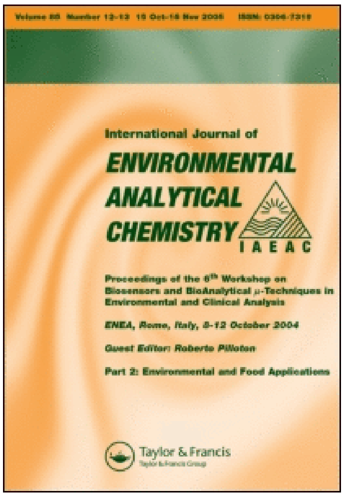

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DETERMINATION OF HEAVY METALS IN LAKE AND RIVER SEDIMENTS BY SELECTIVE LEACHING

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The sequential extraction procedure developed by Ure et al.[1] as a reference method for speciation of heavy metals in sediments has been extended. The three fractions as 1. exchangeable and bound to carbonate, 2. reducible, bound to Fe/Mn oxides, 3. oxidizable, bound to organic and sulfide compounds, were further completed by a strong acid-soluble fraction, the "pseudototal fraction." The extracting solutions were conc. nitric acid and perchloric acid. This fraction has the advantage of giving a better insight into the association mechanism of metals with mineralogical phases of the sediments. Zinc, Ni, Cd, Cr, Cu, and Pb were determined in the extracts. The sum of the contents obtained with the four-step selective leaching method was compared with those obtained with the total acid-soluble procedure and a good agreement was found. Most of the elements were found in the acid-soluble fractions indicating stable species of sediments. The critically examined three-step sequential extraction method should be used to compare the data produced by different laboratories, but the strong acid-soluble fraction of elements could add more valuable information.

Keywords: River and lake sediment; speciation; sequential extraction method; heavy metals; AAS

INTRODUCTION

Soil, and river and lake sediments are basic components of our environment, as they provide nutriment for living organisms and serve as sinks for deleterious chemical species. The composition of sediments reflects the degree of degradation and leaching introduced by weathering, and the influence of external inputs such as contamination introduced by human activities. It is necessary to know

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the mechanisms of the transport of trace metals and their complexes in river and lake to understand their chemical cycles in nature. Metal ion associations can be sorbed to organic and inorganic complexes, coprecipitated as metal hydroxides, sulfides, bound into inert positions of a mineral or soluble metal salt, etc. The sediments can be generally divided in two sections: the oxic surface layer and the anoxic sediment layer; in practice there is a gradient between the two layers, not a really sharp boundary[2]. In the oxic layer the settling particles are subject to chemical degradation that causes a remobilization of contaminants. A central role is played by the anoxic layer in the sediment as it determines the stable phases of the contaminants and metal concentrations in pore waters. Important adsorbents are Fe/Mn hydroxides, carbonates, organic matter and clay minerals.

The selective separation and direct determination of a metal may not give an accurate representation of the actual chemical form of metal present in the sediment. Thus, the individual chemical forms of a trace metal are often defined by the procedures, reagents or extractants that are used to isolate them. For this reason the method is called operationally defined speciation. Operationally defined speciation is often, and conveniently, equated with the quantification of the elements in a specific phase of a sediment, although the procedure may often be insufficiently specific. The procedure can be made more selective by employing several extractants in a defined sequence. Because of the operational nature of these schemes, the standardisation of the procedures becomes essential if results from different laboratories are to be compared. Sequential extraction schemes involving three to eight different fractions were summarized recently[3].

Both single and sequential extraction schemes were critically examined by Ure *et al.*[1] and they have recommended a three-step extraction procedure for sediments. Metals were leached from sediment samples by selective reagents for determination of fractionation patterns into operationally defined fractions: (1) exchangeable and bound to carbonates, (2) bound to Fe/Mn oxides, (3) bound to organic matter and sulfides. The procedure has many limitations, however, as the results given by sequential extraction experiments are more representative of certain operationally defined groups of metal forms and associations than of the true speciation in sediments. These assessment techniques are reasonable as a differentiated approach in the study of interactive processes between water-biota and operationally defined solid phases. The sequential extraction process can be related to a procedure in which the natural sediment is transferred to an appropriate artificial environment and the change in reaction equilibrium is registered. So, the sequential extraction can be used as an operation to reduce the complexity of the natural system and to gain a detailed understanding of trace metal speciation and mobility in sediments.

In some cases, mostly concerning the disposal of the sediments, the total concentration of trace elements is also of importance. Standards for sediments have not been set yet and the procedure usually follows the standards of soils. The sequential extraction method suggested by the BCR[1], does not contain total dissolution of the residual fraction but has often been used in conjunction with an aqua regia 'pseudototal' determination[4,5]. In our work, a four-step method has been developed in which the standard procedure is followed in the first three stages. As a fourth step, the residual fraction of the sediment is partially dissolved in strong acids.

