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Dynamic fractionation of trace metals in soil and sediment samples using rotating coiled column extraction and sequential injection microcolumn extraction: A comparative study

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ABSTRACT

Dynamic fractionation has been recognized as an appealing alternative to conventional equilibrium-based sequential extraction procedures (SEPs) for partitioning of trace elements (TE) in environmental solid samples. This paper reports the first attempt for harmonization of flow-through dynamic fractionation using two novel methods, the so-called sequential injection microcolumn (SIMC) extraction and rotating coiled column (RCC) extraction. In SIMC extraction, a column packed with the solid sample is clustered in a sequential injection system, while in RCC, the particulate matter is retained under the action of centrifugal forces. In both methods, the leachants are continuously pumped through the solid substrates by the use of either peristaltic or syringe pumps.

A five-step SEP was selected for partitioning of Cu, Pb and Zn in water soluble/exchangeable, acid-soluble, easily reducible, easily oxidizable and moderately reducible fractions from 0.2 to 0.5 g samples at an extractant flow rate of 1.0 mL min^{-1} prior to leachate analysis by inductively coupled plasma-atomic emission spectrometry.

Similarities and discrepancies between both dynamic approaches were ascertained by fractionation of TE in certified reference materials, namely, SRM 2711 Montana Soil and GBW 07311 sediment, and two real soil samples as well. Notwithstanding the different extraction conditions set by both methods, similar trends of metal distribution were in generally found. The most critical parameters for reliable assessment of mobilisable pools of TE in worse-case scenarios are the size-distribution of sample particles, the density of particles, the content of organic matter and the concentration of major elements. For reference materials and a soil rich in organic matter, the extraction in RCC results in slightly higher recoveries of environmentally relevant fractions of TE, whereas SIMC leaching is more effective for calcareous soils.

1. Introduction

According to IUPAC recommendations [1], the process of classification and quantification of elements from solid samples according to the bonding to predefined phases or chemical reactivity is defined as fractionation.

Sequential extraction is a well-established approach for fractionation of trace elements (TE) in environmentally relevant solid samples [2,3], such as soils, sediments, solid waste, sludges and airborne particulates. Sequential extraction procedures (SEPs) are based on the successive use of aqueous solutions of increasing aggressiveness encompassing mineral salts, acids and complexing reagents for sequential release of TE associated to targeted phases. In general, sequential extraction provides an insight into the origin, physicochemical mobility, and transport of TE and despite its operationally defined nature the "nominal forms" of SEP assist in the estimation of the amounts of TE in different reservoirs that can be mobilised under changes in the chemical properties of soil [3,4].

Since the late 1970s a considerable number of SEP have been proposed for determining the forms of trace metals and metalloids [3,5] in soil, sediments and sludge samples. Despite their wide use in environmental studies, the conventional batch wise

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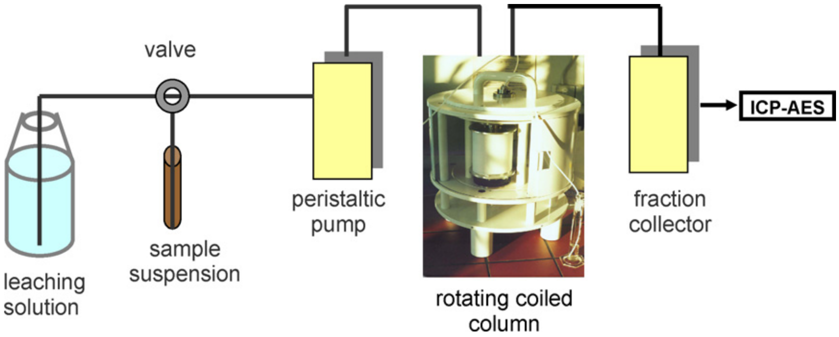

Fig. 1. Schematic diagram of the rotating coiled column set-up for dynamic extraction.

SEP are rather laborious and time consuming [6] and are subjected to several potential errors such as sample contamination and sample losses [7] because of manual operations. Two additional problems recognized [3,8,9] are: (I) the phase overlapping, that is, the possibility of releasing metals associated to different solid compartments by one leaching agent; (II) the metal re-adsorption phenomenon, that is, TE released by the extractant might associate with other undissolved solid components or freshly exposed surfaces within the time frame of the extraction step, thus rendering underestimation of the mobilisable TE pools. Further, SEP are based on steady-state extractions, which cannot mimic environmental scenarios accurately [10] because naturally occurring processes are always dynamic, whereby the ecotoxicological relevance of the information provided is rather questionable [11,12].

To tackle the above drawbacks, novel dynamic (non-equilibrium) fractionation methods, relying on the continuous provision of fresh extractant volume to the solid sample under investigation, have been proposed over the past few years [13–16]. Two dynamic approaches which have proven well suited for fractionation of TE in environmental substrates are the so-called rotating coiled column (RCC) extraction [17] and sequential injection microcolumn (SIMC) extraction [18].

