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Fractionation of elements in soils, sludges and sediments: batch and dynamic methods

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Abstract. Methods and approaches employed in the fractionation of elements according to their physicochemical mobility and bioavailability in soils, sludges and sediments are generalised. Comparative analysis of sequential extraction schemes for heavy metals, arsenic, selenium and phosphorus is performed. Special consideration is given to the flow-through fractionation and kinetic aspects of selective leaching. The bibliography includes 115 references.

I. Introduction

The physicochemical mobility, bioavailability and toxicity of elements in natural sample largely depend on the forms of their existence and the type of binding to the sample matrix. Data on the total contents of elements in soils, sediments and sludges are too scarce to allow considering their possible migration upon changes in the environmental conditions and the probability for released elements to be incorporated in plants and other living organisms. Elements in various forms are analysed using sequential extraction in which the sample is subjected to successive treatment with selective leaching reagents. Aqueous solutions of reagents should mimic, to one or another extent, the natural conditions under which the elements bound to the soil, sludge or sediment matrix are released. For example, a change in the ionic composition of the solution affecting sorption – desorption processes or a decrease in the pH may cause release of elements that are bound to the matrix by weak electrostatic forces or co-precipitated with carbonates ('exchangeable' and 'acid-soluble' forms). A decrease in the redox potential results in dissolution of oxides unstable in reducing media ('reducible' form). The organic matter of soil may be destroyed in an oxidative medium, resulting in dissolution of metal complex compounds with organic ligands ('oxidisable' form). Finally, decomposition of the mineral matrix is accompanied by dissolution of the constituent elements as a result of isomorphous substitution ('residual' form). Sequential extraction may provide knowledge about the origin, physicochemical mobility and bioavailability of elements and also on their possible migration upon the change in the chemical properties of the soil.

According to IUPAC recommendations, sequential extraction of element forms from soils, sludges and sediments is a method of fractionation of elements.[1] The main principle of this fractionation is that each subsequent leachant should either be stronger in chemical action than the previous one or have a different nature.[2] At least eight different fractions of heavy metals can be separated (Table 1). For fractionation of elements (such as arsenic, phosphorus, selenium) existing as anions, specific sequences of reagents are used.[3] Note that fractionation implies isolation of not pure chemical compounds of elements, but their combinations. Each fraction obtained on treatment with a particular leachant represents, most often, a group of compounds with similar properties (in particular, physicochemical mobility and bioavailability). In some cases, individual species of elements are determined in the isolated fractions; however, this aspect is beyond the scope of this review.

Two approaches to classification of fractions of elements are known. According to one approach based on the action of reagents used, the fractions are called 'acid-soluble', 'easily reducible', 'easily oxidisable' and so on. These names reflect the conditions for the release of trace elements bound to a particular soil, sludge or sediment component. According to the second approach, it is assumed that mineral phases of the sample are dissolved by selective reagents; hence, fractions can be referred to as 'carbonate co-precipitated elements,' 'manganese oxide-bound elements', 'iron oxide-bound elements' and so on. These terms are certainly useful for interpretation of the fractionation of elements, but in some cases they can lead to wrong conclusions, because the reagents are by no means always selective and the isolated fractions overlap (elements bound to particular soil components are partly extracted to another fraction when the subsequent reagent is used).

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Table 1. Fractionation of heavy metals. Operationally defined fractions and applied leaching reagents.[2–4]

Fraction	Extracted components (possible forms of binding)	Physicochemical mobility	Bioavailability	Common leachants
Water-soluble	free ions	mobile	easily available	deionised water
Exchangeable (A)	exchangeable ions (metals retained by weak electrostatic interactions)	"	the same	$Ca(NO_3)_2$, $Mg(NO_3)_2$, $CaCl_2$, $MgCl_2$, $CH_3CO_2NH_4$
Acid soluble (B)	carbonates (for non-calcareous soils, other specifically adsorbed forms of metals)	easily mobilisable	"	CH_3CO_2H, CH_3CO_2Na ($pH \leqslant 6$)
Easily reducible (C)	manganese oxides	moderately mobilisable	moderately available	$NH_2OH \cdot HCl$
Easily oxidisable (D)	humic and fulvic acid salts and other organic complexes	the same	the same	$K_4P_2O_7$, $Na_4P_2O_7$, NaClO, NaOH
Moderately reducible (E)	amorphous iron and aluminium oxides	poorly mobilisable	poorly available	$NH_2OH \cdot HCl$, oxalate buffer (pH 3.2)
Moderately and poorly oxidisable (F)	stable organic compounds and sulfides	the same	the same	$H_2O_2 + CH_3CO_2NH_4$
Poorly reducible (G)	crystalline iron and aluminium oxides	"	"	$(NH_4)_2C_2O_4$ + ascorbic acid
Residual	mineral lattice (metals retained within the crystal structure)	immobile	unavailable	HF, HNO_3, $HClO_4$

Generally, the results of speciation analysis of elements depend on the leachant use, contact time of the liquid and solid phases, the intensity of shaking of the mixture, the ratio of the sample weight to the reagent volume and specific features of the soils or sediments studied. The sequential extraction schemes have been repeatedly criticised for the lack of versatility, low selectivity of the leachant with respect to the isolated forms of elements (soluble mineral phases of the sample) and poor reproducibility of the results.[3,4] Note also that for performing sequential extraction, several days of routine work are required, because batch extraction of elements from solid samples (without renewing of reagent solutions) is slow. In addition, estimation of the mobility and bioavailability of element forms is not always correct, as leaching under natural conditions always occurs in the dynamic mode, *i.e.*, the reaction soil solution is continuously renewed. Despite the above-listed drawbacks, batch sequential extraction is widely used for speciation analysis of soils, sludges and sediments. Meanwhile, development of an alternative procedure based on flow-through (dynamic) fractionation of elements is a topical task. In this review, special attention is given to dynamic fractionation methods that are being actively developed in the last decade.

II. Batch sequential extraction

1. Fractionation of forms of heavy metals

The total content of the potentially mobile forms of elements in soils, sludges and sediments can be estimated by single extraction [5] using 1 M solutions of nitric acid, ammonium acetate or ammonium acetate buffer with pH 4.8. The first sequential extraction schemes that provided information on the distribution of elements between various forms appeared in the 1960s.[6,7] Over the last 30 years, dozens of schemes have been proposed and tested;[2–32] the most popular protocols are presented in Table 2. However, none of them can be preferred.

McLaren and Crawford were the first to develop a procedure for the isolation of four extractable fractions.[8] According to this procedure, elements bound to the organic matter of soil are isolated before dissolution of iron and manganese oxides. In 1979, Tessier *et al.*[9] proposed one of the most popular schemes in which also four fractions were isolated, but other reagents were used; metals bound to iron and manganese oxides were leached prior to the extraction of the 'organic/sulfide' form. The Kersten–Förstner [10] scheme is generally based on the Tessier scheme, but allows one to separate heavy metals bound to both manganese and iron oxides. These species have different mobilities and bioavailabilities; therefore, their sequential recovery is important for the evaluation of the potential environmental hazard. Zeien and Brümmer [11] proposed a six-step fractionation of the extractable forms, which made it possible to separate elements bound to manganese oxides and amorphous or crystalline iron oxides. Manganese oxides are dissolved before extraction of the organic compound. Note that according to the scheme proposed by Krishnamurti *et al.*,[12] seven extractable forms of heavy metals can be isolated. The recovery of easily oxidisable (humic and fulvic acids) or poorly oxidisable (refractory organic compounds and sulfides) fractions is carried out in two stages before three-step dissolution of oxides.

