

Is there a future for sequential chemical extraction?†

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Since their introduction in the late 1970s, sequential extraction procedures have experienced a rapid increase in use. They are now applied for a large number of potentially toxic elements in a wide range of sample types. This review uses evidence from the literature to consider the usefulness and limitations of sequential extraction and thereby to assess its future role in environmental chemical analysis. It is not the intention to provide a comprehensive survey of all applications of sequential extractions or to consider the merits and disadvantages of individual schemes. These aspects have been covered adequately in other, recent reviews. This review focuses in particular on various key issues surrounding sequential extractions such as nomenclature, methodologies, presentation of data and interpretation of data, and discusses typical applications from the recent literature for which sequential extraction can provide useful and meaningful information. Also covered are emerging developments such as accelerated procedures using ultrasound- or microwave energy-assisted extractions, dynamic extractions, the use of chemometrics, the combination of sequential extraction with isotope analysis, and the extension of the approach to non-traditional analytes such as arsenic, mercury, selenium and radionuclides.

1. Introduction

The environmental behaviour of potentially toxic elements (PTEs) depends critically on the form in which they occur.² The manner in which an element is bound to the solid components of environmental solids, such as soils or sediments, influences the mobility and, ultimately, the bioavailability and toxicity of the element to organisms. As a result there is considerable interest in improving the understanding of

element–solid phase associations in natural and polluted systems.

Direct determination of the chemical forms of trace elements in environmental samples such as soils can be achieved by means of various instrumental techniques,³ notably synchrotron-based X-ray radiation fluorescence (SXRF),^{4,5} particle-induced X-ray emission (PIXE),⁵ X-ray absorption near edge structure (XANES),⁶ and extended X-ray absorption fine structure (EXAFS)^{4,5} spectroscopy. Although powerful, these

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† This review is dedicated to Allan Ure (see ref. 1) who was instrumental in the development of the BCR sequential extraction procedure and the preparation and certification of reference materials. Allan was involved in the work of various Royal Society of Chemistry analytical chemistry committees and European BCR programmes.



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techniques are not widely available and may offer poor detection limits, meaning that they can be applied only to heavily contaminated samples.^{7–10}

Hence, over the past three decades, interest has increased markedly in the use of indirect approaches such as sequential chemical extraction (Fig. 1). In sequential extraction, a series of reagents is applied to the same sample to sub-divide the total metal content. The ‘vigour’ of the treatment generally increases through the steps of the procedure, from initial mild conditions (*e.g.* shaking with water, a salt solution or dilute acetic acid) to the use of much harsher reagents (*e.g.* hot mineral acid). The PTEs extracted early in the process are thus generally those most weakly bound to the solid phase. Hence, they have greater potential mobility, and environmental impact, than those released later.

In 1991, Ure¹¹ defined chemical speciation as either ‘the *active process* of identification and quantification of the different *defined species forms or phases* in which an element occurs in a material’ or ‘the *description* of the amounts and kinds of species, forms or phases present in the material’. He proposed that speciation be divided into three classes:

(a) *Classical* speciation refers to specific chemical compounds or oxidation states of elements, *e.g.* cerussite (PbCO_3) vs. pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$]; Cr^{III} vs. Cr^{VI} .

(b) *Functional* speciation refers to the observed role or behaviour of the

element, and is characterized by terms such as ‘plant available’ or ‘mobile’ species.

(c) *Operational* speciation refers to the situation where the reagent used to extract the sample defines the species, *e.g.* ‘acetic acid soluble’ or ‘moderately reducible’ species.

Sequential chemical extraction is an example of operational speciation.

Later, IUPAC¹² published a definition of speciation which distinguished the process of identifying species (‘speciation analysis’) from the description of the species themselves. The IUPAC definition of speciation corresponds roughly to the ‘classical’ definition of Ure. Hence, although the term ‘operational speciation’ is still widely used, it is more correct to refer to sequential extraction as a method for ‘fractionation’ of PTEs.

To quote an IUPAC report¹³ on the determination of trace elements bound to soils and sediment fractions, “despite some drawbacks, the sequential extraction method can provide a valuable tool to distinguish among trace element fractions of different solubility related to mineralogical phases. The understanding of the speciation of trace elements in solid samples is still rather unsatisfactory because the appropriate techniques are only operationally defined”. This is the nub of the problem in using sequential extractions. The ever increasing use of sequential extractions indicates that this approach is thought to provide meaningful and useable information and yet in

many papers no real attempt is made to interpret the data other than to say that so much metal is associated with a certain phase. There appear to be many misconceptions in existence, even to the meaning of ‘operationally defined’, which can lead to confusion. The aim of this review is to outline the development and current status of chemical sequential extraction and to highlight some of the issues that still exist in the application of the procedure and interpretation of results.

2. History

The growth in interest in sequential extraction may be traced back to the classic work of Tessier, Bisson and Campbell in 1979.¹⁴ They used a five-stage extraction (Table 1) to fractionate cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc in river sediments containing low levels of PTEs. The reagents used were selected on the basis of their ability to remove analytes from specific, major, sediment phases – either by exchange processes or by dissolution of the target phase. Extraction steps also corresponded with, or at least represented extremes of, important changes in environmental conditions that could affect metal binding in sediments: acidification (*e.g.* in response to an input of acidified rain-water or industrial discharge); reduction (*e.g.* as may occur following post-depositional burial in a sediment column) and oxidation (*e.g.* as might occur following dredging and land-deposition of anoxic sediments).

Sequential extraction was thus originally developed to provide information on potential impacts of sediment-bound PTEs on water quality. However, application to soil soon followed^{15,16} and, by the early 1990s a number of researchers were using the approach to fractionate PTEs (and, in some cases, radionuclides) in a variety of substrates. The use of different procedures, with different numbers of steps, reagents and extraction conditions, meant that it quickly became difficult to draw meaningful comparisons between results obtained in different laboratories. The need for standardization became clear.

The Community Bureau of Reference of the Commission of the European

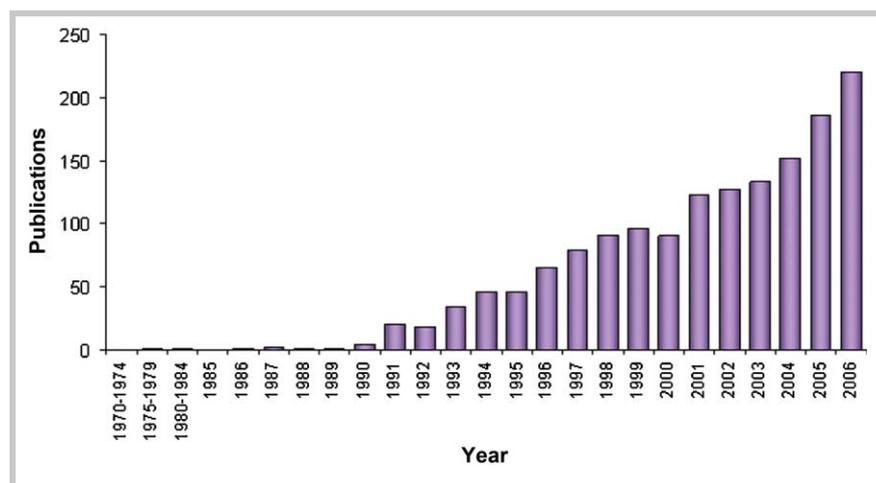


Fig. 1 Growth in publications featuring the use of sequential extraction for fractionation of trace metals (Source: ISI Web of Science; search parameters: ‘sequential extraction’ AND ‘meta*’).

Table 1 The Tessier and (revised) BCR sequential extraction schemes

Tessier (ref. 14)		Revised BCR (ref. 21)	
Reagent	Fraction label and nominal target phase(s)	Reagent	Fraction label
Step 1 1.0 mol l ⁻¹ MgCl ₂ at pH 7.0	Exchangeable	Step 1 0.11 mol l ⁻¹ CH ₃ COOH	Exchangeable, water- and acid-soluble
Step 2 1.0 mol l ⁻¹ CH ₃ COONa adjusted to pH 5 with CH ₃ COOH	Bound to carbonates	Step 2 0.5 mol l ⁻¹ NH ₂ OH·HCl at pH 1.5	Reducible
Step 3 0.04 mol l ⁻¹ NH ₂ OH·HCl in 25% CH ₃ COOH (96 °C)	Bound to Fe–Mn oxides	Step 3 H ₂ O ₂ (85 °C) then 1.0 mol l ⁻¹ CH ₃ COONH ₄	Oxidisable
Step 4 HNO ₃ /H ₂ O ₂ (85 °C) then 3.2 mol l ⁻¹ CH ₃ COONH ₄ in 20% HNO ₃	Bound to organic matter and sulfides	(Step 4) ^a <i>Aqua regia</i>	Residual
Step 5 HClO ₄ /HF	Residual		

^a Although not officially a step in the sequential extraction, it is recommended that the residue at the end of Step 3 be digested with *aqua regia* and the sum of the four fractions be compared with the results of a separate *aqua regia* digestion of the sample.

Communities (BCR) commissioned research which led to the development of a harmonized, three-stage, sediment sequential extraction protocol.^{17,18} The principal difference in this new scheme, with respect to that of Tessier, was that the first two steps of the Tessier scheme were replaced by a single step. In addition, larger sample amounts and extractant volumes were used to allow more representative sampling and to avoid some of the analytical difficulties associated with the use of small extractant volumes. In light of increasing concerns over the specificity of reagents used in sequential extraction procedures (see Section 3), the fractions were labeled according to chemical processes rather than target mineral phases.

Problems were reported with irreproducibility of, in particular, Step 2 of the original BCR procedure (see, for example, ref. 19) and, after a thorough re-evaluation in the late 1990s,²⁰ a revised protocol was recommended²¹ (shown in Table 1). Recognizing the need for improved quality control in sequential extraction, the BCR also led developments such as the production of certified reference materials (CRMs).²² Sediments certified for amounts of analytes extractable by both original^{23,24} and revised^{25,26} BCR sequential extraction protocols were produced (see Table 2). It was also recommended that, when using the revised BCR protocol, an additional step (*aqua regia* digestion of the residue from Step 3) be performed and the sum of the four steps of the sequential extraction be compared with the result of a separate *aqua regia* digestion of the whole soil (pseudototal content). In this way the overall effectiveness of the sequential extraction process and element recoveries can be assessed.

Since the early 1990s, sequential extraction has continued to increase in popularity. In addition to the sediments originally envisaged, the approach has been applied to a wide variety of substrates including agricultural soils,^{27,28} soils amended with organic wastes,^{29–33} rhizosphere soils,^{34–39} urban soils,^{40,41} forest soils,^{42,43} industrial (contaminated) soils,^{44,45} urban sediments (road particulates),⁴⁶ mine spoil,^{47–49} sewage sludge,^{50–52} composts,^{53–56} incinerator ashes,⁵⁷ medical waste fly ash,⁵⁸ airborne particulate matter,^{59,60} electric arc

furnace dust⁶¹ and gas pipeline corrosion products.⁶² Although a large number of different protocols have been reported, the Tessier and BCR schemes remain amongst the most widely used. A comprehensive review of sequential extraction schemes was provided in 2002 by Filgueiras, Lavilla and Bendicho.⁶³ The review of Young *et al.*⁶⁴ is recommended for providing a clear introduction to the development of sequential extractions, some of the limitations such as lack of specificity and some of the recent innovations for improving the procedure. Other reviews have included an overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments,⁶⁵ the use of sequential extraction procedures for the characterization and management of contaminated soils,⁶⁶ the fractionation of metals in atmospheric aerosols⁶⁷ and recent methodological advances, in particular for on-line dynamic fractionation.⁶⁸

An ongoing limitation to the use of sequential extraction has been the availability of only a few reference materials for checking the performance of methods and laboratories. Various authors have therefore attempted to increase the range available by applying standard^{69–80} or other^{81,82} procedures to generate indicative extractable metal concentrations in additional reference materials, typically soils or sediments already certified for their total PTE contents. This has provided useful information (see Table 3). However, such data should be used with care since they are generally generated in a single laboratory and, therefore, not subjected to the same degree of inter-laboratory assessment as occurs during certification of a new reference material. Further work in this area will, however, refine the reliability of published results⁷⁸ and is therefore to be encouraged.

