

# Single and Sequential Extractions for Element Fractionation of Sediment Samples\*

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The BCR recommended sequential extraction procedure and single extraction with EDTA were modified for this study. Single and sequential extraction procedures were applied to four sediment samples coming from industrially polluted region of Eastern Slovakia. This paper describes the preparation of samples, gives analytical results in each extraction step for cadmium, lead, copper, and chromium and brings comparison of these results with total element content analyses realized by independent spectral method. Spectrochemical methods are in general predominantly used for assessment of element contaminants in various components of the environment, though in actual geochemical research the optical method took a representative place as an analytical ending with respect to the element detection.

During last two centuries, which means from the start of industrialization, many changes occurred in the global statement of chemical compounds existing on earth surface. Contamination of widespread territories by foreign matters suggested interest for evaluation of natural and anthropogenic element distribution in environment components (water, soils, sediments). Actual geochemical research has skipped from total element contents observation to the study of elements forms in chosen systems [1]. Total content of element in the sample is not a suitable indicator of biological availability for plants [2]. Element toxicity is dependent on its chemical form, mobility, degree of transformation, and bioavailability, which allow element contaminants to enter the food chain [3]. Knowledge of toxicology sciences, of different degree of toxic effects of several chemical compounds of element contaminants on biological systems, gave birth to the effort of analytical resolution – fractionation of several element-binding forms in environmental and biological materials [4]. Quantification of chemical and binding forms of elements in sediments and soils has given the basis for monitoring of bioavailability and mobility of contaminants in environment [2].

Fractionation through sequential extraction procedure is often used for evaluation of ecotoxicity and bioavailability of chemical and element-binding forms. Determination of broader operationally and functionally defined forms is time-consuming but informative. This kind of fractionation brings more information about potential mobility of metal contaminants. The significance and comparability of extraction results is highly dependent on the used procedure and because of them the interlaboratory uniformity of used leaching procedures is necessary.

In this paper the results of sequential extraction procedure, which is a modification of BCR (Community Bureau of Reference) recommended extraction, and results of single extraction with ethylenediaminetetraacetic acid are presented. The sediment samples from industrially stressed area of Spišsko-Gemerské Rudohoric Mountains were studied.

The natural sediment is a full mixture of several phases, especially of weathering and erosion rests of clay materials, aluminosilicates, iron and manganese hydroxides, sulfides, carbonates, and particles coming from biological and industrial activity, which are transported through liquid phase. River sediment is

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a complicated dynamical system, which is chemically and biologically reactive. Precipitation and adsorption of dissolved metals from aquatic phase by interaction on sediment surface are seldom controlled by the formation of well-defined poorly soluble complex sediments [5]. Fractionation means identification and quantification of different fractions of sediment, on which heavy metals are bound [4]. Presence of elements in sediments and soils is temporary, because soil and sediment are only parts of biochemical cycle of elements in ecosystem.

Time of element abundance in existing form is different, depends on element character, on physicochemical form, kind of chemical binding, mobility, and external conditions of systems.

For understanding of physicochemical process of fixation, mobility, and metal transport serves the method of sequential extraction-fractionation.

For resolution of the existing trace element form in soils, sediments, and sludge many selective extractive advances were developed, which consist in consecutive-sequential leaching of element portion binding on main components of solid phase. Reactive agents are selected on the basis of selectivity for the relevant physicochemical form. The most frequently used leaching scheme became the method suggested by *Tessier* [6]. It was applied and seriously tested by a great number of authors [7–10].

Similarity of soil and sediment matrix allows application and optimization of procedure usual for the evaluation of hygienic state of soils with respect to sediments. In "soil monitoring" in the Slovak Republic for evaluation of hygienic state of soils single extraction with  $0.05 \text{ mol dm}^{-3}$  EDTA for determination of heavy metal contents is used. So specified element contents are marked as releasable contents including different element forms from the aspect of their solubility.

In this work the leaching medium  $0.05 \text{ mol dm}^{-3}$  EDTA for extraction of sediment was applied. Sequential extraction is otherwise time-demanding, but it provides more detailed information about origin, biological and physicochemical availability and mobility of trace elements. Fractionation through the sequential extraction enables to find out the mode of binding of the given element, but not real chemical form of its existence. The sequential extraction procedures after dividing metals into groups on the basis of predefined advances, offer information about environmental risk contamination of water by external condition changes [11, 12]. The method of sequential extraction for this work was recommended by BCR according to the methodology by *Fiedler et al.* [13]. The main reason for uniform methodology establishment rests in need of comparative results produced by different laboratories, as well as in need of reference material preparation, necessity to control the accuracy of their analyses. It deals with three-step sequential extraction. Except of the proposed extraction

steps the first step for elements extractable at water phase and the fifth step for determination of element contents in sediment rest were added. These "element rests" are bound on silicate minerals. Comparison BCR scheme with the most famous and used extraction procedure according to *Tessier* is listed in *R* [14].

