

A Study on the trace metal speciation in the Ružín reservoir sediment

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Štúdium viazania stopových prvkov v sedimente vodnej nádrže Ružín

Pre účely posúdenia možnosti využitia fyzikálnych a fyzikálno-chemických metód separácie, vybraná vzorka sedimentu z Ružína bola podrobená 5-stupňovej procedúre sekvencnej extrakcie (SE) podľa Tessiera (Tessier *et al.*, 1979) a Horowitza (Horowitz, 1991). Vo výluhoch bolo stanovované zastúpenie konštitučných (Fe, Mn, Ca a Mg) ako aj niektorých ťažkých kovov (Cu, Pb, Zn, Ni a Cd). Bolo zistené, že jedna tretina Fe je reaktívna vo forme prevažne amorfných oxyhydroxidov a dve tretiny sú viazané v kryštálových mriežkach silikátov a ílových minerálov. Kryštalické ílové minerály a silikáty viažu 34,3 % Cu, 24,7 % Zn, 41,9 % Pb a 46,3 % Ni. Amorfné oxyhydroxidy Fe(III) a Mn(IV), pravdepodobne pokrývajúce povrch ílových minerálov, však viažu napriek nízkemu zastúpeniu v sedimente až 40,6 % Cu, 44,1 % Zn, 33,8 % Pb a 26,6 % Ni. Humínové látky nakoniec viažu iba 16,1 % Cu, 15,6 % Zn, 19,4 % Pb a 10,0 % Ni.

Key words: bottom sediments, trace metals, separation.

Introduction

Natural waters, i.e. seawaters and freshwaters, are extremely complex dynamic chemical systems consisting of different components, namely various solutes, organic matter and colloidal or particulate material. Hence, a number of chemical processes between metal pollutants dissolved in trace levels and each of these components is expected to take place in the aquatic reservoirs such as rivers, lakes and oceans (see Figure 1) and it is the distribution of the trace metal pollutants between the different chemical species and forms (chemical speciation of the first kind) which determines their geochemical and biological reactivity.

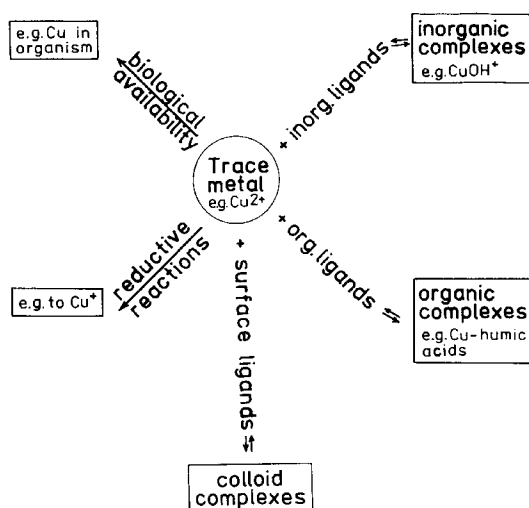


Fig.1. Possible chemical reactions of trace metals (e.g. Cu^{2+}) with various natural water components.

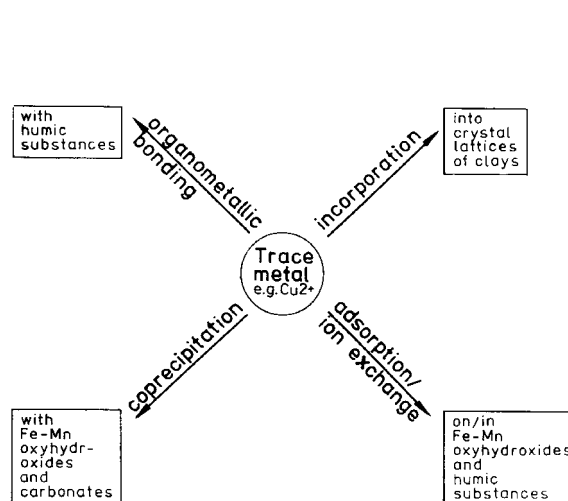


Fig.2. Possible association mechanisms of trace metals (e.g. Cu^{2+}) with various sediment phases in oxic environments.