When selecting a sequential extraction scheme, one should take into account the multicomponent and multiphase structure of solid natural samples. It is important to distinguish, if possible, the most typical mechanism of binding of elements to the soil (sediment) matrix.[7] For example, in the studies of calcareous soils where the formation of poorly soluble compounds is a key mechanism of heavy metal binding, of particular importance is recovery of acid-soluble (carbonate) fraction, while in the case of humus-rich soil horizons, it is determination of elements bound to organic matter.

Water-soluble, exchangeable and acid-soluble heavy metal forms are most mobile and bioavailable; therefore, their determination is exceptionally important for evaluation of

Table 2. Some sequential extraction schemes for heavy metals.

Authors	Leachants	Leaching conditions	Recovered form (without the residual fraction)
McLaren and Crawford [8]	0.05 M $CaCl_2$		exchangeable ions (A)
	2.5% CH_3CO_2H		specifically sorbed ions (B)
	0.1 M $K_4P_2O_7$, pH 10		metals bound to organic matter (D)
	0.1 M $H_2C_2O_4$ + 0.175 M $(NH_4)_2C_2O_4$	pH 3.2	metals bound to oxides (C + E)
Tessier, Campbell, Bisson [9]	1 M $MgCl_2$		exchangeable ions (A)
	1 M CH_3CO_2Na, pH 5		metals bound to carbonates (B)
	0.04 M $NH_2OH \cdot HCl$ + 25% CH_3CO_2H	pH 2, T = 96°	metals bound to manganese and iron oxides (C + E)
	30% H_2O_2; then 3 M $CH_3CO_2NH_4$	pH 2, T = 85 °C	metals bound to organic matter (D + F)
Kersten, Förstner [10]	1 M $CH_3CO_2NH_4$	pH 7	exchangeable ions (A)
	1 M CH_3CO_2H	pH 5	metals bound to carbonates (B)
	0.01 M $NH_2OH \cdot HCl$ + 0.01 M HNO_3	pH 2	metals bound to manganese oxides (C)
	0.1 M oxalate buffer	pH 3	metals bound to iron oxides (E)
	30% H_2O_2; then 1 M $CH_3CO_2NH_4$ in 6% HNO_3	pH 2, T = 85 °C	'sulfide/organic' fraction (D + F)
Zeien, Brümmer [11]	1 M NH_4NO_3	pH 7	exchangeable ions (A)
	1 M $CH_3CO_2NH_4$	pH 6	specifically sorbed ions (B)
	0.1 M $NH_2OH \cdot HCl$ + 1 M $CH_3CO_2NH_4$	pH 6	metals bound to manganese oxides (C)
	0.025 M NH_4 (EDTA)	pH 4.6	metals bound to organic matter (D)
	0.2 M $(NH_4)_2C_2O_4$	pH 3.2	metals bound to amorphous iron oxides (E)
	0.2 M $(NH_4)_2C_2O_4$ + 0.1 M ascorbic acid	boiling	metals bound to crystalline iron oxides (G)
Krishnamurti, Huang, Van Rees, Kozak, Rostad [12]	1 M $Mg(NO_3)_2$	pH 7	exchangeable ions (A)
	1 M $CH_3CO_2NH_4$	pH 5	carbonates (B)
	0.1 M $Na_4P_2O_7$	pH 10	metal-organic complexes (D)
	0.1 M $NH_2OH \cdot HCl$ + 0.01 M HNO_3		easily reducible fraction (C)
	30% H_2O_2; then 1 M $Mg(NO_3)_2$ + 20% HNO_3	pH 2, T = 85 °C	oxidisable organic matter, sulfides (F)
	0.2 M $(NH_4)_2C_2O_4$	pH 3	amorphous iron and aluminium oxyhydroxides (E)
	0.2 M $(NH_4)_2C_2O_4$ + 0.1 M ascorbic acid	pH 3, T = 95 °C	crystalline iron and aluminium oxyhydroxides (G)
Ure, Quevauviller, Muntsu, Griepink,[31] original BCR scheme [a]	0.11 M CH_3CO_2H	t = 16 h	acid-soluble (A + B)
	0.1 M $NH_2OH \cdot HCl$ + HNO_3 (to pH 2)	t = 16 h	reducible (C + E)
	8.8 M H_2O_2; then 1.0 M $CH_3CO_2NH_4$ + HNO_3 (to pH 2)	t = 2 × 1 h, T = 85 °C t = 16 h	oxidisable (D + F)
Rauret, López-Sánchez, Sahuquillo, Rubio, Davidson, Ure, Quevauviller,[32] optimised BCR scheme [a]	0.11 M CH_3CO_2H	t = 16 h	acid-soluble (A + B)
	0.5 M $NH_2OH \cdot HCl$ + HNO_3 (to pH 1.5)	t = 16 h	reducible (C + E + partially G)
	8.8 M H_2O_2; then 1.0 M $CH_3CO_2NH_4$ + HNO_3 (to pH 2)	t = 2 × 1 h, T = 85 °C t = 16 h	oxidisable (D + F)

[a] BCR is the Community Bureau of Reference.

contamination hazard for soils, sludges and sediments. Easily reducible and easily oxidisable fractions are also environmentally significant, because heavy metals they contain may be dissolved (mobilised) upon changes in environmental conditions. Now we consider methods for isolation of each of these fractions

Water-soluble fraction. Although this fraction contains most mobile and bioavailable forms of elements, its recovery is usually neglected.[4] Water-soluble species are represented by free ions or metal complexes, in particular, those with a soluble organic compound. However, the use of distilled water as the leachant faces procedural difficulties, because, first, the content of organic compounds in a sample affects considerably the interaction of the sample with water, and, second, water has no buffer capacity and its extraction properties change as soluble components of the sample pass to the liquid phase. Thus, in most cases, water-soluble and exchangeable fractions are recovered simultaneously using dilute salt solutions.[13]

Exchangeable fraction. Exchangeable (weakly adsorbed) cations are retained in the sample due to weak electrostatic interactions; their behaviour is dictated by ion-exchange processes. A change in the ionic composition of the medium and a decrease in the solution pH result in mobilisation (release) of exchangeable ions.[14, 15] For adequate estimation of the content

of exchangeable metals in soils and sediments, selection of an appropriate reagent is important. The electrolyte cation should have a high displacing ability and have an ionic radius roughly equal to the radius of the extracted metal. In addition, neither cation nor anion of the salt used should react with components of the sample to form precipitates or complexes.[7]