3. Scope and limitations of sequential extraction

Sequential extraction is thus now widely accepted and adopted. The approach has led to improved understanding of the behaviour of PTEs in environmental samples, and generated large amounts of data useful in assessing potential risks from environmental contaminants. However, along with the proliferation in

Table 2 Reference materials specifically certified for sequentially extractable PTEs, together with certified values (mg kg⁻¹)

BCR CRM 601 (metals extractable by the original BCR procedure) ^a					
	Step 1	Step 2	Step 3	Step 4	Pseudototal ^b
Cd	4.14 ± 0.23	3.08 ± 0.17	1.83 ± 0.20		
Cr	0.36 ± 0.04				
Cu	8.32 ± 0.46 ^c				
Ni	8.01 ± 0.73	6.05 ± 1.09	8.55 ± 1.04		
Pb	2.68 ± 0.35	33.1 ± 10.0 ^c	109 ± 13		
Zn	264 ± 5	182 ± 11			
BCR CRM 601 (metals extractable by the revised BCR procedure) ^d					
Cd	4.45 ± 0.67 ^c	3.95 ± 0.53 ^c	1.91 ± 1.43 ^c	1.3 ± 2.2 ^c	11.5 ± 1.9 ^c
Cr	0.35 ± 0.08 ^c	10.6 ± 0.9 ^c	14.4 ± 2.6 ^c	78.2 ± 6.5 ^c	112 ± 9.5 ^c
Cu	10.5 ± 0.8 ^c	72.8 ± 4.9 ^c	78.6 ± 8.9 ^c	60.4 ± 4.9 ^c	230 ± 15 ^c
Ni	7.82 ± 0.84 ^c	10.6 ± 1.2 ^c	6.04 ± 1.27 ^c	50.5 ± 4.3 ^c	78.8 ± 6.7 ^c
Pb	2.28 ± 0.44 ^c	205 ± 11 ^c	19.7 ± 5.8 ^c	38.0 ± 8.7 ^c	288 ± 52 ^c
Zn	261 ± 13 ^c	266 ± 17 ^c	106 ± 11 ^c	161 ± 14 ^c	833 ± 17 ^c
BCR CRM 701 (metals extractable by the revised BCR procedure) ^e					
Cd	7.34 ± 0.35	3.77 ± 0.28	0.27 ± 0.06	0.13 ± 0.08 ^c	11.7 ± 1.0 ^c
Cr	2.26 ± 0.16	45.7 ± 2.0	143 ± 7	62.5 ± 7.4 ^c	272 ± 20 ^c
Cu	49.3 ± 1.7	124 ± 3	55.2 ± 4.0	38.5 ± 11.2 ^c	275 ± 13 ^c
Ni	15.4 ± 0.9	26.6 ± 1.3	15.3 ± 0.9	41.4 ± 4.0 ^c	103 ± 4 ^c
Pb	3.18 ± 0.21	126 ± 3	9.3 ± 2.0	11.0 ± 5.2 ^c	143 ± 6 ^c
Zn	205 ± 6	114 ± 5	45.7 ± 4.0	95 ± 13 ^c	454 ± 19 ^c

^a Uncertainties quoted are half widths of the 95% confidence intervals of the mean values. ^b *Aqua regia*-soluble PTE content. ^c Indicative value. ^d Uncertainties quoted are standard deviations ($n = 7$ for Steps 1–3, $n = 6$ for Step 4 and pseudototal). ^e Uncertainties quoted are half widths of the 95% confidence intervals of the mean values for Steps 1–3, but standard deviations for Step 4 and pseudototal values.

Table 3 Some additional certified reference materials to which Tessier or BCR sequential extraction procedures have been applied

CRM	Type of material	Procedure	PTEs measured	Reference
NIST SRM 2709	Relatively uncontaminated agricultural soil	Tessier	Al, Ca, Cd, Co, Cu, Fe, K, Mn, Ni, (P), Pb, Sr, Ti, V, Zn	69
NIST SRM 2710	Highly contaminated pasture soil	Tessier	Al, Ca, Cd, Co, Cu, Fe, K, Mn, Ni, (P), Pb, Sr, Ti, V, Zn	69
		Original BCR	Cd, Cu, Pb, Zn	70
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	72
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	75
NIST SRM 2711	Moderately contaminated agricultural soil	Revised BCR	Al	77
		Tessier	Al, Ca, Cd, Co, Cu, Fe, K, Mn, Ni, (P), Pb, Sr, Ti, V, Zn	69
		Original BCR	Cd, Cu, Pb, Zn	70
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	72
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	75
NIST SRM 1648 BCR CRM 483	Urban air particulate matter Sewage sludge-amended soil	Revised BCR	Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn	78
		Revised BCR	Cd, Cu, Fe, Mn, Pb, Zn	79
		Original BCR	Cd, Cu, Fe, Mn, Zn	73
		Revised BCR	Cd, Cr, Cu, Ni, Pb, Zn	71
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	72
CW 7	Dust from ventilation shaft of a road tunnel	Revised BCR	Cu, Fe, Mn, Pb, Zn	74
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	75
		Revised BCR	Cd, Cr, Cu, Ni, Pb, Zn	76
		Revised BCR	Al, Cu, Fe, Mn, Pb, Zn	72
		Revised BCR	Al	77
CANMET RSS SO-2	Ferro-humic podzol soil	Revised BCR	Al	77
CANMET RSS SO-4	Black soil	Revised BCR	Al	77
HPS CRM SA-B	Sandy soil	Revised BCR	Al	77
WEPAL SRM RTH 912	Loess soil	Revised BCR	Al	77
RTC NMC RM 025–050	Moderately contaminated soil	Revised BCR	Al	77
GBW 07401	Chinese soil	Original BCR	Tl	80

applications have grown misconceptions about the significance of the results obtained.⁸³ Procedures are often applied uncritically⁸⁴ and, in particular, the operational nature of the extraction procedure is frequently ignored (or – worse – noted but then disregarded) by authors. This issue is discussed in more detail in Section 4.

It is extremely important to appreciate that sequential extraction only divides the PTE content of a test sample into portions soluble in particular reagents under particular conditions. Whilst these reagents are often selected with the intention that they should target well-defined mineral phases – and may indeed do so in many cases – such specificity cannot be guaranteed. Hence, interpretation of the results of sequential extraction in terms of binding of trace metals to specific minerals is unjustifiable, unless additional, X-ray-based, analytical techniques are applied to the residues at each stage in the extraction to identify precisely the solid components remaining.^{84–93}

Schemes continue to be described which are claimed to target specific, well-defined, phases successfully. Poulton and Canfield⁹⁴ developed a scheme to target seven ‘operationally derived’ iron pools in sediment samples and validated the specificity on grain-size-separated sediments. An improved procedure using hydroxylamine hydrochloride and acidified hydrogen peroxide, also used in both the BCR and Tessier schemes, was developed in order to dissolve specifically manganese oxide phases without any significant dissolution of iron oxide phases.⁹⁵

Such papers are, however, heavily outnumbered by papers which report clear evidence for the non-specificity of sequential extraction procedures. The comparison by Parat *et al.*⁹⁶ of three different procedures provided evidence for lack of specificity and the operational nature of the extractions. Sodium acetate, generally defined as extracting exchangeable metals or carbonate-bound metals, could remove considerable amounts of metals in forms other than exchangeable ones. Copper distribution was affected by the position of the oxidation step in the sequence of extraction steps. In a similar comparison, Tokalioglu *et al.*⁹⁷ also concluded that

the amount of metal released at each step of the leaching procedure depended both on the type of reagents used and the sequence in which they were applied. As the measured amount of metal associated with a particular phase is strongly dependent on the extractant and procedure used, it has been suggested that at least two independent procedures should be used.⁹⁸ In most cases this would be considered impractical. Hanahan⁹⁹ found that sodium acetate could also release metals associated with hydroxide minerals. Independent studies of mining wastes¹⁰⁰ and anoxic sediments^{101,102} demonstrated that hydroxylamine hydrochloride can dissolve sulfide minerals so sulfide-bound metals could mistakenly be interpreted as being bound to iron oxide species. Dermatas *et al.*¹⁰³ concluded that lead in the soils of firing ranges could be extracted in any step of the procedure depending on the soil buffering capacity even though scanning electron microscopy revealed 95% of the lead to be in carbonate or oxide forms. Perhaps the most extreme demonstration of the dependency of interpretation on the procedure used was the finding by Doelsch *et al.*¹⁰⁴ that the amendment of a tropical soil with sewage sludge led to an increase of metals associated with the reducible fraction according to one sequential extraction scheme but to a decrease according to another scheme.

A number of other problems have been identified that cannot be explained by specific causes. Mostly unreliable results were obtained for chromium using 11 different schemes,¹⁰⁵ serious discrepancies were found for manganese using an ‘optimized’ BCR procedure,⁷⁵ no reliable data for nickel in unpolluted soils could be obtained using the BCR procedure¹⁰⁶ and systematic under-recovery was observed for a seven-step procedure.¹⁰⁷ In comparison to single extractant procedures, sequential extraction was considered more aggressive and gave higher extractable concentrations.^{108,109}

Although not specifically a problem of sequential extraction but more of speciation studies in general, thought should be given to the effects of sample preparation on metal distribution, in particular in the study of sediments. Sample drying and grinding of sediments has consistently been shown to lead to re-distribution of the metals to more extractable

forms.^{110–112} Unfortunately, the reproducibility of analysis on wet samples was considerably poorer than that for dried samples.¹¹² Freeze-drying did not preserve metal partitioning in anoxic sediment cores.¹¹³ It has been suggested that sediment and soil samples should be sampled and analysed under an inert atmosphere in order to reduce the risk of oxidation.¹¹⁴

There are several reasons why sequential extraction does not determine quantitatively the trace metals associated with specific mineral phases in environmental solids. These include:

- (a) re-distribution of analytes among phases during extraction;
- (b) non-selectivity of reagents for target phases;
- (c) incomplete extraction;
- (d) precipitation of ‘new’ mineral phases during extraction.

A considerable body of evidence has accumulated confirming the importance of these effects. This evidence is based on a large number of studies which fall into two groups – those that have utilized pure and synthetic substrates and those that utilized ‘real’ samples.

3.1 Pure and synthetic substrates

Even before publication of the Tessier sequential extraction, Guy *et al.*¹¹⁵ had demonstrated that low analyte recoveries were obtained when attempting to sequentially extract simple binary mixtures of bentonite, MnO₂ and humic acid that had been spiked with Cu and Pb. This poor performance was attributed to either post-extraction re-adsorption of analytes on residual solids or incomplete dissolution of the target phase. Many studies conducted on model sediments^{116,117} and soils^{118–120} have since confirmed that significant re-distribution of analytes occurs during both Tessier^{116,119,120} and BCR^{117,118} protocols.

Work on sequential extraction of seawater-spiked mineral phases¹²¹ illustrated the non-specificity of the BCR procedure with, for example, the majority of iron oxyhydroxide-bound metals being released in Step 1, rather than in Step 2 (the reduction step) as expected. Non-selectivity was also observed during application of the Tessier extraction to spiked soil components.^{120,122} Whilst

good recoveries of Cu, Pb and Zn (generally >90%) could be obtained when individual components were subjected to a single extraction with their corresponding reagent (indicated in Table 1), significant amounts were also released when reagents were applied to non-target phases. For example, although intended to release 'metals bound to carbonates', it was found that acidified sodium acetate could also remove around 50% of analytes associated with Fe/Mn oxides.¹²⁰

Premature extraction of organically-bound metals has been noted in both the Tessier¹²² and the BCR procedures,^{117,121} and presumably occurs because analytes can be liberated by exchange processes as well as following destruction of the organic matter. It is thus clear that neither Step 4 of the Tessier procedure, nor Step 3 of BCR, can be considered accurately to represent the entire pool of 'metals bound to organic matter'.

3.2 Environmental substrates

The validity of extrapolating results obtained for synthetic substrates – or based on the use of high spike concentrations – has been questioned.¹²³ However, many authors have now reported similar findings for 'real' samples. Re-distribution of lead from manganese oxide to iron oxide phases was shown to occur when samples of a naturally precipitated mixed oxide from a former lead mine were treated with hydroxylamine hydrochloride.⁸⁵ Sequential extraction combined with EXAFS analysis of mine tailings demonstrated significant re-adsorption of lead liberated by Tessier Step 1.¹⁰ This inability of 1.0 mol l⁻¹ MgCl₂ to retain added analytes in soluble forms was also noted by Gomez-Ariza *et al.*¹²⁴ when using a 'standard additions' approach. They also showed that the degree of (re-)adsorption depended critically on the geochemical characteristics of the sediment studied.