The resultant five-step applied extraction distributes the isolated metals to the following fractions:

Water-soluble fraction – characterizes water-soluble share of trace elements in the form of mainly mineral salts, water-soluble and exchangeable fractions are probably not strictly separated [15];

Exchangeable and carbonate fraction – characterizes the share of trace elements absorbed on mineral salts and bound in carbonates, which are released in water phase by change from neutral conditions (pH 7) to soft acid;

Reducible fraction – this is characterized by trace element share bound on Fe and Mn oxides, these are thermodynamically unstable and release elements in water phase by change of redox potential of dissolving medium (water);

Oxidizable organic and sulfide fraction – is characterized through the share of elements bound in organic material and sulfides. These elements are released in water phase in consequence of oxidation and following decomposition of organic matter and sulfides by change of physicochemical conditions;

Residual fraction – defines share of elements fixed in primary and secondary minerals – in mineral lattice, these are not released into water phase under conditions normally probable in environment.

Summary description of the used extraction scheme is in *Fig. 1*.

There are published and discussed results of heavy metal contaminants determinations: Cd, Pb, Cu, and Cr in sediments. They were analyzed after one-step extraction with  $0.05 \text{ mol dm}^{-3}$  EDTA and after sequential extraction described in *Fig. 1*.

The measurements are a part of the project, purpose was to develop and verify an analytical methodology for determination of individual element forms in river sediments. Their allowed limits are listed in the Methodical Instruction of the Slovak Republic Ministry of Environment [16] for contaminated fluvial and bed-load sediments. Works with similar orientation were rarely solved within the frame of Slovakia.

## EXPERIMENTAL

The fluvial sediment samples were taken in industrially stressed region Spišsko-Gemerské Rudohorské Mountains, four sampling places were chosen (*Table 1*).

Fluvial sediment samples were dried at temperatures to  $40^\circ\text{C}$ , then sieved and milled in agate planetary treadmill on fineness under  $0.09 \text{ mm}$ . For

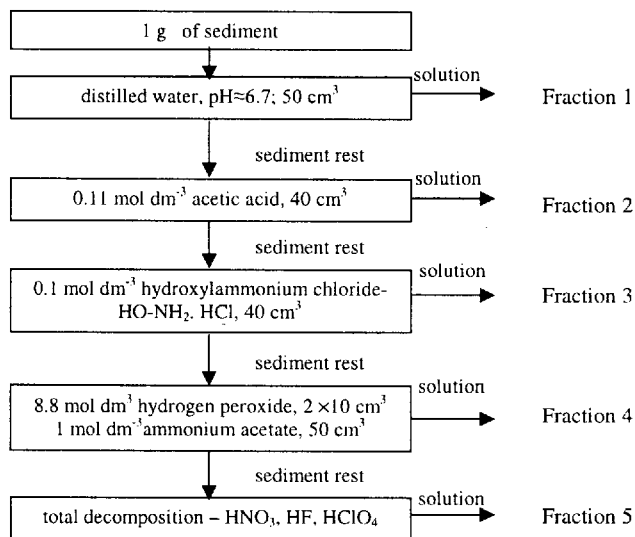


Fig. 1. Description of the applied sequential extraction scheme.

Table 1. Sampling Places of Chosen Region

Description of sample	Place of sampling	River/Stream
River sediment 1	Rudňany - Markušovce	Hornád
River sediment 2	Slovinky	Poráčský jarok
River sediment 3	Richnava	Hornád
River sediment 4	Jaklovce	Hnílec

assessment of extractable element share of Cd, Cu, Cr, and Pb 1 g of homogenized sample was weighted.

Extraction in individual steps was performed in a mechanical shaker for 16 h by sequential extracting agents and besides that for 1 h by simple extraction with  $0.05 \text{ mol dm}^{-3}$  EDTA (number of vibrations 200

$\text{min}^{-1}$ , temperature  $(20 \pm 2)^\circ\text{C}$ ). After finishing the extraction the solution was centrifuged by 4000 rpm, for 20 min. Solutions obtained from individual extraction steps were saved in polyethylene vessel at temperature  $4^\circ\text{C}$ . From the solution prepared in the described way, extractable shares of chosen elements were determined and results are average values of 5 repeated analyses.