In practice, metals held by electrostatic forces are leached with 0.05–1 M solutions of the following salts: $NaNO_3$, KNO_3, NH_4NO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Pb(NO_3)_2$, $CH_3CO_2NH_4$.[2,16,17] Most widely used are 1 M solutions of $MgCl_2$ and $CH_3CO_2NH_4$. However, chlorides and acetates can form fairly stable complexes with some metals. As a result, the equilibrium in the solid phase–liquid system is shifted, resulting in overestimated contents of exchangeable ions. Nitrate anions are more preferable, because they participate only in ion exchange and do not affect complexation.[4,12] The Ca^{2+} ion is the electrolyte cation of choice. The Sr^{2+} and Ba^{2+} ions are characterised by high displacing abilities, which ensures the extraction of the exchangeable fraction of metals.[7] The selectivity of Ba^{2+} with respect to exchangeable metals is lower than that of Ca^{2+}, which may be caused by the possible parallel complexation and/or precipitation reactions involving Ba^{2+} and components of the sample matrix. Thus, calcium nitrate complies with the above requirements and can be used as a reagent ensuring rather selective extraction of exchangeable metals.

It is noteworthy that recovery of the exchangeable fraction with NH_4NO_3, $Ca(NO_3)_2$, $CaCl_2$ or $NaNO_3$ can be used as a one-step extraction procedure to estimate the plant-available metals.[17,18]

Acid-soluble fraction. This fraction contains metals extracted from a soil or sediment sample at a pH value of about 5. Most often, 1 M acetate buffer (pH 5) is used as the extractant for the recovery of the acid-soluble form of elements.[3,9,16] This particulate fraction contains metals co-precipitated with carbonates as well as metals adsorbed specifically on the surface of clay minerals, organic matter and iron and manganese hydroxides. In addition, as pH decreases from 7 (at this pH the exchangeable fraction is operationally defined) to 5, weakly adsorbed cations that have not been extracted in the previous stage also pass to the liquid phase.

In the studies of soils and sediments with high carbonate contents, incomplete dissolution of carbonates in the acetate buffer is observed in some cases. The metals co-precipitated with carbonates can be recovered at the subsequent stages of extraction, which results in the overlap of the isolated fractions.[19]

The acid-soluble fraction is obtained using not only acetate buffer solutions, but also 0.1–1 M solutions of acetic acid. As the acetic acid concentration increases, the degree of metal extraction increases and the difference between the metal contents in the acid-soluble fractions extracted by 0.11 M and 1 M acetic acid solutions can reach an order of magnitude.[20]

Easily reducible fraction. The manganese and iron oxyhydroxides are key binding sites for heavy metals in soils, sludges and sediments. These oxides are unstable under reducting conditions: reduction of Fe(III) and Mn(IV) by the reaction with, for example, hydroxylamine hydrochloride is accompanied by their dissolution.[4] The reducible fraction can be isolated in three steps, namely, the isolation of easily reducible (manganese oxides), moderately reducible (amorphous iron and aluminium oxides) and poorly reducible (crystalline iron and aluminium oxides) fractions.[11,12,21]

The easily reducible fraction is most readily available and, hence, environmentally significant. The use of a 0.01–0.1 M solution of hydroxylamine hydrochloride acidified to pH 2 is believed to ensure selective dissolution of manganese oxides with minor leaching of iron oxides.[10,22,23] However, at low pH, partial extraction of metals bound to organic matter can take place and their content in the easily reducible fraction would be overestimated. It is more expedient to use a non-acidified (pH 3.6) 0.1 M solution of hydroxylamine hydrochloride. This leaching agent was shown to have no noticeable influence on the organic matter or iron and aluminium oxides.[24]

Easily oxidisable fraction. The organic matter in soils, sludges and sediments is mainly represented by macromolecular compounds (humic substances and resins), carbohydrates, proteins, peptides, amino acids, fats and so on. Under oxidising conditions, organic matter is destroyed and the metals bound to it are released. Since heavy metals can form stable complexes with the soil organic matter, this way of binding may predominate in some cases.

A 'mild' leachant, potassium/sodium pyrophosphate (0.1 mol litre^{-1}, pH 10.0), has long been used to recover organic complexes of iron and aluminium.[25,26] This reagent is included in many sequential extraction protocols[8,12,21] and is considered to be selective with respect to easily oxidisable fraction containing metals, most of all, as humates and fulvates. However, the efficiency of potassium/sodium pyrophosphate at pH 10 is rather low.[27] A mixture of 0.1 M solutions of $K_4P_2O_7$ and KOH (pH 11–12) has been proposed to increase the solubility of metal–organic complexes.[7] Note that at this high pH, manganese oxides can also be partially dissolved; hence, the easily reducible fraction should be isolated prior to pyrophosphate extraction.

Some researchers believe that the easily oxidisable fraction should be called more correctly 'the pyrophosphate-extractable fraction' or 'the fraction containing metal–organic complexes'.[28] This cannot be argued because this fraction is isolated most often by reagents having no oxidising properties. The dissolution of humate- and fulvate-bound metals can also be carried out using a potent complexing agent, ethylenediaminetetraacetic acid (EDTA).[7,11] However, EDTA solutions can also dissolve metals bound to iron oxides due to formation of Fe–EDTA chelates with high stability constants.

If the organic matter of soil is destroyed on heating in the presence of such oxidants as sodium hypochlorite in alkaline medium[29,30] or hydrogen peroxide,[9,14,31,32] not only metal–organic complexes are dissolved, but also stable organic compounds and sulfides. In this case, it is impossible to estimate the content of environmentally significant (moderately mobilisable) fraction of metals represented by humates and fulvates.

The diversity of the reagents used, inadequate standardisation of sequential extraction schemes and low reproducibility of fractionation have prevented for a long time correct comparison of the results obtained in different laboratories. In 1993, fifteen European institutes have started a joint project within the BCR Programme.† The following tasks were set: (i) development of a simplified three-step scheme for sequential extraction of elements; (ii) interlaboratory testing of the scheme; (iii) certification of the contents of three extractable forms of heavy metals in a standard sediment sample.[31] The

† Later 'Standards, Measurements and Testing Programme of the European Commission'.

work on the project was outlined in a number of publications (see, for example, Refs 20, 31–43).