Radiotracers have provided further insight into the behaviour of PTEs undergoing sequential extraction. Radionuclides have the advantage that they can be added in very small quantities that do not alter significantly the total analyte concentrations in the sample. When aliquots of ¹⁰⁹Cd, ⁶⁵Zn and ²¹²Pb were added at the start of

Step 1 of the BCR extraction of a CRM, it was found that only 20–30% of copper and zinc,¹²⁵ but 60–90% of lead,¹²⁶ were scavenged from the acetic acid solution by the (solid) reducible fraction. When ²¹²Pb was instead added to the reagent at the start of BCR Step 2, 35–85% of the activity partitioned into the solid phase but, when added at the start of BCR Step 3, the tracer remained in solution.¹²⁶

Incomplete dissolution of carbonates during Step 1 of the BCR protocol has been demonstrated by X-ray analysis of the residue at the end of the extraction step, for both urban canal sediment⁸⁶ and soil.⁸⁴ The latter study focused on a calcareous soil, where the amount of acetic acid added was insufficient to dissolve the *ca.* 27% dolomite present. Carbonate-bound metals were not recovered until Step 2 or even Step 3 of the procedure, and the increased pH of the extract – resulting from neutralization of the acid – interfered with the partitioning of elements in subsequent steps (an effect also observed in carbonate-rich urban soils).⁴¹ The ability of a sample to alter (raise) markedly the initial pH of an added extractant, with subsequent decrease in solubility of extracted analytes, was also noted by Bermond in a detailed investigation of the role of H⁺ in sequential extraction,¹²⁷ and was one of the factors that led to revision of the original BCR extraction.²⁰

Enhanced dissolution efficiency can sometimes be achieved by repeating an extraction step before progressing to the next,^{84,128,129} and it has been suggested that use of such replicate extractions, together with careful monitoring of the pH,^{84,129} major element content,¹²⁹ or redox potential¹²⁹ of the extracts, can be a useful strategy.

Extraction yields are also low if the ratio of volume of extractant to mass of sample (*v* : *m*) is too low.¹³⁰ The recommendation that large extractant volumes should be used has implications, however, for analytical detection of the extracted metals. It is important to define clearly a constant *v* : *m* ratio as extractability of metals varies with the ratio, highlighting the operational nature of the procedure.¹³¹

The re-distribution of PTEs can also result from the formation, during the extraction process, of new mineral phases not originally present in the sample. This

can make results extremely difficult to interpret. For example, Zhu *et al.*¹³² interpreted fractionation data, obtained following the addition of a variety of phosphate amendments to soil, as indicating that such treatments could transform lead from non-residual to residual forms, thus successfully reducing the potential for plant uptake of this PTE. However, Scheckel *et al.*^{90,133} demonstrated that, in heavily phosphate-amended soil, insoluble lead phosphate (pyromorphite) was formed only during the sequential extraction process itself.

Artifacts can also originate from reagents applied. Significant amounts of aluminium, iron and lead were extractable from forest soils under reducing conditions but this fraction would be underestimated if sodium pyrophosphate were used in a previous step.¹³⁴ Lead mobility in forest soils could therefore also be underestimated. Another example is the precipitation of insoluble oxalates following use of acidified ammonium oxalate (Tamm's reagent).^{86,135}

It is well known that soils and sediments do not contain discrete particles of different minerals, but consist of complex mixtures of components.^{115,116} This means that, even where a reagent is completely specific, the intended target mineral phase could be inaccessible due, for example, to occlusion within a dissimilar mineral coating.¹³⁶ Whilst this problem may be overcome by grinding the sample finely, grinding will expose new faces of solid components and increase the surface area for leaching, meaning that the data subsequently generated by sequential extraction may no longer reflect accurately the likelihood of PTE mobilization under the original environmental conditions.

4. Issues

4.1 Nomenclature

It is perhaps surprising that there is no commonly accepted abbreviation for sequential extractions. This, together with the fact that SE should not be used as it is already used for supercritical extraction, has resulted in a number of different abbreviations being used for essentially the same thing. These abbreviations include SCE (sequential chemical extraction), SEP (sequential

extraction procedure), SES (sequential extraction scheme), SET (sequential extraction test), SSD (selective sequential dissolution), SSE (both selective sequential extraction and sequential selective extraction) and SSEP (short sequential extraction procedure).

No official distinction is made between the two BCR procedures which exist. Papers frequently refer to 'the BCR' method or protocol but rarely to the specific procedure being employed. Only by looking at the detail in the method description can the reader determine which method was used. Confusion is greatest when authors refer to one of the two methods but then present details for the other method. It is not unknown for authors to state that they have used 'the BCR method' and to give references to both methods. It remains a mystery as to which one they actually used. Some authors do distinguish between the two methods by referring to them as the 'original' and 'revised' or 'modified' methods. Even this can lead to confusion. Does a reference to a revised BCR procedure mean that the authors have used the officially revised scheme or that they have themselves altered one of the two BCR procedures to meet their own requirements? One can in fact have a modified 'revised BCR procedure'. Confusion could be reduced greatly if there were some generally accepted way of distinguishing between the two procedures. Simple ways would be to redefine the BCR procedures as the 'BCR (1993)' and 'BCR (1999)' schemes or as the 'BCR1' and 'BCR2' schemes.

Why is this important? There is increasing evidence that the two BCR procedures can produce very different results, in particular for lead. Mossop and Davidson,⁷⁴ Sutherland and Tack¹³⁷ and Bacon *et al.*¹³⁸ have all compared the two BCR procedures and found significant differences between the two methods. It could be concluded that the modifications incorporated into the second procedure had been successful in attacking more completely the oxide phases but for lead the order of magnitude shift from the 'oxidisable' fraction to the 'reducible' fraction leads to severe problems of interpretation. This is best illustrated by the study of Jensen *et al.*¹³⁹ in which the 'original' BCR procedure was used to study the speciation of lead

in industrially polluted soils. Most lead was extracted in the 'oxidisable' fraction and it was concluded that lead adsorbed preferentially to organic matter. The conclusions would probably have been quite different had the 'revised' BCR procedure been used.

These findings emphasize the operational nature of the procedure. There appears to be growing awareness that sequential extraction procedures are operationally defined and that the results cannot be interpreted as metals being bound to specific phases. Reference to specific phases continues to happen, however, and, more confusingly, mixed terminology is frequently used. It is not unusual to read sentences like "The association of heavy metals with operationally defined solid phase fractions (carbonates, iron and manganese oxides, sulfides/organics and residual) was assessed". What is the message that this gives? That the procedure, as defined by the operations carried out, targets the specific phases listed successfully? Or that the procedure is defined by the operations carried out and that the names given to each fraction are the nominally targeted phases and used for convenience rather than accuracy?

Most authors probably use the names of specific phases as a matter of convenience. The discussion of data is, however, frequently based on association of metals with specific phases. It is difficult to find a terminology which is accurate and yet simple to use. Relatively few papers have followed the examples set by Kersten *et al.*¹⁴⁰ who referred to 'exchangeable', 'reducible', 'oxidisable' and 'residual' fractions, or Gobeil *et al.*¹⁴¹ who referred to 'acetate buffer extractable Pb' and 'hydroxylamine/acetic acid extractable Pb'. The BCR method has never been presented as targeting specific phases and terms such as 'reducible' and 'oxidisable' fractions are preferred. This, however, is still rather vague even though probably the best manageable option. The differences between the two BCR procedures highlight the fact that the 'reducible' fraction, as defined by the original BCR procedure, is different from the 'reducible' fraction as defined by the revised BCR procedure. To be accurate one would have to refer to the 'fraction reducible in 0.1 M hydroxylamine hydrochloride at

pH 2' or the 'fraction reducible in 0.5 M hydroxylamine hydrochloride at pH 1.5'. This is clearly very clumsy and impractical. Perhaps the only solution is to define the fractions in the Methods section by the operations used and to refer to them simply as fraction 1, 2, 3, *etc.* Phrases such as 'operationally defined Fe and Mn oxides (reducible fraction)' are best avoided.

4.2 Methodology

Although authors frequently cite, for example, the BCR method as the procedure they used, close inspection can reveal that there are differences between the conditions as specified by the BCR procedure and those described by the authors. This applies in particular to the shaking conditions. Researchers can only use equipment they have available so, combined with a common lack of understanding of the term 'end-over-end shaker', extractions can be performed under a range of conditions. Jensen *et al.*,¹³⁹ for example, followed the BCR procedure yet used a shaking speed of 100 rpm (type of shaker unspecified). Not all laboratories have air conditioning so extractions carried out in southern Europe will probably be outside the temperature range specified by the BCR procedure. These divergencies from the specified procedures are rarely recorded.

Do these divergences matter? Probably not, but the true answer is that we don't know because these aspects have not been thoroughly investigated. The energy being placed into the shaking process could well influence the extraction efficiency but most shaking is carried out overnight so the extraction should be complete in that timescale. If too much energy is placed into shaking, however, samples could effectively be centrifuged rather than shaken. There are good reasons for choosing a shaking speed that keeps the solid phase in suspension and for maintaining conditions such as temperature constant throughout a study. In this way one can have confidence that the data have been obtained under the same conditions and therefore are comparable. If data from one study are to be compared with those from another study then consistency of methodologies and extraction conditions becomes important.

4.3 Presentation of data

Sequential extraction can generate a vast quantity of data. For each sample analysed using the four-step BCR procedure, five results are obtained for each element determined. Some procedures can have seven or eight steps. It is not always easy to present large datasets in a manner that is clear and easy to interpret. The use of bar charts is space-efficient and visually acceptable and so is widely adopted. Bar charts work particularly well if colour is used, but they are often less effective in black and white. Also, the large numbers needed in some studies can result in a reduction in size and a reduction in clarity of presentation (see, for example, Davidson *et al.*⁴¹).

Unfortunately, the data in bar charts are in most cases presented as a percentage (with respect to either pseudototal values or the sum of the steps of the sequential extraction). This can be misleading unless the absolute levels of metals are also provided. For example, Fig. 2(a) suggests that element A has the greatest potential for mobilization and hence presents the greatest risk (assuming the three analytes have equal toxicities). However, when the same data are presented in terms of concentration [Fig. 2(b)], it becomes clear that all three elements have exactly the same concentrations in each of Steps 1, 2 and 3.

Potential confusion can easily be avoided by displaying the absolute amounts of metal in each fraction (see, for example, Ettler *et al.*¹⁴²) or by presenting bar charts for both analyte concentrations and analyte fractionation patterns in the same figure, exemplified by Gonnee and Paytan¹⁴³ in a recent study of barium in sediments using a five-step sequential extraction procedure.

Authors frequently base their discussion solely on the relative amounts of

elements in each fraction and this can be misleading. Statements such as ‘percentage Pb bioaccessibility was the lowest in the most contaminated soils’ could be misinterpreted because the most contaminated soils by definition have the highest concentrations so they could easily have the highest absolute amount of ‘bioaccessible lead’ even though the percentage is the lowest. Reimer *et al.*¹⁴⁴ considered the high arsenic levels in crushed rocks to be unavailable because only 10% was easily extracted, yet low concentrations of arsenic in organic soils were ‘more available’ because 10–50% was extracted. It is the absolute amount, however, that is important. This was recognized by Abollino *et al.*¹⁴⁵ when they justified presentation of relatively small extractable amounts of aluminium because ‘0.004% Al extracted into the exchangeable fraction corresponds to 3.1 mg kg⁻¹ of the element’.

Some studies^{146–148} have used a ‘Risk Assessment Code’ to assess the environmental impact of contaminated river sediments. In this code the degree of risk is related to the relative amount of metals associated with the ‘carbonate’ and ‘exchangeable’ fractions. A value of <1% is considered to present no risk to the aquatic environment even though 1% of a large concentration could still be harmful. It is questionable whether a risk assessment should be based on the percentage of metal extracted in a particular fraction.

A similar caveat applies to the presentation of PTE mobility series based on the proportion (percentage) of each element released by the initial step or step(s) of a sequential extraction. Considering again the hypothetical sequential extraction presented in Fig. 2, a mobility series for elements A, B and C could be proposed based on Step 1

[A(36%) > B(20%) > C(4%)] or on the fractions associated with non-residual components [Σ (Steps 1–3): A(91%) > B(50%) > C(9%)]. Both are potentially misleading and fail to properly emphasize the fact that a very small proportion of a large amount of PTE could be much more significant than a high proportion of a small amount.

4.4 Interpretation of data

Once data have been acquired then they must be interpreted. The interpretation depends strongly on the context and aim of the study so that one metal pool could be considered as ‘bioavailable’ in studies of plant uptake yet ‘mobile’ or ‘labile’ in leaching studies. Surprisingly, many studies still make no attempt to interpret the data obtained within a clearly-defined context.

Interpretation is not aided by the dependence on the operations used to obtain individual fractions. Not only is it necessary to understand the context of the sample but also the implications of adopting a particular procedure. It is important to understand the differences between the two BCR procedures so that appropriate conclusions can be drawn. It is important to understand that the Tessier and BCR procedures will not necessarily give the same results. For example, Mn is extracted from agricultural soils predominantly in the reducible fraction of the BCR procedure, but predominantly in the residual fraction of the Tessier scheme.²⁸ It is therefore important to realize that comparison with data from outside a study should only be done with caution.

Consistent interpretation of the outputs of sequential extraction is further hampered by the large variations that exist in authors’ definitions of ‘bioavailable’, ‘mobile’ and ‘labile’ pools.