For determination of studied elements in each leached fraction the following analytical methods were applied: for Cr, Cu, and Pb – atomic emission spectrometry with inductively coupled plasma and ultrasonic nebulization of sample, for Cd – atomic absorption spectrometry with electrothermal atomization. AES measurements were carried out by spectrometer Liberty 200 (Varian) with ultrasonic nebulizer (Cetac) and AAS measurements by atomic absorption spectrometer SpectrAA-400 with electrothermal atomizer GTA-96 (Varian). For the determinations of total element contents in studied fluvial sediments roentgen-fluorescent spectrometry has been applied and measurements were realized by spectrometer SpectroX-LAB.

## RESULTS AND DISCUSSION

The column diagrams listed in Figs. 2–5 represent distribution of studied elements throughout the process of extraction, summary content, which is the sum of contents in five leaching steps, comparison of summary contents with results of total element analyses obtained by roentgen-fluorescent spectrometry, and results of single extraction with  $0.05 \text{ mol dm}^{-3}$  EDTA. The running of five-step extraction allows the following discussion:

– Extraction from sediment to water phase (1st step) for studied elements does not overlap 1.5 %

Distribution of Cd in sediment samples

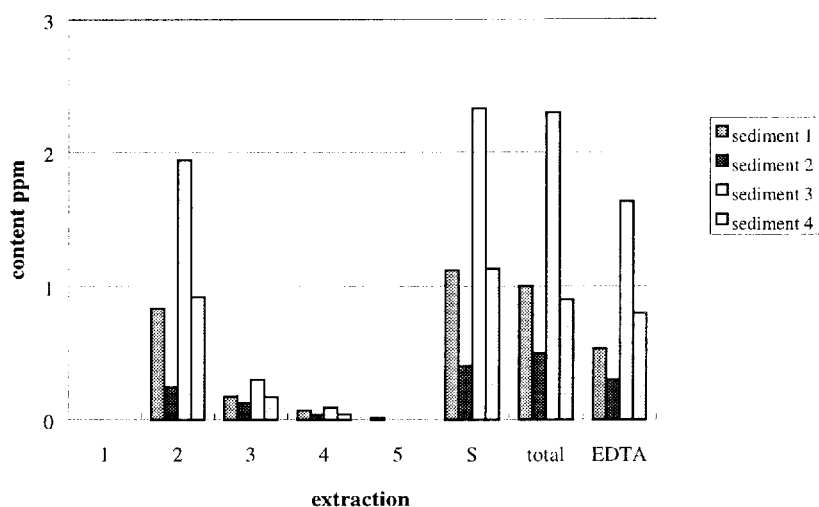


Fig. 2. Distribution of cadmium in sediment samples. Notice: 1–5 – extraction steps, S – summary content, which is the sum of the contents in five leaching steps, total – total element content analysis obtained by the XRF method, EDTA – single extraction with  $0.05 \text{ mol dm}^{-3}$  EDTA.

Distribution of Pb in sediment samples

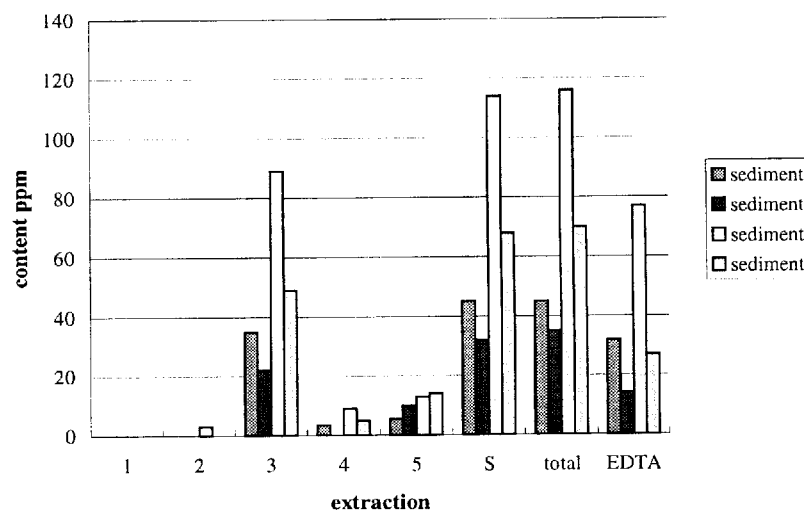


Fig. 3. Distribution of lead in sediment samples. Denotation as in Fig. 2.

