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Continuous-flow fractionation of selenium in contaminated sediment and soil samples using rotating coiled column and microcolumn extraction

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ABSTRACT

Dynamic fractionation is considered to be an attractive alternative to conventional batch sequential extraction procedures for partitioning of trace metals and metalloids in environmental solid samples. This paper reports the first results on the continuous-flow dynamic fractionation of selenium using two different extraction systems, a microcolumn (MC) packed with the solid sample and a rotating coiled column (RCC) in which the particulate matter is retained under the action of centrifugal forces. The eluents (leachants) were applied in correspondence with a four-step sequential extraction scheme for selenium addressing “soluble”, “adsorbed”, “organically bound”, and “elemental” Se fractions extractable by distilled water, phosphate buffer, tetramethylammonium hydroxide, and sodium sulphite solutions, respectively. Selenium was determined in the effluent by using an inductively coupled plasma atomic emission spectrometer.

Contaminated creek sediment and dumped waste (soil) samples from the abandoned mining area were used to evaluate resemblances and discrepancies of two continuous-flow methods for Se fractionation. In general, similar trends were found for Se distribution between extractable and residual fractions. However, for the dumped waste sample which is rich in organic matter, the extraction in RCC provided more effective recovery of environmentally relevant Se forms (the first three leachable fractions). The most evident deviation was observed for “adsorbed” Se (recoveries by RCC and MC are 43 and 7 mg kg^{-1}, respectively). The data obtained were correlated with peculiarities of samples under investigation and operational principles of RCC and MC.

1. Introduction

Selenium is an element with diverse properties of its species, which are of environmental and ecotoxicological concern. Se is essential for animals and humans and its deficiency can cause diseases. At the same time Se is toxic even at relatively low concentrations that are higher than those needed for health care. The common range of Se in soils is 0.01–2 mg kg^{-1}, but the distribution varies from almost zero up to 1250 mg kg^{-1} [1]. Physicochemical mobility and bioaccessibility of Se in soil environments strongly depend on its individual species and type of binding with the sample matrix [1–4]. Se occurs at four oxidation states. Depending on soil conditions, it can exist as selenate (VI), selenite (IV), elemental Se (0), and selenide (-II). In addition, it is associated with sulfur and various organic compounds, either complexed or built into the molecular and high-molecular structures. All these species can be present in soils and sediments concomitantly, which makes the chemistry of Se in the environmental compartments quite complex. In general, selenate is fairy soluble and thus available to plants, whereas selenite can be adsorbed onto the soil surfaces. Elemental Se and metal selenides are both insoluble under reducing conditions, and their oxidation in soil is slow [1]. Hence, estimating the risks associated with Se in sediments or soils as well as possible remedies require a detailed understanding of its biogeochemistry and thus its speciation [2].

There is no validated analytical methodology for the determination of Se species in relevant concentrations in soils [1]. In order to understand and evaluate Se distribution and ensuing physicochemical mobility, sequential extraction has been generally used [1–6]. Sequential extraction procedures (SEP) are based on the successive use of aqueous solutions of increasing aggressiveness encompassing salts, acids as well as reducing, oxidizing, and complexing reagents for sequential release of trace elements associated to targeted phases. According to the recommendations of International Union of Pure and Applied Chemistry (IUPAC) [7], this process of classification and quantification of elements in solid samples

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Table 1
Physicochemical properties and elemental analysis of the experimental samples.

Parameter	B 26571	B 26575
Sample type	Creek sediment	Dumped waste, bore core 350–360 cm
pH (H_2O, 1:5)	6.9	5.9
Organic C (%)	6.2	11.5
Fe_2O_3 (%)	3.4	6.2
SiO_2 (%)	28.3	18.7
CaO (%)	2.8	4.7
Zn (mg kg^{-1})	79500	92800
Cu (mg kg^{-1})	3050	31100
Se (mg kg^{-1})	215	228