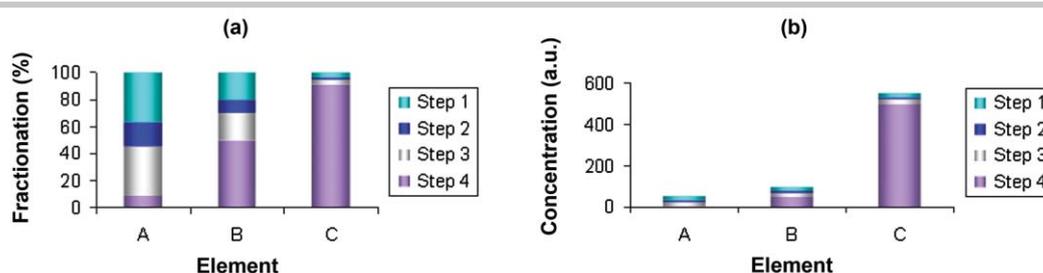


Fig. 2 Hypothetical results of a BCR-type extraction, presented as (a) percentage fractionation patterns and (b) absolute concentrations.

Bioavailability is a complex and evolving concept,¹⁴⁹ but has recently been defined as the 'degree to which chemicals present in the soil may be absorbed or metabolized by a human or ecological receptor or are available for interaction with biological systems'.¹⁵⁰ Whilst it is entirely legitimate to use sequential extraction as a tool to deduce information on the potential bioavailability of PTEs, due emphasis must be placed on 'potential'. A large number of factors (physical, chemical and physiological) affect whether an element will be incorporated into an organism: even those elements extracted early in a sequential extraction are not necessarily currently bioavailable and may never become so.

Similar comments apply to the designation of PTEs in particular fractions as 'mobile' or 'labile'. Whether mobilization will actually occur depends on a large number of additional environmental factors, including the prevailing pH, redox conditions, and availability of solid and colloidal particulate phases for re-adsorption. Sequential extraction can thus only indicate the potential, rather than the actual, mobility of soil- and sediment-bound species.

Despite the fact that sequential extraction schemes are designed with increasing reagent activities as one proceeds through the steps, few authors interpret the data as reduced availability or mobility passing through the stages of the extraction.^{147,151} This is probably because knowing that one fraction is more available than another is not necessarily helpful and researchers prefer to try to put absolute qualities to their data.

The majority of papers define the 'bioavailable/mobile pool' as the most easily extracted fractions (corresponding to the first step of the BCR procedures and the first two steps of the Tessier procedure).^{152–185} However, a substantial number of papers define the 'bioavailable/mobile pool' as all fractions except the residual fraction (corresponding to all three steps of the BCR procedure or all four steps of the Tessier method).^{78,79,186–202} It goes without saying that these two definitions can result in quite different interpretations of data. There are also a number of intermediate definitions in which the reducible fraction^{203–210} or oxidisable fraction^{211–217}

was considered to represent the 'bioavailable/mobile' pool, either together with the easily extractable pool or on their own. Distinction is also made in some studies between the easily reducible pool (more mobile) and less easily reducible pool (less mobile).^{218,219} In contrast the reducible^{220,221} or oxidisable^{222,223} fractions have been specifically described as immobile or unavailable.

There are, however, some subtle (and some less subtle) nuances to the meaning of 'bioavailable' or 'mobile' fractions. Whereas the 'water soluble' and 'carbonate' fractions have been defined simply as 'mobile'¹⁵⁵ or 'bioavailable',¹⁵⁷ other descriptions of the 'exchangeable' fraction range from 'mobilizable',¹⁸³ the fraction with 'greatest potential for chemical remobilization',¹⁸¹ the 'form of high mobility and potential bioavailability',¹⁷⁹ 'readily available',¹⁵⁶ to 'highly mobile and bioavailable'.¹⁵³

Interpretation is clearly not straightforward and, to quote De Vries *et al.*,²²⁴ 'despite numerous sequential extraction schemes, specific information on the availability of those pools in view of its relation with dissolved concentrations, readily available for plant uptake or leaching to groundwater is lacking'.

Improved understanding of the relationships between results of sequential extraction and measured biological uptake can be obtained by analyzing samples of biota in parallel with sequential extraction of the soils or sediments on which they live. Many studies of this type have appeared in recent years, focusing on a variety of organisms: microbes;^{40,225,226} plants (lettuce,^{227–230} alfalfa,²³¹ wheat,^{226,232–235} maize,²³⁶ brassicas,^{132,182,237} trees,²³⁸ rice,²³⁹ peanut,²⁴⁰ basil,²⁴¹ Swiss chard,²⁴¹ sea rush,²⁴² tall fescue,²⁴³ tea,²⁴⁴ corn,²⁴⁵ parsley,²³⁰ dill²³⁰ and onion²³⁰) and animals (mussels,^{246–249} rag worms,²⁴⁹ fish,²⁵⁰ spiders,²⁵¹ earthworms^{44,174,252,253} and rats²⁵⁴). However, considerable further research is needed.^{255,256}

There is contradictory evidence as to whether a correlation exists between extractable concentrations of metals and some observable biological effect such as plant uptake. Whereas no correlation was found between uptake by wheat,²³⁴ sorghum²⁵⁷ or plantain²⁵⁸ and extractable metal contents, good correlation has been found between plant uptake and the

metal concentrations extracted in the first fraction of sequential extraction schemes.^{244,259–262} Up to 19% of the 1500 mg kg⁻¹ lead found in polluted paddy fields was extracted in the first step of a sequential extraction procedure and corresponded to a high uptake of lead by rice plants.²⁶¹ Removal of copper from contaminated soil by poly(amido-amine) dendrimers correlated well with the 'exchangeable and carbonate-bound' copper fractions.²⁶³ Uptake of metals by vegetables,²³⁰ corn²⁶⁴ and sugarcane²⁶⁵ all correlated with either the 'exchangeable' or 'carbonate-bound' fractions together with the 'organic' fraction which were therefore considered to be 'bioavailable'. In contrast the uptake of copper and zinc from sludge-amended soils correlated with the metals extracted in the 'reducible' fraction.²⁶⁶ In pot trials, zinc uptake seemed to correlate with all extractable fractions.²⁶⁷

The contradiction in evidence is exemplified by two studies on the uptake of metals by plants following amendment of soil with sewage sludge. Mendoza *et al.*²⁵⁷ found that uptake by sorghum of metals did not correspond to the availability predicted by sequential extraction. The authors concluded that neither single nor sequential extractions provided a good prediction of metal bioavailability. Pedra *et al.*²⁶⁸ on the other hand concluded that both total and extractable metal concentrations gave adequate predictions of plant uptake.

Evidence from the use of direct bio-accessibility assays has also proved somewhat contradictory. Use of a microbiological biosensor for lead indicated that the first stage of the BCR procedure overestimated the 'bioavailable' fraction of lead and that a single extraction with CaCl₂ gave a better correlation.²⁶⁹ Similarly, a bioluminescence assay gave a lower 'bioavailable' fraction of lead than the first stage (1 M sodium acetate) of a sequential extraction test.²⁷⁰ The bioluminescence assay gave a higher value for 'bioavailable' copper, however, than the oxidation step of the sequential extraction procedure. Use of a stable-isotope-dilution procedure revealed that there was no correspondence between the isotopically labile cadmium pool in soils, often taken as representing the bioavailable pool, and the first fraction of a sequential extraction procedure.²⁷¹ This

led the authors to state that 'results suggest that conventional SEPs may be of limited utility for predicting bioavailability, for example, during ecological risk assessment'.

In contrast to these findings, a good correlation was found between 'bioaccessible' cadmium, as measured using a physiologically-based *in vitro* test, and water-soluble and 'exchangeable' cadmium.²⁷² A reduction in the 'bioavailability' of lead, measured with an *in vivo* test using rats, when biosolids were incorporated into contaminated soils was reflected by a change in partitioning towards 'less available' phases as measured by sequential extraction.²⁵⁴ In a study on the toxicity to microorganisms of copper in soils, a correlation existed between IC₅₀ (a measure of toxicity) and the exchangeable copper fraction but not with any of the other fractions.²⁷³ The bioavailability of mercury in sediments, measured using the assimilation efficiency in the clam, correlated well with mercury identified as bound to Fe/Mn oxide, amorphous organosulfur or the mineral lattice but not with mercury identified as bound to organocomplexes.²⁷⁴

In addition, or as an alternative, to bioassay, some authors have compared sequential extraction with the use of well-established, single extraction procedures, generally assumed to provide a reasonable estimate of plant-available PTEs in soil, e.g. diethylenetriamine pentaacetic acid (DTPA)^{52,182,254,275–277} and ethylenediamine tetraacetic acid (EDTA).^{276,278–281} Relationships between sequential extraction data and results of physiologically-based extraction tests designed to estimate PTE bioaccessibility in humans – following (usually) accidental intake of contaminated soil or sediment – are also beginning to be explored.^{133,226–228,269,272}

5. Recent applications

Given the problems and uncertainties associated with sequential extraction analyses, one would be forgiven for wondering why anybody bothers using them. The fact that sequential extraction continues to see increased use suggests that researchers see the procedure as providing useful information. Examples of applications already cited in previous

sections indicate that under certain conditions the information provided by sequential extractions correlates well with observable effects. An additional example is the fascinating find that high levels of 'bioavailable' copper in contaminated beach sediments, as measured by sequential extraction, correlated with low biodiversity.²⁸² Is this direct evidence of a link between 'bioavailable' copper measured by sequential extraction and a toxic effect?

Sequential extractions are relatively complicated, time-consuming and expensive and so should be only used when appropriate. They are not a very cost-effective method, for example, for predicting plant uptake of metals from contaminated soils. There is generally no advantage over the traditional use of single extractants such as EDTA²⁸ or CaCl₂.²⁶⁹ Similarly, single extractants have been found better than sequential extractions for the study of sediments.²⁸³ Even the use of multiple single extractants, essentially those used in the Tessier sequential scheme, has been proposed as a preferred option.²⁸⁴ This last proposal raised a number of issues such as double-accounting, however, which lie outside the scope of this review.

The lack of specificity is in itself not a major disadvantage in environmental studies. The chosen operations match conditions found within the environment, in particular the redox conditions, so it can be argued that it is more important to know the levels of metals susceptible to release under reducing or under oxidising conditions rather than to know the specific phases that are being attacked.

Taken together with other information, sequential extraction can provide information on natural processes within soils and sediments. Whereas soil organic matter was considered to play an important role in immobilizing lead in forest soils,⁴³ the Fe–Mn oxides controlled metal mobilization in sediments contaminated by mining activity.²⁸⁵ The finding from isotope analysis that anthropogenic lead had penetrated no deeper than 10 cm in forest soils was consistent with the observation that lead below this depth was in a residual form.²⁸⁶ In environments dominated by limestone, carbonate species played a major role in the

'self-purification' of waters²⁸⁷ which was seasonal.²⁸⁸

Sequential extraction is widely used to assess the impact of human activity such as mining on the environment.^{45,47,289,290} Such studies are enhanced if a link can be demonstrated between metal fractionation and a biological effect such as intake by fish.²⁵⁰ These studies are most effective when comparing two different states. Changes can be observed in metal fractionation in the sediments of an estuary and those of its upper catchment in a mining area²⁹¹ or between contaminated river sediments and mud.¹⁰⁸ Seasonal changes in metal partitioning have been observed for sediments.²⁹² The activity of indigenous sulfur-oxidising bacteria in contaminated sediments changed metal distributions with consequent remobilization of metals.²⁹³ Human activity can have an impact in a wide range of cases including the addition of copper to reservoirs as an algicide,²⁹⁴ the use in road construction of ashes from the incineration of municipal waste⁵⁷ and the generation of urban air particulates.⁶⁰ Sequential extraction has been used with other tests to investigate the effectiveness of leach tests which are widely used to assess release of metals from mineral processing waste.⁴⁹

Classic examples of 'before and after' application of sequential extraction are the numerous studies on the clean-up of wastes and the remediation of contaminated sediments and soils. In all these studies, sequential extraction is used to determine metal partitioning both before and after the treatment thereby allowing an assessment of the effectiveness of the treatment to be made. Here is a strength of sequential extractions. Although it might not be possible to assign metals to specific soil phases, a general change in their reactivity can be identified and the consequences for their 'bioavailability' or 'mobility' assessed. There are two major approaches to the remediation of contaminated soils and sediments. One is the removal of metals through techniques such as acid washing,²⁹⁵ the use of chelating agents^{296–298} or other extractants,²⁹⁹ microbially-produced surfactants^{300,301} or flotation techniques.³⁰² Sequential extraction can be used to evaluate the potential of electro-dialytic remediation of harbour sediments, a

technique which requires the metals to be in a mobile form.³⁰³ Similarly, the use of biodegradable chelating agents is only effective if the metals are present in mobile forms.²⁹⁶ The effectiveness of electrokinetic remediation methods was highly dependent on soil type and conditions.^{304,305} The observation³⁰⁴ that up to 76% copper could be removed from one soil but that copper was only redistributed between fractions in another soil led to a caution against generalization of the remediation process.

