



ESTIMATION OF THE MOBILITY OF HEAVY METALS IN THE ENVIRONMENT USING SEQUENTIAL EXTRACTION PROCEDURES

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Abstract

Applicability and relevance of two sequential extraction procedures for the fractionation of element content of sediments and soils are presented in this comparative study. An agricultural soil sample from Nagyhörcsök and a contaminated lake sediment from Gödöllő was selected as samples representing different level of pollution. Element content of the samples was fractionated using the original BCR procedure which was originally developed for the fractionation of heavy metal content in aquatic sediments. As an alternative for more adequate characterization of environmental mobilization a new procedure was applied that is based on sequential extraction with supercritical CO₂, subcritical H₂O and their 1:10 mixture in a supercritical fluid extractor (SFE).

Keywords

Heavy metals, environmental mobility, sequential extraction, sediment, soil, gravitation dust

1 INTRODUCTION

Risk assessment of heavy metal contamination in the soil/water/atmosphere system is based on fractionation of metallic element content of environmental samples according to their environmental mobility. (The expression fractionation in this paper is used according to IUPAC recommendations [1] in which the term of species, speciation analysis, element speciation and fractionation are clearly defined.) Mobility of an element according to the solubility of the different binding classes can be estimated by solvents sequentially applied which contain increasingly more and more aggressive reagents [2]. The first sequential extraction procedure for characterization of mobility of heavy metals in aquatic sediments was developed by Tessier et al. [3] who classified the metal content of sediments according to solubility and binding forms of metallic species. Based on this essential work several 5-8-step sequential extraction schemes were developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed [4]. The total time demand of these procedures is usually 5-6 days, while duration of the applied batch leaching steps is determined by the long setting up time of partition and other heterogeneous equilibria. The European Union (EU) member states attempted to harmonize these methods and the Community Bureau of Reference (BCR, now Standard, Measurement and Testing Programme) recommended a simplified three-stage sequential extraction procedure and developed a sediment reference material (CRM 601) certified for Zn, Cd, Pb, Ni, Cr, and Cu amounts extractable by the proposed procedure [5]. In this method the water soluble, the weakly adsorbed and the carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step, so it does not model the primary natural pathways of mobilization with water dissolution and bicarbonate formation. Due to the numerous operations and reagents applied, there is a risk of contamination during the whole procedure. Readsorption of extracted metals during the phase separation can lead to analyte losses. In the extracts the high reagent's concentrations may cause strong matrix effects during the spectrochemical element detection.



The original BCR procedure was modified to avoid the analyte losses during the second leaching step due to the pH instability [6]. The BCR procedure in its original and modified versions was successfully applied to aquatic sediments and soils [7, 8, 9], but its application can be problematic in some cases (e.g. samples with high carbonate or organic matter content). As an alternative to the BCR procedure, a continuous flow sequential extraction procedure was developed in our laboratory a few years ago [10]. The samples were mixed in appropriate rate with pure quartz sand (SiO_2) weighed into a column of a supercritical fluid extractor (SFE). Firstly supercritical CO_2 , then under the same conditions subcritical H_2O and finally their 1:10 ratio (V/V) mixture were applied as extractants as it is described in Table 1.

Table 1: Scheme of the sequential extraction in the supercritical fluid extractor (SFE)

Step	Extractant	Chemical information	Duration
1	Supercritical CO_2 (in SFE)	CO_2 -soluble mobile organic bound fraction	60 min
2	Subcritical H_2O (in SFE)	Water soluble fraction	60 min
3	$\text{H}_2\text{O}/\text{CO}_2$ (10:1) (in SFE)	Carbonate bound fraction	60 min
4	$\text{HNO}_3/\text{H}_2\text{O}_2$ (out of SFE)	Residual	

Firstly an apolar organic fraction which can contain organic pollutants, too can be obtained by this procedure. In the 2nd step the water-soluble, and in the 3rd step the carbonate-bound fraction can be collected. The present paper will compare the application of the original (unmodified) BCR and the above mentioned continuous flow ($\text{CO}_2/\text{H}_2\text{O}/\text{H}_2\text{O}+\text{CO}_2$) sequential extraction onto a soil and a sediment sample.

2 EXPERIMENTAL

2.1 Samples

A sediment sample was selected from the Gödöllő – Isaszeg lake system study [8]. This sample has a relatively high organic carbon and CaCO_3 content ($\text{CaCO}_3 = 7.6\%$, $\text{TOC} = 11\%$). A soil sample was selected from a field experiment of heavy metal contamination performed by Research Institute for Soil Science and Agrochemistry (RISSAC) at Nagyhorcsók experiment site [11]. The selected untreated soil sample contains $\text{CaCO}_3 = 4.8\%$ and $\text{TOC} = 3.5\%$. The BCR 701 lake sediment sample was used as described in the original BCR information [12, 13].