First, the procedures for the preparation of leachant solutions and extraction conditions for each of the three steps were described in detail.[31,33] Thus, the main factors that could have adverse effect on the reproducibility were seemingly eliminated. However, in testing the original BCR scheme for speciation analysis of Cd, Cr, Cu, Ni, Pb and Zn present in the reference lake sediment sample CRM 601, copper and chromium extracted in the second stage (reducible fraction) and copper, chromium and zinc extracted in the third stage (oxidisable fraction) were not certified due to the poor reproducibility of the results.[34] The effects of several parameters (pH, reagent concentration, time and temperature of extraction) on the recovery of elements were studied in order to elucidate the reasons for deviations between the results.[35,36] It was found that poor reproducibility is mainly typical of the second step (isolation of the reducible forms of elements on treatment with hydroxylamine hydrochloride). In a modified (optimised) BCR scheme,[32] reducible species are leached using higher concentration of hydroxylamine hydrochloride (0.5 mol litre^{-1} instead of 0.1 mol litre^{-1}) and more acidic medium (pH 1.5 instead of 2.0). Using the optimised scheme, all extractable forms of Cd, Cr, Cu, Ni, Pb and Zn in the reference lake sediment sample BCR 701 were certified.[37] This scheme was also tested in relation to reference samples of soils [CRM 483,[38,39] SRM 2710, SRM 2711 (Ref. 40)], sludges[41] and road dust sediments.[42]

It is noteworthy that modification of the BCR scheme was accompanied by a decrease in its selectivity. Indeed, an increase in the hydroxylamine hydrochloride concentration and especially a decrease in the pH to 1.5 result in not only leaching of reducible forms of elements, but also partial dissolution of the organic matter of soil and release of metals bound.[3,4,7] Thus, data on the contents of metals in reducible species may be overestimated and, correspondingly, the metal contents in oxidisable species would be underestimated. Nevertheless, the optimised BCR scheme is currently the only one that is used for certification of samples and permits rather correct comparison of data on element fractionation obtained in different laboratories.[20,43]

Special place among heavy metals belongs to mercury. Due to the large number and diversity of mercury forms with specific physical and chemical properties, the sequential extraction procedures used to study metals such as copper, lead, cadmium and zinc are hardly applicable to mercury. In terms of the degree of binding to soil particles, forms of mercury are classified into water-soluble (ion-exchangeable), complexed, adsorbed and chemically bound to mineral components. Water-soluble forms include chlorides, sulfates, nitrates and soluble organic complex compounds. In coordination compounds, mercury shows high affinity to organic compounds and S-containing ligands. Mercury complexes with humus substances influence the bioavailability of mercury for living organisms including methylating bacteria. Mercury can interact with humus substances through thiol (strong binding), carboxy and phenolic groups (weak binding).[44]

Thus, sequential extraction of mercury should comprise steps that ensure the separation of the following metal forms: soluble mercury(II) compounds; mercury(II) complexes with fulvic and humic acids; mercury(II) sulfide and, finally, the residual (mercury ions bound to humus and retained in the mineral lattice).[45] There are several procedures of sequential extraction of mercury forms, which comprise 2 to 6 steps depending on the purpose of investigation. The most accurate data on the contents of various biogeochemical mercury fractions in soils and sediments are provided by the scheme developed by Bloom *et al.*[46] According to this scheme, the following fractions are operationally defined: water-soluble ($HgCl_2$, $HgSO_4$), acid-soluble (HgO), organic-bound (mercury humates, Hg_2Cl_2), strongly bound (Hg^0, elements retained in the mineral lattice) and sulfide fractions (HgS, HgSe, HgAu). Note that leaching of the 'organic' fraction is performed with a solution of potassium hydroxide, whereas strongly bound and 'sulfide' forms are solubilised by acids.

2. Fractionation of arsenic, selenium and phosphorus

Special sequences of reagents are used for fractionation of anionic As, P and Se.[3,47,48] It should be borne in mind that these elements may exist in soils, sludges and sediments in different oxidation states, which influences their properties including toxicity. The results of fractionation allow one to estimate the potential mobility and bioavailability of elements, but in some cases, they are debatable because sequential extraction requires both oxidative and reductive conditions where the initial oxidation state of the element can be changed.[3,49]

For the fractionation of arsenic forms, numerous leachant sequences have been proposed.[3,47–53] Since the chemical properties of arsenic and phosphorus are similar, some sequential extraction schemes proposed for phosphorus were also used for speciation analysis of arsenic.[50,51] According to these schemes, NH_4Cl, NH_4F, NaOH and H_2SO_4 are used to isolate first the exchangeable fraction of arsenic and then its aluminium-, iron- and calcium-bound forms. A distinctive feature of these schemes is that the forms bound to iron and aluminium are isolated in alkaline medium next after extraction of the exchangeable fraction.[3]

Recently, a new optimised scheme for arsenic form fractionation has been proposed.[52,53] Leachants used for extraction of various forms of metals, selenium and phosphorus, in particular NH_4NO_3, CH_3COONa, $NH_2OH \cdot HCl$, EDTA, NH_4OH and NH_4F, have been tested. Some reagents proved to be either inefficient for the extraction of arsenic or insufficiently selective for dissolution of the required mineral phase of the sample. The final version of the sequential extraction scheme for arsenic (Table 3) includes four steps, in particular, isolation of non-specifically sorbed and specifically sorbed fractions and fractions bound to amorphous iron oxide and crystalline iron oxide using $(NH_4)_2SO_4$, $NH_4H_2PO_4$, $(NH_4)_2C_2O_4$ and an $(NH_4)_2C_2O_4$–ascorbic acid mixture at 96 °C, respectively.[53] Despite the general limitations of element form fractionation, in this particular case, the selectivity of the leachant with respect to the fractions obtained was confirmed by chemical analysis data for soil extracts and model mineral phases and by X-ray diffraction microanalysis of soils. The scheme was recommended for the evaluation of the potential mobility of arsenic during land remediation and upon changes in the environmental conditions.[53]

A number of leachants are used for selenium fractionation.[3] A variety of reagents [water, phosphate buffer (pH 7), HNO_3, HCl, $CH_3CO_2NH_4$, NaOH, $(CH_3)_4NCl$] were tested for analysis of contaminated sediment samples.[54] The developed optimised scheme for the sequential extraction of selenium includes four steps (see Table 3). Particular selenium compounds (selenates, selenites, elemental selenium, organic-bound selenium) were determined in the fractions by chromatographic methods. It was noted that pyrophosphate extraction, which is used to isolate humic and fulvic acids, can also be

Table 3. Sequential extraction schemes for arsenic, selenium and phosphorus.

Authors	Leachants	Leaching conditions	Recovered form (without the residual fraction)
Fractionation of arsenic			
Wenzel, Kirchbaumer, Prohaska, Stingeder, Lombi, Adriano [53]	0.05 M $(NH_4)_2SO_4$		non-specifically sorbed
	0.05 M $(NH_4)H_2PO_4$		specifically sorbed
	0.2 M $(NH_4)_2C_2O_4$	pH 3.25	amorphous iron and aluminium oxides
	0.2 M $(NH_4)_2C_2O_4$ + 0.1 M ascorbic acid	pH 3.25, T = 96 °C	crystalline iron and aluminium oxides
Fractionation of selenium			
Ponce de León, de Nicola, Montes Bayón, Caruso [54]	H_2O		soluble (selenites, selenates)
	0.5 M $KH_2PO_4 + K_2HPO_4$	pH 7	adsorbed (selenates, organic compounds)
	5% $(CH_3)_4N \cdot HCl$		water-insoluble selenites, organic compounds
	1 M Na_2SO_3	pH 7	elemental selenium, residual extracted fraction
Fractionation of phosphorus			
Ruban, López-Sánchez, Pardo, Rauret, Muntau, Quevauviller [55]	1 M NaOH, 1 M HCl		phosphorus bound to iron and aluminium, 'apatite' phosphorus
	1 M HCl, calcination at 450 °C, then 1 M HCl		'inorganic' phosphorus, 'organic' phosphorus
	calcination at 450 °C, then 3.5 M HCl		total phosphorus (extracted with concentrated HCl)

employed for speciation analysis of selenium to isolate the easily oxidisable fraction.