The second approach to the remediation of soils is through the use of inorganic amendments to immobilize metals.^{306–308} Sequential extraction is used to confirm that metals are bound in less extractable forms after amendment of the soils. Relatively large amounts of a mixture of lime and fly ash reduced the leachability of metals, but if insufficient amendment was added the leachability of some metals could actually increase.³⁰⁹ Some procedures were only partially successful. Addition of 1% iron grit to soil, for example, successfully decreased the availability of arsenic and chromium and resultant uptake by plants but had no effect on copper uptake.³¹⁰ In contrast, amendment of contaminated soil with a mixture of coal fly ash and peat reduced the leachability of copper and lead substantially.³¹¹ The most widely used inorganic amendment is the addition of phosphate to soils to immobilize metals.^{132,312–317} These studies consistently found that lead was converted into pyromorphite, a stable lead mineral, but the effectiveness has been reported to be greater for a soluble form than for the widely used rock phosphate³¹² and to be dependent on grain size.³¹⁵ Sequential extraction was used to assess the effect on plant uptake of mine tailings with sewage sludge.³¹⁸ Organic amendments such as humic acids³¹⁹ also immobilized metals in contaminated soils. Heat treatment alone was sufficient to fix radionuclides in soils.³²⁰

Amendment of soils with organic wastes is widely seen as a beneficial means of utilizing these wastes, but there are clear implications in the possible introduction of harmful compounds including metals into soils and the wider ecosystem. Analysis of sewage sludges revealed that metal partitioning within

the sludge was strongly influenced by the stabilization treatment used in production of the sludge.^{52,321} Most studies have, however, addressed the question of what happens to the metal distribution once the sludge is introduced into the soil. Although significantly increased amounts of extractable metals have been reported for sludge-amended soils³²² or for soils irrigated with waste water³²³ and no change in zinc distribution has been observed,³⁰ the general observation is that metal availability reduces and the metals become associated with residual phases in the soil.^{29,324–326} Whereas cadmium introduced into soil with chicken or pig manure was found predominantly in the unavailable residual fraction,³²⁷ cadmium spike added to municipal waste composts was associated in the soil mainly with the relatively bioavailable fractions.³²⁸ In calcareous soils, most of the metals in sewage sludge became associated with the ‘carbonate’ and other relatively available fractions.³²⁹ Soils amended with paper mill sludges,³¹ tannery sludges³³ and municipal solid waste compost³² have also been investigated. The thermal treatment given by forest fires reduced metal availability in sludge-amended forest soils.³³⁰

Composting of organic wastes is seen as a means of reducing metal availability prior to introducing the waste into soil. Composting of municipal solid waste changed metal partitioning with a shift to residual forms.⁵⁴ Although some studies confirmed that composting of sewage sludge reduces the ‘availability’ of metals,^{51,55,56,331} this was not found consistently and increases in cadmium⁵¹ and lead⁵⁰ ‘availability’ have been reported. Analysis of a range of different composts confirmed that composting altered the metal distribution within the waste but also that the changes in distribution depended on the source of the compost.⁵³ The removal of heavy metals from sewage sludge prior to use as a fertilizer has been investigated using chelating agents,³³² bacterial leaching³³³ or electrokinetic treatment.^{334–336} Liming of sewage sludge to make the sludge stable for storage had the effect of redistributing copper in the oxidisable fraction to both the exchangeable and the residual fractions.³³⁷ Metals in incinerator fly ash could be made

less reactive by amending the ash with clays.³³⁸ Cement-stabilized sewage sludge, intended for use as an artificial soil in earth works, had reduced levels of ‘available’ zinc but increased levels of ‘available’ copper.³³⁹

Studies on natural processes in soils help us to understand the action of plant exudates within the rhizosphere in increasing the bioavailability of trace elements.^{34,38,39,42,340,341} Such studies can also provide a better understanding of how hyperaccumulator plants mobilize and take up heavy metals and so can be used for phytoremediation.^{35,36,48,342,343} The effectiveness of phytoremediation can be improved by adding a chelating agent such as EDTA to the soil in order to increase the ‘bioavailability’ of the metals.^{243,344} The effectiveness of microbial recolonization of mine tailings has also been demonstrated.²²⁵ Other soil processes studied include the role of mycorrhiza in immobilizing metals and thereby protecting the host plants,³⁷ the effect of earthworms on metal availability in contaminated soils⁴⁴ and changes in metal partitioning resulting from increased humic acid levels in soils.³⁴⁵

Recent studies provide good examples of the wide range of environmental issues to which sequential extractions have been applied. Over time, zinc introduced into soil became less ‘available’, a so-called ‘aging’ process.³⁴⁶ Snowmelt runoff resulted in episodic releases of oxidation products from mine waste deposits³⁴⁷ whereas metals washed from roads into retention ponds were firmly bound in the sediments.³⁴⁸ A comparison of road de-icing compounds found that whereas the use of NaCl had no significant effect on cadmium ‘bioavailability’, the use of potassium formate reduced cadmium ‘bioavailability’ in soils significantly and was therefore the preferred option.³⁴⁹ Industrial discharges of chelating agents directly into the River Nile were considered to result in great remobilization of metals in the river sediments.³⁵⁰ A modern problem is the primitive processing of e-waste in China which has led to serious contamination of waters and sediments and could be impacting on both the health of local residents and the quality of the downstream environment.³⁵¹

6. Emerging developments and trends

6.1 Ultrasound- and microwave-assisted extraction

A major disadvantage of sequential extraction is that it is time-consuming. For example, the BCR procedure involves three periods of overnight shaking. Together with *aqua regia* digestion of the residue, and analysis of extracts and digests, this means that an entire week may be required to obtain results from a batch of samples – a fact hardly likely to encourage widespread use of the approach in busy, environmental monitoring laboratories. Also, whilst shaking can be carried out unattended, procedures such as oxidation and acid digestion are labour-intensive. There is thus considerable interest in developing new approaches that generate information similar to conventional sequential extraction but are faster to implement.

Ultrasound is increasingly finding applications in analytical chemistry as a tool for rapid and efficient leaching of analytes from samples³⁵² and various authors have attempted to develop ultrasound-assisted sequential extraction procedures. Perez-Cid *et al.*³⁵³ used the reagents recommended in the original BCR protocol and a sample of urban sewage sludge to develop the first such extraction, reported in 1998. Sonication conditions were optimized so that the amounts of metals extracted in the various steps matched, as far as possible, those obtained by conventional shaking. Ultrasound-assisted versions of the Tessier protocol, developed for both sewage sludge³⁵⁴ and river sediment,³⁵⁵ soon followed.

Various workers have since developed and applied ultrasound-assisted variants of both Tessier^{356,357} and BCR^{73,76,307,358–363} extractions. However, uncertainties remain about whether these truly access the same phases as standard procedures, as demonstrated, for example, by difficulties experienced in obtaining similar fractionation patterns for matrix elements such as iron^{73,358} by conventional and ultrasonic extraction – even though results for trace elements were similar. Many extraction procedures have been developed on the basis of reference materials but have yet to be proved on real samples.^{73,360,362,364} Some

have been optimized specifically with a view to application only to a particular sample type, *e.g.* sewage sludge.^{76,353,354} Whether such methods are transferable to other substrates remains somewhat questionable.³⁵⁸

Microwave-assisted sequential extraction procedures also exist. Again, most research has focused on well-established extraction schemes. Microwave-assisted protocols simulating the Tessier extraction have been developed based on lagoon sediment,³⁶⁵ sewage sludge,³⁶⁶ river sediment,³⁶⁷ and fly ash.^{368,369} Protocols based on the BCR extraction are reported for estuarine,³⁶⁰ marine³⁷⁰ and freshwater³⁶² sediment, and also for fly ash.³⁶⁸ Work has also been conducted on pond sediment,³⁷¹ vehicle exhaust particulates,³⁷¹ calcareous soils³⁷² and, uniquely, coal.³⁷³ Use of a set of microwave-assisted single extractions as a time-saving alternative to conventional sequential extraction has also been proposed.^{374,375}

There is considerable merit in the development of these rapid approaches. However, the physical processes involved in ultrasound or microwave treatment are not the same as mechanical agitation. Also, considerable heating can occur in steps normally performed at room temperature. Owing to the operational nature of sequential extraction, the development of ultrasound- or microwave-assisted protocols that give similar performance to conventional shaking for all types of substrates seems unrealistic. More probable is the acceptance of standard protocols, perhaps using the same reagents as the Tessier or BCR procedures but not necessarily generating the same PTE fractionation patterns as conventional shaking, which can be used by laboratories to obtain harmonized data.

6.2 Dynamic extraction

An alternative means to achieve rapid results is to load the soil or sediment sample into a suitable container and perform the sequential extraction in continuous flow mode. Fritted centrifuge tubes,^{345,376–378} micro-columns^{379–382} and rotating coiled columns^{383–387} have been used for this purpose. Dedicated extraction cells³⁸⁸ have been developed including one

combining continuous-flow operation and microwave irradiation.³⁸⁹

Performing sequential extraction in dynamic mode overcomes potential problems associated with analyte re-adsorption during prolonged contact between extract and residual solids.³⁹⁰ The extractograms obtained provide information on element associations^{391–393} and, with use of suitable reagent flow rates, some systems can be coupled directly to FAAS,³⁸¹ ICP-OES³⁸³ or ICP-MS^{379,388} instruments. Also, the change from thermodynamic (*i.e.* equilibrium) to kinetic control of the leaching process has been claimed to represent more accurately environmental processes such as the percolation of rainwater through a soil profile. The reagents applied are usually similar to those used in conventional sequential extraction, although some authors have selected non-specific reagents, such as increasing concentrations of nitric acid.³⁷⁹

Workers at the British Geological Survey have developed and successfully applied a rapid extraction in which a series of non-specific extractants is drawn through the sample by centrifugation, and the resulting extractograms interpreted by chemometrics to obtain information on geochemical associations of PTEs.^{345,376–378} Dynamic sequential extraction has been recently reviewed by Miro and co-workers.^{68,394}

6.3 Use of chemometrics

As in many other areas of analytical science, the past decade has seen a marked increase in the application of multivariate data analysis procedures as tools in the interpretation of results obtained by sequential extraction. Not only is it possible to assess relationships between (sometimes large numbers of) sampling sites and analytes, it is also feasible to include additional parameters, such as general soil or sediment characteristics, to gain a better overall insight into factors governing the environmental behaviour of PTEs.^{395,396} Most authors employ principal components analysis (PCA), but there are recent studies involving use of the Tucker N-way method³⁹⁷ and fuzzy clustering algorithms.³⁹⁸

Chemometric processing of data obtained from sediment fractionation

studies has helped inform decisions about land management,³⁹⁹ provided insight into the geochemical effects of urbanization,⁴⁰⁰ revealed associations between various groups of metals^{194,401–403} and provided information about anthropogenic sources of contaminants in lakes⁴⁰⁴ and river systems.^{192,223,405–408} Pollution source apportionment has also been achieved in street dusts.^{79,202} Sewage sludge has been studied to evaluate its suitability for use as an agricultural amendment.⁴⁰⁹

An early application of PCA to results obtained in the Tessier extraction of soil reference material SRM 2710 provided clear evidence of non-specificity.⁴¹⁰ Later studies explored correlations between results of different extraction procedures.²⁸¹ The combination of correlation analysis, PCA and hierarchical cluster analysis has been used to investigate relationships between metals recovered in the various steps of the BCR sequential extraction and plant uptake in an urban garden.⁴¹¹ Chemometric treatment has also been used to study the effects of land-use⁴¹² on soil metals and to identify soils requiring remediation on the basis of high concentrations of PTEs in easily extractable forms.¹⁴⁵

6.4 Sequential extractions combined with stable isotope analysis

Although sequential extractions alone can provide useful information on the association of metals with different reactive phases in soils and sediments, combined with isotope analysis they become a powerful technique which can provide information on the origin of the metal and on soil processes. Whereas total concentration and bulk isotope analysis revealed no penetration of anthropogenic lead into soil profiles, the combination of sequential extraction and isotope analysis demonstrated this clearly.⁴¹³ When combined with precise isotope analysis, use of this approach was able to distinguish between the lead in residual components from three nominally identical soils.⁴¹⁴

Because of concern arising from the widespread dispersion of lead throughout the environment, this approach has been applied principally to the study of lead which, fortuitously, has a variable isotopic composition in nature. Typical

studies include those on estuarine sediments,⁴¹⁵ freshwater sediments,^{416,417} agricultural soil,⁴¹⁸ organic-rich soils,⁴¹⁹ forest soils⁴²⁰ and contaminated soils.⁴²¹ In forest soils⁴²² and contaminated marine sediments,¹⁴⁰ most anthropogenic lead was associated with 'organic matter' whereas, in lake sediments,⁴²³ anthropogenic lead was associated predominantly with the 'oxide-hydroxide' fraction.