EXPERIMENTAL

Sampling

Sediment samples were collected at two different places. The lake sediment samples were collected from Lake Balaton near Keszthely at a depth of 0.03–0.42 m from the surface of the sediment. A fibre-glass boat was driven to the selected sampling site and a special home-made sampling device was used to collect the sediments. Thus, samples were taken and they were immediately carried to the laboratory, air-dried and stored in glass bottles (Ure *et al.*[1,6]). Five portions from a depth of 0.03–0.06, 0.12–0.15, 0.21–0.24, 0.30–0.33, and 0.39–0.42 m, respectively, were thoroughly investigated. The sediments of River Malom were taken above and below a waste water discharge, over a 3 km length of the river at 14 sites, for monitoring the pollution. The upper 10 cm was sampled and the samples were treated in the same way as those from the lake.

Leaching Procedures and Reagents

The sediment samples were subjected to the sequential leaching extraction procedure developed by Ure *et al.*[1]. This method was completed with a further step, and the concentrations of elements in the residual fractions were determined. Along with the sequential leaching procedure the total acid-soluble element concentration was also determined after the digestion in a mixture of conc. $HNO_3 + H_2O_2 + HClO_4$. Analytical-reagent grade solutions (Reanal and Spectrum 3D, Hungary, and Aldrich) were used without further purification.

The extractants applied for the sediment samples were as follows:

- Solution "A": 0.11 mol/L CH_3COOH (pH = 2.8)

- Solution “B”: 0.1 mol/L $NH_2OH.HCl$, (HNO_3 pH = 2)
- Solution “C”: 8.8 mol/L H_2O_2, (HNO_3 pH = 2–3)
- Solution “D”: 1 mol/L NH_4OAc, (HNO_3 pH = 2),
- Solution “E”: 3.75 mL conc. HNO_3 + 1.25 mL $HClO_4$

The sequential leaching procedure was carried out in 30 mL glass centrifuge tubes (diameter 25 mm) with three replicates.

-1. (exchangeable and bound to carbonate) fraction: 20 ml of solution “A” was added to 0.5 g sediment in the centrifuge tube and extracted by shaking for 16 hours at ambient temperature, then the extract was separated by centrifugation for 15 minutes at a speed of 2500 rpm. The supernatant liquid was separated, 0.5 mL of spectroscopically pure HNO_3 was added and the solution was filled up to 50 mL in a volumetric flask. The residue was washed by adding 20 mL of distilled water, shaken for 15 min and centrifuged. The supernatant was decanted and discarded. The cake was broken up using a glass rod prior to the second step.

-2. (acid reducible, bound to Fe/Mn oxide) fraction: 20 mL of solution “B” was added to the residue from step 1 in the centrifuge tube and extracted by shaking 16 hours at ambient temperature. The extract was separated by centrifugation and decantation as in step 1. Washing and handling the solutions and solid residue, respectively, were carried out as in step 1.

-3. (oxidizable, bound to organic matter + sulfide) fraction: 5 mL of solution “C” was carefully added to the residue in the centrifuge tube. The vessel was covered with a watch glass and digested at room temperature for 1 hour with occasional manual shaking. The digestion was continued for 1 hour at 85 °C and the volume was reduced to a few mL by further heating of the uncovered vessel on a sand bath. A further aliquot of 5 mL of solution “C” was added. The covered vessel was heated again to 85 °C and the sample was digested for 1 hour. After cooling, the volume of the liquid was reduced for a few mL. To the cool moist residue a 25 mL of extracting solution “D” was added and the mixture was shaken for 16 hours at ambient temperature. The extract was separated by centrifugation and decantation as in step 1.

-4. (strong acid-soluble) fraction: solution “E” (3.75 mL conc. HNO_3 + 1.25 mL $HClO_4$) was added to the residue from step 3. The digestion was accomplished in 2 hours at 100 °C in water bath. After cooling 1.5 mL conc. HNO_3 and double distilled water were added to the mixture, the solution was filtered and made up to 50 mL.

The total elemental content of the non-silicate bound fraction of the original sediment was determined after digestion in strong acid-mixture. In a glass vessel 1 g of sediment sample was weighed and the mixture of conc. 10 mL HNO_3 + 5 mL H_2O_2 + 5 mL $HClO_4$ was added. The sample was heated for 2 hours at

100 °C on a sand bath. The volume of the liquid was reduced to a few mL and, after cooling, 5 mL cc HNO_3 and double distilled water were added to the mixture, filtered and made up to 100 mL. The solution was stored at 4 °C prior to analysis.

In all cases three replicate samples were extracted and measured. With each batch of extractions, blank samples, (vessel + solutions with no sediment,) were carried through the complete procedure. Before extraction, all glassware and plastic vessels were treated in a solution of 10 m/m % HNO_3 for 24 hours and washed by double distilled water.

AAS Measurements

Metal concentration of the fractions was determined by atomic absorption spectrometry, in an electrothermal atomization mode using Perkin- Elmer 5100 PC, HGA 600 graphite furnace (GEM software); Perkin-Elmer 303, HGA 70 graphite furnace, instruments. The calibrant solutions were prepared from 1 g/L of each metal (Merck standard solutions) and freshly diluted before use. Linear regression method was used to calculate the calibration curves.

RESULTS AND DISCUSSION

Ure *et al.*[1] performed an interlaboratory study of sediment sequential extraction and it was found that Zn concentrated mostly in the exchangeable and bound to carbonate fractions. In the three-step procedure the CV (coefficient of variance) fell between 10 and 25 %. They did not measure the strong acid-soluble fraction, however, it was indicated that the total elemental content should be measured separately. The relative binding strength of Zn in lake and river sediments determined by the present, modified 4-stage sequential leaching procedure can be seen in Figures 1/a and b.