2.2 BCR sequential extraction procedure

The BCR sequential extraction procedure was carried out according to the original protocol [5, 12] (Fig. 1). In the present investigation nitric acid/ H_2O_2 digestion was applied in a Milestone 1200 MEGA microwave oven according to our former studies for gaining the residual fraction [8] instead of aqua regia digestion.

2.3 Sequential extraction in the supercritical fluid extractor (SFE)

The solid samples were mixed manually with SiO_2 (Reanal) in a mass ratio of 1:20. Stainless steel extraction columns were filled as follows: first a layer of 1 g SiO_2 , then 10 g of sample- SiO_2 mixture (and SiO_2 for the procedure blank measurements, respectively), and the remaining volume was filled with SiO_2 again. Extractions were performed in a supercritical fluid extractor consisting of two Jasco PU 980 HPLC pumps (the CO_2 pump was cooled to -6°C), a Jasco CO 980 column oven and Jasco 880-81 back pressure regulator (heated to 60°C). Solvents were applied as presented in Table 1 but the



duration of the 3rd step was extended to 90 min according to our optimization study [14]. The extractions were performed under the following conditions: solvent flow rate $1 \text{ cm}^3 \text{ min}^{-1}$, oven temperature: 80°C , pressure: 27 MPa. Extracts were collected in polyethylene bottles and analyzed by inductive coupled plasma optical emission spectrometry (ICP-OES) and inductive coupled plasma mass spectrometry (ICP-MS), respectively. The measured concentrations were corrected by subtracting the concentrations of the procedure blank.

2.4 Element analytical detection

Concentration of Zn, Cd, Pb, Ni, Cr and Cu in the BCR extracts was measured with a Jobin Yvon 24 sequential ICP optical emission spectrometer. Operation parameters were set up according to the manufacturer's instructions. Calibration for each type of extract was performed by Merck multielement standard with matrix-matching dilution.

Concentration of Al, Ca, Fe, K, Na, P, S in the SFE extracts was measured with a Perkin Elmer Optima 3300 DV ICP optical emission spectrometer, while other elements (As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Er, Gd, Ge, Hg, Ho, In, La, Li, Lu, Mg, Mn, Mo, Ni, Pb, Sc, Se, Sr, Ti, V, Y, Yb, Zn) in these extracts were determined with a Thermo Elemental X series ICP mass spectrometer. Operation parameters were set up according to the manufacturer's instructions.

3 RESULTS

3.1 BCR procedure

The extracted concentrations related to sample dry weight obtained in soil, sediment and BCR 701 samples are presented in Fig. 1. It can be observed that the measured concentrations of Zn, Cd and Pb in the BCR 701 sample are in good agreement with the certified values but extraction efficiency of Ni, Cr and Cu is less than that of modified BCR procedure as it was experienced in our preliminary study, too [9].

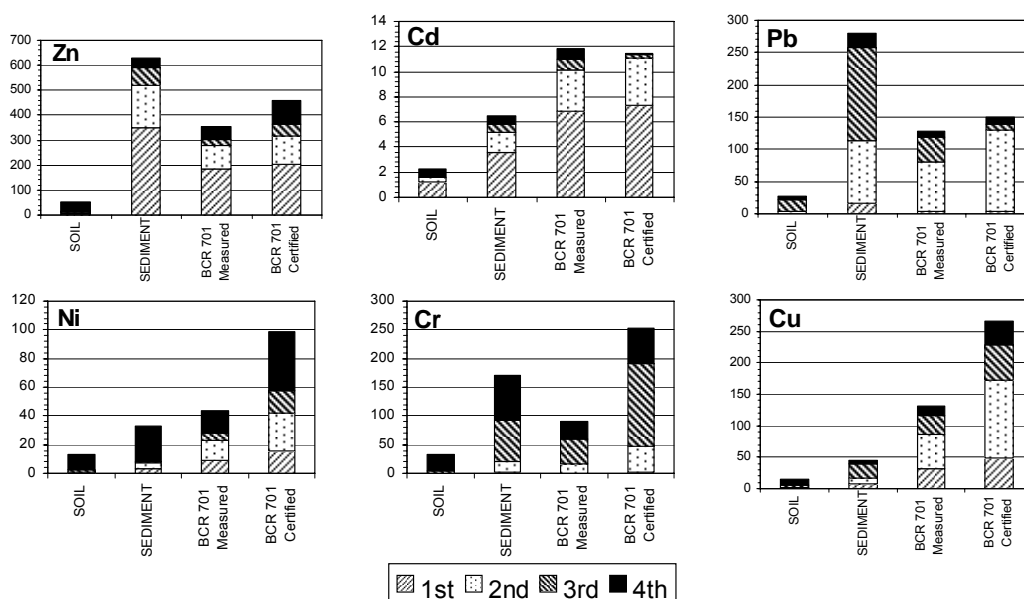


Figure 1: Extracted element concentrations (mg kg^{-1} related to dry weight) obtained by the unmodified BCR sequential extraction in BCR 701, soil and sediment samples



3.2 SFE procedure

The extracted concentrations of Pb, Cu, Zn and Cd related to the sample dry weight from soil, sediment and gravitation dust samples obtained by SFE sequential procedure are summarized in Fig. 2. The other elements listed in the experimental part were also detected, but their concentration could not be evaluated reliably after the correction with the procedure blank.

