

ORIGINAL PAPER

A new method of evaluation of element pollutant mobility
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Received 9 November 2006; Revised 21 June 2007; Accepted 2 July 2007

This paper is dedicated to the memory of Erika Krakovská

The application of a strong chelating agent for the screening test of element mobility in sedimentary systems was investigated. Single-step and sequential extraction procedures were applied to four sediment samples collected from an industrially polluted region of Eastern Slovakia. A sequential extraction procedure (SEP), recommended by the Institute for Reference Materials and Measurements (IRMM), was applied and used as a reference extraction method. A single-step extraction with 0.05 mol dm⁻³ ethylenediaminetetraacetic acid (EDTA) was adapted for sediments when extraction conditions were optimised. The extraction efficiency of the single-step procedure was compared with that of SEP. The contents of elements extracted by Na₂EDTA were in good agreement with the sum of the first three steps of the SEP for Fe, Mn, and Co. Na₂EDTA can therefore be considered capable to extract the majority of elements associated with the reducible sedimentary phase – bound to Fe and Mn oxides in the regional geological conditions of the monitored region. Thus, Na₂EDTA extraction of Fe and Mn can serve as an economical, time-saving supplementary test for the IRMM procedure.

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Keywords: Fe, Mn, Co, extractable forms, element mobility, sediments

Introduction

Quantification of extractable forms of Fe, Mn, and trace metals in contaminated sediments and soils provides the basis for element mobility studies in environment (Batley, 1990; Slaveykova & Wilkinson, 2005). Changes of iron release into a water solution induce the trace element mobility changes, transport of elements through the environment components and a change in the water's potential to affect the aquatic life (Ussher et al., 2004; Laan et al., 2004; Howitt et al., 2004). Fractionation, using sequential extrac-

tion methods, gives comprehensive information on the potential mobility of metal contaminants. It is, however, a time consuming procedure. There are strongly recommended standard SEPs (Gleyzes et al., 2002), but the risk assessment of contaminants requires a meaningful tool for obtaining primary information on metal lability changes in sedimentary systems (Vojteková et al., 2003a, 2003b; Vojteková & Krakovská, 2006). The application of single-step extraction procedures is interesting both from economical and from time-saving point of view. For example, an optimised Na₂EDTA sediment extraction takes six hours while

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[‡]Presented at the XVIIIth Slovak Spectroscopic Conference, Spišská Nová Ves, 15–18 October 2006.

Table 1. Sampling places characterisation

Sediment sample	Soil sample*	Sampling place	Geographic coordinates		River/stream
			Longitude	Latitude	
Sediment 1	Soil 1, 2	Rudňany–Markušovce	20° 38′	48° 54′	Hornád
Sediment 2	Soil 3	Slovinky	20° 45′	48° 53′	Poráčsky jarok
Sediment 3	Soil 4	Richnava	20° 50′	48° 56′	Hornád
Sediment 4	Soil 5	Jaklovce	21° 00′	48° 53′	Hnilec

*Soil samples were collected in the distance from 10 m to 15 m from the bank of the streams.

the modified IRMM extraction requires 64 hours in total.

In this work, the standard soil extraction procedure using 0.05 mol dm^{-3} EDTA for sediments was modified and compared with the results of the SEP recommended by IRMM (Fiedler et al., 1994). The extraction time and solid mass to extraction solution volume ratio were optimised. Previous kinetic and equilibrium experiments indicated a need for longer extraction time and increased solid to solution ratio for polluted sediments in comparison with extraction conditions of the standardised EDTA extraction (extraction time 1 h, solid mass to extraction solution volume ratio of 1:10) (Sommers & Lindsay, 1979; Pickering, 1986).

The method of sequential extraction used in this work was slightly modified with respect to the regional geological conditions. Apart from the usual three steps of the IRMM procedure, the first step (for elements extractable into the water phase) and the fifth step (digestion of the sediment residue) were added (Mackových, 2000; Tessier & Campbell, 1988). A comparison of the two extraction procedures was done using four sediment samples from the industrially stressed area of the Spišsko–Gemerské Rudohorie Mountains (Bodiš et al., 2000).