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Among the chemical reactions, association with colloids and particles forming suspended and bottom sediments is a key process in the cycling of trace metals in natural waters on a wide range of timescales (chemical speciation of the second kind). In fact, it has been found that trace metals occurring in most rivers are predominantly carried by suspended particles and only a small fraction is transported in the soluble form (Horowitz, 1991; Moore and Ramamoorthy, 1984). Natural sediments are complex mixtures of various phases, namely residues of weathering and erosion such as clays and other aluminosilicates and iron and aluminum oxyhydroxides and sulfides, and substances produced by biological activity, both organic (living microorganisms, biological detritus and humic substances) and inorganic (carbonates, phosphates and silica) (Tessier, 1992). Therefore, the following mechanisms of the association (generally termed „sorption“) of trace metals with the specific phases of natural sediments can be considered to take place in oxic environments as opposed to anoxic environments where precipitation of trace metal sulfides may dominate (Figure 2): (1) coprecipitation with hydrous iron and manganese oxides and carbonates, (2) adsorption and cation exchange on/in clays, hydrous iron and manganese oxides and humic substances, (3) organometallic bonding with humic substances, and (4) incorporation in the crystal structure of clays and other aluminosilicates (Horowitz, 1991; Tessier, 1992).

Use of total concentration as a criterion to assess the potential effects of the sediment contamination implies that all forms (phases) of a given trace metal have an equal impact on the environment. Such an assumption is untenable (Tessier et al., 1979). It is evident that just the speciation of trace metal pollutants with the various sediment phases determines their specific impact on the environment. Also, the type of the phase specific bonding of trace metals in contaminated natural sediments specifies suitable methods of their potential cleaning and utilization (Langen et al., 1994). Although more time consuming, a common analytical method of evaluating particular trace metal-sediment phase associates is the method of sequential extractions (SE), adapted from the methods of soil and sediment chemical analysis. The concept of the SE procedure is the partitioning of a solid material into specific phases or fractions that are selectively extracted, i.e. liberated and released into solution (leached) along with the associated trace metals, by using appropriate reagents arranged in the increasing strength (Horowitz, 1991; Langen et al., 1994; Tessier, 1992; Tessier et al., 1979; Tessier et al., 1980).

The purpose of this preliminary study was to examine the speciation of selected trace metals (Cu, Zn, Pb, Ni, and Cd) in the Ružín reservoir sediment by using two different SE procedures, namely after Tessier et al. (1979) and Horowitz (1991), with the aim of evaluating possibilities of its physical and/or physico-chemical treatment.

Materials and Methods

Sampling

The single point samples of the oxic sediments were collected in March 1993 from the streams and rivers flowing into and out the Ružín reservoir as well as from this reservoir itself, dried at 105 °C and sized. Based on the total concentration analyses of all samples, i.e. highest total concentrations of trace metals associated, the SE procedure was applied only to the sample taken at the place where the tributary stream Hnilec enters the Ružín reservoir. Only the < 45 µm fraction was used for all analyses. For more details, see Gecik (1994).

SE procedure and chemical analysis

The following five-fraction (step) SE procedure was adopted for the determination of the trace metals speciation:

- 1. exchangeable (adsorbed and exchanged),*
- 2. bound to carbonates,*
- 3. bound to iron and manganese oxides,*
- 4. bound to organic matter (humic substances), and*
- 5. residual (primary and secondary minerals).*

Since numerous reagents are used to „selectively“ extract the same sediment phase/fraction (and associated trace metals), the SE procedure (extracting reagents and conditions) applied must be well defined. The difference in the five-fraction SE procedure, as defined by Tessier et al. (1979) and Horowitz (1991), consists in the kind of the extraction reagents used as well as in the time of their action within particular extraction steps.

Table 1. Description of the five-fraction SE procedure after Tessier et al. (1979).