RCC traditionally used for separation and purification of organic [19] and inorganic [20] solutes by countercurrent chromatography (support-free liquid–liquid partition chromatography) have been recently exploited in liquid–solid systems [21] for continuous leaching of trace metals [22–24] and arsenic [25] from contaminated soils, lake and river sediments. The solid sample (typically 0.5 g) is retained as a stationary phase, whereas leaching solutions of mineral acids, electrolytes, and complexing agents are successively pumped through via a peristaltic pump. The fractionation of TE is performed on a planetary centrifuge furnished with a vertical one-layer coiled polytetrafluoroethylene (PTFE) column, as shown in Fig. 1. During the experimental protocol the spiral column rotates around its axis and simultaneously revolves around the central axis of the unit with the aid of a planetary gear. The information on metal/metalloid chemical forms and metal soil phase associations obtained by adapting various SEP to leaching in RCC has been critically discussed and contrasted with that of traditional batch wise tests [17,22,25], yet no comparison with dynamic SEP methods has been reported so far.

The other approach, SIMC extraction, exploits the liquid handling capabilities of the second generation of flow analysis, that is, sequential injection (SI) analysis [26] for automatic fractionation of TE in solid samples as contained in a microcolumn inserted in the flow network [18,27–29], as shown in Fig. 2. The core of SI is a multiposition valve, the central port of which is connected to a bi-directional syringe pump operating as a liquid driver. The valve is equipped with six, eight or ten peripheral ports that can communicate with the central port via an internal rotary conduit of the valve. Thus, through this conduit, the syringe pump can be made to address each of the ports of the valve. The analytical sequence in SIMC fractionation comprises the consecutive aspiration of the individual extractants from different external ports of the valve, which, via flow reversal, are exposed sequentially to the sample contained in a microcartridge attached to another peripheral position whereby TE associated with different mineralogical phases are released.

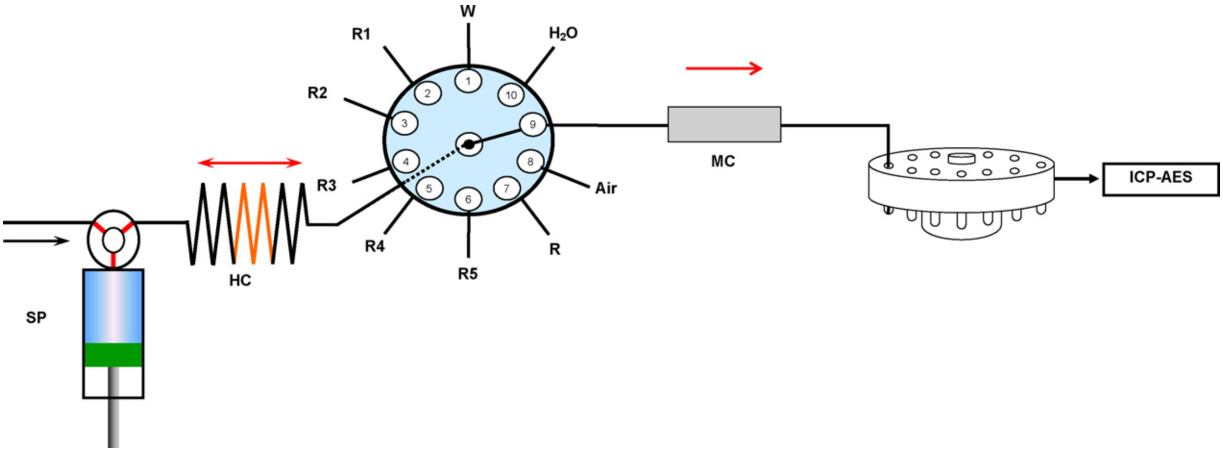

Fig. 2. Schematic diagram of the sequential injection flow network for microcolumn extraction. R_1: 0.05 mol L^{-1} $Ca(NO_3)_2$; R_2: 0.43 mol L^{-1} CH_3COOH; R_3: 0.1 mol L^{-1} $NH_2OH \cdot HCl$ pH 3.6 (non-acidified); R_4: 0.1 mol L^{-1} $K_4P_2O_7$ at pH 11 (adjusted with KOH); R_5: 0.1 mol L^{-1} $(NH_4)_2C_2O_4$ at pH 3.2; R: 0.25 mol L^{-1} KNO_3; W: Waste; SP: syringe pump; SV: selection valve; HC: holding coil; MC: microcolumn.

Table 1
Physicochemical properties of the experimental soil and sediment samples assayed.

Parameter	SRM 2711	GBW 07311	A01725	A91295
Sampling site	Montana, USA, till layer of the wheat field	NR	Bitterfeld, Central Germany, riverine area	Moscow, Russia, lawn (industrial area)
Sample description (type)	Pasture soil	Stream sediment	Anthropogenic transformed floodplain soil	Anthropogenic transformed urbo-soil
Horizon, depth (cm)	NR	NR	A, 0-20	A, 0-10
Particle size (μm)	<74	NR	<250	<250
pH (H_2O, 1:5)	8.5	7.4	4.2 ± 0.1	8.1 ± 0.1
Organic C (%)	1.2 ± 0.1	0.21 ± 0.01	14.6 ± 0.2	5.6 ± 0.1
Fe_2O_3 (%)	4.13 ± 0.08[a]	4.4 ± 0.2[a]	5.6 ± 0.4	4.2 ± 0.1
Al_2O_3 (%)	12.3 ± 0.2[a]	5.5 ± 0.2[a]	9.3 ± 0.1	3.9 ± 0.1
CaO (%)	4.0 ± 0.1[a]	0.47 ± 0.08[a]	0.66 ± 0.08	6.0 ± 0.1

[a] Certified values; NR: Not reported.

