropogenic sediment from the Lintich tailings impoundment is characterized by a markedly acidic character with high total contents of Cu, Pb, and Zn. The natural lake sediments from the Ružín water reservoir reflect the influence of different river ecosystems (Hornád and Hnilec Rivers) on the quality of the lake ecosystem. The total contents of the monitored metals were higher in the reservoir sediments than in the Hornád River sediments. Sampling the river sediment can be used to monitor the impact of water flow on the partitioning of metals between water and sediment.

The Cu, Pb, and Zn contents in milligrams of metal extracted from kilograms of dry sediment sample determined using both extraction reagents are shown in Fig. 9. In Fig. 10, these contents are expressed as the percentage of metal in the MF extracted with the more effective agent and in the residual fraction (RF), which is constituted by forms that are potentially mobilizable under extreme environmental changes (the forms bound to oxides and/or sulfides) and forms that are tightly bound to the sediment matrix, which are not mobilized under any conditions (forms bound to quartz and silicates).

From the results graphically depicted in Fig. 9, it is possible to assess the suitability of the extraction agent for a particular sample type and element. AA was more effective at extracting all metals from Lintich tailings and Zn from all types of sediments. EDTA was more effective at extracting Cu and Pb from natural sediments. The differences between the extraction efficiencies of the

Table 4 Chemical composition of the particle surface material in the anthropogenic sediment samples

Sample	Content/weight %										
	O	Al	Si	K	Ca	Mg	Fe	S	Ba	Cu	Pb	Zn
LD1 (Fig. 7a)	15	2.2	8.6	0.8	0.7	–	1.9	23	–	–	–	48
LD2 (Fig. 7b)	15	1.5	7.5	0.9	–	–	–	–	–	–	75	–
LD3	31	3.2	8.7	1.2	0.9	–	1.6	12	41	–	–	–
LD4	16	–	–	3.9	–	–	38	43	–	–	–	–
LL1 (Fig. 8a)	38	2.5	15	0.8	0.7	–	1.3	9.9	32	0.7	–	–
LL2 (Fig. 8b)	42	8.4	25	3.4	1.7	1.3	28	–	–	–	5.2	1.3
LL3	25	3.6	11	1.3	1.1	1.1	28	28	–	–	–	–
LL4	24	10	23	3.9	1.5	0.7	3.5	5.8	26	–	–	–