Phosphorus is not a trace element but rather a major nutrient element. Nevertheless, determination of phosphorus forms is an important task in the studies of soils, sludges and sediments. Within the framework of the Standards, Measurements and Testing Programme of the European Commission, four procedures of sequential extraction of phosphorus were compared. As a result, a new procedure based on the protocol of Williams *et al*.[56] was proposed.[55] This procedure included three parallel experiments: sequential extraction of the iron- and aluminium-bound forms and calcium-bound forms with sodium hydroxide and hydrochloric acid, respectively; sequential extraction of so-called organic and inorganic phosphorus fractions; determination of total phosphorus (see Table 3).

Apart from the sequential extraction of arsenic, selenium and phosphorus forms, determination of individual compounds of these elements in various oxidation states is often carried out;[57, 58] however, as has already been noted, this aspect of speciation analysis of soils, sludges and sediments is beyond the scope of the present review.

III. Methods for dynamic fractionation of elements

It has been noted above that all sequential extraction procedures are labour-consuming (usually, they require several days of routine work). For example, determination of four forms of elements according to the McLaren scheme requires 65 h (without the time of recovery of the residual fraction).[8] The isolation of element forms by BCR schemes requires 50 h (the whole procedure including isolation of the residual fraction and determination of the contents of elements in the fractions lasts for two weeks).[31, 32] The batch extraction of element forms from solid samples (without renewing of extractant solutions) occurs slowly. Recently, attempts have been made to accelerate extraction by microwave treatment [59, 60] or sonication.[61, 62] However, in any case, estimates of the mobility and bioavailability of forms of elements made under batch conditions are not always correct because leaching processes in nature take place under dynamic conditions. Usually, batch extraction faceds two major problems related to the selectivity and completeness of fraction isolation: phase overlap [63, 64] and re-adsorption (elements transferred to the solution can be adsorbed on undissolved soil components).[63, 65]

These problems can be solved by an alternative strategy based on flow-through (dynamic) fractionation of elements accompanied by renewing of leachant solutions. Dynamic extraction makes use of big columns, stirred flow cells, rotating coiled columns and microcolumns.

Big columns. For estimating the mobilities of elements under dynamic conditions as close as possible to the natural conditions, cumbrous non-metal columns filled with several kilogrammes (most often, 1 to 10) of soil,[66, 67] sediment or compost [68] are used. Leachant solutions are passed through the columns at a flow rate of 0.1 – 10 litres per 24 h. The large weight of the sample ensures sample representativeness. Despite the fact that with dense packing of a big column, by no means the whole surface of the sample is accessible for the reagents, laboratory experimental data obtained with big columns are comparable with the results obtained by field lysimeters.[69, 70]

Big columns proved useful for the study of the behaviour of metals that get into soil with contaminated water;[71, 72] the key factors affecting immobilisation of heavy metals in soils and sediments;[73, 74] and applicability of various adsorbents for remediation of metal-contaminated soils;[75, 76] and also for increasing the efficiency of single or sequential extraction for soil cleanup.[77]

Leaching in big columns is a tiring time-consuming procedure, which, however, allows detailed investigation of hydrogeological processes [78] and correct estimation of the probability of release of heavy metals, for example, during acid rains.

Stirred flow cells. Of considerable interest are studies describing a10-ml stirred cell covered with membrane filters.[79, 80] This device is quite simple. A sample (0.25 to 5 g) is magnetically stirred in the cell. Solutions of leachants are supplied by a peristaltic pump mounted either upstream (positive pressure) or downstream (negative pressure) of the cell.

A number of three- and four-step sequential extraction schemes have been used for flow-through fractionation of heavy metals,[79,81] arsenic[82] and phosphorus[83] in soils and sediments. Unlike batch extraction, dynamic fractionation in a cell can be automated, which shortens the time required to isolate each fraction. Using a stirred flow cell, it is also possible to study the effect of the eluent flow rate, specific features of the sample and other parameters on metal re-adsorption in each extraction stage.[84]

The main drawback of the cell is partial refreshment of the pumped-through reagent solutions. The great 'dead volume' of the device results in overlap of the isolated fractions. In addition, the flow rate of the mobile phase is unstable, which may have an adverse effect on the reliability and reproducibility of the results. Using the modified cell with variable flow direction, one can avoid accumulation of particles on the membrane filter and attain a constant eluent flow rate.[85] This cell was used for fractionation of elements according to the BCR scheme (the sample weight was 0.25 g, the elements in the eluate were determined on-line by inductively coupled plasma mass spectrometry).

Rotating coiled columns. Traditionally, rotating coiled columns are used for separation and purification of organic[86] and inorganic[87] compounds by counter-current chromatography. The method is based on the distribution of substances to be separated between the non-miscible phases of a two-phase liquid system. The stationary liquid phase is held in the column by the centrifugal forces arising as the column rotates around its own axis with simultaneous revolution of a planetary centrifuge around the central axis; the mobile liquid phase is continuously fed into the column. The absence of a sorbent or a solid support for the stationary phase is a specific feature of rotating coiled columns.

It was shown[88] that these columns can be used to separate both solutes and solid particles not only in liquid–liquid, but also in liquid–solid systems. Rotating coiled columns have been used for dynamic fractionation of heavy metals[89,90] and arsenic[91] in contaminated soils, sludges and sediments. A ground solid sample (usually weighing 0.5 g) was held by centrifugal force as the stationary phase in a 20-ml column (with an inner diameter of 1.5 mm), while aqueous solutions of salts, acids and complexing agents were continuously pumped through the column. The eluents were selected in conformity with original[31] and optimised[32] BCR schemes, the McLaren and Crawford scheme,[8] the Kersten–Förstner scheme[10] (fractionation of heavy metals) and an optimised scheme proposed by Wenzel *et al.*[53] (fractionation of arsenic). Leaching of elements from solid samples is a long-lasting process; however, the use of dynamic multistage extraction in rotating coiled columns allowed the time it takes to recover each fraction to be reduced to 1–2 h.