A striking common finding in the studies using lead isotopic composition is that lead in the different extracted fractions, no matter the operations used, is isotopically distinct. Even though sequential extractions should not be considered as targeting specific phases, the results of these studies indicate that the operations are extracting distinct fractions. The unequal isotopic distribution of lead between different fractions was true even at depths in St Lawrence sediments where no industrial lead was to be expected.¹⁴¹

Although most studies exploiting the variable isotopic composition of strontium to investigate the provenance of strontium in soils and sediments have used single extractant tests, some use of sequential extraction combined with highly precise strontium isotope analysis has been made. Yokoo *et al.*⁴²⁴ demonstrated that an extraction scheme, designed to attack specific mineral phases, could be used to identify the provenance of both wet and dry deposition in loess and sand from China. A combination of strontium and neodymium isotopic compositions and rare-earth element concentrations in acid-insoluble phases proved most suitable for characterizing dry deposition. Xu and Marcantonio⁴²⁵ used sequential extraction combined with strontium isotope analysis to investigate the distribution of elements in suspended particulates in the Mississippi River.

The development in recent years of highly precise mass spectrometers for isotope analysis has revealed that other elements can have variable isotopic composition and so could be suitable for this type of study. Emmanuel *et al.*⁴²⁶ investigated the use of iron isotopes as a tool for quantifying iron cycling in soils and demonstrated that extracted fractions have distinct $\delta^{57}\text{Fe}$ signatures which could be used to calculate the isotopic composition of mixing end members.

Although all the studies previously cited exploited natural variations in isotopic composition, it is also possible to spike samples with enriched stable isotopes in order to investigate the incorporation of the spikes into different soil fractions and to study the long-term trace element dynamics in soils. Ahnstrom and Parker²⁷¹ monitored the incorporation of cadmium spike into soil fractions defined by a five-step procedure to measure the total labile pool ('E-value') and the labile cadmium in each extracted fraction. The fact that no correspondence was found between the isotopically labile pool, often taken to represent the bioavailable pool, and the first step of the extraction procedure led the authors to conclude that 'conventional sequential extraction procedures may be of limited utility for predicting bioavailability, for example, during ecological risk assessments'.

6.5 Application to 'non-traditional' analytes

The vast majority of sequential extraction literature focused on a small suite of PTEs: cadmium, chromium, copper, iron, lead, manganese, nickel and zinc. However, the approach is now being used more widely, with standard extraction procedures being applied to 'non-traditional' elements such as arsenic, mercury, selenium and radionuclides. Success has been limited, however, because of the markedly different chemistries of these elements from the metals and it is common practice for dedicated schemes to be developed for these other elements.

6.5.1 Arsenic. Of these other elements, arsenic has received the most attention. Although Sahuquillo *et al.*⁴²⁷ applied the BCR procedure to the study of arsenic, the procedure has not generally been used because it is not considered to supply the information needed, in particular with respect to binding to oxides.⁴²⁸ The Tessier scheme has seen slightly more application but extraction of arsenic from synthetic mineral mixtures showed the scheme to be unsuitable.⁴²⁹ The study of arsenic is in fact marked by the large number of individual dedicated schemes which can be highly complex. Even though a few of these schemes have

become fairly widely accepted and applied, they tend to be revised to meet the specific needs of studies. These schemes, presented in detail in the review of Hudson-Edwards *et al.*,⁴³⁰ can have several steps designed to target specific phases. It is not unknown for eight-step procedures to be applied,^{431,432} and the procedure used by Kim *et al.*⁴³³ was considered to consist of ‘only’ seven steps. The discussion in such studies is almost without exception in terms of specific soil or sediment phases.

Applications of arsenic speciation very much mirror those of heavy metal speciation. Studies of the natural distribution of arsenic, in particular in areas of high natural concentrations, included those on sediments,^{434,435} peat⁴³⁶ and coal.⁴³⁷ The majority of studies has, however, been targeted at assessing the mobility and availability of arsenic in mine wastes,^{432,438–445} contaminated sediments^{431,446–450} and contaminated soils.^{451–453} A particular application is to the behaviour of arsenic in paddy fields⁴⁵⁴ and other soils⁴⁵⁵ irrigated with waters with high natural concentrations of arsenic and to sequestration of arsenic in rice plants.⁴⁵⁶ The mobility of organo-arsenic pesticides in soils is of concern^{457–460} as demonstrated by the study of Sarkar *et al.*⁴⁶¹ in which it was shown that arsenic was less bioavailable in soils with high concentrations of amorphous oxides, in particular of aluminium and iron. The concentrations in the soluble fractions correlated well with results from a physiologically-based extraction test. Phytoremediation of contaminated soils^{462–464} and the use of iron to stabilize contaminated soils⁴³³ or to purify waters⁴⁶⁵ have also received attention. An extraction procedure designed for the study of soils was applied to the analysis of lichens because most arsenic was present in trapped soil particles.⁴⁶⁶ The study of Han *et al.*⁴⁶⁷ on the speciation of arsenic in poultry waste was notable for defining the fractions operationally and not as specific phases. Over 47% of arsenic in the wastes was water-soluble, but when applied to soils, 72% of arsenic was extracted in the residual phase.

6.5.2 Mercury. As with the extraction schemes for arsenic, those for mercury tend to be quite complex and numerous

schemes have been developed. Although the BCR scheme has been applied to the speciation of mercury in sediments,⁴⁶⁸ almost without further exception the schemes used have been developed to address the particular chemistry of mercury. The five-step scheme of Bloom *et al.*⁴⁶⁹ has been the most widely adopted by researchers and is curious in that the second stage is defined as the ‘human stomach acid’-soluble fraction. Whereas the relevance of this to studies of soil ingestion by humans is clear, the relevance to the mobility of mercury in soils and sediments is less obvious. Other fractions were defined as ‘water soluble’, ‘organo-chelated’, ‘elemental mercury’ and ‘mercuric sulfide’. The sum of the concentrations in the ‘water soluble’ and ‘human stomach acid’-soluble fractions correlated well with results from *in vitro* bioaccessibility tests. The six-step scheme of Hall and Pelchat⁴⁷⁰ gave specific extraction when applied to single minerals but, when the minerals were mixed with granite, problems of re-adsorption and inappropriate assignment to specific phases occurred. Not all extraction schemes are complex. A two-step scheme was designed specifically to target sulfide-bound mercury in soils.⁴⁷¹ The simple three-step scheme of Han *et al.*⁴⁷² was based on extractability and not on targeted phases to quantify ‘mobile’, ‘semi-mobile’ and ‘non-mobile’ fractions. Although the procedure was proposed for routine analysis in the assessment of environmental mobility of mercury, it appears to have seen little use.

The limitations of sequential extractions for mercury speciation have been highlighted. Kim *et al.*⁴⁷³ found that specific phases were dissolving in the ‘wrong’ fractions of their procedure (Bloom *et al.*⁴⁶⁹) and reported ‘inconsistencies in speciation results between different extraction protocols’ which ‘might not yield accurate information’. In a comparison of different extraction schemes, Sladek and Gustin⁴⁷⁴ found that identification of specific mercury phases could only be made with caution and that the schemes overestimated the release of mercury from mine wastes. They concluded that ‘these methods require more extensive evaluation before they can be considered as a predictive measure of *in situ* volatilization and removal *via* water’. On the other hand,

Fernandez-Martinez *et al.*,⁴⁷⁵ whilst acknowledging that it was not possible to identify individual species, found differences in availability between soils and considered that the method ‘provides detailed information about mobility in soils’.

Mercury speciation has been applied predominantly to mine wastes,^{473,474,476} contaminated soils^{475,477–483} and contaminated sediments.^{484–487} An investigation into the use of willow trees to stabilize mercury in contaminated land found that the root systems were effective in trapping ‘bioavailable’ mercury.⁴⁸⁸

6.5.3 Selenium. A critical evaluation of two sequential extraction schemes for the speciation of selenium in soils and sediments demonstrated that most of the steps were not specific and that extraction could remove substantial proportions of non-targeted components.⁴⁸⁹ Nevertheless the authors considered that the schemes could provide useful information and optimized one of the schemes to provide accurate quantification of selenium fractions (soluble/exchangeable, adsorbed, elemental and ‘organically associated’). Warning was given, however, that the results should be interpreted with caution. After comparing various extraction schemes for selenium, Kulp and Pratt⁴⁹⁰ designed a seven-step scheme to provide a comprehensive and environmentally relevant budget of both bioavailable and insoluble species in geological materials. Although most fractions were operationally defined (for example, water-soluble and acetic acid-soluble), some were specific (for example, organic). All the fractions were associated with specific targeted phases. The six-step scheme of Lim and Goh⁴⁹¹ was developed following the testing of the specificity of a wide range of extractants and was intended to be used for identification of the size fractions in contaminated soils which presented the greatest environmental hazard. De Leon *et al.*⁴⁹² discussed the mechanisms of extraction and recommended a relatively simple procedure. They applied a further layer of speciation analysis in that each of the fractions was further analysed by HPLC–ICP–MS to determine the species (selenite, selenate, elemental selenium and organic selenium) extracted at each stage.

Schemes for selenium speciation can be either relatively simple or relatively complex and range from a three-step procedure to assess selenium in agricultural soils⁴⁹³ to the seven-step procedure of Kulp and Pratt.⁴⁹⁰ Sequential extractions have been applied to the study of selenium in soils,^{492–495} contaminated sediments,⁴⁹⁶ mine tailings⁴⁹⁷ and coal-bearing rocks.⁴⁹⁸

6.5.4 Radionuclides. Natural and synthetic radionuclides have also received attention.⁴⁹⁹ Sequential extraction procedures have been developed specifically for actinides, for example by NIST.^{500–502} A successful method to prevent post-extraction re-adsorption of plutonium by the addition of citrate to sequential extracts was recently reported.⁵⁰³

Sequential extraction procedures have been applied to investigate uranium geochemistry in rivers,⁵⁰⁴ fertilizer-amended soils⁵⁰⁵ and Moroccan black shale oil.⁵⁰⁶ Environmental contamination arising from uranium mining^{507–509} and the technological enhancement of natural radionuclides by phosphates mining⁵¹⁰ and production,^{511–513} coal burning and pyrite roasting⁵¹⁴ and other industrial processes⁵¹⁵ have been investigated. Studies have indicated that relatively small proportions of the transuranic elements plutonium and americium occur in easily extractable forms in contaminated soil^{516–518} and sediment.⁵¹⁹ Hence, the potential for migration of these, highly chemically- and radio-toxic elements, once released to the environment, is generally rather limited.

Fractionation data have clarified the role of microbes in the geochemical cycling of ⁹⁹Tc⁵²⁰ and of fungi in the cycling of ¹³⁷Cs;^{521,522} the importance of sediments as a sink for ⁹⁹Tc⁵²³ and ¹³⁷Cs⁵²⁴ (released from the Sellafield nuclear reprocessing facility, Cumbria, UK); and the factors affecting the migration and fate of ⁶⁰Co,⁵²⁵ ¹³⁷Cs,^{526,527} ^{239/240}Pu⁵²⁷ and ⁹⁰Si⁵²⁶ in soil. The approach has been used in assessing the efficiency of a heating method for immobilization of radionuclides in contaminated soil³²⁰ and as part of laboratory-based studies of radionuclide migration in rock fractures⁵²⁸ relevant to the design of nuclear waste repositories.

Sequential extraction has also provided considerable insight into the physico-chemical behaviour of radionuclides released by the Chernobyl accident (April 1986).⁵²⁹ It is now widely accepted that the majority of radiocaesium is strongly bound to soil components,^{530–533} whereas ⁹⁰Sr is found predominantly in easily extractable forms, except close to the reactor where there is a strong influence of deposited fuel particles.^{530,531,533} Similar findings have been reported for river sediments in the Chernobyl area⁵³⁴ and confirmed by column and batch leaching experiments.⁵³⁵

6.5.5 Other elements. There is a tendency in the study of other elements to apply a standard procedure. The BCR procedure has been applied to study the release of strontium and barium from mine tailings⁵³⁶ and the bioavailability of tungsten in abandoned mine spoil.⁵³⁷ In addition, the BCR procedure has been used to study aluminium in mine wastes^{538,539} and data have been presented for aluminium in six geological reference materials.⁷⁷ The Tessier procedure, on the other hand, has been applied to the speciation of boron,⁵⁴⁰ thallium⁵⁴¹ and vanadium⁵⁴² in soils and of antimony in sediments.⁵⁴³ Dedicated schemes have been developed for the study of antimony⁵⁴⁴ in soils and of barium in sediments.¹⁴³ A five-step scheme was used to study the solubilization of gold by microbes in soils from a gold mine.⁵⁴⁵ Although a seven-step procedure was devised to study the uptake of thallium by hyperaccumulator plants, the fractions were effectively grouped into two fractions – ‘easily accessible’ and ‘less accessible’.⁵⁴⁶ Platinum in road tunnel dusts and in gully sediments was found to be extracted only in either ‘mobile’ or ‘easily mobilised’ fractions and could therefore present a risk to the environment.⁵⁴⁷

7. Concluding remarks

Sequential extraction is an important and widely applied tool for gaining information on potential mobility (hence, potential bioavailability and toxicity) of PTEs in the environment. Despite the limitations highlighted in this review, the usefulness of sequential extraction is

evident from considerable insights it has provided over almost three decades into the environmental behaviour of PTEs. Applications of the approach continue to expand, and now encompass more elements and substrates than were probably ever envisaged by early workers in the field.