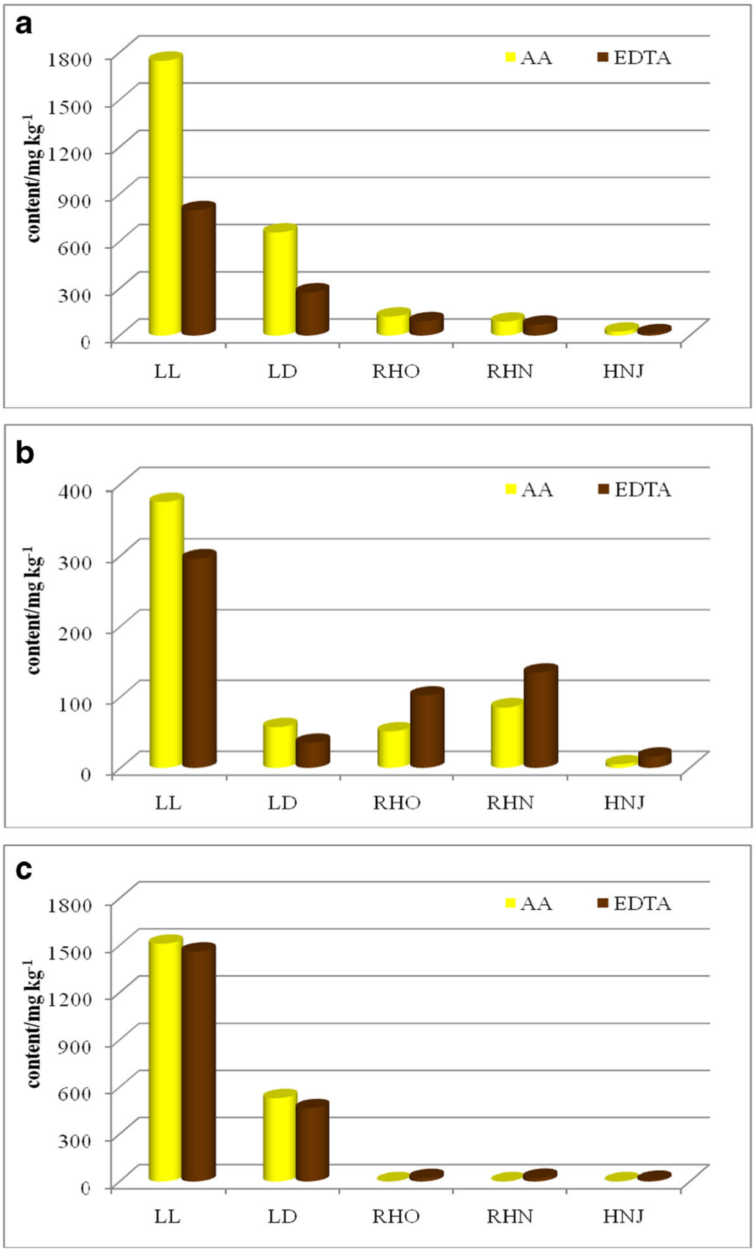

Fig. 9 Contents of Zn (**a**), Cu (**b**), and Pb (**c**) in the MFs extractable by AA and EDTA

two agents for the sludge sediment were metal-dependent and decreased in the following order: Zn, Cu, and Pb. The mobilizable metal contents in the LL sample (Lintich lagoon) were higher than those in the LD sample (Lintich dam), and the mobilizable metal contents in anthropogenic sediment were higher than those in the natural sediments. Our results can also be used to deduce the preferred association of elements with the sediment phases. Since the TOC content (organic matter extractable by EDTA) was higher than the TIC content (carbonate material extractable by AA) in the lake sediment samples and the EDTA extraction efficiency for Zn, Cu, and Pb was higher than that of AA, the preferred association of Zn was likely with carbonate material, and that of Cu and Pb with organic matter. The higher amount of Zn extracted by AA from the tailing material also indicates the association of Zn with hydroxide or sulfate phases.

The percentage contents of the metals, graphically depicted in Fig. 10, represent the proportion of metal that is mobile upon mild changes in environmental

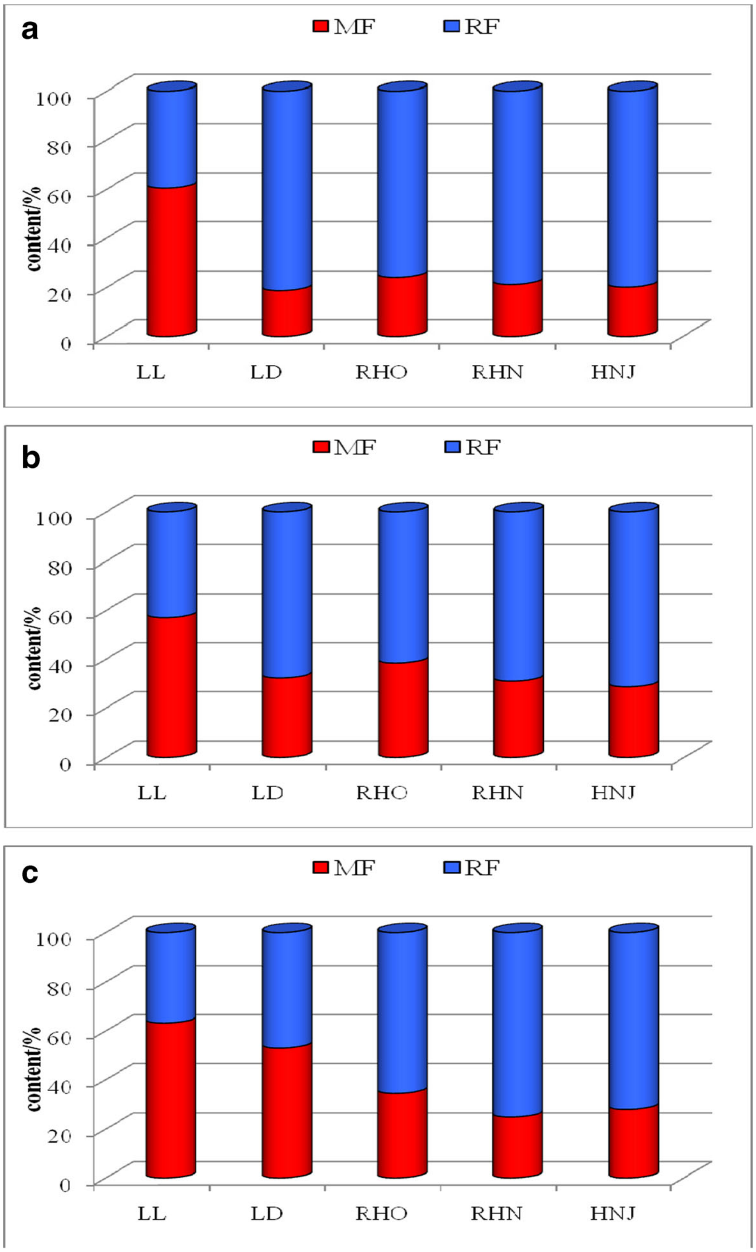

Fig. 10 Percentage contents of Zn (**a**), Cu (**b**), and Pb (**c**) in the MF and RF