A comparative analysis of the results obtained by dynamic fractionation and batch sequential extraction of elements was carried out. It was found that continuous renewing of the eluent in a rotating column eliminates the re-adsorption problems and provides the possibility to estimate correctly the contents of heavy metals and arsenic in the most mobile, environmentally significant fractions (in the case of batch extraction, these values were underestimated severalfold in some cases).[89–91]

A hyphenated method of fractionation and determination of element forms based on on-line detection of elements in the eluate from a rotating column by inductively coupled plasma atomic emission spectroscopy was proposed.[92,93] Using this method, one can monitor dynamic leaching of both trace elements (As, Cd, Pb, Cu, Zn, Ni, Cr) and matrix components of the sample (Fe, Mn, Al, Ca, S) on a real-time basis (Fig. 1). This possibility was used in testing of a new fractionation procedure and investigation of the leachant selectivity with respect to sample mineral phases being dissolved.[93] Characteristic features of binding of heavy metals to matrix components of some soils were studied.[94] It was shown that it is possible to consider the presence or absence of an operating source of soil pollution by a particular metal from the positions and shapes of peaks in the elution curve corresponding to the exchangeable fraction of the element. The knowledge about the competitive binding of metals to the organic matter and mineral structures of soil can be gained by comparing the elution profiles of acid-soluble and pyrophosphate-extractable fractions. The time-resolved elution peaks of iron and aluminium oxides and metals bound to them attest to different mechanisms of their dissolution. As an example, Fig. 2 shows the extraction curves for heavy metals and major elements of a contaminated municipal soil sample.

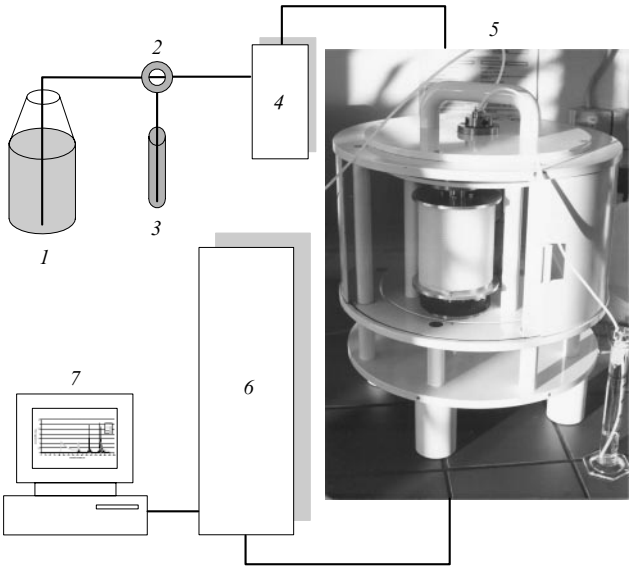


Figure 1. Diagram of a hyphenated method of the dynamic fractionation and determination of elements using a rotating coiled column.[93,94]
(*1*) Leachant solution, (*2*) multiway valve, (*3*) sample suspension, (*4*) peristaltic pump, (*5*) rotating coiled column, (*6*) multielement detector, (*7*) computer.

It is noteworthy that by varying the design parameters of the rotating column, one can increase the representativeness of the sample. Thus with an increase in the inner diameter of the rotating coiled column from 1.5 to 3.4 mm, the weight of the held sample can be increased from 0.5 to 5 g.[95]

Rotating columns can also be used to separate soil particles according to the grain size composition. By obtaining the clay, silt and sand fractions and determining various forms of heavy metals in each fraction, one can gain detailed information on the distribution of elements in the sample and their possible migration in the environment.[96]

Microcolumns. The continuous refreshment and a steady flow rate of the eluent are attained by using either rotating columns or cylindrical microcolumns (the latter are usually filled with 5–25 mg of the sample)[97,98] or microcartridges with quartz filters.[99,100] The use of flow injection analysis (FIA) is suitable for leaching in three different modes of flow-

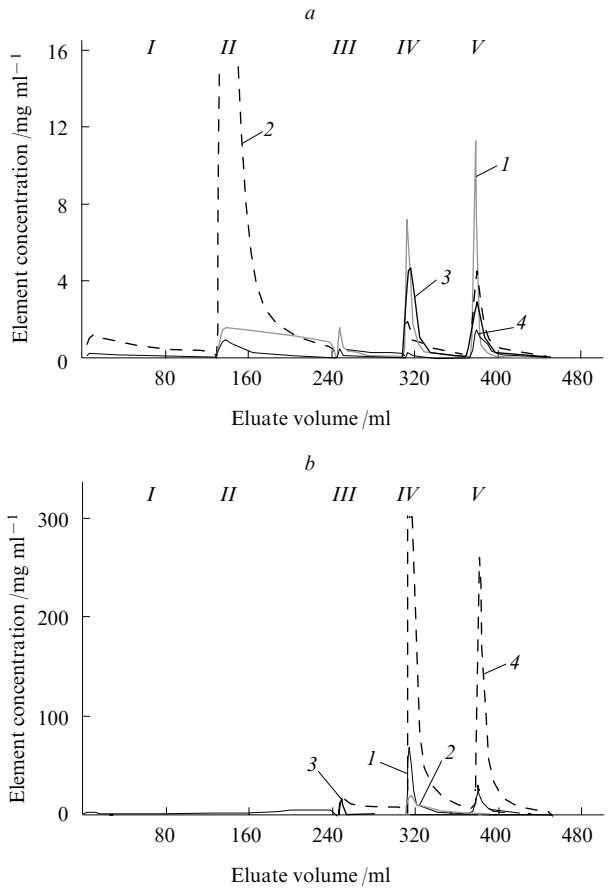


Figure 2. Elution curves of heavy metals and major elements obtained for a sample of contaminated municipal soil using a rotating coiled column.[94]
Sample weight 0.5 g; eluent flow rate 1 ml min^{-1}; on-line ICP AES determination of elements in the eluate every 24 s (this corresponds to 0.4 ml of the eluate). Eluent: (*I*) 0.05 M $Ca(NO_3)_2$ (exchangeable fraction); (*II*) 0.4 M CH_3CO_2H (specifically sorbed fraction); (*III*) 0.1 M $NH_2OH \cdot HCl$, pH 3.6 (manganese oxide-bound elements); (*IV*) 0.1 M $K_4P_2O_7$, pH 11 (elements bound to organic complexes); (*V*) 0.1 M $(NH_4)_2C_2O_4$, pH 3.2 (amorphous iron and aluminium oxide-bound elements). After recovery of each fraction, 5 ml of water was pumped through.
a: (*1*) Cu, (*2*) Zn, (*3*) Pb, (*4*) Ni; *b*: (*1*) Al, (*2*) S, (*3*) Mn, (*4*) Fe.