The establishment of quality control/quality assurance tools, including harmonization of different flow-through leaching tests, is still the bottleneck for further development and application of dynamic fractionation methods. Thus, the aim of this work is to critically compare and evaluate the two promising approaches stated above, that is, continuous-flow RCC extraction and SIMC extraction. A series of reference materials and real soil samples with different mineralogical composition and particle size distribution were used for comparative investigations. To the best of our knowledge, this is the first research directed at the harmonization of dynamic fractionation of TE in environmentally relevant solid samples.

2. Experimental

2.1. Samples and sequential extraction scheme

Two standard reference materials, *namely,* SRM 2711 and GBW 07311 and two real soils, *namely*, A91295, A01725 were used for validation and comparative purposes (Table 1). SRM 2711 is a pasture soil collected in the till layer of a wheat field (Montana, MT) prepared by National Institute of Standards of Technology (NIST). The GBW 07311 material is stream sediment from National Research Center of China. The two selected real soils (A91295 and A01725) were subjected to anthropogenic contamination and are characterized by different contents of major components governing the behavior of TE. Both samples are lawn soils taken, respectively, in Moscow industrial area and floodplain area in Central Germany (Bitterfeld) influenced by former ore processing and chemical industry. The maximum acid soluble contents of major elements in real samples were determined using a microwave digester (Milestone, MLS-1200 Mega, Sorisole, Italy) prior to detection by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with cross-flow pneumatic nebulization.

The sequence of extractants used for dynamic fractionation of TE (Table 2) has been chosen according to recent studies on the selectivity of leachants towards given mineralogical fractions of soils [30–32]. This five-step leaching procedure has been successfully applied to continuous-flow fractionation of trace elements in a series of soil, sediment and sludge samples using RCC [24,33].

2.2. Preparation of standard solutions and glassware

The overall chemicals used for sequential extraction were of analytical grade. For SIMC extraction, the following chemicals were employed: calcium nitrate (Probus, Badalona, Spain), glacial acetic acid (Scharlau, Barcelona, Spain), hydroxylamine hydrochloride (Panreac, Barcelona, Spain), potassium pyrophosphate (Panreac), and ammonium oxalate (Probus). For extraction in RCC, calcium nitrate, glacial acetic acid, hydroxylamine hydrochloride, ammonium oxalate (all from Merck, Darmstadt, Germany) and potassium pyrophosphate (Riedel-de-Haën, Seelze, Germany) were used.

Stock standard metal solutions of Cu, Zn and Pb (100–1000 mg L^{-1}) for ICP-AES calibration were prepared either from pure metals (Merck) for Cu and Zn or from lead nitrate (Probus) for Pb following standard APHA methods [34]. Standard working solutions were prepared by appropriate dilution of the stock solution with Milli-Q water (Millipore Synthesis A10, Millipore Corporation, Billerica, MA). All glassware used was previously cleaned and soaked in 10% (v/v) HNO_3 and rinsed with Milli-Q water.

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

The continuous leaching of heavy metals 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

Table 2
Five-step fractionation procedure for sequential extraction of trace elements.

Step	Reagent	Leached fraction	Metal species	Mobility/Potential biological availability
1	0.05 mol L^{-1} $Ca(NO_3)_2$	Water soluble and exchangeable	Ions bound to the sample matrix by weak electrostatic interactions	Mobile/easily available species
2	0.43 mol L^{-1} CH_3COOH	Acid-soluble	Carbonates and other specifically adsorbed forms of metals	Easily mobilisable/available species
3	0.1 mol L^{-1} $NH_2OH{\cdot}HCl$ pH 3.6 (non-acidified)	Easily reducible	Elements bound to Mn oxyhydroxides	Readily mobilisable/available species
4	0.1 mol L^{-1} $K_4P_2O_7$ + KOH to adjust pH 11	Easily oxidizable (pyrophosphate extractable)	Elements bound to humates and fulvates (organometallic complexes)	Readily mobilisable/available species
5	0.1 mol L^{-1} $(NH_4)_2C_2O_4$ pH 3	Moderately reducible	Elements bound to amorphous and poorly crystalline Fe and Al oxyhydroxides	Poorly mobilisable/available species

Table 3
Operating conditions of inductively coupled plasma atomic emission spectrometers.