Fraction	Trace metal speciation	Extraction reagent/Conditions
1	adsorbed and exchanged	1 M sodium acetate (NaOAc), pH 8, 1 h
2	bound to carbonates	1 M sodium acetate (NaOAc) + acetic acid (HOAc), pH 5, 3 h
3	bound to iron and manganese oxides	0.04 M hydroxylamine hydrochloride (NH ₂ OH) + 25 % acetic acid (HOAc), pH 2, 90 °C, 3 h
4	bound to organic matter	30 % hydrogen peroxide (H ₂ O ₂) + 0.02 M nitric acid (HNO ₃), pH 2, 80 °C, 5 h
5	residual	hydrofluoric acid (HF)+perchloric acid (HClO ₄), 5 h

To liberate *exchangeable* metals, 1 M sodium acetate (NaOAc) (a reagent currently used in measuring the cation exchange capacity in soil) was used at pH 8.2. For selectively dissolving *carbonate* fraction, the procedure involved 1 M NaOAc and adjustment of pH to 5 with acetic acid (HOAc). The selectively leaching of *iron and manganese oxides*, involved the combined action of hydroxylamine hydrochloride-acetic acid (NH₂OH.HCl+HOAc) reducing these metals to their ferrous and manganese forms, respectively, and keeping their large amounts in solution. Hot hydrogen peroxide (H₂O₂) in a nitric acid (HNO₃) medium was used to destroy or oxidize *organic matter*. Finally, for dissolving *residual* primary and secondary minerals, the hydrofluoric acid-perchloric acid (HF-HClO₄) mixture was chosen. The residue from an extraction step was submitted to the next extraction step after filtration. Constituent and trace metal concentrations in the respective leachates were determined by atomic absorption spectroscopy (Perkin Elmer model 1100 B) operated using the air-acetylene flame.

Table 2. Description of the five-fraction SE procedure after Horowitz (1991).

Fraction	Trace metal speciation	Extraction reagent/Conditions
1	adsorbed and exchanged	1 M MgCl ₂ , pH 7, 1 h
2	bound to carbonates	1 M sodium acetate, pH 5, 1 h
3	bound to iron and manganese oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid or hydrochloric acid, 1 h
4	bound to organic matter	0.1 M sodium hydroxide, 1 h
5	residual	hydrofluoric acid + hydrochloric acid, 5 h

Extraction reagents applied in each of the five steps are different from the above. See Table 2 for comparison.

X-ray diffraction

The X-ray diffraction analysis (Mikrometa Chirana, Czechoslovakia) was performed on the initial (unleached) sediment sample as well as on the leached residues.

Results and Discussion

Concentrations of constituent (Fe, Mn, Ca, and Mg) and trace (Cu, Pb, Zn, Ni, and Cd) metals, as determined by the Tessier's SE procedure in the Ružín sediment leachates, are listed in Table 3a and 3b, respectively. Figure 3 shows the same data in percentage. Analogously, Table 4a and 4b summarizes concentrations of the constituent and trace metals, as determined by the Horowitz's SE procedure, and Figure 4 depicts the same data in percentage. When evaluating the data obtained using the Tessier's SE procedure, it can be seen that Fe accumulates mainly in the fraction 5 (77.3 %) and 3 (21.4 %), which fact indicates that about one third of Fe is present as reactive, presumably amorphous oxyhydroxides, and two thirds incorporated in the crystal lattices of clay minerals and silicates. This is in agreement with the finding of Tessier (Tessier et al., 1980) on river sediments in Quebec. Mn accumulates in the fraction 3 (45.9 %) and 5 (29.5 %) but it is also present in the fraction 2 (16.1 %) and 4 (7.0 %). A major part of Ca is concentrated in the fraction 2 (59.2 %) and 1 (33.1 %), while Mg dominates the fraction 5 (82.8 %). It is possible that Ca forms calcite, that however was not detected by the X-ray diffraction analysis, and Mg is a part of silicates. Figure 5 shows the X-ray diffraction spectrum of the initial Ružín sediment sample. It can be seen that quartz, muscovite, plagioclase and chlorite are the major minerals in this sediment. It was also observed that the pattern