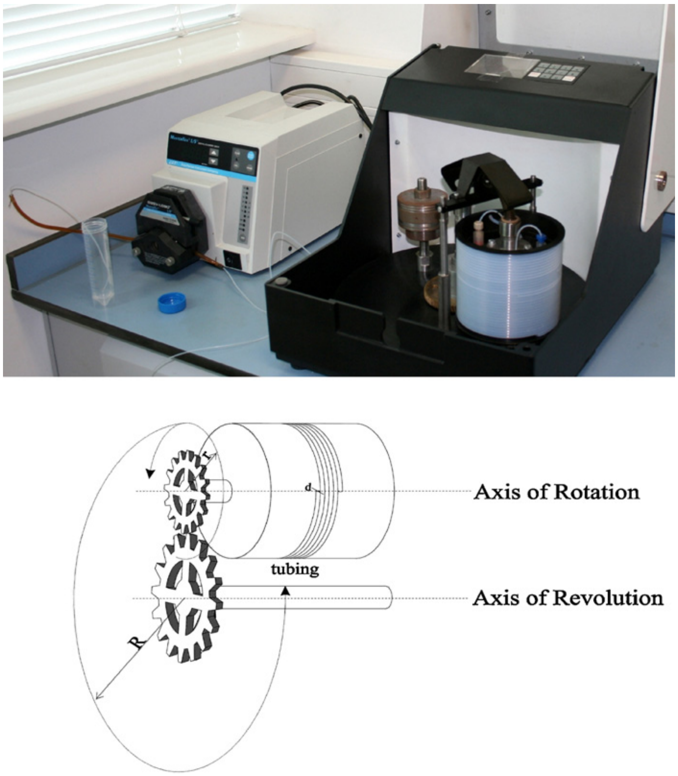

Fig. 1. Planetary centrifuge with a vertical column drum. Photo and schematic representation.

according to the bonding to predefined phases or chemical reactivity is defined as fractionation.

So far, the fractionation of Se in soils and sediments has been performed under batch extraction conditions using different sequences of leaching reagents [1–6]. Despite their wide use in environmental studies, the conventional batch-wise SEP are rather laborious and time consuming [8] and are subjected to several potential errors such as sample contamination and sample losses because of a series of shaking, centrifugation, and filtration operations. Additional problems are the phase overlapping and the re-adsorption phenomenon. Besides, SEP based on steady-state extractions – resulting in equilibrium – cannot mimic environmental scenarios accurately because naturally occurring processes are always dynamic, whereby the ecotoxicological relevance of the information provided may be rather questionable [9]. The above problems can be minimized using dynamic (non-equilibrium) fractionation methods, relying on the continuous supply of fresh extractant volume to the solid sample under investigation [10,11]. Two dynamic approaches which have proven well suited for the fractionation of trace elements in environmental substrates are the so-called rotating coiled column (RCC) extraction [12] and microcolumn (MC) extraction [13–15]. In RCC, the particulate sample (usually 500 mg) is retained by centrifugal forces whereas different eluents are continuously pumped through. No membranes or filters are used. In MC, filters should be selected considering both particle size and packed solid amount. For soils, no backpressure has been observed for fractionation of up to 300 mg by resorting to polytetrafluoroethylene (PTFE) filters with 1.0 μm pore size. However, filters of 0.45 μm pore size are mandatory for reliable fractionation of sediments. Each approach has advantages and limitations which are the result of the particular column designs and operational parameters. RCC and MC as flow-through dynamic extraction assemblies have been critically compared taking as example the fractionation of Cu, Pb and Zn in soil and sediment samples [16]. Notwithstanding the different extraction conditions set by both methods, similar trends of metal distribution between separated fractions were generally found.

To the best of our knowledge, there are no published data on the dynamic fractionation of Se in soils and sediments. Therefore, this is the first research in this direction. The sequence of leaching reagents proposed by Ponce de León et al. [6] has been chosen for the dynamic fractionation of Se using RCC and MC continuous-flow extraction. The efficiency of two approaches for the recovery of environmentally relevant Se species from anthropogenic contaminated samples has been evaluated.