Distribution of Cu in sediment samples

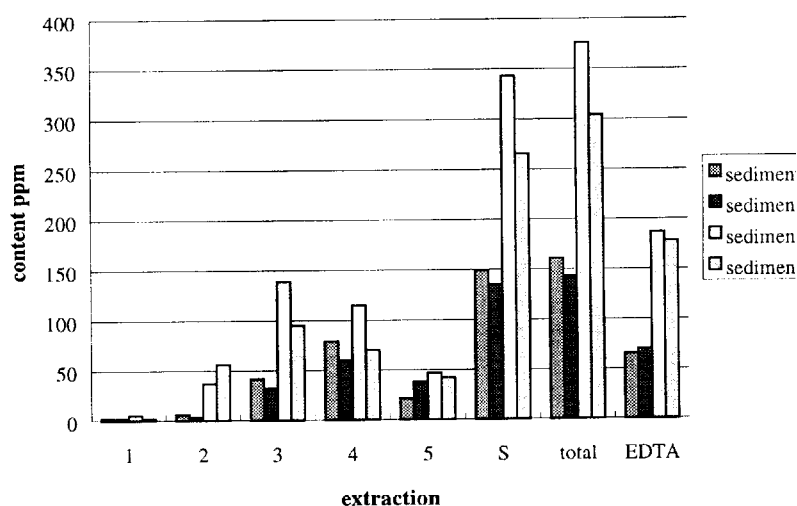


Fig. 4. Distribution of copper in sediment samples. Denotation as in Fig. 2.

of total contents. This fact shows that in the natural system water—sediment dynamic equilibrium was achieved and present 1.5 % leached element share by extraction into water represents solubility due to pH changes of water used by extraction;

– Cadmium in all sediment samples is extracted mostly in the second step ( $0.11 \text{ mol dm}^{-3}$  acetic acid), namely in dependence on the sample in the range 60–80 % of total element contents. During the second, third, and fourth steps, which represent exchangeable, carbonate, reducible, and organic-sulfide fraction, practically 100 % of cadmium content is leached. It can mean high potential mobility of this contaminant in bleeding area, which could be achieved by environment pH changes (Fig. 2);

– Lead is practically leached in all four samples in the third step ( $0.1 \text{ mol dm}^{-3}$  hydroxylammo-

nium chloride), in amount 70–80 % of total content (Fig. 3);

– Copper is already leached into distilled water (step) and by all sediments does not overlap 1.5 % of total element contents, in surroundings of  $0.11 \text{ mol dm}^{-3}$  acetic acid (2nd step) the extracted share is moved percentage scope 2.2–18.6 % and in the third step (in  $0.1 \text{ mol dm}^{-3}$  hydroxylammonium chloride) in range 23–40 %. The content maximum corresponds to the sample with the maximal copper content (sediment 3). In the fourth step ( $8.8 \text{ mol dm}^{-3}$  hydrogen peroxide and  $1 \text{ mol dm}^{-3}$  ammonium acetate) this interval was 33–53 % and at the residual step 13–28 % (Fig. 4);

– Chromium is not leached in the first and second steps at all, in the third and fourth steps it is extracted by all samples only to 6 % of total content

Distribution of Cr in sediment samples

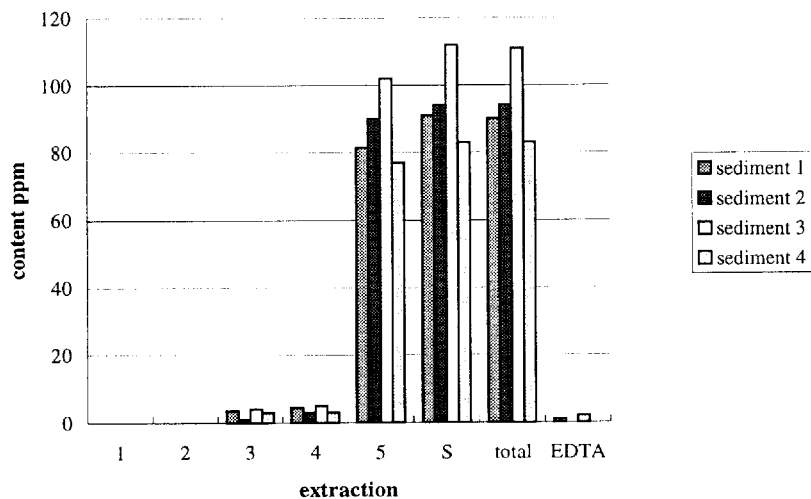


Fig. 5. Distribution of chromium in sediment samples. Denotation as in Fig. 2.

and so more than 90 % of total chromium contents in analyzed samples remain till the residual step (total decomposition) of the leaching procedure (Fig. 5). This fact shows that Cr is incorporated in the lattice structure of sediment.