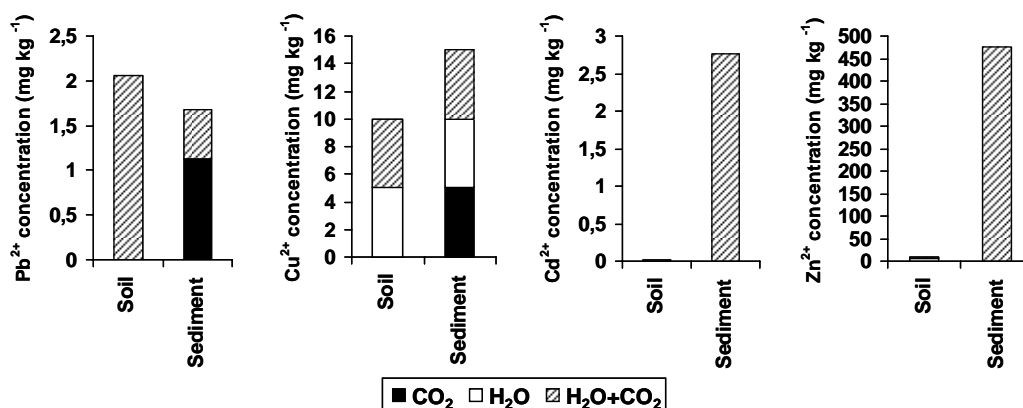


Figure 2: Extracted Pb, Cu, Zn and Cd concentrations (mg kg^{-1} related to dry weight) in the fractions obtained by the SFE sequential extraction of the soil and sediment samples

The results show that the easily mobilizable copper, cadmium and zinc content in the sediment is higher than in the soil sample, whereas lead content in the soil sample is higher than that of the sediment. The ratio of the fraction extracted by subcritical water-carbon dioxide mixture (i.e. the carbonate-bound fraction) is significant in case of all four elements. However, lead (and to a less extent copper) could also be detected in the fraction extracted by supercritical carbon dioxide (i.e. bound to organic material) in case of the sediment sample. The latter results are in good agreement with our former studies on the BCR sequential extraction of the sediments from the Gödöllő-Isaszeg fishpond chain [8].

3.3 Comparison of results gained from BCR and SFE procedures

Comparison of extracted amounts by BCR 1st step [BCR(1)] and SFE 2nd + 3rd step [SFE(2+3)] is summarized in Table 2. It can be observed that the sum of the water soluble (SFE 2nd step) and the carbonate bound (SFE 3rd step) fractions can be higher than the amount gained by BCR 1st step, however, lead was found in much higher concentration in the BCR (1) fraction of the sediment.

Table 2: Comparison of the element contents (mg kg^{-1} related to dry weight) found in the 2nd and 3rd step of the SFE procedure [SFE (2+3)] and 1st step of the BCR procedure [BCR (1)] extracts (n.d.: not detected)

Sample	Extract	Cd	Cr	Cu	Ni	Pb	Zn
Soil	SFE (2+3)	n.d.	n.d.	n.d.	n.d.	2.06	n.d.
	BCR (1)	1.27±0.04	n.d.	1.16±0.01	n.d.	0.29±0.02	5.83±0.01
Sediment	SFE (2+3)	2.76	n.d.	n.d.	1.76	0.54	475
	BCR (1)	3.55±0.01	1.68±0.01	7.39±0.07	3.67±0.01	16.76±0.04	349±1



4 CONCLUSION

On the basis of our results it can be established that the total heavy metal contamination level of the studied sediment sample is higher than that of the soil sample. The information about environmental mobility of element content of different kind of solid environmental samples gained by BCR procedure is limited to six elements (heavy metals) in sediments according to its validation [12, 13]. By this procedure the water soluble and carbonate bound fractions cannot be distinguished, while they are measured together, however, it characterizes the heavy metal mobilization by redox reactions in the aquatic environment better. The SFE procedure offers an alternative to the BCR procedure for the characterization of the above mobilization pathways for different kind of samples. During the 1st extraction step by supercritical CO₂ the apolar organic adsorptive layer is removed from the surface of particles, thus the hydration and dissolution in water is promoted. The extracted amount by SFE (2+3) step is commensurable with BCR (1) step. SFE (2+3) extracted amount is higher than BCR (1) in some cases, while it contains a significant amount of metals complexed with water soluble humic acids [15]. The SFE extracts are more diluted than those of BCR, matrix effects are lower, and it requires a better detection power than ICP-OES e.g. ICP-MS. Further improvement of the SFE method should be performed, so columns of smaller size can be used for the same sample amount with less SiO₂, so that the blank values will decrease.

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