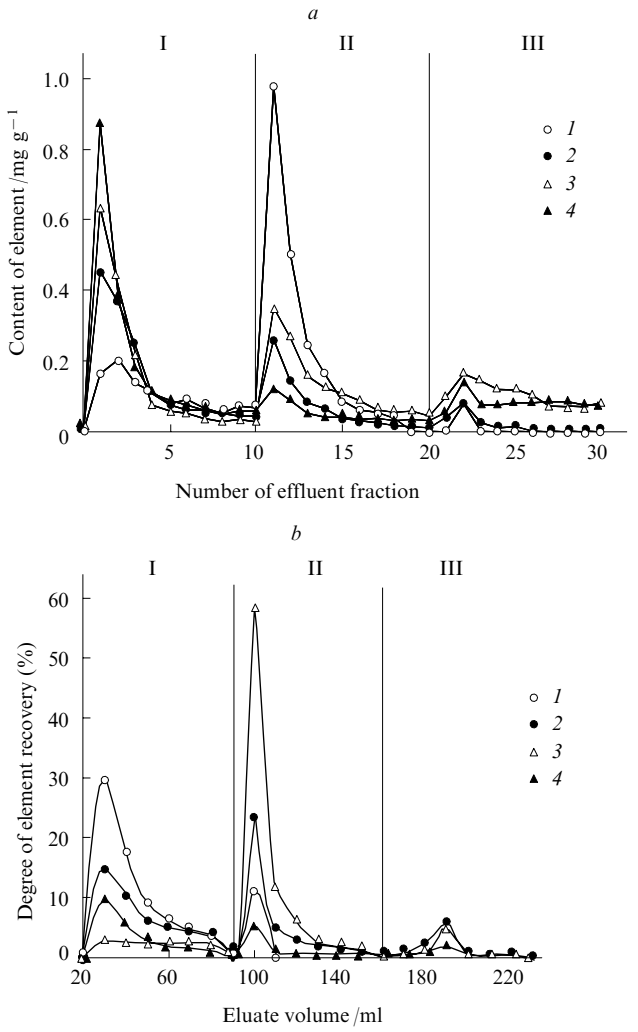


Figure 3. Extraction curves of metals obtained for the soil sample SRM 2710 using the sequence of eluents corresponding to the original BCR scheme.
(*a*) Flow-through fractionation in a microcolumn.[103] Sample weight 25 mg; internal volume of the column 0.36 ml; eluent flow rate 3 ml min^{-1}; volume of recovered eluate fractions 5 ml; (*1*) Pb, (*2*) Cu, (*3*) Zn, (*4*) Mn.
(*b*) Flow-through fractionation in a rotating coiled column.[90] Sample weight 500 mg; internal volume of the column 20 ml; eluent flow rate 1 ml min^{-1}; volume of recovered eluate fractions 10 ml; (*1*) Cd, (*2*) Cu, (*3*) Pb, (*4*) Zn.
The roman numerals designate the extraction stages.

through (dynamic) extraction, batch extraction and extraction with eluent recycling. In the first case mentioned, a leachant solution is continuously pumped through the microcolumn.[97,98] In the second case, pumping is stopped after the column has been filled with the eluent (stopped-flow mode) in order to increase the contact time of the sample and the leachant.[100] The use of eluent recycling along a closed loop also increases the contact time between the liquid and solid phases. During recycling, eluate microsamples are taken to monitor the concentrations of the extracted elements in the liquid phase.[99] It should be emphasised that the optimal conditions for recovery of the forms of elements from a particular sample are determined by the extractant efficiency, the kinetic lability of the leached form of the element and re-adsorption processes.

Owing to the possibility of determination of elements in the eluate by mass spectrometry or other instrumental methods, microcolumns have become a potent tool for investigation of leaching processes on a real time basis.[97–99] However, note that sequential extraction of elements using microcolumns is better suitable for fast screening of thoroughly homogenised samples.[101] The relatively low capacity of the columns (the sample weight usually does not exceed 50 mg) still prevents their extensive use in the analysis of soils, sludges and sediments. ‡

Despite the considerable difference between the dynamic extraction protocols in microcolumns and rotating coiled columns, the use of the two methods for the fractionation of heavy metals in a homogenised reference soil sample SRM 2710 gave quite comparable results (Fig. 3).[90,103]

‡ Recently it was shown[102] that in a microcolumn of an improved design, the sample weight can be increased to 0.3 g.

Fractionation in the dynamic mode has some advantages over the batch fractionation. This can be seen when comparing characteristics of these modes given below.

Batch extraction	Dynamic extraction
Sequential extraction in the batch mode with intermediate sample centrifugation steps	Continuous extraction in the dynamic mode
Long-lasting labour-consuming procedures requiring several days	Fractionation requires several hours, in some cases, complete automation is possible
The problem of re-adsorption of extracted elements arises	Continuous renewal of the eluent minimises re-adsorption problem
Lower degree of recovery of the most mobile (easily available and environmentally hazardous) forms of heavy metals and arsenic	Higher degree of recovery of the most mobile (easily available and environmentally hazardous) forms of heavy metals and arsenic
Poor possibility of studying mobilisation processes of elements in the solid phase – soil solution systems	Using elution curves, one can evaluate the efficiency of the leaching reagents and the capacity of binding sites and gain important additional information on the kinetics of element extraction and predict the dynamics of their possible mobilisation under natural conditions
Does not require special equipment	Requires special equipment and trained personnel
Several parallel samples can be analysed	Only one sample can be analysed

IV. Kinetic aspects of selective leaching processes

Any leaching (dissolution) process comprises three main stages.[104] The first stage is approach of the leachant to the solid surface through either molecular diffusion or convection. At the second stage, chemical reactions at the solid – liquid interface take place, and at the third stage, the ions or molecules of the sample being dissolved are withdrawn to the solution bulk. If the whole process rate is limited by the rate of the first or third stage, the course of the process is governed by the laws of diffusion kinetics. If the second stage is the rate-limiting stage, the process follows the laws of chemical kinetics. Some processes obey mixed kinetics.

External and internal diffusion (external and internal mass transfer) are distinguished.[105] In the former case, the mass transfer is limited by the rate of diffusion through a liquid layer: a mobile solution layer with a concentration nearly equal to the saturation concentration is formed near the surface of the sample, and the reagent and the solutes diffuse through this solution, the diffusion determining the rate of the whole process. The internal diffusion controls the process rate if either leaching from cracks (pores) or transport of the dissolved substance and the reagent through the formed shell of the solid reaction product is the slowest stage. When the process is governed by internal diffusion, the rate of leaching does not depend on the flow rate of the liquid with respect to the dissolved sample but depends appreciably on the sample porosity; the process rate is directly proportional to the reagent concentration. The rate of dissolution and leaching of minerals and other solids is determined, in most cases, by the rate of diffusion.[105, 106] The extraction processes of the forms of elements are, most often, also diffusion-controlled, the key role being played by external diffusion processes. The dissolution (and leaching) rate decreases according to a logarithmic law following an increase in the solute concentration (c) in the liquid phase[106] and, taking into account the heterogeneous mass transfer, it is expressed by the kinetic equation[107]

$$\frac{dc}{dt} = \frac{k_0 DS(c_{eq} - c)}{V\delta},$$

where dc/dt is the rate of variation of the solute concentration in the solution bulk, k_0 is the rate constant for leaching, D is the diffusion coefficient of the compound being dissolved, S is the surface area being dissolved, c_{eq} is the saturation concentration, V is the solution volume, δ is the diffusion layer thickness.

In the general case, k_0 depends on the physical and chemical properties of reacting species, the design of the leaching device and the reaction mass flow rates. Under stationary experimental conditions

$$\frac{dc}{dt} = k(c_{eq} - c),$$

the kinetic constant k is directly proportional to the diffusion coefficient and inversely proportional to the thickness of the diffusion layer.