conditions and the proportion that is immobile under certain conditions. Increasing the total metal content in the sediment will increase its content in the individual fractions. Based on these data, it is possible to assess the mobility of the metals between the sediment and the surrounding ecosystem. The highest metal mobility was found in the Lintich sediment sample (tailings lagoon), which had the highest content of the metals in the MF. However, the mobility decreased moving towards the tailings dam, and the mobilities of Zn and Cu became comparable to the mobilities of these elements in the natural sediments. The metal mobilities decreased in the order of Pb, Zn, and Cu in the anthropogenic sediment and Cu, Pb, and Zn in the natural sediments. Within the Ružín reservoir ecosystem, the mobility of the metals in the Hornád River inflow area was slightly higher than that in the Hnilec River area inflow.

Conclusions

On the basis of the results obtained in this study, the following conclusions can be drawn:

(a) the phase composition, total contents of matrix elements, and TIC and TOC contents confirmed that the matrix compositions of anthropogenic and natural sediments differ depending on their origin and the location in the environment;

(b) the different properties of the sediment sample matrix also affect the mobility of elements in the surrounding ecosystems and are crucial in selecting a suitable extractant for determining the MF of metals;

(c) XRD analysis confirmed, in all the sediment samples, the predominant quartz and silicate phases, but for selection of reagent this information should be supplemented by determining the total contents of the matrix elements and determining the particle composition of the particular particles;

(d) the content of sulfur and its form, which is dependent on the external conditions of the sediment, is an important information for the selection of reagent. Contact with atmospheric oxygen, as it was in the case of anthropogenic sediment, supports the transformation of sulfide phases of sulfur into sulfate phases, which are soluble in AA; the association of metals with these phases is significant in terms of mobility assessment;

(e) the 16-h AA extraction, which is more time-consuming than EDTA extraction, is required to evaluate the mobility of metals in acidic sediments and to evaluate Zn mobility;

(f) the 1-h EDTA extraction is sufficient to evaluate the mobility of Cu and Pb in sediments with a higher organic matter content or lower total contents of these metals; and

(g) anthropogenic sediments containing tailings (waste from sulfide ore processing) with deposited material that is acidic are significant source of heavy metals to the surrounding ecosystem. Higher mobility of the monitored elements was noticed from the sediment of the lagoon than from the sediment of the dam. This finding indicates that the dam, which was subjected to different conditions than the lagoon, forms some protecting wall before the distribution of the contamination.

Funding information This research was supported by the Slovak Grant Agency for Science VEGA 1/0631/17.

References

Abollino, O., Malandrino, M., Giacomino, A., & Mentasti, E. (2011). The role of chemometrics in single and sequential extraction assays: a review part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition. *Analytica Chimica Acta, 688*, 104–121.

Anju, M., & Banerjee, D. K. (2010). Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. *Chemosphere, 78*, 1393–1402.

Anju, M., & Banerjee, D. K. (2011). Association of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. *Environmental Monitoring and Assessment, 176*, 67–85.

Cappuyns, V. (2012). A critical evaluation of single extractions from the SMT program to determine trace element mobility in sediments. *Applied and Environmental Soil Science, 2012*, 1–15. https://doi.org/10.1155/2012/672914.

Cappuyns, V., & Swennen, R. (2008). “Acid extractable” metal concentrations in solid matrices: a comparison and evaluation of operationally defined extraction procedures and leaching tests. *Talanta, 75*, 1338–1347.

Chaudhary, S., Banerjee, D. K., Kumar, N., & Yadav, S. (2016). Assessment of bioavailable metals in the sediments of Yamuna flood plain using two different single extraction procedures. *Sustainable Environment Research, 26*, 28–32.

Favas, P. J. C., Pratas, J., Gomes, M. E. P., & Cala, V. (2011). Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: Environmental implications. *Journal of Geochemical Exploration, 111*, 160–171.