In the sediment sample of Lake Balaton, the concentration of Zn ranged between 17 and 39 mg/kg, and there was no linear correlation with the depth of the sediment column. The exchangeable and bound to carbonate fractions were found to be in the range of 20 to 35 %, and were unrelated to the oxic or anoxic nature of the samples. The reducible and oxidizable fractions proved to be entirely insignificant, whereas, the strong acid-soluble fraction reached 45–65 % of the total Zn content. It means that at least half of the Zn in the lake sediments is in stable form and in natural conditions the Zn-compounds can be found as solid species.

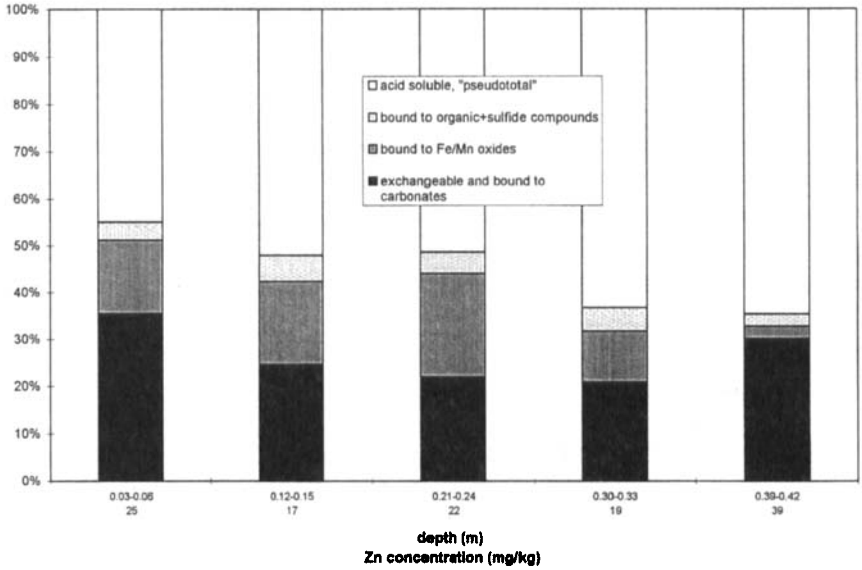

FIGURE 1/a Distribution of Zn in sediment samples (Lake Balaton) and total Zn content, mg/kg.

In an industrially polluted river, the sediment samples contained much higher concentrations of Zn, namely 170–825 mg/kg. Sample 1 was collected above of the discharge of the waste water and it can always be considered as a reference

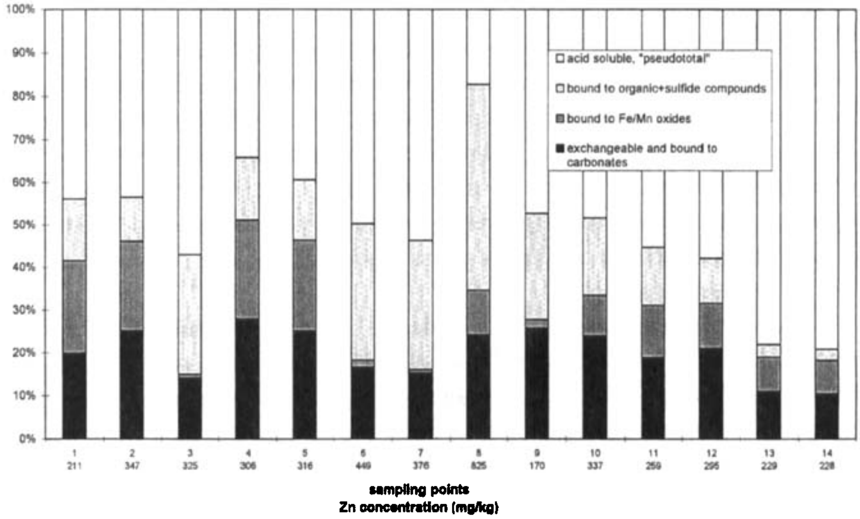

FIGURE 1/b Distribution of Zn in sediment samples (River Malom) and total Zn content, mg/kg.

point. At sampling point 8, the water slows down in a bend, so the suspended solid materials have more time to settle to the bottom of the river. Consequently, the first 10 cm of the sediment is richer in aggregated solids resulting in a more elevated elemental concentration (825 mg/kg Zn). Figure 1/b shows a dominant strong acid-soluble, 'pseudototal' fractionation pattern, while the exchangeable ion content is only 20 % on average. Samples were collected in the upper 10 cm of the sediment, and this part of the oxic sediment was in an equilibrium with the water body. The results of the sequential leaching experiments give the picture that the oxidizable (3.) and strong acid-soluble, 'pseudototal' (4.) fractions are together between the 55 and 90 % and the Zn mainly accumulated in the stable fractions.