2. Experimental

2.1. Samples and reagents

Two anthropogenic 90 μm sieved samples were under study (Table 1). Both samples have been taken in the old abandoned mining area (Mansfeld region, Germany). B 26571 is a creek sediment sample collected near the abandoned tailings. Sample B 26575 is taken from a bore core of dumped non-ferrous ore processing waste at a depth of about 3.6 m below surface. This sample is relatively rich in organic carbon (11.5%) and by convention may be regarded as an anthropogenic transformed soil sample. The total element contents in the samples were determined by energy dispersive X-ray fluorescence spectrometry (EDXRF) (X-LAB 2000, Spectro A.I.).

All chemicals used for the preparation of leaching solutions (Table 2, scheme by Ponce de León et al. [6]) were analytically grade reagents.

2.2. Continuous-flow fractionation in a rotating coiled column (RCC)

The continuous leaching of selenium was performed on a planetary centrifuge with a vertical one-layer coiled column drum developed and fabricated in the Institute of Analytical Instrumentation of St. Petersburg, Russia. A schematic illustration of the RCC set-up is shown in Fig. 1. The planetary centrifuge has a revolution radius $R = 140$ mm and a rotation radius $r = 50$ mm. The β value ($\beta = r/R$) is 0.36. The two axes of the instrument are parallel. The column was made of a PTFE tube with an inner diameter of 1.5 mm and total inner capacity of 20 mL. The tube length was about 10 m.

Before commencing the leaching procedure, the spiral column was filled with distilled water (the first eluent), after which the solid sample (about 300 mg) was introduced into the column (in the stationary mode) as a suspension in 10 mL of the water at a flow rate of 10 mL min^{-1}. After this, extra 5 mL of water were added into the sample test-tube and injected into the column. Then, while the column was rotated, aqueous solutions of different reagents, used as the mobile phase, were continuously fed to the column inlet at a flow rate of 1.0 mL min^{-1} using a peristaltic pump (Minipuls

Table 2
Two representative sequential extraction schemes for the fractionation of Se in soils and sediments. Reactants and corresponding fractions.

Protocol	Step	Reagents/conditions	Fraction	Extracted species
Ponce de León et al. [6]	1	Distilled water (24 h at 37 °C)	"Soluble" Se	Non-adsorbed selenite and selenate species; (methane seleninic acid) [3]
	2	0.5 mol L^{-1} KH_2PO_4/K_2HPO_4, pH 7 (24 h at 37 °C)	"Adsorbed" Se	Selenate (mostly for sediments [5,6]), selenite (mostly for soils [3]) and unidentified high molecular weight selenium species [6] adsorbed onto the surface of sample components
	3	5% tetramethylammonium hydroxide (24 h at 37 °C)	"Organically bound" Se	Non-soluble in water selenite, organically bound selenium species
	4	1.0 mol L^{-1} Na_2SO_3, pH 7 (24 h at 37 °C)	"Elemental" Se	Elemental selenium and remaining extractable selenium
Zhang and Moore [5] modified by Wright et al. [2]	1	0.25 mol L^{-1} KCl (2 h at 25 °C)	"Soluble/exchangeable" Se	Non-adsorbed selenite and selenate species
	2	0.1 mol L^{-1} K_2HPO_4, pH 8.0 (2 h at 25 °C)	"Adsorbed" Se	Selenate (mostly for sediments [5,6]), selenite (mostly for soils [3]) species adsorbed onto the surface of sample components
	3	0.1 mol L^{-1} NaOH (4 h at 25 °C)	"Organically associated" Se	Inorganic Se, predominantly Se(IV) [3], associated with organic soil components
	4	0.25 mol L^{-1} Na_2SO_3, pH 7.0 (4 h in ultrasonic bath; rinsed twice with 0.25 mol L^{-1} Na_2SO_3)	"Elemental" Se	Predominantly elemental Se
	5	5% NaOCl, pH 9.5 (30 min at 90 °C)	"More recalcitrant forms" of organic Se	Selenium associated with refractory organic compounds, metal selenides, remaining extractable selenium

3, Abimed-Gilson, Langenfeld, Germany). The solid sample was retained inside the rotating column as the stationary phase under the action of centrifugal force field throughout the experiment. The recovery of different forms of selenium was achieved by successive changing the eluents according to the scheme proposed by Ponce de León et al. [6] (Table 2). Sub-fraction volume was 15 mL. Since the inner volume of the rotating column and connecting tubes is known, the individual fractions were differentiated by recalculating the volume of the effluent. It should be noted that the mixture effects of extracting agents in the column of 1.5 mm inner diameter are negligible. In some cases, if two successive eluents are of different nature (for example, acidic and basic) and can react with each other, additional washing steps (pumping few milliliters of water) are required [11]. However, if the sequence of leaching reagents proposed by Ponce de León et al. [6] is applied, there is no need in intermediate washing steps.