Feketeová, Z., Hulejová Sládkovičová, V., Mangová, B., & Šimkovic, I. (2015). Biological activity of the metal-rich post-flotation tailings at an abandoned mine tailings pond (four decades after experimental afforestation). *Environmental Science and Pollution Research, 22*, 12174–12181.

Franks, D. M., Boger, D. V., Côte, C. M., & Mulligan, D. R. (2011). Suistainable development principles for the disposal of mining and mineral processing. *Resources Policy, 36*, 114–122.

Heikkinen, P. M., Räisänen, M. L., & Johnson, R. H. (2009). Geochemical characterization of seepage and drainage water quality from two sulphide tailings impoundments: acid mine drainage versus neutral mine drainage. *Mine Water and the Environment, 28*, 30–49.

Jamshidi-Zanjani, A., Saeedi, M., & Li, L. Y. (2015). A risk assessment for bioavailability of metals in sediments: Anzali International Wetland case study. *Environmental Earth Sciences, 73*, 2115–2126.

Lee, G., Faure, G., Bigham, J. M., & Williams, D. J. (2008). Metal release from bottom sediments of Ocoee Lake no. 3, a primary cachment area for the Ducktown Mining District. *Journal of Environmental Quality, 37*, 344–352.

Lintnerová, O., Šucha, V., & Streško, V. (1999). Mineralogy and geochemistry of acid mine Fe-precipitates from the main Slovak mining regions. *Geologica Carpathica, 50*(5), 395–404.

Mahanta, M. J., & Bhattacharyya, K. G. (2011). Total concentrations, fractionation and mobility of heavy metals in soils of urban area of Guwahati. India. *Environmental Monitoring and Assessment, 173*, 221–240.

Maranhão de, T. A., Silva, J. S. A., Bascuñan, V. L. A. F., Oliveira, F. J. S., & Curtius, A. J. (2011). Analysis of acetic acid extraction solutions by inductively coupled plasma mass spectrometry for the classification of solid waste. *Microchemical Journal, 98*, 32–38. https://doi.org/10.1016/j.microc.2010.10.007.

Morillo, J., Usero, J., & Rojas, R. (2008). Fractionation of metals and As in sediments from a biosphere reserve (Odiel salt marshes) affected by acidic mine drainage. *Environmental Monitoring and Assessment, 139*, 329–337.

Navarro, M. C., Pérez-Sirvent, C., Martínez-Sánchez, M. J., Vidal, J., Tovar, P. J., & Bech, J. (2008). Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. *Journal of Geochemical Exploration, 96*, 183–193.

Nordstrom, D. K. (2011). Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. *Applied Geochemistry, 26*, 1777–1791.

Peng, J. F., Song, Y. H., Yuan, P., Cui, X. Y., & Qiu, G. L. (2009). The remediation of heavy metals contaminated sediment. *Journal of Hazardous Materials, 161*, 633–640.

Rao, C. R. M., Sahuquillo, A., & Lopez-Sanches, J. F. (2008). A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water, Air, & Soil Pollution, 189*, 291–333.

Rao, C. R. M., Sahuquillo, A., & Lopez-Sanchez, J. F. (2010). Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. *Analytica Chimica Acta, 662*, 128–136.

Salvarredy-Aranguren, M. M., Probst, A., Roulet, M., & Isaure, M. P. (2008). Contamination of surface waters by mining wastes in the Milluni Valley (Cordillera Real, Bolivia): mineralogical and hydrological influences. *Applied Geochemistry, 23*, 1299–1324.

Schneider, I. L., Teixeira, E. C., Rodrigues, M. L. K., & Rolim, S. B. A. (2014). Metal content and distribution in surface sediments in an industrial region. *Anais da Academia Brasileira de Ciências, 86*(3), 1043–1061.

Sun, Y., Zhou, Q., Xie, X., & Liu, R. (2010). Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *Journal of Hazardous Materials, 174*, 455–462.

Šestinová, O. (2012). *The forms study occurrence of metals in the sediments from the water reservoir Ružín No.I and their phytotoxicity and genotoxicity.* Dissertation, Institute of Geotechnics, Košice: Slovak Academy of Sciences.

Šestinová, O., Findoráková, L., Hančuľák, J., & Šestinová, L. (2015). Study of metal mobility and phytotoxicity in bottom sediments that have been influenced by former mining activities in Eastern Slovakia. *Environmental Earth Sciences, 74*, 6017–6025.

Ure, A. M., Davidson, C. M., & Thomas, R. P. (1995). Single and sequential extraction schemes for trace metal speciation in soil and sediment. *Quality Assurance for Environmental Analysis*: Elsevier Science B. V.