Parameter	Spectrometer Perkin-Elmer OPTIMA 5300 DV	Spectrometer CIROS, Spectro A.I.
RF generator power (W)	1300	1400
Frequency of RF generator (MHz)	40	27.12
Carrier gas flow rate (L/min)	0.7	0.9
Coolant gas flow rate (L/min)	15	14
Auxiliary gas flow rate (L/min)	0.2	0.8
Max integration times (s)	5	3
Nebulizer	Gem tip cross-flow nebulizer en Cap N068-0503	Cross-flow
Analytical wavelength (nm)		
Cu	324.754	324.754
Pb	220.351	168.215/220.351
Zn	213.856	213.856

filled, using a peristaltic pump (Minipuls 3, Abimed-Gilson, Langenfeld, Germany), with 0.05 mol L^{-1} solution of calcium nitrate, whereupon a two-way valve was switched and the solid sample (about 0.5 g) was introduced into the column (in the stationary mode) as a suspension in 10 mL of the same solution. Afterwards, a surplus of 5 mL of calcium nitrate was injected into the column. Then, while the column was rotated at 800 rpm, aqueous solutions of different reagents, used as the mobile phase, were continuously delivered to the column at the same flow rate as in the SIMC fractionation, that is, 1.0 mL min^{-1}. The solid sample was retained inside the rotating column as the stationary phase under the action of a centrifugal force field throughout the experiment. The recovery of different forms of TE was achieved following the fractionation protocol described in (Table 2). Each of the first two reagents (calcium nitrate and acetic acid) was pumped through the column during 120 min. The other three reagents were pumped during 60 min. 5 mL of water were pumped between extraction steps. After the leaching procedure has been finished, the residue of the solid sample was removed from the column in a quiescent mode by pumping water at 10 mL min^{-1}.

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). The operational conditions are given in Table 3. In order to consider the changing matrix conditions for leachate analysis, a matrix-matched calibration with the different leaching solutions was applied.

2.4. Sequential injection microcolumn (SIMC) extraction

The extraction system for dynamic microcolumn fractionation used in this work is schematically illustrated in Fig. 2. It comprises a 5000-step bi-directional syringe pump (SP) (Crison Instruments, Alella, Barcelona, Spain) for handling of leaching reagents and delivery to the solid containing microcolumn; a 10-port multiposition selection valve (SV) (Crison Instruments, Alella Barcelona) for selection of appropriate extractants; and a 45 position autosampler (Micro Sampler Crison, Alella, Barcelona) for collection of leachates.

The automatic SP is furnished with a 5 mL syringe (Hamilton, Switzerland) and a three-way solenoid valve at its head, which allows connection with either the flow-manifold or the carrier (water) reservoir. The central port of the SV is connected to SP via a holding coil (HC), which consists of 3.0 m long PTFE tubing (1.5 mm i.d.), with an inner volume of 5.3 mL. All outlets of the SV were connected through PEEK ferrules with rigid PTFE tubing (1.5 mm i.d.).

The extraction microcolumn employed in this work has been described in detail elsewhere [18]. It was made of PEEK, and comprises a central dual bi-conical shape sample container for facilitating mixing of sample with extractants. It is equipped with filters and filter supports and caps at both ends. Membrane filters (Fluoropore TM, Millipore, 13 mm diameter) with 0.45 and 1.0 μm pore sizes were used for sediment and soil samples, respectively.

For instrumental control of SP, SV and autosampler, the software package AutoAnalysis 5.0 (Sciware, Palma de Mallorca, Spain) was used. The developed software based on dynamic link libraries (DLLs) at 32 bits comprises a single and versatile protocol, which allowed the implementation of individual DLLs for control of the instrumentation [35].

Notwithstanding the fact that SI facilitates the application of various operational modes of extraction [29], a forward-flow approach was herein selected as being the one commonly applied in RCC extraction.

Before initialization of the extraction cycle, a 150 μL air plug is aspirated from port 8 of SV into HC. The role of the air segment is to prevent dispersion of the leaching reagent into the carrier solution. Afterward, SP is set to aspirate 5.0 mL of 0.05 mol L^{-1} $Ca(NO_3)_2$ from port 2 into HC at a flow rate of 10.0 mL min^{-1}. The entire extractant plug was then dispensed at 1.0 mL min^{-1} from HC directly to port 9 and then passed through the microcolumn, allowing leaching to take place. For each three cycle runs, the extracts from the microcolumn are collected in a plastic vial, thus totally amounting to 15 mL. The above analytical protocol is repeated eight times, whereby 120 mL of salt solution is utilised in the first fractionation step. Thereafter, 0.43 mol L^{-1} CH_3COOH was automatically aspirated from port 3 and the collection of eight 15 mL subfractions is effected.

Prior to continuing with the ensuing extraction step, a washing protocol is implemented by aspiration of 5.0 mL of Milli-Q water from port 10 into HC and then passed through the microcolumn and collected in a new plastic vial. The amount of metals leached in the cleansing step is summed to the content of the subfractions collected in the previous extraction.

Identical procedures are executed for the remainder of extractants, *viz.*, 0.1 mol L^{-1} $NH_2OH{\cdot}HCl$, 0.1 mol L^{-1} $K_4P_2O_7$ and 0.1 mol L^{-1} $(NH_4)_2C_2O_4$ which are automatically aspirated from the respective valve ports. However, a mere of four 15 mL subfractions are herein collected for a complete set because of faster release of metal solid-phase associations.

Determination of concentrations of individual metal species in the various fractions was performed by a Perkin-Elmer OPTIMA 5300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES). The operational conditions are compiled in Table 3. Alike in RCC extraction, a matrix-matched calibration was utilised.