of the spectrum is not changed after submitting the sample to the subsequent leachings (steps 1-4 only). Crystalline clay minerals and silicates (fraction 5) account for 34.3 % Cu, 24.7 % Zn, 41.9 % Pb and 46.3 % Ni. However, amorphous Fe and Mn oxyhydroxides (fraction 3), although representing only a small fraction of the sediment, are the most important scavengers of the trace metals (40.6 % Cu, 44.1 % Zn, 33.8 % Pb, and 26.6 % Ni). Humic substances (fraction 4) bind a minor portion of the trace metals (16.1 % Cu, 15.6 % Zn, 19.4 % Pb, and 10.0 % Ni). A special association of Cd, i.e. the prevalence of its exchangeable and adsorbable and/or carbonate forms (fraction 1 and 2), was found, although the concentration levels are slightly higher than the detection limit.

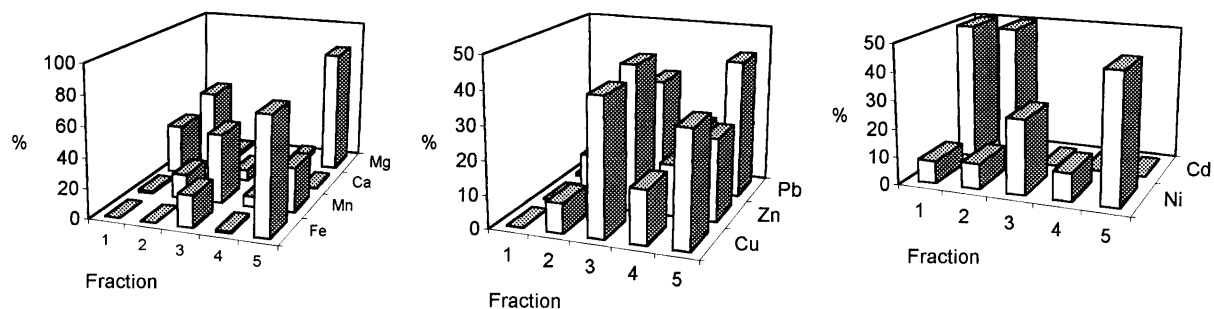


Fig.3 a-c. Concentrations of constituent (Fe, Mn, Ca, and Mg) and trace metals (Cu, Pb, Zn, Ni, Cd) in the leachates (%). Tessier's SE procedure.

Table 3. Concentrations of the constituent (a) and trace (b) metals in the leachates ($\mu\text{g.g}^{-1}$). Tessier's SE procedure.

(a)	Concentration ($\mu\text{g.g}^{-1}$)			
	Leachate	Fe	Mn	Ca
1	3	22	2640	200
2	12	224	4720	120
3	12760	640	560	400
4	775	97	9	187
5	46134	412	46	4381
Σ	59684	1395	7975	5288

(b)	Concentration ($\mu\text{g.g}^{-1}$)				
	Leachate	Cu	Zn	Pb	Ni
1	1.6	1.6	2.4	12.0	0.8
2	99.2	112.8	13.6	13.5	0.8
3	452.0	322.0	108.0	40.0	-
4	179.0	113.7	62.0	15.0	-
5	381.0	180.4	134.0	69.6	-
Σ	1112.8	730.5	320.0	150.2	1.6

However, the data obtained using the Horowitz's SE procedure have been found to be different from these obtained using the Tessier's SE procedure in the matter of constituent as well as trace metal concentrations. In general, total concentrations of constituent and trace metals (with the exception of Pb) are appreciably lower. Essentially, the total concentration Fe is only ca. one quarter. But there are also dramatic differences in the distribution of the metals into particular phases of the sediment. Accumulation of trace metals in the fraction 1 to 3 is evident. Concomitantly, all trace metals, with the exception of Ni, are almost totally absent in the fraction 4 and 5.