In response to the title of this review, we consider sequential extraction to have a healthy future in the 21st century but that its continued usefulness, in particular for environmental monitoring, requires researchers to be aware of the limitations. Studies based on sequential extractions are more likely to be successful if certain conditions are met:

(a) A ‘standard’ sequential extraction scheme (*e.g.* the revised BCR procedure) should be used whenever possible because of the availability of reference materials and the possibility of direct comparison between studies. The experimental work should be adequately validated through use of mass balance and/or certified reference materials.

(b) When using such a ‘standard’ scheme it is critical that the specified procedure is adhered to strictly or, at the very least, any variations should be reported.

(c) There should if possible be some degree of comparison within a study – that is, comparing the difference in ‘before and after’ situations, spatial or temporal variability, the effect of some form of treatment or other changes within a system. Because of their operational nature and the difficulty in interpretation, sequential extraction procedures are not particularly suited for absolute studies – that is, identifying the distribution of metals between specific soil phases without reference to any other analyses.

(d) Data should be presented in terms of absolute concentrations instead of or in addition to percentage values

(e) Data should be interpreted according to the ‘operational speciation’ definition of Ure.¹¹ For example, PTEs recovered in Step 2 of the BCR procedure should be described as associated with the ‘reducible fraction’, rather than as being ‘bound to iron/manganese oxyhydroxides’.

(f) It is important that sequential extractions are not applied uncritically and users should take cognizance of the

scope and limitations of the approach. Phenomena such as non-specificity and re-adsorption can occur to widely variable extents, depending on the substrate and PTE studied.

(g) Care should be taken when drawing inferences concerning bioavailability based on sequential extraction results. Although, in general, it is reasonable to expect that PTEs liberated early in a sequential extraction have the potential for more immediate environmental impact than those found in residual fractions, relationships between the results of sequential extraction and observed bioavailability depend on the element, the substrate, the organism studied and the exposure route.

Studies into the fundamental mechanisms of sequential extraction procedures are to be encouraged as these provide us with an improved understanding of the metal speciation within the matrix and the solid phases attacked by the extractants. Our understanding of the relationship between extractability on the one hand and mobility and bioavailability on the other needs to be improved. The availability of a wider range of reference materials would help ensure the production of reliable data and ease the comparison of data produced by different studies.

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References

- 1 D. Littlejohn, C. Davidson, J. Bacon and P. Quevauviller, *J. Soils Sediments*, 2006, **6**, 62.
- 2 A. M. Ure and C. M. Davidson, *Chemical Speciation in the Environment*, Blackwell, Oxford, 2nd edn, 2002.
- 3 J. J. D'Amore, S. R. Al-Abed, K. G. Scheckel and J. A. Ryan, *J. Environ. Qual.*, 2005, **34**, 1707.
- 4 A. Manceau, M. A. Marcus, N. Tamura, O. Proux, N. Geoffroy and B. Lanson, *Geochim. Cosmochim. Acta*, 2004, **68**, 2467.
- 5 M. P. Isaure, A. Laboudigue, A. Manceau, G. Sarret, C. Tiffreau, P. Trocellier, G. Lambelle, J. L. Hazemann and D. Chateigner, *Geochim. Cosmochim. Acta*, 2002, **66**, 1549.
- 6 J. S. Bang and D. Hesterberg, *J. Environ. Qual.*, 2004, **33**, 891.

- 7 T. A. Kirpichtchikova, A. Manceau, L. Spadini, F. Panfili, M. A. Marcus and T. Jacquet, *Geochim. Cosmochim. Acta*, 2006, **70**, 2163.
- 8 T. Karlsson, P. Persson and U. Skjellberg, *Environ. Sci. Technol.*, 2005, **39**, 3048.
- 9 E. Welter, W. Calmano, S. Mangold and L. Troger, *Fresenius' J. Anal. Chem.*, 1999, **364**, 238.
- 10 J. D. Ostergren, G. E. Brown, G. A. Parks and T. N. Tingle, *Environ. Sci. Technol.*, 1999, **33**, 1627.
- 11 A. M. Ure, *Microchim. Acta*, 1991, **2**, 49.
- 12 D. M. Templeton, F. Ariese, R. Cornelis, L. G. Danielsson, H. Muntau, H. P. Van Leeuwen and R. Lobinski, *Pure Appl. Chem.*, 2000, **72**, 1453.
- 13 J. Hlavay, T. Prohaska, M. Weisz, W. W. Wenzel and G. J. Stinger, *Pure Appl. Chem.*, 2004, **76**, 415.
- 14 A. Tessier, P. G. C. Campbell and M. Bisson, *Anal. Chem.*, 1979, **51**, 844.
- 15 A. C. Chang, A. L. Page, J. E. Warneke and E. Grgurevic, *J. Environ. Qual.*, 1984, **13**, 33.
- 16 P. O. Scokart, K. Meeusverdinne and R. Deborger, *Int. J. Environ. Anal. Chem.*, 1987, **29**, 305.
- 17 P. Quevauviller, G. Rauret, H. Muntau, A. M. Ure, R. Rubio, J. F. López-Sánchez, H. D. Fiedler and B. Griepink, *Fresenius' J. Anal. Chem.*, 1994, **349**, 808.
- 18 A. M. Ure, P. Quevauviller, H. Muntau and B. Griepink, *Int. J. Environ. Anal. Chem.*, 1993, **51**, 135.
- 19 C. M. Davidson, P. C. S. Ferreira and A. M. Ure, *Fresenius' J. Anal. Chem.*, 1999, **363**, 446.
- 20 A. Sahuquillo, J. F. López-Sánchez, R. Rubio, G. Rauret, R. P. Thomas, C. M. Davidson and A. M. Ure, *Anal. Chim. Acta*, 1999, **382**, 317.
- 21 G. Rauret, J. F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure and P. Quevauviller, *J. Environ. Monit.*, 1999, **1**, 57.
- 22 H. D. Fiedler, J. F. López-Sánchez, R. Rubio, G. Rauret, P. Quevauviller, A. M. Ure and H. Muntau, *Analyst*, 1994, **119**, 1109.
- 23 P. Quevauviller, G. Rauret, J. F. López-Sánchez, R. Rubio, A. Ure and H. Muntau, *Sci. Total Environ.*, 1997, **205**, 223.
- 24 J. F. López-Sánchez, A. Sahuquillo, H. D. Fiedler, R. Rubio, G. Rauret, H. Muntau and P. Quevauviller, *Analyst*, 1998, **123**, 1675.
- 25 G. Rauret and J. F. López-Sánchez, *Int. J. Environ. Anal. Chem.*, 2001, **79**, 81.
- 26 M. Pueyo, G. Rauret, D. Lück, M. Yli-Halla, H. Muntau, P. Quevauviller and J. F. López-Sánchez, *J. Environ. Monit.*, 2001, **3**, 243.
- 27 A. Mocko and W. Waclawek, *Anal. Bioanal. Chem.*, 2004, **380**, 813.
- 28 J. M. Alvarez, L. M. Lopez-Valdivia, J. Novillo, A. Obrador and M. I. Rico, *Geoderma*, 2006, **132**, 450.
- 29 D. Chaudhuri, S. Tripathy, H. Veeresh, M. A. Powell and B. R. Hart, *Environ. Geol.*, 2003, **45**, 115.
- 30 M. S. Yoo and B. R. James, *Soil Sci.*, 2003, **168**, 686.
- 31 S. Z. Zhang, S. X. Wang, X. Q. Shan and H. Z. Mu, *Biol. Fertil. Soils*, 2004, **40**, 237.
- 32 P. Bhattacharyya, A. Chakraborty, K. Chakrabarti, S. Tripathy and M. A. Powell, *Chemosphere*, 2005, **60**, 1481.
- 33 A. K. Gupta and S. Sinha, *Chemosphere*, 2006, **64**, 161.
- 34 S. Tao, Y. J. Chen, F. L. Xu, J. Cao and B. G. Li, *Environ. Pollut.*, 2003, **122**, 447.
- 35 H. Al-Najar, R. Schulz and V. Romheld, *Plant Soil*, 2003, **249**, 97.
- 36 J. Yanai, N. Mabuchi, N. Moritsuka and T. Kosaki, *Soil Sci. Plant Nutr.*, 2004, **50**, 423.
- 37 Y. Huang, S. Tao and Y. J. Chen, *J. Environ. Sci. (China)*, 2005, **17**, 276.
- 38 Y. Yu and Q. X. Zhou, *Biol. Fertil. Soils*, 2006, **42**, 450.
- 39 S. H. Ru, J. P. Xing and D. C. Su, *J. Plant Nutr.*, 2006, **29**, 921.
- 40 Y. G. Yang, C. D. Campbell, L. Clark, C. M. Cameron and E. Paterson, *Chemosphere*, 2006, **63**, 1942.
- 41 C. M. Davidson, G. J. Urquhart, F. Ajmone-Marsan, M. Biasioli, A. D. Duarte, E. Diaz-Barrientos, H. Grcman, L. Hossack, A. S. Hursthouse, L. Madrid, S. Rodrigues and M. Zupan, *Anal. Chim. Acta*, 2006, **565**, 63.
- 42 S. Inaba and C. Takenaka, *Water, Air, Soil Pollut.*, 2005, **162**, 285.
- 43 P. Sipos, T. Nemeth and I. Mohai, *Environ. Geochem. Health*, 2005, **27**, 1.
- 44 T. Lukkari, S. Teno, A. Vaisanen and J. Haimi, *Soil Biol. Biochem.*, 2006, **38**, 359.
- 45 W. D. Brady, M. J. Eick, P. R. Grossl and P. V. Brady, *Soil. Sediment Contam.*, 2003, **12**, 541.
- 46 D. J. Robertson, K. G. Taylor and S. R. Hoon, *Appl. Geochem.*, 2003, **18**, 269.
- 47 M. S. V. Basilio, K. Friese, J. C. de Lena, H. A. Nalini and H. M. P. Roeser, *Quim. Nova*, 2005, **28**, 822.
- 48 P. S. Kidd and C. Monterroso, *Sci. Total Environ.*, 2005, **336**, 1.
- 49 S. R. Al-Abed, P. L. Hageman, G. Jegadeesan, N. Madhavan and D. Allen, *Sci. Total Environ.*, 2006, **364**, 14.
- 50 Y. X. Chen, Y. M. Hua, S. H. Zhang and G. M. Tian, *J. Hazard. Mater.*, 2005, **123**, 196.
- 51 D. Gao, G. D. Zheng, T. B. Chen, W. Luo, W. Gao, Y. A. Zhang and Y. X. Li, *J. Environ. Sci. (China)*, 2005, **17**, 957.
- 52 A. Fuentes, M. Llorens, J. Saez, A. Soler, M. I. Aguilar, J. F. Ortuno and V. F. Meseguer, *Chemosphere*, 2004, **54**, 1039.
- 53 Y. Y. Liu, T. Imai, M. Ukita, M. Sekine and T. Higuchi, *Environ. Technol.*, 2003, **24**, 1517.
- 54 K. Szymanski, B. Janowska and R. Sidelko, *Asian J. Chem.*, 2005, **17**, 1646.
- 55 G. D. Zheng, T. B. Chen, D. Gao and W. Luo, *Water Sci. Technol.*, 2004, **50**, 75.
- 56 J. W. C. Wong and A. Selvam, *Chemosphere*, 2006, **63**, 980.
- 57 J. Kumpiene, A. Lagerkvist and C. Maurice, *Soil. Sediment Contam.*, 2006, **15**, 429.
- 58 S. Sukandar, K. Yasuda, M. Tanaka and I. Aoyama, *Environ. Pollut.*, 2006, **144**, 726.