2.5. Dissolution of solid residues and determination of total concentration of metals

The environmental solids and residues leftover after the sequential extraction scheme were digested for quantification of total metal concentrations and immobilised metal fractions, respectively. The microwave digestion procedure, which was used for the quantification of total metal concentrations and analysis of residues in SIMC extraction, can be regarded as a modified version of the

EPA Method 3051 [36], named microwave-assisted acid digestion for sediments, sludges, soils, and oils. Digestions were performed in a closed-vessel microwave digestion system (MLS-1200 Mega, Milestone, Sorisole, Italy). Weighed solid samples (0.20 g) or residual solids remaining after fractionation were digested using 2.0 mL of concentrated HNO_3 (65%, Merck, Darmstadt, Germany) and 6 mL of concentrated HCl (37%, Riedel-de-Haën, Seelze, Germany).

The microwave digestion program consists of five steps as detailed as follows: 5 min at 250 W; 5 min at 400 W; 5 min at 650 W; 5 min at 250 W; and 5 min at 0 W. After cooling, if needed, the digests were filtered through cellulose acetate filters (Schleicher & Schuell, 589/2, Dassel, Germany). The clear digests were diluted further with Milli-Q water to adjust the analyte concentrations within the linear range of ICP-AES.

After RCC extraction, the residue was partly dissolved in aqua regia employing a closed microwave digestion device (Multiwave, Perkin-Elmer). Briefly, 1.2 mL of concentrated nitric acid (65%) and 3.6 mL of concentrated hydrochloric acid (30%), both suprapur quality (Merck), were added to the residue. The samples were heated in three steps to 260 °C starting with a ramp from 500 to 800 W in 8 min, followed by a ramp to 1000 W in 3 min whereupon this temperature was held constant for additional 20 min. After cooling down 10 min at 0 W in the device and further 30 min outside the resulting solution was transferred to centrifuge beakers. The undissolved residue was separated by centrifugation. The supernatant was transferred to 25 mL polyethylene bottles and filled to volume with Milli-Q water. The resulting solution was analysed using ICP-AES.

3. Results and discussion

3.1. Critical comparison of RCC and SIMC as flow-through dynamic extraction assemblies

Each approach apparently has advantages and limitations which are the result of the particular column designs and operational parameters as detailed below.

3.1.1. Equipment

In itself the microcolumn is a relatively simple tool. The planetary centrifuge furnished with RCC is a rather sophisticated device which could constrain its applicability.

3.1.2. Column volume

The volume capacity of the RCC is 20 mL, yet the internal volume of the biconical column in SIMC is merely 750 μL [37]. Therefore, the leached TEs are less diluted in SIMC fractions, thereby fostering a more accurate quantitation of mobile pools. Nevertheless it should be noted that narrow sharp peaks of trace and major elements were on-line detected when fast leaching processes were investigated by using RCC [24,33].

3.1.3. Weight and particle size distribution of assayed samples

A limitation of SIMC as compared to RCC is the maximum amount of solid that can be handled with no adverse back-pressure or clogging effects. Despite the optimal hydrodynamic conditions of the biconical column with respect to cylindrical containers, samples up to merely 300 mg could be fractionated in SIMC [27,37]. Highly heterogeneous samples should be better handled in RCC where the tubular column is typically filled with 0.5 g [17,22–25]. It should be however emphasised that if the sample weight of half a gram is considered to be insufficient for assurance of sample representativeness it can be increased up to 5.0 g by exploiting coiled columns with larger tubing bore [38].

The SIMC system has been proven suitable for fractionation of solids with heterogeneous particles ≤2 mm [27,29] which cannot be handled in conventional RCC because of smaller column i.d., *viz.*, 1.5 mm. If needed however, special rotating columns with larger tubing bore may be used [38].

3.1.4. Retention of particulate matter

In RCC, the solid sample is retained by centrifugal forces whereas different eluents are continuously pumped through. No membranes or filters are used. This is a notable advantage of RCC as compared to SIMC. In the latter, filters should be selected attending both particle size and packed solid amount. For soils, no backpressure has been observed for fractionation of up to 300 mg by resorting to PTFE filters with 1.0 μm pore size. However, filters of 0.45 μm pore size are mandatory for reliable fractionation of sediments.

Another drawback of SIMC concerns to sample peptization, which eventually lead to a breach of membrane as a consequence of backpressure increase. Peptization is the process by which colloidal soil particles are dispersed from an aggregated to a dispersed state. This process is accelerated by a decrease of the ionic strength of the extractant as a consequence of the increase of the double layer thickness of colloids. This phenomenon was particularly observed during changeover from the fourth to fifth extractant whenever Milli-Q water was used for rinsing the remaining environmental solid. To tackle this problem, the cleansing step was effected using a saline solution of 0.25 mol L^{-1} KNO_3, in lieu of water, to increase the ionic strength of the washing solution.

3.1.5. Operational modes

Owing to the versatility of fluid delivery by SP, four operational modes for SIMC extraction are potentially feasible, namely, uni-directional flow, bi-directional flow, multi bi-directional flow and stopped-flow, which might be easily accommodated in a single SI set-up with no need for manifold re-configuration [29]. Further, the high-precision SP features steady pumping of extractants through the packed columns [11,39] with no need for periodical recalibration of the liquid driver. SIMC protocols also are fully automated by user-friendly software, including the change of extractants during the analytical sequence.

Up to now uni-directional flow and stopped-flow modes have been used for the extraction in RCC. Protocols are however only semi-automated. The flow rate should be controlled and the liquid driver (peristaltic pump) should be periodically recalibrated, which is a limitation of the RCC system.