Tessier *et al.*[7] found in sediments that exchangeable and organic Zn was relatively low. Martin *et al.*[8] employed a five-step modified Tessier procedure for analysis of sediments collected in the Loire, Rhone, Gironde and Huanghe rivers. It was found that the half of Zn concentrated in the exchangeable fraction and an other 10 % of Zn in the carbonate associated portion. Different patterns were obtained by Sakellariadou[9] in the investigation of marine sediments from the Mediterranen Sea off Thraki, northern Greece. Results based upon the sequential extraction of 177 samples (modified Tessier procedure) show that the Zn was mostly enriched in the reducible (28 %), oxidizable (15 %) and residual (50 %) fractions, and no exchangeable Zn has been identified in the samples. These findings refer to the importance of strong acid-soluble, 'pseudototal' fractions, since, depending on the nature of the samples, this portion should play an important role on the characterization and disposal of sediments.

Fractionation patterns of Ni in the lake and river sediments are shown in Figures 2/a and b, respectively. The concentration of Ni in the Lake Balaton sediments ranged between 45 and 58 mg/kg, two fractions (bound to organic and sulfide compounds and strong acid-soluble) contained the 85 % of total Ni. The oxidizable fraction was 40–60 %, and the reducible (bound to Fe/Mn oxides) was <3 %. There is no considerable difference among the 5 samples collected in different depths of the sediment column. Oxic sediments from Malom river contained 28–400 mg/kg Ni and the strong acid-soluble, 'pseudototal' fraction was generally dominant. Depending on the distance from the waste water discharge (between sampling sites 1 and 2), the Ni content considerably varied, from the 28 mg/kg background (this value is even much smaller than we found in the Lake Balaton) up to 400 mg/kg at sampling site 8. In the detailed study of Ure *et al.*[1] the Ni distributed almost evenly among the exchangeable, oxidizable, and reducible fractions. However, there was no extraction step on the acid-soluble content of metals, and the total Ni content has not been published either. Thomas *et al.*[10] applied the same three-stage sequential extraction procedure that

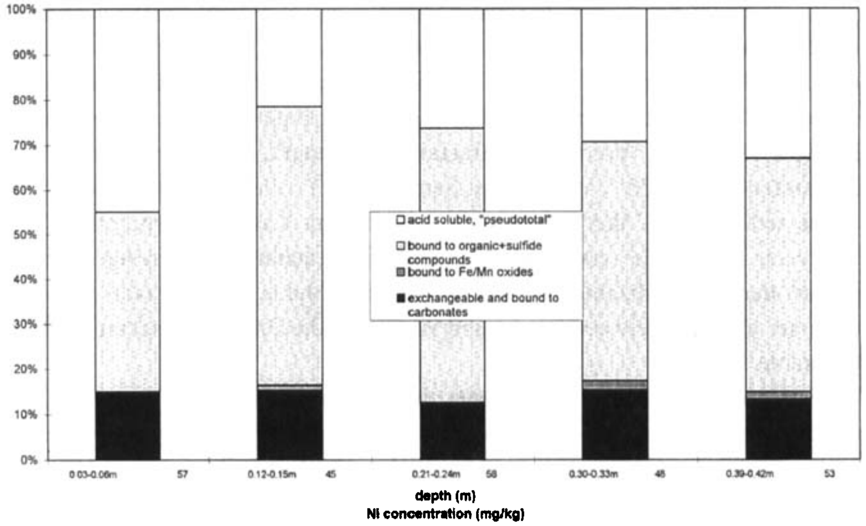

FIGURE 2/a Distribution of Ni in sediment samples (Lake Balaton) and total Ni content, mg/kg.

was suggested earlier[1] to two river sediments from an industrial region of East Catalonia, Spain. The partitioning of Ni was different in each sediment and could indicate differences in the source of the elements. In one sediment, 70–80

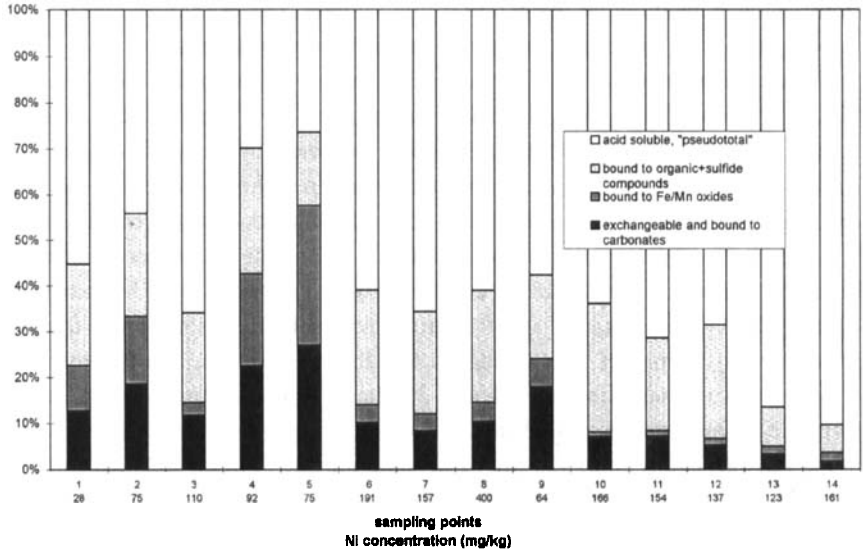

FIGURE 2/b Distribution of Ni in sediment samples (River Malom) and total Ni content, mg/kg.