Experimental

Collection and pre-treatment of sediment samples

Topographical localisation of the selected sampling region and the list of sampling sites are given in Fig. 1 and Table 1. The collection of sediment samples was carried out in accordance with the Methodical Instruction of the Slovak Ministry of Environment No 549/1998-2 (1998). The depth of physical and biological raise of the sediment is approximately 20 cm; therefore, a 20 cm thick layer was collected from the sediment surface. Original samples comprised sand, silt and clay fractions. Sediment particle size ranged from $1 \mu\text{m}$ to $3000 \mu\text{m}$. Samples were dried at 40°C and passed through a 0.125 mm stainless steel sieve. A fraction with the particle size smaller than 0.125 mm was milled on an agate planetary treadmill to grain size under 0.09 mm . Half-gram portions of the



Fig. 1. Topographical location of the sampling area in Slovakia; scale 1:500 000. Four sampling places (1–4) of four sediment and five soil samples (details in Table 1).

Table 2. Standard and modified procedures for single-step extraction with 0.05 mol dm^{-3} EDTA salts

	Standard procedure	Modified procedure
Extraction agent	$(\text{NH}_4)_2\text{EDTA}$	Na_2EDTA
Extraction time	1 h	1–6 h
Temperature	$(20 \pm 2)^\circ\text{C}$	$(20 \pm 2)^\circ\text{C}$
Extraction ratio	1:10	1:50, 1:100, 1:150
pH of extraction agent	7	3–7
Extraction vessel	250 cm^3 PE (washed by H_2O , 4 mol dm^{-3} HNO_3 and 0.05 mol dm^{-3} EDTA-salt)	
Filtration	“paper with blue stripe” $\Theta = 18.5 \text{ cm}$	

homogenised samples were weighted for the determination of the content of extractable Fe, Mn, and Co.

Sample analysis procedure

The standard soil extraction procedure with 0.05 mol dm^{-3} $(\text{NH}_4)_2\text{EDTA}$ (Ure et al., 1995) was modified for the sediments. Original and modified conditions of the extraction procedure are given in Table 2. The modified five-step extraction procedure (Table 3) distributes the isolated metals into the following fractions: water-soluble, acid-extractable (exchangeable and carbonate), reducible (bound to Fe and Mn

Table 3. Standard and modified IRMM procedure for sequential extraction

Extracted fraction↓	Standard IRMM procedure (Fiedler et al., 1994)	Modified IRMM procedure (Mackových, 2000; Tessier and Campbell, 1988)
Water-soluble	–	Deionised water, pH \approx 6.7
Acid extractable	0.11 mol dm ⁻³ CH ₃ COOH, pH = 3	0.11 mol dm ⁻³ CH ₃ COOH, pH = 3
Reducible	0.1 mol dm ⁻³ HONH ₂ · HCl, pH = 2	0.1 mol dm ⁻³ HONH ₂ · HCl, pH = 2
Oxidisable	8.8 mol dm ⁻³ H ₂ O ₂ , 1 mol dm ⁻³ CH ₃ COONH ₄ , pH = 2	8.8 mol dm ⁻³ H ₂ O ₂ , 1 mol dm ⁻³ CH ₃ COONH ₄ , pH = 2
Residual	–	HNO ₃ , HF, HClO ₄

oxides), oxidisable (organic and sulphide) and residual.

All stock standards and chemicals were obtained from the Sigma–Aldrich group and Merck (Darmstadt, Germany). Distilled water was cleaned by reverse osmosis (Purelab Option R3, Elga) and by an ion exchanger (Purelab Clasic). Deionised water was used in all experiments. Ion exchange and reversal osmosis were used. The pH value of water was 6.7. Working standard solutions were prepared by dilution of stock standard solutions by deionised water.

For the single-step extraction procedure 0.05 mol dm⁻³ Na₂EDTA solution (pH – changed within 3 and 7, adjusted with HCl, NH₄OH, alternatively) was prepared. The pH of untreated Na₂EDTA solution was 4.7. For sequential extraction procedure, the solutions of 0.11 mol dm⁻³ acetic acid (CH₃COOH), 0.1 mol dm⁻³ hydroxylammonium chloride (HONH₂ · HCl), concentrated H₂O₂ acidified with nitric acid-water solution ($\varphi(\text{HNO}_3)/\varphi(\text{H}_2\text{O}) = 1:1$) to pH between 2 and 3, and 1 mol dm⁻³ ammonium acetate (NH₄OOCCH₃) were used.