3.1.6. Contact between solid and liquid phases

In SIMC, the extractant flows through a packed particulate matter. Preferential flow channels for the leachant may be formed, thus lowering the effective contact surface between the samples and leaching solution. In RCC, particles may be either fixed to a given position at the column walls or migrate within the column thereby increasing the effective surface area. Behavior of particles inside RCC is primarily dependent on their size and density as well as on the design and the operational variables of the planetary centrifuge [40].

3.2. Fractionation of trace elements in environmental solids by SIMC and RCC

According to the selected sequential extraction scheme, five leachable fractions are separated (see Table 2). Trace metals in exchangeable and acid soluble fractions (mobile and easily mobilisable forms of TE, respectively) are considered, in general, to be easily bioavailable. Hence, these two fractions are of particular

Table 4

Extractable amounts of Pb, Cu, and Zn (mg kg^{-1}) in soil samples and certified reference materials obtained by sequential injection microcolumn (SIMC) extraction and continuous-flow fractionation in a rotating coiled column (RCC).

Element/stage		1	2	3	4	5	Residual	Sum[d]	MW digestion	Recovery (%)
Soil A91295										
Cu	RCC	<LOD[a]	294 ± 10	8.0 ± 0.7	124 ± 8	153 ± 11	107 ± 9	686 ± 11	791 ± 40	87
	SIMC	7.1 ± 0.4	422 ± 15	13 ± 2	111 ± 13	138 ± 16	55 ± 13	747 ± 26		94
Pb	RCC	<LOD[a]	<LOD[a]	<LOD[a]	128 ± 11	41 ± 4	49 ± 5	218 ± 10	232 ± 10	94
	SIMC	2.3 ± 0.2	30 ± 2	12 ± 5	133 ± 9	38 ± 6	30 ± 4	245 ± 12		105
Zn	RCC	177 ± 18	1643 ± 110	48 ± 5	71 ± 6	126 ± 12	320 ± 23	2385 ± 95	2719 ± 147	88
	SIMC	396 ± 41	1817 ± 105	37 ± 4	131 ± 2	145 ± 5	266 ± 26	2793 ± 90		103
Soil A01725										
Cu	RCC	12.8 ± 1.5	25 ± 3	0.40 ± 0.06	48 ± 3	32 ± 2	55 ± 6	173 ± 4	172 ± 17	100
	SIMC	10 ± 2	2.4 ± 0.3	2.4±0.3	24.1 ± 0.1	12 ± 4	119 ± 2	170 ± 9		99
Pb	RCC	3.1 ± 0.5	8.2 ± 0.9	5 ± 2	46 ± 3	100 ± 12	310 ± 25	472 ± 18	450 ± 50	105
	SIMC	5.4 ± 0.8	46 ± 3	4.5 ± 0.7	19.6 ± 1.5	15.3 ± 0.5	387 ± 16	478 ± 15		106
Zn	RCC	51 ± 5	15 ± 2	3.1 ± 0.6	12.3 ± 1.5	15 ± 2	200 ± 18	296 ± 28	303 ± 24	97
	SIMC	41 ± 2	1.9 ± 0.4	0.71 ± 0.08	8.6 ± 1.4	<LOD[b]	244 ± 23	297 ± 21		98
SRM 2711										
Cu	RCC	<LOD[a]	32 ± 2	0.60 ± 0.04	25 ± 2	8.1 ± 0.7	54 ± 5	120 ± 6	114 ± 7 (114[c])	105
	SIMC	0.85 ± 0.03	21.0 ± 1.0	0.6 ± 0.1	18 ± 2	6.3 ± 0.8	62 ± 7	109 ± 6		96
Pb	RCC	<LOD[a]	798 ± 65	124 ± 13	65 ± 6	66 ± 6	78 ± 8	1131 ± 59	1098 ± 6 (1162[c])	97
	SIMC	2.5 ± 0.6	571 ± 35	91 ± 8	121 ± 7	23 ± 5	271 ± 71	1080 ± 57		93
Zn	RCC	<LOD[a]	88 ± 7	2.9 ± 1.6	32 ± 3	26 ± 3	218 ± 13	366 ± 20	360 ± 20 (350.4[c])	104
	SIMC	<LOD[b]	60 ± 8	5.8 ± 1.4	2.4 ± 0.4	3.2 ± 0.8	275 ± 14	346 ± 11		99
GBW 07311										
Cu	RCC	0.20 ± 0.05	13.7 ± 1.4	5 ± 3	9.0 ± 0.7	7 ± 4	53 ± 5	88 ± 5	77 ± 12 (78.6[c])	114
	SIMC	<LOD[b]	3.6 ± 1.0	2.5 ± 0.3	7.7 ± 1.1	5.9 ± 0.2	61 ± 5	81 ± 8		103
Pb	RCC	<LOD[a]	118 ± 11	320 ± 27	7.1 ± 0.6	91 ± 8	136 ± 15	672 ± 32	577 ± 31 (636[c])	106
	SIMC	2.77 ± 0.06	91 ± 18	238 ± 10	35 ± 2	75 ± 5	225 ± 26	664 ± 36		104
Zn	RCC	7.5 ± 0.9	64 ± 7	55 ± 6	2.5 ± 0.3	36.6 ± 3.8	199 ± 10	365 ± 10	365 ± 18 (373[c])	98
	SIMC	4.1 ± 0.2	14.5 ± 1.7	22.1 ± 0.6	9.7 ± 1.5	14.1 ± 0.2	326 ± 17	393 ± 11		105

Results are expressed as the mean of three replicates ± standard deviation.