% of the total concentration of Ni was found in the oxidizable fraction, probably associated with the sulfide component, whereas in the other sample, most of the Ni partitioned equally between exchangeable and bound to organic + sulfide phase. Considering our findings, 30–90 % of Ni (in sample 14 it was 144 mg/kg Ni) was associated with the strong acid-soluble, 'pseudototal' fraction and it should be in stable form under normal environmental circumstances. Sediment samples collected at northern Greece[9] show a similar fractionation pattern; 65 % of Ni concentrated in the residual fractions and there was no exchangeable metal identified by the modified Tessier method. It seems that a considerable part of metal can be found associated with or in the silicate minerals.

Both of the sediments studied show similar distribution of Pb (Figures 3/a and b). Significant amounts of Pb were found mainly in the strong acid-soluble, 'pseudototal', and bound to organic + sulfide fractions, which was not unexpected, as lead forms stable organic complexes and resistant sulfides. The river sediment was polluted with one magnitude higher concentration of Pb compared to the lake one (Figure 3/b). In the lake sediments the exchangeable + bound to carbonate and bound to Fe/Mn oxides fraction are <10 % (Figure 3/a). This indicates that only 0.4 mg/kg of Pb can be in equilibrium with the water body. At this point of the lake this is a negligible pollution, and should be considered as a natural background level.

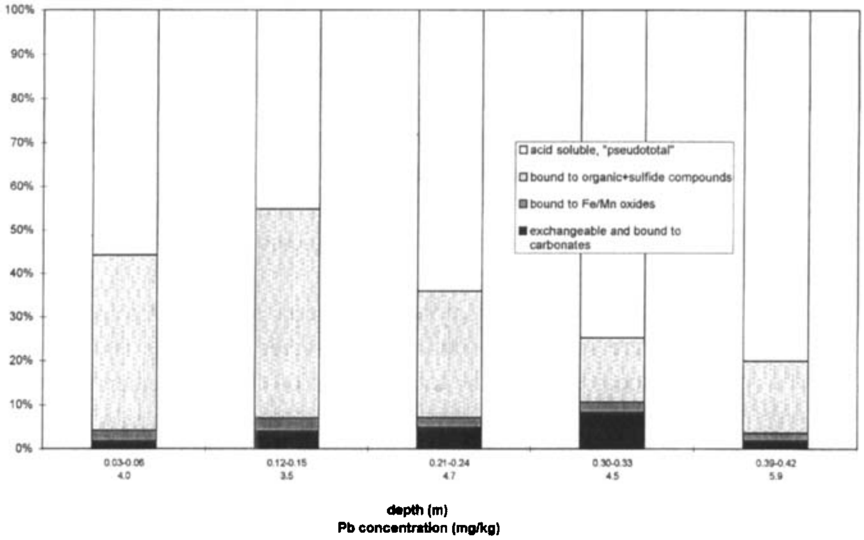

FIGURE 3/a Distribution of Pb in sediment samples (Lake Balaton) and total Pb content, mg/kg.

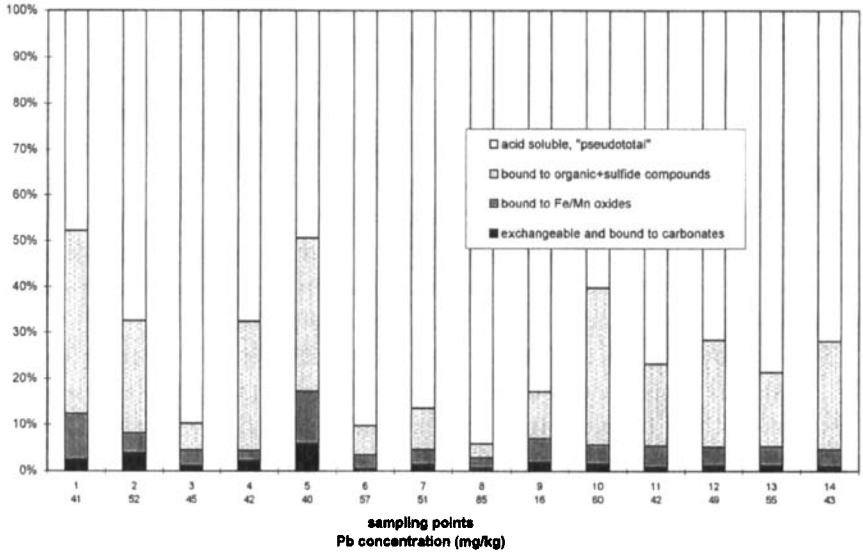

FIGURE 3/b Distribution of Pb in sediment samples (River Malom) and total Pb content, mg/kg.