Single-step extraction procedure

The original protocol for 0.05 mol dm⁻³ EDTA extraction of soils was optimised. The extraction time of 1 h to 6 h, pH of the extractant between 3 and 7 and the sample mass to extractant volume ratio were tested (Table 2). 25 cm³, 50 cm³, or 75 cm³ of 0.05 mol dm⁻³ Na₂EDTA were added to 0.5 g of sediment sample in a 100 cm³ polyethylene vessel. The tightly closed vessels were shaken for 1–6 h. Optimisation of the extraction time was performed at pH = 4.7. Optimisation of the sample mass to extractant volume ratio was done for four pilot sediment samples. pH optimisation of the extraction agent was carried out for the most contaminated Sediment 3. The Na₂EDTA acidity was adjusted to pH 3–7 and the extraction time was set to 1 h. The extractant was separated by filtration and stored in a polyethylene vessel. This solution was then used in the determination of extractable element portions in the sample. Decomposition of the sediment residue was carried out as in the sequential extraction (see Step 5 below).

Sequential extraction procedure

Each step of the sequential extraction was performed in a mechanical end-over-end shaker for 16 h (200 min⁻¹, temperature (20 ± 2) °C). After finishing the extraction, the solution was centrifuged at 4000 min⁻¹ for 20 min. Solutions obtained from the individual extraction steps were stored in polyethylene vessels at the temperature of 4 °C. Extractable portions of the chosen elements were determined from the solutions prepared in the described way. All experiments were repeated five times.

Step 1 was used to obtain water-soluble fraction of the elements. 50 cm³ of distilled water was added to 0.5 g of sediment sample in a 100 cm³ polyethylene vessel. The tightly closed vessel was shaken for 16 h. After the extraction, the extractant was separated by centrifugation and poured into a polyethylene vessel. This solution was used in the determination of the water-soluble part of the sample. The solid residue was used in the next extraction step.

Step 2 served to separate acid-extractable fraction of the elements. 40 cm³ of 0.11 mol dm⁻³ acetic acid were added to the solid residue from the extraction step 1 and shaken together in a 100 cm³ polyethylene vessel for 16 h. The solution was then centrifuged and stored in a polyethylene vessel. It was used in the determination of the exchangeable and carbonate parts of the sample. The solid residue was washed with 20 cm³ of deionised water, shaken and centrifuged for 15 min and then used in the next extraction step. Determined values of Fe, Mn, and Co concentration in the washing water were under the detection limit of the method in all extraction steps.

Step 3 afforded reducible fraction of the associated metals. The residue from the previous step was slurried in a 100 cm³ polyethylene vessel by a 40 cm³ of 0.1 mol dm⁻³ hydroxylammonium chloride solution adjusted to pH 2 with HNO₃. After shaking for 16 h, the extractant was separated by centrifugation and poured into a polyethylene vessel. This solution was used in the determination of the reducible part of the sample. The solid residue was washed with 20 cm³ of deionised water, shaken, centrifuged for 15 min and used in the next extraction step.

Step 4 was used to determine the oxidisable frac-

tion of the studied metals. In this step, 10 cm³ of 8.8 mol dm⁻³ hydrogen peroxide were carefully added to the previous solid residue in little aliquots, to avoid loss due to violent reaction. The vessel was occasionally shaken at room temperature for 1 h. Then, it was placed on a sand bath heated to 85 °C and evaporated to dry state. The same procedure was repeated while adding another 10 cm³ of H₂O₂ and the sediment residue was evaporated to complete dryness. The vessel content was quantitatively transferred to the extraction vessel, then 50 cm³ of 1 mol dm⁻³ ammonium acetate were added and the extraction process was carried out as in the steps described above.

Solid residue obtained after the fourth extraction step was wetted and digested in an acid mixture of HF, HClO₄, and HNO₃. 10 cm³ HF and 1 cm³ HClO₄ were added to the remaining solid residue. The vessel content was shortly shaken by hand, placed on a sand bath and evaporated to the point of white fumes formation. 10 cm³ of HF were added and the sample was evaporated to the complete dryness. 5 cm³ of HNO₃ (diluted with water in volumetric ratio of 1:1) were then added to the residue and digested for 20 min. The cooled solution was transferred to a 50 cm³ volumetric flask, filled up to the mark with distilled water and transferred to the polyethylene vessel once more.