After the leaching procedure has been finished, the residue of the solid sample was removed from the stopped column by pumping water at a flow rate of 10 mL min^{-1} and then filtered for the following digestion.

The collected fractions of the effluent were directly analysed without filtration by ICP-AES (CIROS, Spectro A.I., simultaneous spectrometer with CCD working in axial torch position). A matrix matched calibration was utilized by employing spiked leaching solutions.

2.3. Continuous-flow fractionation in a packed microcolumn (MC)

A particulate solid sample (about 300 mg) was placed into the microcolumn (Fig. 2). As described in [17], the extraction MC unit employed in this work is made of polyoxymethylene that can tolerate the extractants used. The unit comprises two polyoxymethylene end-caps, PTFE membrane supports designed for maximizing extractant flow through the entire sample, silicone gaskets and a cylindrical sample container (height of 22 mm and diameter of 47 mm) with an approximate inner volume of 2.8 mL. To avoid the sample loosing during the experiment, two microfibre filters (Whatman, Maidstone, UK) were put at the inlet and the outlet of the MC. The silicone gaskets were used to prevent leakage. Alike RCC extraction, different eluents were sequentially pumped through the MC at a flow rate of 1.0 mL min^{-1}. Since the inner volume of the microcolumn and connecting tubes is known, the individual fractions were differentiated by recalculating the volume of the effluent. Sub-fraction volume was 15 mL.

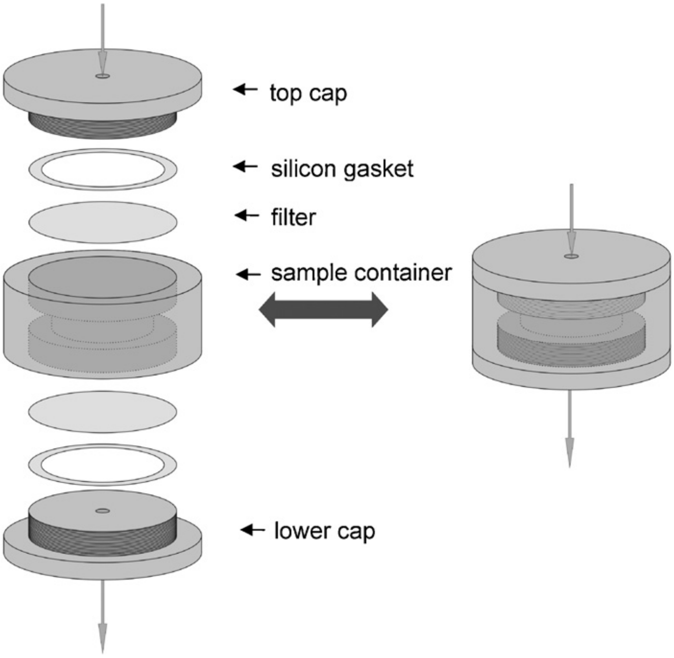

Fig. 2. Schematic representation of a cylindrical microcolumn for continuous-flow extraction.

The collected fractions of the effluent were analysed by ICP-AES.

2.4. Analysis of residual fractions

The residue after RCC extraction was separated by filtration (0.45 μm; cellulose acetate, Sartorius). Both the residues after MC extraction (fixed on Whatman filters) and the residues after RCC were partly dissolved in aqua regia employing a closed microwave digestion device (Multiwave, Perkin-Elmer). The procedure is described in detail in our previous work [16]. Clean filters were used as blank samples. The resulting solution was analysed using ICP-AES.