[a] LOD in RCC ($3\sigma_{\text{blank}}$): 0.2 mg kg^{-1} Cu; 0.4 mg kg^{-1} Pb; 0.06 mg kg^{-1} Zn in $Ca(NO_3)_2$, 0.3 mg kg^{-1} Pb in CH_3COOH, 0.06 mg kg^{-1} Pb in $NH_2OH{\cdot}HCl$.

[b] LOD in SIMC [44]: 0.6 mg kg^{-1} Cu; 0.7 mg kg^{-1} Zn in $Ca(NO_3)_2$, 0.9 mg kg^{-1} Zn in $(NH_4)_2C_2O_4$.

[c] Certified value.

[d] Standard deviations are calculated on the basis of the three sums obtained in each triple series.

interest for environmental monitoring, investigation on groundwater pollution and ecotoxicological assessment of contaminated sites. The reducible and oxidizable forms are relatively stable under standard soil conditions, however, easily reducible (hydroxylammonium extractable) and easily oxidizable (pyrophosphate extractable) fractions may be readily mobilised and hence are also environmentally relevant. The moderately reducible fraction is poorly mobilisable/available but this pool of TE might be of interest for geochemical and soil science research.

The results of fractionation of TE in certified reference materials and real samples as obtained using SIMC and RCC extraction are presented in Table 4. The contents of TE in residual fractions and maximum acid soluble concentrations of metals in the samples under investigation are given as well. The total recoveries of elements in the five leachable fractions plus residuals are within the range 93–106% and 87–114% for SIMC and RCC extraction, respectively, with reproducibilities given as relative standard deviations below 15% in both methods, thereby confirming the accuracy and reliability of both SIMC- and RCC-based methods for partitioning of environmental solids. The distribution of TE between leachable and residual fractions is clearly illustrated in Fig. 3.

As can be seen in Fig. 3 and Table 4, despite the different liquid (free column volume) to solid ratios SIMC and RCC yielded similar characteristic patterns of TE distribution in both SRM 2711 soil and GBW 07311 sediment. Nevertheless, the quantitative values of TE content in individual fractions are different to some extent. In all cases, the total recoveries of Cu, Pb, and Zn in the five leachable fractions are higher if dynamic extraction in RCC is used. The most evident deviations are observed for individual acid-soluble and pyrophosphate extractable fractions. For example, the contents of acid-soluble Cu in GBW 07311 as recovered by using RCC and SIMC are 13.7 and 3.6 mg kg^{-1}, respectively. Hence, for the two reference materials assayed, the continuous-flow leaching in RCC provides more effective recovery of environmentally relevant metal forms. These partitioning results might be explained attending the particular means of extraction 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 [40], large particles of high density are under the experimental conditions used in this work fixed to a given position at the column walls throughout the leaching experiment. 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 pseudostationary and migrate axially within the RCC during the SEP. In addition it should be noted that clay (<2 μm) and silt (2–50 μm) granulometric fractions of soils are often characterized by ten times higher content of metals in mobile forms than the sand (>50 μm) fraction [41]. The improved extractability of TEs in RCC from homogenized, finely sieved reference materials might be thus explained.

The operation principle of dynamic SIMC extraction differs significantly from that of RCC extraction. Particulate matter is here retained as a packed-bed column through which the extractant flows. As a consequence of the application of an uni-directional flow extraction mode, soil particles are quiescent within the column.