Analytical methods and equipment

Atomic emission spectrometry with inductively coupled plasma was used for the determination of Fe, Mn, and Co in each extracted fraction. The measurements were carried out on a Varian spectrometer Liberty 200 with a Cetac ultrasonic nebulizer. X-ray fluorescence spectrometry (XRF) was applied for the determination of total element contents in the studied fluvial sediments. Measurements were performed on a Spectro X-LAB 2000 spectrometer. Experimental conditions of the ICP OES and XRF measurements were described by Mackových (2000). The standard IRMM extraction procedure recommends using CRM 601 as the certified reference material, but no certified values for Fe, Mn, and Co are available, only informative ones (Sutherland & Tack, 2002). Accuracy of the single-step and the sequential extraction and the results of Fe, Mn, and Co analyses was evaluated by comparing the sum of the contents determined in each extraction step with those of the reference analyses made using XRF. CRM required for the comparison of the sequential extraction element determination and the single-step element determination of leached element portions in the chelating agents is not commercially available.

Results and discussion

The results of extraction and determination of Fe, Mn, and Co in four sediment samples are presented in

Table 4. The investigation of the accuracy of single-step and sequential extractions shown in this table brought acceptable results. The results of the total elemental content analysis of Fe, Mn, and Co obtained by the XRF method are in good agreement with those determined using sequential or Na₂EDTA extraction. The recovery degrees of these three methods were between 80 % and 101 % for Fe, 79 % and 101 % for Mn and 92 % and 102 % for Co.

The amount of Fe extracted in the first and second steps of sequential extraction was not significant and did not exceed 0.2 % of the total elemental content of all sediment samples. The extracted amount of Fe in the third step ranged between 4.8 % and 17.3 % depending on the sample matrix. In the fourth step, the obtained values were between 1.4 % and 5.2 %. The fifth mineralisation step yielded values from 80 % to 94 % of the total Fe content.

Mn was extracted mainly in the second step in all of the samples when the values obtained represented up to 74 % of the total elemental content. This fact documents the predominant presence of compounds such as MnCO₃ in the studied sediments (Bodiš et al., 2000). The extracted amount of Mn in the third step, the reducible fraction, ranged between 6 % and 11.2 % of the total Mn content. The recovery yield of the fifth step was from 12.2 % to 23.1 % of the total Mn content.

The low water solution mobility of Co is reflected by the amount extracted in the first step being under the detection limit of the used analytical method. The amount of Co extracted in the second, third, and fourth steps represented up to 21 % of the total element content. The yield of the fifth mineralisation step ranged from 52 % to 62.5 % of the total Co content.

With respect to the single-step EDTA extraction optimisation, it is possible to conclude that the optimised extraction ratio of the studied elements was 1:150 for each sediment when an increase of the extracted element amounts ranged from 11 % to 30 % compared to the standard procedure. The optimised time was six hours, which is illustrated, for the Fe extraction, in Fig. 2a. Experiments for Mn and Co were performed analogously. The suitability of the six-hour extraction was confirmed also here as follows from a decrease in the relative standard deviations of five repeated extractions (Figs. 2b, 3c, 3d). The six-hour extraction could thus be more appropriate for macroelements and more contaminated sediments.

The pH optimisation experiments showed that the highest recoveries of Fe can be observed in an extraction medium with pH 3 (Fig. 3). The extracted contents of Mn and Co show a gentle decrease at pH 3, which is in agreement with the proportionality of the present dissociated forms of the EDTA salt. The pH value of 3 is, however, improbable in real water-sediment systems. It should be more relevant to adjust