It is not the objective of this short communication to discuss the above disproportion between the data obtained using the above SE procedures. Nevertheless, one can notice an interesting agreement of our data obtained after the Tessier's SE procedure with these obtained by Tessier et al. (1979) on the Piereville sediment sample (Figure 6). Of course, although any direct comparison is not generally justified, it is worth mentioning that e.g. the Fe contents are comparable in both sediment samples. In the Piereville sediment, however, most trace metals are more uniformly distributed between its fractions. On the other hand, the distributions of Ni as well as Cd in both samples are in close agreement.

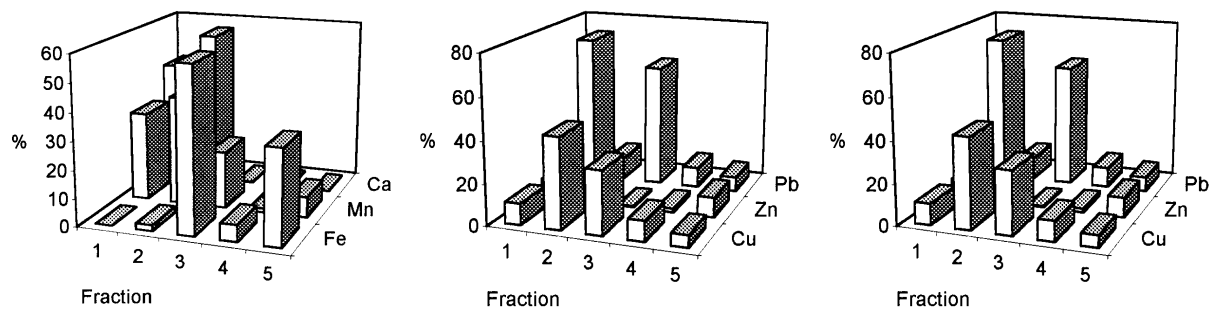


Fig.4 a-c. Concentrations of constituent (Fe, Mn, and Ca) and trace metals (Cu, Zn, Pb, Ni, Cd) in the leachates (%). Horowitz's SE procedure.

Table 4. Concentrations of the constituent (a) and trace (b) metals in the leachates ($\mu\text{g}\cdot\text{g}^{-1}$). Horowitz's SE procedure.

(a)	Concentration ($\mu\text{g}\cdot\text{g}^{-1}$)			
	Leachate	Fe	Mn	Ca
1		1.9	249	3809.5
2		289.5	305	4896.0
3		8376.5	160	29.2
4		849.2	11	27.1
5		4800.0	58	10.0
Σ		14317.1	783	8771.8

(b)	Concentration ($\mu\text{g}\cdot\text{g}^{-1}$)					
	Leachate	Cu	Zn	Pb	Ni	Cd
1		41.6	29.4	16.6	10.9	1.3
2		175.2	266.7	13.7	7.6	0.8
3		122.3	1.9	75.3	2.8	0
4		39.4	6.2	12.3	4.9	0
5		23.3	32.2	8.9	13.3	0
Σ		401.8	336.4	126.8	39.5	2.1