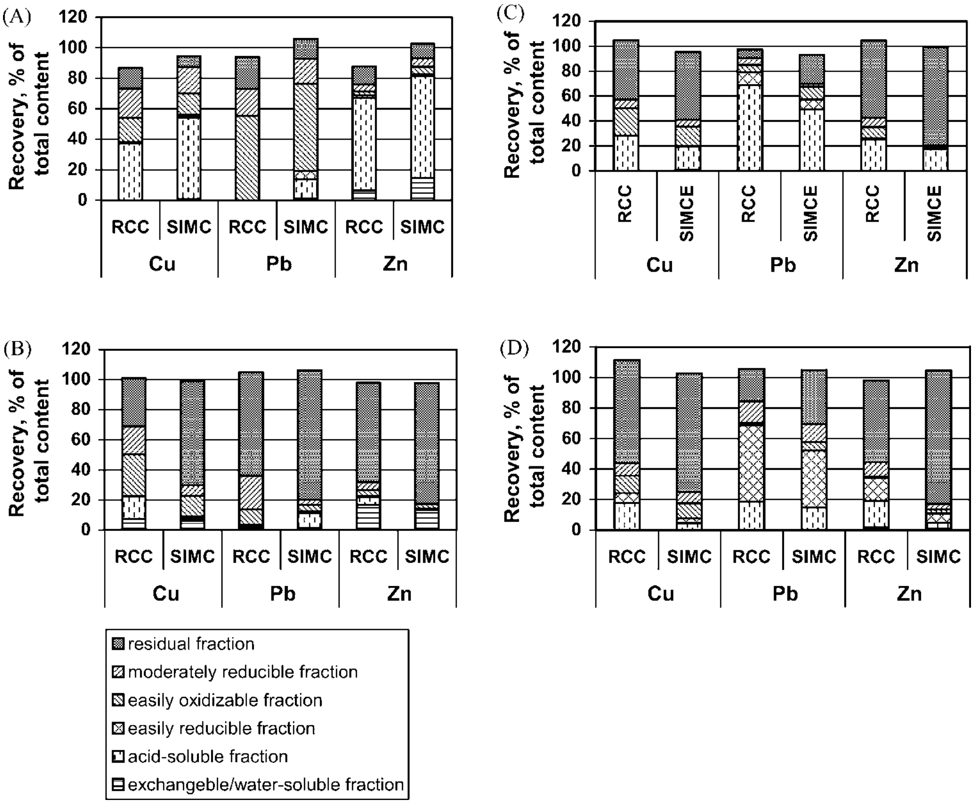

Fig. 3. Distribution of trace metal fractions (recoveries, % of metal content as obtained by microwave digestion) in soil samples A91295 (A), A01725 (B), reference material SRM 2711 (C), and standard sediment sample GBW 07311 (D) as obtained by using dynamic RCC extraction and SIMC extraction.

The lower extractability in SIMC for standard reference materials is most likely due to the stagnant nature of the overall soil/sediment particles and the eventual formation of preferential flow channels for the extractant. By attaching the sample container to one of the peripheral ports of SV and withholding the entire substrate in the lower conical cavity of the column, fluidized-bed like mixing conditions might be however attained, which in turn would lead to improved TE leachability [28].

With regard to the 250 μm-sieved real soil A91295 sample, SIMC and RCC extraction also provide similar patterns for TE distribution. In contrast to reference materials, SIMC provides improved recoveries for the exchangeable fraction of Zn, acid-soluble fractions of Cu and Pb, and pyrophosphate extractable fraction of Zn. It should be also noted that the pools of immobile (residual) TE in RCC (107 mg kg^{-1} Cu, 49 mg kg^{-1} Pb and 320 mg kg^{-1} Zn) significantly exceeded those of SIMC (55 mg kg^{-1} Cu, 30 mg kg^{-1} Pb and 266 mg kg^{-1} Zn). It should be borne in mind that this sample is a calcareous soil because it is characterized by a high content of calcium oxide (6%). In calcareous soils, where the formation of poorly water soluble compounds appears to be one of the main mechanisms for uptake of TE, the determination of the “carbonate” fraction is of great importance. However, in RCC large limestone particles containing specifically sorbed metals might be actually fixed (pressed) at the column walls [40], generating a capillary-like stationary soil column which leads to a decreased extraction efficiency as compared to the packed column in the SIMC method. Yet, increased extractability in RCC could be accomplished by either decreasing the sample weight from 0.5 up to 0.2 g, or by appropriate lowering of the centrifugal force field via accurate control of the column rotation speed [40].

As to the 250 μm-sieved real sample A01725, the results obtained using RCC and SIMC are dissimilar. In general, the extraction in RCC results in significantly higher recoveries of leachable fractions for the suite of TE. The soil assayed is very rich in organic carbon (14.6%) and hence contains a considerable amount of organic matter that participates in the competitive binding of metals. Binding centers can be located inside humus clods which are hardly available for leaching reagents. Migration of organic-rich particles with low density inside the RCC might enhance the mixing of solid and liquid phase and, consequently, the extraction efficiency. In packed columns, however, organic clods are most likely agglomerated. The decreased surface area of soil particles might thus explain the lower extractability of TE in SIMC method.

In general, both investigated techniques are valuable for dynamic fractionation of TE in environmental solids. The comparative data are in acceptable agreement, especially taking into account the uncertainties typically reported when analysing soil samples [2,12] and the operationally defined nature of both fractionation methods. It is of common knowledge that 15 European institutions worked during 6 years according to the Standards, Measurements and Testing Programme of the European Commission (formerly BCR Program) in order to certify extractable contents of heavy metals in two lake sediment samples using a single standard fractionation protocol [42,43]. This demonstrates the inherent difficulties for quality assurance of analytical data in fractionation tests.

4. Conclusions

This work has been focused on the generalization of similarities and discrepancies between two dynamic leaching methods, the so-called RCC extraction and SIMC extraction, which should be regarded as appealing alternatives to batch wise steady-state leaching tests.

The partitioning of TE was studied using a five-step sequential extraction scheme and available certified reference materials plus real soil samples. The experimental results presented in this article revealed that the physicochemical properties of the samples which most significantly affect the leachability of trace elements in flow-through dynamic fractionation methods are the size and density of soil/sediment particles, the contents of organic matter and the limestone nature of the soil.

We have set the basis for the harmonization of dynamic fractionation using RCC and SIMC for accurate determination of overall mobilisable pools of TE in environmental substrates for ascertainment of worse-case scenarios. Further work is to be focused on the analysis of a wide range of samples with variable composition and particle size distribution and optimization of analytical parameters for extraction as well.

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