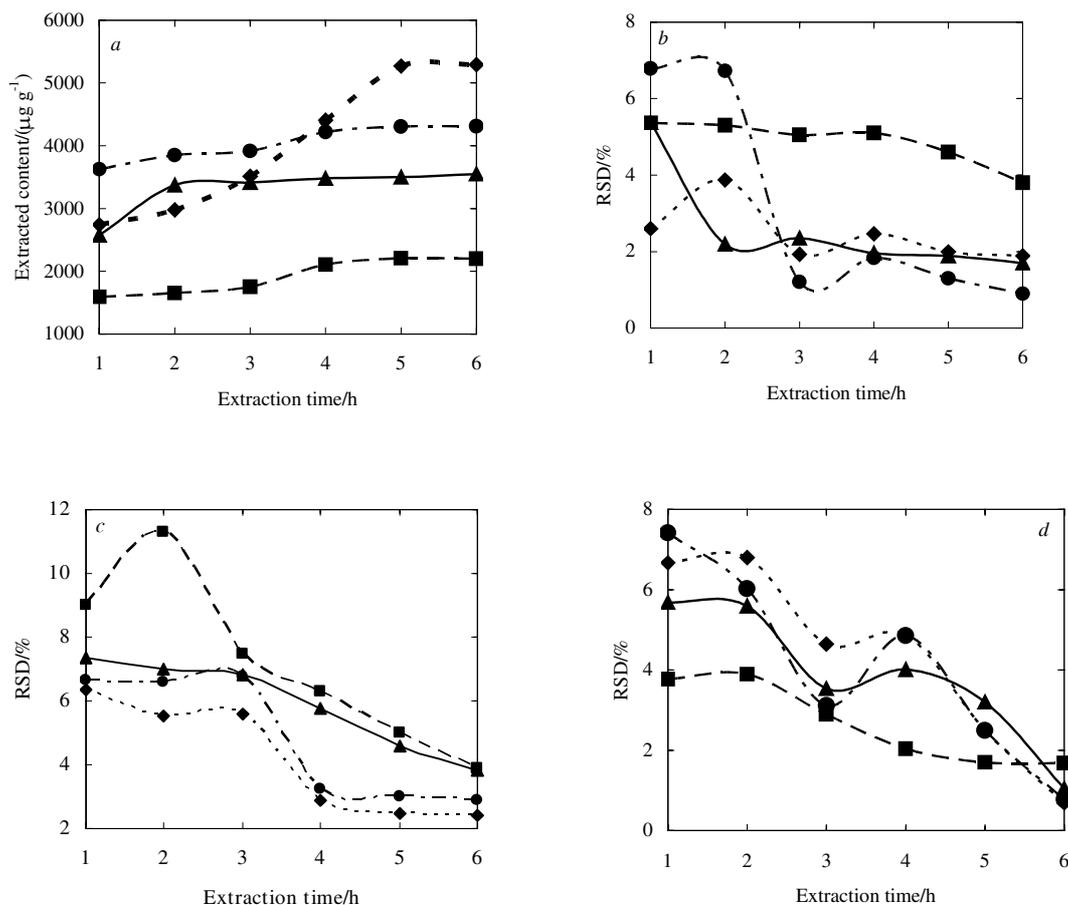


Fig. 2. Optimisation of extraction time; $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$ without pH modification ($\text{pH} = 4.7$) for the sediment samples 1 (triangles), 2 (squares), 3 (circles), and 4 (diamonds). Extracted content of Fe (mean of 5 repeated experiments) (a) and relative standard deviations (RSD) of the extracted amount of Fe (b), Co (c), and Mn (d).

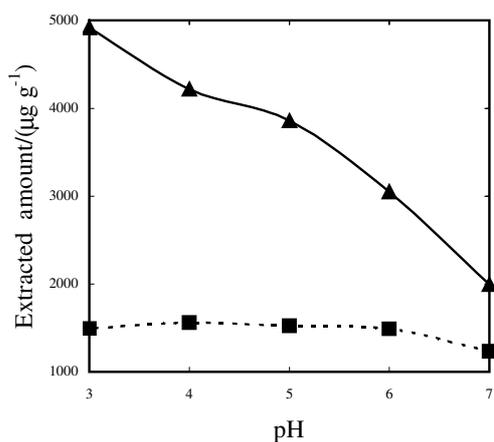


Fig. 3. Optimisation of pH for extraction of Fe (triangles) and Mn (squares) with $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$ in Sediment 3. Relative standard deviation (RSD) values of the extracted content in replicate experiments were in the interval 5–8 %.

the EDTA extraction pH according to the acidity of surface water.

When the single-step and sequential extraction

procedures are compared with respect to the metal removal ability, it is possible to conclude that the optimised single-step procedure enabled the extraction of potentially mobile forms in the extent corresponding to the overall extraction efficiency of the first three steps of SEP (Table 4). As the extraction of Fe and Mn in the fourth extraction step of SEP is concerned, oxidation conditions have to be created for the release of the metal portions in their sulphide forms. Therefore, the optimised Na_2EDTA extraction enables the release of the most environmentally important reducible sediment phase and also of all elemental contaminants associated with Fe and Mn oxides.