Content magnitudes of total element contents for sediment samples, analyzed by the XRF method, are in accordance with the sum of contents (*i.e.* counts of contents of individual steps). It is documented in Figs. 2–5. Single extraction is suitable to discuss as follows:

– Cadmium is for all four samples extracted with  $0.05 \text{ mol dm}^{-3}$  EDTA similarly as with  $0.11 \text{ mol dm}^{-3}$  acetic acid, which separates exchangeable and carbonate fraction by sequential extraction. Figs. 2–5 document that results of the second step of sequential extraction are in agreement with the results of extraction with EDTA;

– In the case of lead, the small contents in the first and second extraction steps are determined (values are in average on the level of detection limit of the method), and the results of extraction with EDTA are comparable with the results of the third sequential extraction step (by all four sediment samples). The third step represents reducible element fraction (extraction into  $0.1 \text{ mol dm}^{-3}$  hydroxylammonium chloride);

– Values of copper content in surroundings of  $0.05 \text{ mol dm}^{-3}$  EDTA are by all studied samples higher than the sum of contents of the first, second, and third extraction step. It could be said that into EDTA is in some sediment samples partly extracted also the share bound on organic matter and sulfides, it means part from the fourth step of sequential extraction;

– Chromium is practically not extracted in accordance with the results from sequential extraction (chromium content is in average on the level of detection limit of the method), which is verified only by the presence of chromium of geogenic origin.

Ethylenediaminetetraacetic acid is not able to release from the sediment chromium bound in silicate matrix.

## CONCLUSION

Following the presented facts, it is possible to state that with the applied extraction agents the behaviour of sediments from all sampling areas is very similar, and results of five-step sequential extraction well correspond with the total content determinations realized by roentgen-fluorescent spectrometry. Estimated values of concentration of monitored elements show mobility of studied element forms and availability of five-step sequential extraction for monitoring chosen toxic elements in sediments.

From the sediment matrix of chosen sampling areas with  $0.05 \text{ mol dm}^{-3}$  EDTA it is possible to extract shares corresponding to the first four steps of sequential extraction. Extraction efficiency is (for chosen sediment samples) element-specific and dependent on the composition of sediment matrix.

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## REFERENCES

1. Flórián, K., Matherny, M., and Pliešovská, N., *Microchim. J.* 51, 26 (1995).
2. Broekaert, J. A. C., Gücer, S., and Adams, F., *Metal Speciation in the Environment*. Springer-Verlag, Heidelberg, 1990.
3. Kimáková, T., *Slov. vet. čas.* 25, 213 (2000).
4. Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., Van Leuwen, H. P., and Lobinski,

- R., *Pure Appl. Chem.* 72, 1453 (2000).
5. Hakansson, K., Karlson, S., and Allard, B., *Sci. Total Environ.* 43, 87 (1989).
  6. Tessier, A. and Campbell, P. G. C., *Anal. Chem.* 60, 1475 (1988).
  7. Van Valin, R. and Morse, J. W., *Mar. Chem.* 11, 535 (1982).
  8. Rapin, F. and Förstner, U., *Proc. Int. Conf. on Heavy Metals in the Environment*, p. 1074. Springer-Verlag, Heidelberg, 1983.
  9. Martin, J. M., Nirel, P., and Thomas, A. J., *Mar. Chem.* 22, 313 (1987).
  10. Kim, N. D. and Fergusson, J. E., *Sci. Total Environ.* 105, 191 (1991).
  11. Mackových, D., *Candidate Dissertation Work*. Technical University Košice, 1994.
  12. Krakovská, E. and Mackových, D., *Chem. Pap.* 50, 121 (1996).
  13. Fiedler, H. D., Lopez-Sanchez, J. F., Rubio, R., Raurer, G., Quevauviller, P., Ure, A. M., and Muntau, H., *Analyst* 119, 1109 (1994).
  14. Vojteková, V., Mackových, D., Krakovská, E., Remeteiová, D., and Tomko, J., *Proc. of Int. Conf. "Hutní Analytika"*, p. 134. Luhačovice, 2002.
  15. Kuznetsov, V. A. and Shimko, G. A., *Method of Sequential Leaching in Geochemical Research*. Nauka i Tekhnika, Minsk, 1990.
  16. *Methodical Instruction of the Slovak Republic Ministry of Environment from 27th August 1998 No. 549/1998-2, for risk evaluations of contaminated fluvial and bed-load sediments.*