3. Results and discussion

3.1. Representative sequential extraction schemes for Se and their applicability to dynamic fractionation

The batch-wise fractionation of Se in soils and sediments and the speciation analysis of the separated fractions have been extensively discussed in the literature [1–6]. According to the published data a sequential extraction protocol proposed by Zhang and Moore [5] and modified by Wright et al. [2] (Table 2) seems to be the most suitable SEP that allows one to evaluate Se distribution and ensuing physicochemical mobility [1]. “Soluble/exchangeable”, “adsorbed” and “organically associated” Se fractions can be mobilizable/available under environmental conditions whereas “elemental” Se and “more recalcitrant forms” of organic Se are hardly mobilizable/available. The SEP developed by Ponce de León et al. [6] (Table 2) is less “popular”. However, it has some advantages and does not conflict with the protocol proposed by Zhang and Moore [5] and modified by Wright et al. [2]. The Ponce de León scheme addresses water-soluble fraction (mobile and directly available to biota), “adsorbed” Se, “organically bound” Se (mobilizable/available fractions), and “elemental” Se (hardly mobilizable/available). The first three fractions are of particular importance for risk assessment. Different concentrations of applied reagents were tested and the optimized values were included in the final scheme [6]. It was demonstrated that the basic extraction by 5% tetramethylammonium hydroxide is more appropriate than the conventional extraction by 0.1 mol L^{-1} NaOH. Besides, the Ponce de León protocol utilizes the unified conditions at all the extraction steps whereas the modified Zhang and Moore SEP requires specific conditions (e.g. ultrasonic bath or heating) at different extraction steps.

Hence, it looks reasonable to use the sequence of leaching reagents proposed by Ponce de León et al. [6] for the dynamic (continuous-flow) fractionation of Se. The contact time of 24 h between particulate sample and extractant needed for the separation of each fraction under batch conditions does not represent an obstacle. Multi-step extraction processes occurring both in RCC and MC enable the contact time needed for the recovery of each fraction to be significantly reduced. For example, it has been shown that the RCC extraction of exchangeable/acid soluble trace metals within 1 h may be even more efficient than the conventional batch extraction within 16 h [18].

3.2. Fractionation of selenium in environmental solids using RCC and MC

According to the selected sequential extraction scheme, four leachable fractions of Se are separated (see Table 2). The extractograms obtained for samples B 26571 and B 26575 using RCC and MC are shown in Fig. 3. As is seen, for creek sediment sample B 26571 elution profiles are similar, though deviations in peaks height are observed. In contrary, for dumped waste (soil) sample B 26575 the continuous-flow extraction methods lead to different results. The elution curve obtained by using MC is characterized by rather broadened peaks. This might be attributed to peculiarities of the sample under study and different operational principles of RCC and MC. Sample B 26575 is relatively rich in organic matter (11.5% of organic carbon) and Se binding centres may be hardly available for the eluent. In RCC, both solid particles and liquid solutions are subjected to the action of a complex asymmetrical force field generated in a planetary centrifuge. The behavior of particles, including their migration, is influenced by particle size and density as well as by the operation and configuration parameters of the planetary centrifuge, including rotation speed, eluent flow rate, tubing bore, column rotation and revolution radii. According to earlier observations [19] made for polydisperse particulate matter (e.g. soil samples), large particles of high density are fixed to a given position at the column walls under the experimental conditions used in this work. However, particles smaller than 10 μm migrate within the column, thereby increasing the effective surface area for extraction. Even larger particles with low density, e.g. those rich in organic matter, might become pseudo stationary and migrate axially within the RCC throughout the leaching experiment. In MC, particulate matter is retained as a packed-bed column through which the extractant flows. As a consequence of the application of an uni-directional flow mode, soil particles are quiescent within the column and the formation of preferential flow channels for the extractant is possible thus decreasing the effective contact interface between the sample and eluent.