The extractability of Fe and Mn into $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$ could reflect the mobility of all other contaminating trace elements of sediments and soils (columns 4–9 of Table 4), which is also conformable with the contents of metal contaminants in sediments determined in our previous studies (Vojteková et al., 2003a, 2003b; Vojteková & Krakovská, 2006) and with the Fe and Mn distribution in the soils which were collected in the examined region (Table 5). The analysed soils were practically collected from the same places as the sediments (Fig. 1 and Table 1). The same five-

Table 4. Comparison of single-step EDTA extraction, five-step sequential extraction, and total content analysis by XRF for sediments

Sediment	Extraction step	Mean content* \pm uncertainty/ $(\mu\text{g g}^{-1})$								
		Fe	Mn	Co	As	Sb	Pb	Cu	Cr	Ni
Sediment 1	1	32 \pm 3	6 \pm 1	< 0.002	0.4 \pm 0.1	1.2 \pm 0.2	< 0.004	2.0 \pm 0.4	< 0.002	< 0.002
	2	9 \pm 2	739 \pm 15	3.0 \pm 0.6	< 0.1	1.0 \pm 0.1	< 0.004	6 \pm 1	< 0.002	4.0 \pm 0.8
	3	3477 \pm 174	125 \pm 5	5 \pm 1	6.2 \pm 0.6	1.0 \pm 0.1	35 \pm 4	42 \pm 4	4.0 \pm 0.8	8 \pm 2
	4	1331 \pm 67	55 \pm 6	4.0 \pm 0.8	0.7 \pm 0.1	0.9 \pm 0.1	4 \pm 1	79 \pm 8	5 \pm 1	4.0 \pm 0.8
	5	20520 \pm 513	189 \pm 7	20 \pm 2	16.7 \pm 2.0	24.5 \pm 1.5	6 \pm 2	21 \pm 2	82 \pm 8	17 \pm 2
	Sum	25396 \pm 635	1114 \pm 22	32 \pm 3	24.0 \pm 2.3	28.6 \pm 1.7	45 \pm 5	150 \pm 15	–**	33 \pm 3
	EDTA Extraction	3550 \pm 177	884 \pm 18	7 \pm 2	6.4 \pm 0.6	7.1 \pm 0.7	38 \pm 4	78 \pm 8	4.0 \pm 0.8	9 \pm 2
	EDTA Sum	27436 \pm 686	1185 \pm 24	31 \pm 3	22.5 \pm 2.3	29.1 \pm 1.7	44 \pm 4	155 \pm 16	–**	36 \pm 4
	XRF	31700 \pm 159	1418 \pm 14	33 \pm 2	20 \pm 1	34 \pm 1	45 \pm 3	161 \pm 8	91 \pm 5	38 \pm 2
	Recovery XRF–SEP/%	80	79	97	120	84	100	93	–	87
Recovery XRF–EDTA/%	87	84	94	113	86	98	96	–	95	
Sediment 2	1	22 \pm 2	5 \pm 1	< 0.002	0.20 \pm 0.03	0.4 \pm 0.1	< 0.004	2.0 \pm 0.4	< 0.002	< 0.002
	2	< 0.004	561 \pm 11	3.0 \pm 0.6	< 0.1	0.3 \pm 0.1	< 0.004	3.0 \pm 0.6	< 0.002	2.0 \pm 0.4
	3	2324 \pm 116	84 \pm 9	6 \pm 1	2.3 \pm 0.2	0.6 \pm 0.1	21 \pm 2	32 \pm 3	1.0 \pm 0.2	5 \pm 1
	4	669 \pm 7	27 \pm 3	4.0 \pm 0.8	0.3 \pm 0.1	0.4 \pm 0.1	< 0.004	62 \pm 6	3.0 \pm 0.6	3.0 \pm 0.6
	5	45940 \pm 459	203 \pm 7	22 \pm 2	25.8 \pm 2.6	20.0 \pm 1.2	9 \pm 2	39 \pm 4	90 \pm 9	21 \pm 2
	Sum	48955 \pm 979	880 \pm 18	35 \pm 4	28.6 \pm 5.2	21.7 \pm 2.4	30 \pm 6	138 \pm 14	–	31 \pm 3