In the river sediment, the Pb was fairly evenly found among the 14 samples except samples 8 and 9. The amount of Pb was the highest one at site 8 (85 mg/kg), and the next sample contained always the lowest quantity (16 mg/kg). River sediments collected in Spain[10] gave the same picture; Pb was found only in the oxidizable fraction; in the other two fractions, it was below the detection limit. Fractionation pattern of Pb in marine sediments[9] demonstrates that reducible and residual fractions are the major associations (>85 %). This also underlines our suggestion, namely, the three-step sequential extraction procedure does not explore a considerable portion of metal pollution. The strong acid-soluble, 'pseudototal' (extracted by $HNO_3 + HClO_4$) or bound to silicates, 'total' (extracted by $HF + HNO_3$) fractions furnish a better picture on the real distribution of toxic elements in sediment samples.

Recently, it was found that the fractionation patterns of Cr and Cu in different sediment samples were somewhat similar[1,9,10]; organic + sulfide and residual fractions contained the >90 % of the total amount of the two elements. Therefore, only the distribution of Cr is discussed. The concentration of Cr ranged between 1 and 5 mg/kg in the lake sediment (Figure 4/a), and the exchangeable and bound to carbonates, as well as bound to Fe/Mn oxides fractions were negligible (the Cu concentration varied from 3 to 12 mg/kg). Sediment samples collected at the bottom layer (0.39–0.42 m) contained the highest amount of Cr and Cu in the combined stable organic complexes-sulfides and silicate fractions.

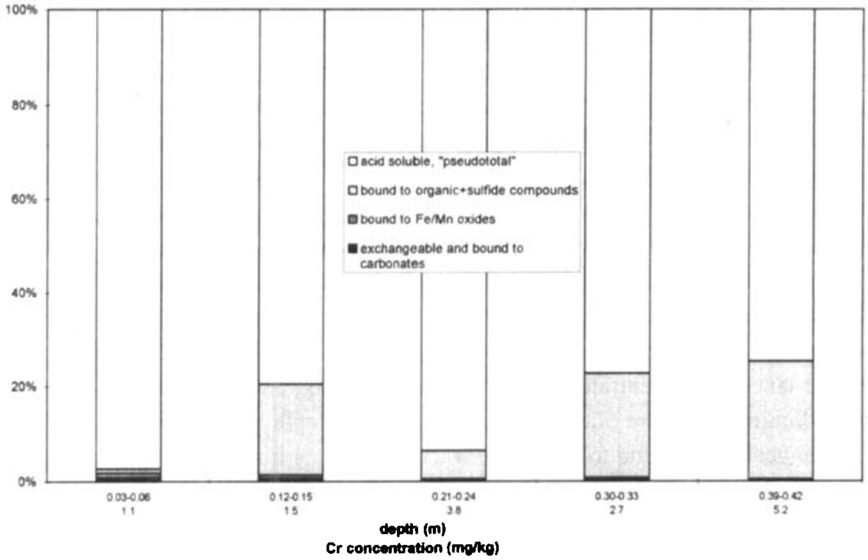

FIGURE 4/a Distribution of Cr in sediment samples (Lake Balaton) and total Cr content, mg/kg.

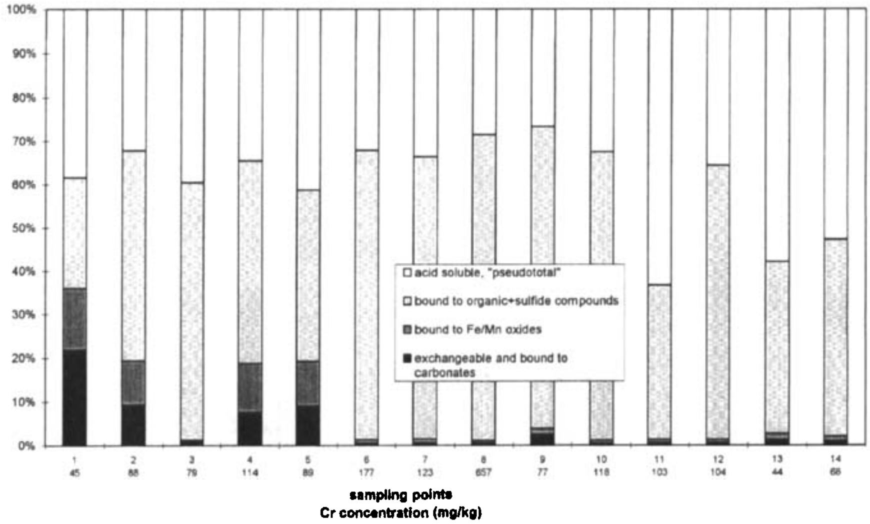

FIGURE 4/b Distribution of Cr in sediment samples (River Malom) and total Cr content, mg/kg.

In the river sediments, sometimes two orders of magnitude higher concentrations of metals were measured (Figure 4/b). The background level of Cr was obtained as 45 mg/kg (site 1.) and at the sampling site 8., 657 mg/kg of Cr was measured. Similarly, the 55 mg/kg Cu found at the unpolluted part of the river sediment increased to 1274 mg/kg at site 8. It is quite obvious that, due to intensive industrial activities and the lack of the appropriate water purification technology, the Malom river is heavily polluted by Cr and Cu. Upon disposal of the sediments on to any agricultural area great care should be taken.