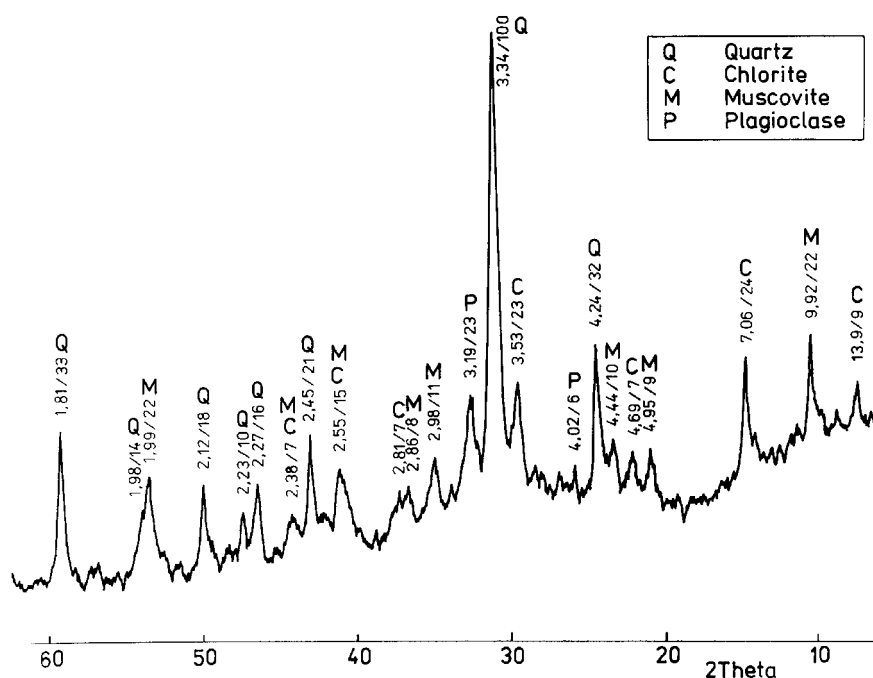


Fig.5. Diffractogram of the Hnilec sediment sample (numbers at the diffraction peaks describe the corresponding interplanar spacings in angströms and relative intensities).

Pliešovská et al. (1997) applied a modified (six-step) Tessier's SE procedure for an averaged sample of the sediment from Ružín. Unfortunately, they analyzed only Cd, Co and Pb so that the comparison with the presented data cannot be done. In any case, however, they also consider the fraction 3 to be the most important scavenger of trace metals.

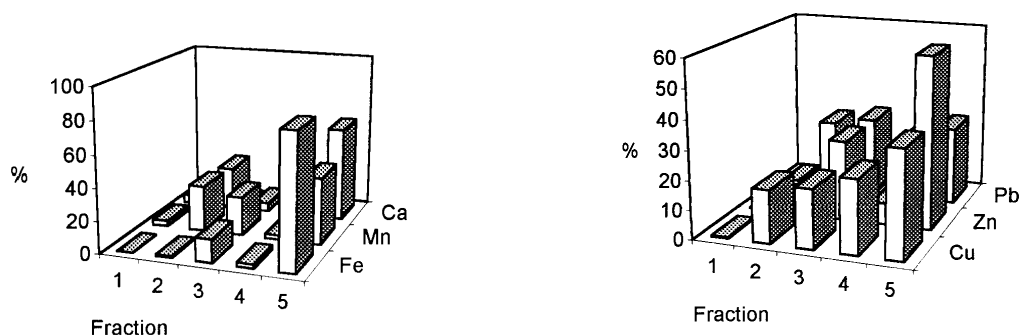


Fig.6 a-b. Concentrations of constituent (Fe, Mn, Ca) and trace metals (Cu, Zn, Pb) in the leachates (%). Pierville sediment. Tessier's SE procedure.

Conclusions

The sequential extraction (SE) procedure is advantageous in that it enables to evaluate a potential environmental availability of trace metals associated with specific sediment phases under various environmental conditions. Particularly, a major proportion of trace metals studied (25 to 50 %), being associated with mineral lattices, is essentially unavailable and it is not expected to be released into solution over a reasonable time span under the condition normally encountered in natural waters. On the other hand, the next considerable proportion of the trace elements (27 to 44 %), associated with ferro-manganese coatings, is probably available as Fe-Mn oxides, thermo-dynamically unstable under anoxic conditions. The rest of the trace metals, i.e. organics-associated (10 to 20 %) can be also available. Exchanged and adsorbed trace metals, although readily available, represent a relatively minor percentage (< 1 %). Finally, most Cd can be easily available, as it was identified in the exchangeable and carbonate forms only. The SE procedure provides an useful technological information in respect of separation methods (e.g. flotation) that could be used in cleaning the sediments.

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