	EDTA Extraction	2199 \pm 110	641 \pm 13	7 \pm 2	2.2 \pm 0.2	2.0 \pm 0.2	21 \pm 2	90 \pm 9	1.0 \pm 0.2	8 \pm 2
	EDTA Sum	48310 \pm 483	927 \pm 19	38 \pm 4	27.6 \pm 3.0	22.3 \pm 2.5	32 \pm 3	140 \pm 14	–	31 \pm 3
	XRF	48400 \pm 242	1110 \pm 11	38 \pm 1	29 \pm 2	23 \pm 1	35 \pm 2	143 \pm 8	94 \pm 5	34 \pm 3
	Recovery XRF–SEP/%	101	79	92	99	94	86	96	–	91
Recovery XRF–EDTA/%	100	84	100	95	97	91	98	–	91	
Sediment 3	1	23 \pm 2	7 \pm 1	< 0.002	1.4 \pm 0.1	1.5 \pm 0.2	< 0.004	5 \pm 1	< 0.002	< 0.002
	2	18 \pm 2	954 \pm 19	5 \pm 1	< 0.1	0.5 \pm 0.1	4 \pm 1	37 \pm 4	< 0.002	11 \pm 1
	3	4066 \pm 203	120 \pm 4	8 \pm 2	22.1 \pm 1.3	1.5 \pm 0.2	85 \pm 9	137 \pm 14	4.0 \pm 0.8	14 \pm 1
	4	1067 \pm 53	58 \pm 6	5 \pm 1	4.8 \pm 0.5	0.5 \pm 0.1	9 \pm 2	120 \pm 12	5 \pm 1	4.0 \pm 0.8
	5	24890 \pm 622	158 \pm 6	29 \pm 3	49.9 \pm 3.0	41.5 \pm 2.5	13 \pm 1	46 \pm 5	102 \pm 10	27 \pm 3
	Sum	30064 \pm 769	1297 \pm 26	47 \pm 5	78.2 \pm 6.6	45.5 \pm 2.7	111 \pm 6	345 \pm 34	–	56 \pm 6
	EDTA Extraction	4310 \pm 216	1092 \pm 22	7 \pm 2	39.4 \pm 2.4	9.2 \pm 0.9	88 \pm 9	214 \pm 21	4 \pm 0.8	24 \pm 2
	EDTA Sum	32807 \pm 820	1345 \pm 27	50 \pm 5	76.9 \pm 6.8	44.6 \pm 4.9	114 \pm 6	345 \pm 34	–	59 \pm 6
	XRF	35700 \pm 178	1433 \pm 14	49 \pm 3	77.0 \pm 3.8	47 \pm 1.7	116 \pm 3	376 \pm 16	111 \pm 6	57 \pm 3
	Recovery XRF–SEP/%	84	91	98	102	97	96	92	–	98
Recovery XRF–EDTA/%	92	94	102	100	95	98	92	–	104	
Sediment 4	1	60 \pm 6	21 \pm 4	< 0.002	0.20 \pm 0.03	0.8 \pm 0.2	< 0.004	2.0 \pm 0.4	< 0.002	< 0.002
	2	80 \pm 8	1183 \pm 24	7 \pm 1	0.20 \pm 0.03	< 0.1	< 0.004	56 \pm 6	< 0.002	6 \pm 1
	3	7804 \pm 390	94 \pm 9	8 \pm 2	10.6 \pm 1.1	2.0 \pm 0.2	48 \pm 5	97 \pm 10	3.0 \pm 0.6	7 \pm 1
	4	1073 \pm 54	30 \pm 3	3.0 \pm 0.6	0.7 \pm 0.1	0.3 \pm 0.3	5 \pm 1	99 \pm 10	4.0 \pm 0.8	2.0 \pm 0.4
	5	36005 \pm 900	276 \pm 10	20 \pm 2	41.7 \pm 2.5	37.6 \pm 2.3	15 \pm 2	45 \pm 5	77 \pm 8	20 \pm 2
	Sum	45022 \pm 450	1604 \pm 32	38 \pm 4	53.4 \pm 5.5	40.7 \pm 4.6	68 \pm 7	299 \pm 30	–	35 \pm 4
	EDTA Extraction	5293 \pm 265	1236 \pm 25	11 \pm 2	3.8 \pm 0.4	3.5 \pm 0.4	37 \pm 4	215 \pm 22	3.0 \pm 0.6	10 \pm 2
	EDTA Sum	48155 \pm 482	1580 \pm 31	38 \pm 4	51.6 \pm 5.3	42.6 \pm 4.8	68 \pm 7	301 \pm 30	–	38 \pm 4
	XRF	50800 \pm 254	1596 \pm 16	39 \pm 2	52 \pm 3	43.0 \pm 1.6	70 \pm 4	304 \pm 30	84 \pm 5	42 \pm 4
	Recovery XRF–SEP/%	89	101	97	103	95	97	98	–	83
Recovery XRF–EDTA/%	95	99	97	99	99	97	99	–	90	

*Mean value of 5 repeated extraction experiments.