The chemical speciation of Cd varies widely and reflects the oxidation state of the sediment. Under anoxic conditions, Cd is highly immobile[11] that means it can only be released after strong oxidation with H_2O_2. In the sediment samples of the lake the concentration of Cd was <0.2 mg/kg, and the oxidizable fraction was dominant (Figure 5/a). Depending upon the depth of the layers the ratio of exchangeable + bound to carbonate fraction changes from 40 % (upper layer) to 10 % (at the depth of 0.21–0.24 m) and the importance of the reducible fraction considerably increased. However, due to the very low concentration of Cd, the natural environment in the Lake Balaton shows the background values.

One order of magnitude higher amount of Cd was found in the sediment of Malom river at site 1 (2.2 mg/kg). This point located upstream of the waste water discharge point (Figure 5/b). The total Cd content of other sediment samples (site 2–14), indicated that the waste water was not polluted by Cd.

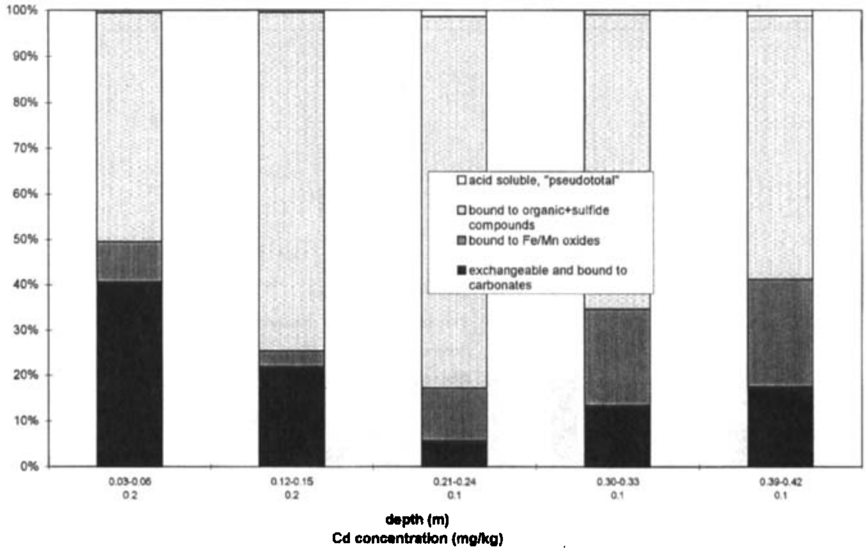

FIGURE 5/a Distribution of Cd in sediment samples (Lake Balaton) and total Cd content, mg/kg.

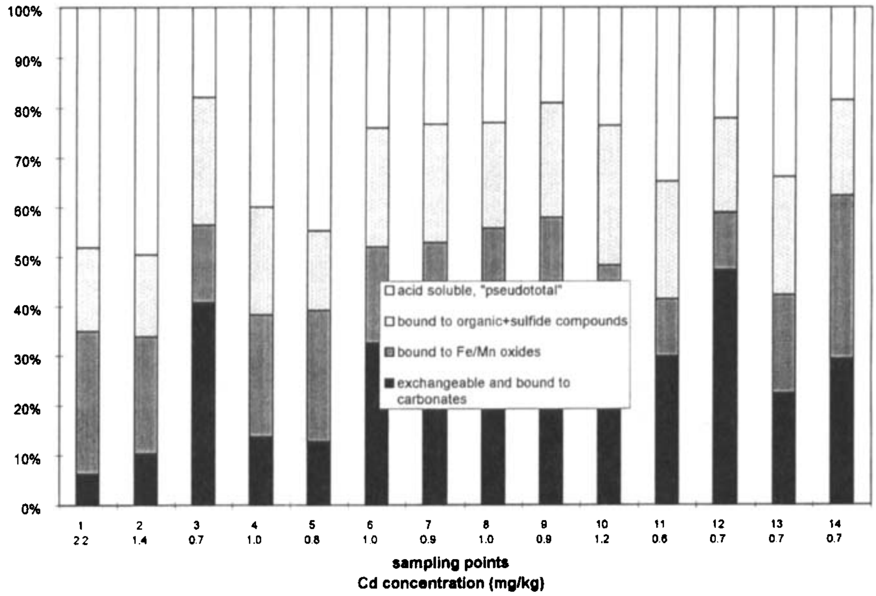

FIGURE 5/b Distribution of Cd in sediment samples (River Malom) and total Cd content, mg/kg.

Nevertheless, the significance of the fact that exchangeable + bound to carbonate and the reducible fractions have been greatly increased. This is important when considering sludge disposal landfill. Thomas *et al.*[10] obtained two different fractionation patterns for two river sediments but the values were considered too low to be interpreted accurately. An evaluation of sequential extraction procedures for natural sediments was reported by Lee *et al.*[12]. In their study of anoxic harbor sediment heavily contaminated with Cd, the electron beam microprobe was used to obtain direct evidence of trace metal partitioning. Cadmium was found to be most frequently associated with sulfur (in about 90% of the particles). Thermodynamic calculations also suggested the formation of CdS. However, when the samples were studied by sequential extraction, exchangeable (34%), carbonate (36%), and reducible oxide-bound (22%) Cd represented the major fractions. This disagreement is probably due to improper sample handling. Proper sample preparation and experimental conditions are the main prerequisite for attaining reliable data.