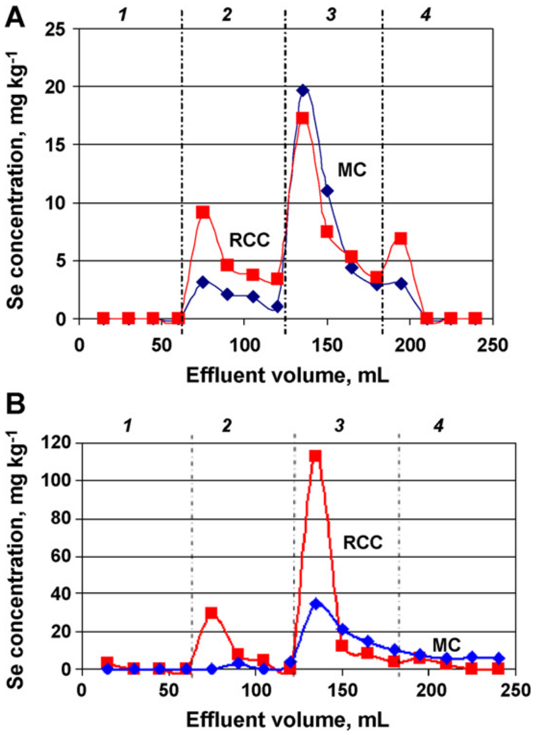

Fig. 3. Leaching profiles of Se as obtained by MC (♦) and RCC (■) extraction for creek sediment sample B 26571 (A) and dumped waste (soil) sample B 26575 (B). Eluent composition: *1*, *2*, *3*, *4* (see Table 2). Flow rate 1.0 mL min^{-1}.

The results of Se fractionation in studied samples as obtained by RCC and MC extraction are given in Table 3. The distribution of Se between leachable and residual fractions is clearly illustrated in Fig. 4. As can be seen, for creek sediment sample B 26571, RCC and MC yielded quite similar characteristic patterns of Se distribution. Nevertheless, the quantitative values of Se content in individual fractions were slightly different. The continuous-flow extraction in

Table 3
Results of the fractionation of selenium (mass fraction, mg kg^{-1}) in the studied samples. Values represent means ($n = 3$) ± SDs.

Sample	Step 1	Step 2	Step 3	Step 4	Residual fraction	Sum	Total (XRF)	Recovery, %
B 26571								
RCC	<LOD	18 ± 2	34 ± 2	7 ± 1	125 ± 4	184 ± 5	215	85
MC	<LOD	12 ± 2	42 ± 3	12 ± 2	121 ± 5	186 ± 7	215	87
B 26575								
RCC	3 ± 1	43 ± 2	101 ± 3	7 ± 1	109 ± 9	263 ± 10	228	115
MC	<LOD	7 ± 1	54 ± 6	16 ± 2	142 ± 11	219 ± 13	228	96

RCC resulted in more efficient leaching of “adsorbed” Se, whereas MC extraction provided higher recoveries of “organically bound” and “elemental” Se. The Se contents in the residual fractions and the sum of leachable and residual fractions were nearly the same for both methods. The mobile (and direct available for biota) water-soluble fraction was not determined in the sediment sample. It should be noted that the most considerable amount of extractable Se is “organically bound” though sample B 26571 is characterized by relatively low value of organic carbon (6.2%).

For dumped waste (soil analogue) sample B 26575, the results as obtained by RCC and MC extraction are different (Table 3) though the general tendencies of Se distribution between extractable and residual fractions are similar (Fig. 4). As is seen, the most considerable amount of leachable Se is also “organically bound” which may be expectable for a sample rich in organic matter. The total recoveries of Se in the four leachable fractions are higher if dynamic extraction in RCC is used. The most evident deviations are observed for individual “adsorbed” and “organically bound” fractions. For example, the contents of “adsorbed” Se (predominantly selenite and high molecular weight selenium species adsorbed onto the surface of iron(hydr)oxides and other sample components) as recovered by using RCC and MC are 42.9 and 7.1 mg kg^{-1}, respectively. Besides, RCC extraction enables the water-soluble fraction of Se (mainly non-adsorbed selenite and selenate species) to be determined. Hence, for sample B 26575, the continuous-flow leaching in RCC provides more effective recovery of environmentally relevant Se forms (the first three leachable fractions). As has been discussed above, this may be attributed to different operational principles of RCC and MC. In particular, the migration of organic-rich particles with low density inside the RCC might enhance the mixing of solid and liquid phases and, consequently, the extraction efficiency. In packed columns, organic clods are most likely agglomerated, whereby the decreased surface area of sample particles might lead to the lower extractability of Se.