**Mineralisation step is not suitable for chromium. The value presented in the 5th step of the sequential analysis is calculated as the difference between the total content obtained by XRF and in the first four extraction steps. The experimental conditions were described in detail by Mackových (2000).

Sum – sum of element contents obtained in the individual extraction steps, EDTA Extraction – element content extracted into Na₂EDTA during the extraction time of 6 h, EDTA Sum – sum of EDTA Extraction and content present in the mineralised sediment residue after Na₂EDTA extraction, XRF – total element content determined by XRF, Recovery XRF–SEP – recovery degree of SEP calculated as the ratio of the Sum- and XRF-values, Recovery XRF–EDTA – recovery degree of the EDTA extraction calculated as the ratio of the EDTA Sum- and XRF-values.

step sequential extraction was applied to the five soil samples. In all of the soil samples, Mn and Fe were distributed similarly as in the sediments (Tables 4 and

5). It means that the majority of the mobile and potentially mobile parts of Fe and Mn soil contents are extracted in the first three steps of SEP.

Table 5. Distribution of Fe and Mn contents in the soils sampled at the same sample places as the sediments determined using the five-step process of sequential extraction

Soil	Extraction step	Mean content* \pm uncertainty/ $(\mu\text{g g}^{-1})$	
		Fe	Mn
Soil 1	1	21 \pm 2	3.0 \pm 0.6
	2	18 \pm 2	78 \pm 9
	3	1298 \pm 65	84 \pm 8
	4	289 \pm 14	5 \pm 1
	5	16585 \pm 415	94 \pm 9
Sum		18198 \pm 455	264 \pm 11
XRF		20000 \pm 20	333 \pm 3
Recovery XRF–SEP/%		91	79
Soil 2	1	42 \pm 4	8 \pm 2
	2	< 0.004	188 \pm 8
	3	1617 \pm 81	335 \pm 7
	4	448 \pm 22	31 \pm 3
	5	25940 \pm 649	265 \pm 11
Sum		28019 \pm 700	825 \pm 17
XRF		29100 \pm 29	1100 \pm 11
Recovery XRF–SEP/%		96	75
Soil 3	1	44 \pm 4	8 \pm 2
	2	< 0.004	148 \pm 6
	3	1712 \pm 586	327 \pm 7
	4	432 \pm 22	29 \pm 3
	5	26015 \pm 650	259 \pm 10
Sum		28175 \pm 704	820 \pm 16
XRF		29900 \pm 30	1092 \pm 22
Recovery XRF–SEP/%		94	75
Soil 4	1	43 \pm 4	4.0 \pm 0.8
	2	< 0.004	290 \pm 12
	3	2212 \pm 111	194 \pm 8
	4	352 \pm 18	12 \pm 1
	5	33125 \pm 828	189 \pm 8
Sum		35696 \pm 899	687 \pm 14
XRF		36500 \pm 37	860 \pm 9
Recovery XRF–SEP/%		98	80
Soil 5	1	28 \pm 3	28 \pm 3
	2	38 \pm 4	136 \pm 14
	3	3199 \pm 160	125 \pm 13
	4	712 \pm 36	25 \pm 3
	5	39010 \pm 975	573 \pm 11
Sum		42986 \pm 1075	886 \pm 18
XRF		43600 \pm 44	999 \pm 10
Recovery XRF–SEP/%		99	89

*The symbols and definitions are the same as in Table 4.

With respect to the results presented above and published previously (Vojteková et al., 2003a, 2003b; Vojteková & Krakovská, 2006), it is possible to state that a single-step leaching procedure into a strong chelating agent is able to release mobile and potentially mobile metal forms associated with specific phases of sediments and soils. It is also possible to evaluate the extractability of other contaminating elements present in the sediments from the extractabil-

ity of Fe and Mn. Extraction with 0.05 mol dm⁻³ Na₂EDTA can be used for screening control of sediment and soil pollution under locally tested conditions. It is applicable as an economical, time-saving supplementary test for the recommended and attested IRMM sequential extraction procedures and as a fast alarm indicator of element mobility changes in sedimentary systems and soils. Such information about stream sediment/soil pollution is usually sufficient for decision-making in the area of environmental protection.

Acknowledgements. The authors would like to express their gratitude to the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences for financial support (Grant Project VEGA No. 1/4450/07).

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