The total elemental content of the sediments is of importance to compare the values to that of the standard methods. In our study, after the step 3., the residue was further extracted by strong acids and only the silicate phases have not been digested. So, the sum of the 4 steps gave the ‘pseudototal’ elemental content of

TABLE I Pseudototal element contents found by summing the contents measured in the 4 steps of the sequential extraction procedure (Σ1–4) compared with pseudototal contents of the whole original sediment found by a single digestion (single)

Sampling	Cd mg/kg		Cr mg/kg		Cu mg/kg		Ni mg/kg		Pb mg/kg		Zn mg/kg	
sites	*Σ1–4.*	*single*	*Σ1–4.*	*single*	*Σ1–4.*	*single*	*Σ1–4.*	*single*	*Σ1–4.*	*single*	*Σ1–4.*	*single*
1	2.4 ± 0.3	2.2 ± 0.2	45 ± 8	45 ± 13	53 ± 6	56 ± 2	31 ± 4	28 ± 5	46 ± 4	41 ± 5	227 ± 68	211 ± 11
2	1.5 ± 0.2	1.4 ± 0.1	103 ± 9	88 ± 19	203 ± 21	185 ± 6	75 ± 8	75 ± 8	57 ± 6	52 ± 5	377 ± 22	347 ± 16
3	1.4 ± 0.6	0.7 ± 0.1	66 ± 15	79 ± 41	258 ± 48	186 ± 6	84 ± 10	110 ± 9	32 ± 4	45 ± 5	259 ± 54	325 ± 15
4	1.1 ± 0.2	1.0 ± 0.1	100 ± 10	114 ± 43	203 ± 19	236 ± 7	82 ± 9	92 ± 6	46 ± 8	42 ± 4	300 ± 14	306 ± 10
5	0.9 ± 0.1	0.8 ± 0.1	99 ± 8	89 ± 36	155 ± 12	174 ± 4	74 ± 6	75 ± 10	38 ± 5	40 ± 4	287 ± 6	316 ± 10
6	1.5 ± 0.2	0.9 ± 0.3	189 ± 18	177 ± 57	588 ± 55	453 ± 47	161 ± 20	191 ± 42	50 ± 8	57 ± 10	387 ± 37	449 ± 10
7	1.0 ± 0.2	0.9 ± 0.2	111 ± 13	123 ± 75	308 ± 17	277 ± 15	104 ± 10	157 ± 54	46 ± 7	51 ± 3	310 ± 27	376 ± 8
8	1.0 ± 0.2	1.0 ± 0.1	629 ± 69	657 ± 19	1553 ± 122	1274 ± 91	362 ± 35	400 ± 60	78 ± 6	85 ± 2	817 ± 30	825 ± 38
9	1.2 ± 0.2	0.9 ± 0.1	60 ± 12	77 ± 11	225 ± 32	233 ± 30	64 ± 14	64 ± 20	21 ± 3	16 ± 2	169 ± 20	170 ± 42
10	1.7 ± 0.6	1.2 ± 0.6	87 ± 9	118 ± 23	243 ± 15	276 ± 7	105 ± 9	166 ± 30	63 ± 25	60 ± 21	297 ± 27	337 ± 21
11	1.2 ± 0.6	0.6 ± 0.2	76 ± 14	103 ± 3	190 ± 22	215 ± 5	88 ± 24	154 ± 16	49 ± 22	42 ± 10	240 ± 17	259 ± 8
12	1.6 ± 0.7	0.7 ± 0.2	76 ± 17	104 ± 6	183 ± 21	188 ± 5	75 ± 18	137 ± 34	56 ± 22	49 ± 10	240 ± 19	295 ± 4
13	1.2 ± 0.2	0.7 ± 0.3	37 ± 4	44 ± 18	58 ± 10	59 ± 5	62 ± 14	123 ± 12	53 ± 16	55 ± 10	172 ± 21	229 ± 14
14	1.3 ± 0.8	0.7 ± 0.1	50 ± 9	68 ± 9	85 ± 19	92 ± 2	55 ± 18	161 ± 18	52 ± 14	43 ± 6	189 ± 15	228 ± 5

the sediment samples. These values were compared to the results of the digestion of the whole sediment with strong acids (HNO_3, H_2O_2 and $HClO_4$) in one step (single extraction) (Table I). Except for Cd at concentrations near the detection limit the sum of the four steps agreed well with the pseudototal content found by acid digestion of the whole sediment. Along with the mean values the confidence limits were also calculated. Only 0.5 mg samples were extracted, and due to the heterogeneity of sediments, the three parallel determinations have been, in some samples, slightly disagreed. The harmony between the two data sets was good. The four-step sequential extraction procedure was appropriate for the determination of metals in sediments.

CONCLUSIONS

Sequential extraction procedures offer the advantage to simulate, to a certain extent, the various natural environmental conditions. In our method the first three-stage was in fully accordance with that was developed by BCR, so it should allow the data produced by different laboratories to be compared worldwide. The fourth step, (strong acid-soluble, 'pseudototal' fraction), enables a deeper understanding the association of elements with the compounds of sediments.

Acknowledgement

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