Note that in the dissolution of powders (ground solid samples), the observed reaction rate differs from the true rate at the interface.[104] In this case, the rate of dissolution is affected by a change in the reaction surface, which is either decreased or increased during leaching. The results will be correct only provided that the surface is equally accessible, which is possible only in rare cases, for example, in the dissolution of rotating discs. Thus, the results of studies of leaching kinetics of elements from soils and sediments under usual batch extraction conditions are somewhat arbitrary. Nevertheless, the obtained data are important for the understanding of processes of possible mobilisation of elements upon changes in the environmental conditions.

The kinetics of batch leaching of elements is studied by two methods. According to the first one, aliquots of the liquid phase are withdrawn at certain intervals during stirring of the sample and the reagent solution; according to second one, experiments with a series of weighed portions are carried out, the contact time of the liquid and solid phases being varied from several minutes to 24 h. In the opinion of some researchers (see, for example Ref. 108), the latter method is preferred.

In some cases, kinetic curves provide additional knowledge about the mobilities of the recovered element forms. For example, depending on the sample type, the acid-soluble forms of metals extracted with acetic acid can be 'labile' (rapidly extractable), 'moderately labile' (slowly extractable) and 'inert'.[109, 110] The labile (rapidly leached) forms are considered to be the most environmentally hazardous. In terms of their mobility, forms of elements are classified on the basis of calculated kinetic constants for the diffusion-controlled extraction[107, 111]

$$c = c_{eq}(1 - e^{k't}),$$

where c is the concentration of the element in the leaching solution at time instant t, c_{eq} is the equilibrium concentration of the element, k' is the rate constant for leaching.

The kinetics of leaching of elements was studied using different leachants (including EDTA) and their sequences.[68, 107–111] Primary attention was devoted to the modified BCR scheme. Using model soil compounds (goethite and humic acids) as examples, some fundamental differences between the behaviour of the reducible and oxidisable forms extracted with hydroxylamine hydrochloride and hydrogen peroxide, respectively, were found.[112] It was shown that elements bound to iron hydroxides (goethite) are, as a rule, more labile than the elements bound to the organic matter of soil.

The results of sequential extraction of arsenic combined with the data on the kinetics of its single extraction with EDTA proved useful for evaluation of the behaviour and possible migration of this element in slightly contaminated soils.[113] Examination of the kinetic curves led to the conclusion that arsenic exists mainly as labile forms that are easily extracted with chelating reagents. It was also shown that the fraction rapidly extracted with EDTA corresponds to the sum of the exchangeable and specifically sorbed fractions operationally defined in the sequential extraction scheme, whereas the fraction slowly extracted with EDTA corresponds to arsenic bound to amorphous iron hydroxides and organic matter.

Flow-through fractionation is a powerful tool for investigation of the dynamics of leaching of elements from soils, sludges and sediments.[80, 90, 99] It was mentioned in the previous Section that the elution profiles (extraction patterns) can be used to elucidate the capacity of binding sites; the extractant volume needed for quantitative recovery of a particular fraction of the sample; and the kinetic lability of the elements in various forms. A comparison of the elution curves of trace and major elements provides information about the leachant selectivity with respect to the sample phases being dissolved and specific features of element binding to the structures of soils and sediments.[94] If leaching occurs rather slowly, it is sufficient to determine the elements in the recovered eluate fractions with a volume of 5–15 ml. In the case of fast dissolution, it is preferred to carry out on-line determination, *i.e.*, to use hyphenated methods of element fractionation and determination.[93, 102]

The possibility of determination of quantitative characteristics of mass transfer during dynamic leaching of elements was demonstrated. The effective coefficients of external-diffusion mass transfer of heavy metals and arsenic during their dynamic extraction from soils, sludges and sediments in a rotating column were calculated using deterministic model of sorption–desorption dynamics describing the behaviour of trace components in the stationary solid sorbent–mobile liquid phase system.[114] According to the results, in the reference samples of soil (SRM 2710) and sediments (BCR 601, CRM 701), the mass transfer coefficients of Cd, Cu, Ni, Pb and Zn determined for flow-through extraction with a 0.11 M acetic acid vary over a broad range, from 2.4×10^{-3} to 1.2×10^{-1} s^{-1}. Undoubtedly, high contents of heavy metals in acid-soluble forms are hazardous for the environment. However, from quantitative parameters of the mass transfer of elements determined for leaching in rotating coiled columns, one can consider the dynamics of possible mobilisation of heavy metals upon the change in the pH of the soil solution. For example, if the mass-transfer coefficient does not exceed 10^{-2} s^{-1}, the release of a 'moderately labile' element is extended in time, while in the case of high mass transfer coefficients (from 4×10^{-2} s^{-1}), the whole 'store' of a heavy metal in the acid-soluble form passes almost immediately into the liquid phase and becomes available for living organisms. Thus, flow-through fractionation of elements not only provides more correct (compared to batch sequential extraction) determination of the contents of elements in most mobile and bioavailable fractions but also allows one to predict the dynamics of element release upon a change in the environmental conditions.

V. Conclusion

Currently, sequential extraction is the key method of fractionation of forms of elements present in soils, sludges and sediments and having different physicochemical mobilities, bioavailabilities and ecotoxicological relevance. In a study of the particular sample, it seems expedient, first, to determine the overall contents of elements; second, to estimate tentatively the contents of the mobile forms by single extraction (for example, with an ammonium acetate buffer); third, if the content of the mobile forms is rather high, fractionation of elements should be carried out. The particular extraction protocol depends on the range of elements to be determined, the type and degree of sample contamination and the probable changes in the environmental conditions (acidity, redox potential) that can influence the sample.

The three-step BCR scheme [32] developed within the framework of the Standards, Measurements and Testing Programme of the European Commission and the relevant reference samples with certified contents of extractable forms of heavy metals form a sound basis for comparison of the results obtained in different laboratories. However, each of the isolated fractions (acid-soluble, reducible and oxidisable ones) can contain forms of elements differing in mobility and bioavailability, thus preventing correct evaluation of the contamination of the soil or sediment. Thus, in the studies of contaminated samples with high contents of elements in one or several of the listed fractions, it is necessary to carry out sequential extraction of exchangeable, acid-soluble (specifically sorbed), easily reducible (bound to manganese oxides) and easily oxidisable (bound to organic ligands) forms of elements. Thus, development and testing of a unified scheme for selective isolation of these ecotoxicologically relevant fractions is a topical task. Studies of the dissolution mechanisms of various mineral phases and their reactions with the leachant are very important for this purpose.[115]

In the routine analysis of soils and sediments, batch sequential extraction still remains the preferred method. Dynamic fractionation, which has a number of obvious advantages, is quite promising for solution of a number of fundamental and practical problems of analytical chemistry, soil science and environmental monitoring; it is indispensable for the analysis of highly contaminated samples, estimation of the efficiency and selectivity of the reagents used, investigation of the leaching kinetics of elements, prediction of the dynamics of their possible mobilisation under natural conditions. Comparative analysis and harmonisation of methods of dynamic fractionation of elements in soils, sludges and sediments is an important problem the solution of which requires a large body of experimental work.

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