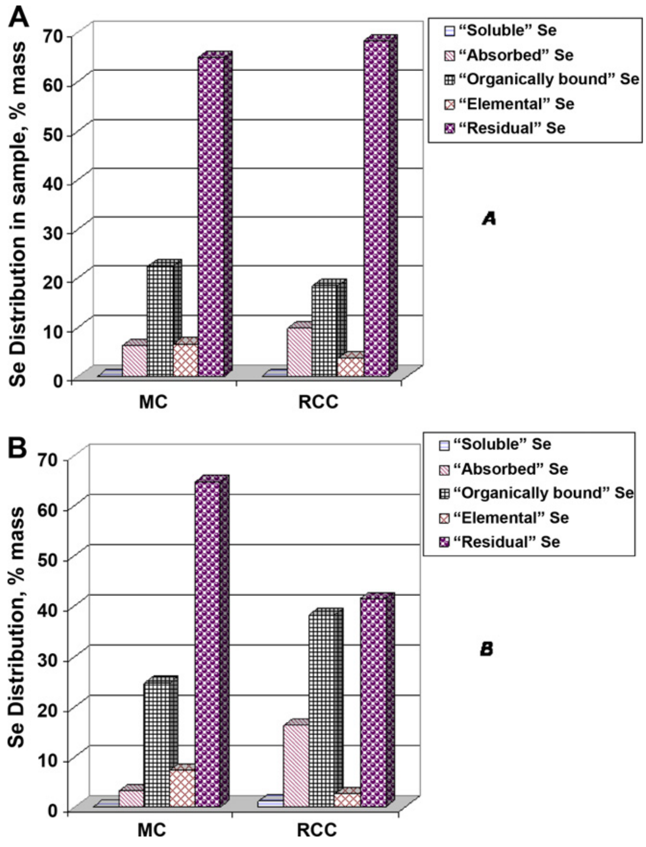

Fig. 4. Distribution of Se between leachable and residual fractions (recoveries, % of total content) in creek sediment sample B 26571 (A) and dumped waste (soil) sample B 26575 (B) as obtained by using continuous-flow RCC and MC extraction.

With regard to the hardly mobilizable/available “elemental” Se (sulphite extractable fraction) in B 26575, its recovery by using MC is somewhat higher than by using RCC. Elemental Se is capable of forming a complex with sulphite, thus making it soluble. Moreover, sulphite solution can also extract other forms of selenium which were not previously extracted from the sample. Hence, lower “elemental” Se content as recovered by RCC may be explained by more efficient leaching of Se at first three steps.

For two samples under investigation, the total recoveries of Se in the four leachable fractions plus residuals are within the range 87–96% and 85–115% for MC and RCC continuous-flow extraction, respectively, with reproducibility’s given as relative standard deviations below 15% for individual extractable fractions (except water-soluble fraction), thereby confirming the acceptable accuracy and reliability of both methods.

4. Conclusions

It has been demonstrated that the continuous-flow extraction in RCC and MC can be successfully applied to the dynamic fractionation of Se in environmental solids. Moreover, elution profiles provide additional information on the dynamics of Se release at the sequential dissolution of different sediment/soil components.

Despite the different extraction conditions set by two dynamic methods, similar trends of selenium distribution between leachable and residual fractions were in generally found. However, quantitative values for the dumped waste (soil) sample as obtained by RCC and MC are dissimilar. The RCC extraction results in more effective recovery of environmentally relevant “water soluble”, “adsorbed” and “organically bound” Se fractions. The deviations observed may be attributed to peculiarities of solid and liquid phases mixing in RCC and MC depending on sample properties (e.g. content of organic matter). Nevertheless, the comparative data can be considered to be in acceptable agreement, especially taking into account the uncertainties typically reported when analysing soil/sediment samples and the operationally defined nature of fractionation methods.

The work is to be continued. The analysis of a wide range of samples with variable composition and physicochemical parameters as well as optimization of extraction conditions will contribute to the harmonization of dynamic fractionation of Se (and other trace elements) using RCC and MC.

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