- 59 F. Fujiwara, M. Dos Santos, J. Marrero, G. Polla, D. Gomez, L. Dawidowski and P. Smichowski, *J. Environ. Monit.*, 2006, **8**, 913.
- 60 E. Dabek-Zlotorzynska, M. Kelly, H. D. Chen and C. L. Chakrabarti, *Chemosphere*, 2005, **58**, 1365.
- 61 G. Laforest and J. Duchesne, *J. Hazard. Mater.*, 2006, **135**, 156.
- 62 N. Kaewkhomdee, C. Kalambaheti, S. Predapitakkun, A. Siripinyanond and J. Shiwatana, *Anal. Bioanal. Chem.*, 2006, **386**, 363.
- 63 A. V. Filgueiras, I. Lavilla and C. Bendicho, *J. Environ. Monit.*, 2002, **4**, 823.
- 64 S. D. Young, H. Zhang, A. M. Tye, A. Maxted, C. Thums and I. Thornton, *Soil Use Manage.*, 2005, **21**, 450.
- 65 A. Sahuquillo, A. Rigol and G. Rauret, *TrAC, Trends Anal. Chem.*, 2003, **22**, 152.
- 66 O. Abollino, A. Giacomino, M. Malandrino and E. Mentasti, *Ann. Chim. (Rome, Italy)*, 2005, **95**, 525.
- 67 P. Smichowski, G. Polla and D. Gomez, *Anal. Bioanal. Chem.*, 2005, **381**, 302.
- 68 M. Miro and E. H. Hansen, *Microchim. Acta*, 2006, **154**, 3.
- 69 X. D. Li, B. J. Coles, M. H. Ramsey and I. Thornton, *Analyst*, 1995, **120**, 1415.
- 70 M. D. Ho and G. J. Evans, *Anal. Commun.*, 1997, **34**, 363.
- 71 G. Rauret, J. F. López-Sánchez, A. Sahuquillo, E. Barahona, M. Lachica, A. M. Ure, C. M. Davidson, A. Gomez, D. Lück, J. Bacon, M. Yli-Halla, H. Muntau and P. Quevauviller, *J. Environ. Monit.*, 2000, **2**, 228.
- 72 R. A. Sutherland and F. M. G. Tack, *Anal. Chim. Acta*, 2002, **454**, 249.
- 73 E. Dabek-Zlotorzynska, M. Kelly, H. Chen and C. L. Chakrabarti, *Anal. Chim. Acta*, 2003, **498**, 175.
- 74 K. F. Mossop and C. M. Davidson, *Anal. Chim. Acta*, 2003, **478**, 111.
- 75 J. Kubova, V. Stresko, M. Bujdos, P. Matus and J. Medved, *Anal. Bioanal. Chem.*, 2004, **379**, 108.
- 76 T. G. Kazi, M. K. Jamali, A. Siddiqui, G. H. Kazi, M. B. Arain and H. I. Affidi, *Chemosphere*, 2006, **63**, 411.
- 77 P. Matus, J. Kubova, M. Bujdos and J. Medved, *Anal. Chim. Acta*, 2005, **540**, 33.
- 78 B. L. Lerner, A. J. Seen and A. T. Townsend, *Anal. Chim. Acta*, 2006, **556**, 444.
- 79 S. Kartal, Z. Aydin and S. Tokalioglu, *J. Hazard. Mater.*, 2006, **132**, 80.
- 80 M. Jakubowska, W. Zembrzusi and Z. Lukaszewski, *Talanta*, 2006, **68**, 1736.
- 81 G. E. M. Hall, G. Gauthier, J. C. Pelchat, P. Pelchat and J. E. Vaive, *J. Anal. At. Spectrom.*, 1996, **11**, 787.
- 82 D. Gomez, M. Dos Santos, F. Fujiwara, G. Polla, J. Marrero, L. Dawidowski and P. Smichowski, *Microchem. J.*, 2007, **85**, 276.
- 83 P. M. V. Nirel and F. M. M. Morel, *Water Res.*, 1990, **24**, 1055.
- 84 M. Sulkowski and A. V. Hirner, *Appl. Geochem.*, 2006, **21**, 16.
- 85 E. Tipping, N. B. Hetherington, J. Hilton, D. W. Thompson, E. Bowles and J. Hamilton-Taylor, *Anal. Chem.*, 1985, **57**, 1944.
- 86 J. Dodd, D. J. Large, N. J. Fortey, A. E. Milodowski and S. Kemp, *Environ. Geochem. Health*, 2000, **22**, 281.
- 87 W. Calmano, S. Mangold and E. Welter, *Fresenius' J. Anal. Chem.*, 2001, **371**, 823.
- 88 C. Ianni, N. Ruggieri, P. Rivaro and R. Frache, *Anal. Sci.*, 2001, **17**, 1273.
- 89 F. C. Dominguez, J. Rodriguez and C. D. Y. Pomes, *Can. J. Anal. Sci. Spectrosc.*, 2002, **47**, 60.
- 90 K. G. Scheckel, C. A. Impellitteri, J. A. Ryan and T. McEvoy, *Environ. Sci. Technol.*, 2003, **37**, 1892.
- 91 B. Dold, *J. Geochem. Explor.*, 2003, **80**, 55.
- 92 X. Wan, W. Wang, T. M. Ye, Y. W. Guo and X. B. Gao, *J. Hazard. Mater.*, 2006, **134**, 197.
- 93 J. S. Manchanda, V. K. Nayyar and I. M. Chhibba, *Chem. Speciation Bioavailability*, 2006, **18**, 27.
- 94 S. W. Poulton and D. E. Canfield, *Chem. Geol.*, 2005, **214**, 209.
- 95 A. Neaman, F. Moue, F. Trolard and G. Bourrie, *Appl. Geochem.*, 2004, **19**, 973.
- 96 C. Parat, J. Leveque, S. Dousset, R. Chaussod and F. Andreux, *Anal. Bioanal. Chem.*, 2003, **376**, 243.
- 97 S. Tokalioglu, S. Kartal and G. Birol, *J. Environ. Monit.*, 2003, **5**, 468.
- 98 P. Tlustos, J. Szakova, A. Starkova and D. Pavlikova, *Cent. Eur. J. Chem.*, 2005, **3**, 830.
- 99 C. Hanahan, *Environ. Geol.*, 2004, **45**, 864.
- 100 J. L. Laca, M. P. da Silva, R. Garcia, M. T. Sevilla, J. R. Procopio and L. Hernandez, *Environ. Pollut.*, 2003, **124**, 291.
- 101 E. Peltier, A. L. Dahl and J. F. Gaillard, *Environ. Sci. Technol.*, 2005, **39**, 311.
- 102 E. D. Burton, I. R. Phillips and D. W. Hawker, *Soil. Sediment Contam.*, 2006, **15**, 253.
- 103 D. Dermatas, G. Shen, M. Chrysochoou, D. G. Grubb, N. Menounou and P. Dutko, *J. Hazard. Mater.*, 2006, **136**, 34.
- 104 E. Doelsch, B. Deroche and V. Van De Kerchove, *Chemosphere*, 2006, **65**, 286.
- 105 J. Kalembkiewicz and E. Soco, *Pol. J. Environ. Stud.*, 2005, **14**, 593.
- 106 E. Fernandez, R. Jimenez, A. M. Lallena and J. Aguilar, *Environ. Pollut.*, 2004, **131**, 355.
- 107 K. A. Kryc, R. W. Murray and D. W. Murray, *Anal. Chim. Acta*, 2003, **487**, 117.
- 108 S. R. G. Barreto, J. Nozaki, E. De Oliveira, V. F. Do Nascimento, P. Henrique, A. Aragao, I. S. Scarminio and W. J. Barreto, *Talanta*, 2004, **64**, 345.
- 109 L. Leleyter and F. Baraud, *C. R. Geosci.*, 2005, **337**, 571.
- 110 G. E. M. Hall, J. E. Vaive, P. Pelchat, G. F. Bonham-Carter, D. A. Klizapetelle and K. Telmer, *Geochem.: Explor., Environ., Anal.*, 2006, **6**, 163.
- 111 Y. Z. Lu, D. M. Dong, Y. Fu, X. E. Shen, M. Yuan and W. T. Sun, *Chem. J. Chin. Univ.*, 2006, **27**, 449.
- 112 W. Baeyens, F. Monteny, M. Leermakers and S. Bouillon, *Anal. Bioanal. Chem.*, 2003, **376**, 890.
- 113 T. Hjorth, *Anal. Chim. Acta*, 2004, **526**, 95.
- 114 K. Zehl and J. W. Einax, *J. Soils Sediments*, 2005, **5**, 164.
- 115 R. D. Guy, C. L. Chakrabarti and D. C. McBain, *Water Res.*, 1978, **12**, 21.
- 116 C. Kheboian and C. F. Bauer, *Anal. Chem.*, 1987, **59**, 1417.
- 117 P. P. Coetzee, K. Gouws, S. Pluddemann, M. Yacoby, S. Howell and L. Dendrijver, *Water SA*, 1995, **21**, 51.
- 118 M. Raksataya, A. G. Langdon and N. D. Kim, *Anal. Chim. Acta*, 1996, **332**, 1.
- 119 X. Q. Shan and C. Bin, *Anal. Chem.*, 1993, **65**, 802.
- 120 I. M. C. Lo and X. Y. Yang, *Waste Manage. (Amsterdam, Neth.)*, 1998, **18**, 1.
- 121 C. Whalley and A. Grant, *Anal. Chim. Acta*, 1994, **291**, 287.
- 122 J. L. G. Ariza, I. Giraldez, D. Sanchez-Rodas and E. Morales, *Talanta*, 2000, **52**, 545.
- 123 N. Belzile, P. Lecomte and A. Tessier, *Environ. Sci. Technol.*, 1989, **23**, 1015.
- 124 J. L. Gomez-Ariza, I. Giraldez, D. Sanchez-Rodas and E. Morales, *Anal. Chim. Acta*, 1999, **399**, 295.
- 125 M. D. Ho and G. J. Evans, *Environ. Sci. Technol.*, 2000, **34**, 1030.
- 126 E. A. Gilmore, G. J. Evans and M. D. Ho, *Anal. Chim. Acta*, 2001, **439**, 139.
- 127 A. Bermond, *Anal. Chim. Acta*, 2001, **445**, 79.
- 128 Z. S. Ahnstrom and D. R. Parker, *Soil Sci. Soc. Am. J.*, 1999, **63**, 1650.
- 129 G. Rauret, R. Rubio, J. F. López-Sánchez and E. Casassas, *Int. J. Environ. Anal. Chem.*, 1989, **35**, 89.
- 130 J. T. van Elteren and B. Budic, *Anal. Chim. Acta*, 2004, **514**, 137.
- 131 O. R. La, C. M. Barra, N. Sobrinho, N. Mazur and A. C. X. Velloso, *Quim. Nova*, 2003, **26**, 323.
- 132 Y. G. Zhu, S. B. Chen and J. C. Yang, *Environ. Int.*, 2004, **30**, 351.
- 133 K. G. Scheckel, J. A. Ryan, D. Allen and N. V. Lescano, *Sci. Total Environ.*, 2005, **350**, 261.
- 134 J. M. Kaste, A. J. Friedland and E. K. Miller, *Water, Air, Soil Pollut.*, 2005, **167**, 139.
- 135 C. M. Davidson, A. S. Hursthouse, D. M. Tognarelli, A. M. Ure and G. J. Urquhart, *Anal. Chim. Acta*, 2004, **508**, 193.
- 136 Q. Tu, X. Q. Shan and Z. M. Ni, *Sci. Total Environ.*, 1994, **151**, 159.
- 137 R. A. Sutherland and F. M. G. Tack, *Adv. Environ. Res.*, 2003, **8**, 37.
- 138 J. R. Bacon, P. Cooper and I. J. Hewitt, *Chin. J. Geochem.*, 2006, **25**, 202.
- 139 P. E. Jensen, L. M. Ottosen and A. J. Pedersen, *Water, Air, Soil Pollut.*, 2006, **170**, 359.
- 140 M. Kersten, C. D. Garbe-Schönberg, S. Thomsen, C. Anagnostou and A. Sioulas, *Environ. Sci. Technol.*, 1997, **31**, 1295.
- 141 C. Gobeil, W. K. Johnson, R. W. Macdonald and C. S. Wong, *Environ. Sci. Technol.*, 1995, **29**, 193.
- 142 V. Ettler, M. Mihaljevic, O. Sebek, M. Molek, T. Grygar and J. Zeman, *Environ. Pollut.*, 2006, **142**, 409.
- 143 M. E. Gonnee and A. Paytan, *Mar. Chem.*, 2006, **100**, 124.

- 144 K. J. Reimer, C. A. Ollson and I. Koch, *Biogeochem. Environ. Important Trace Elem.*, 2003, **835**, 166.
- 145 O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, M. Aceto and R. Barberis, *Water, Air, Soil Pollut.*, 2006, **173**, 315.
- 146 C. K. Jain, *Water Res.*, 2004, **38**, 569.
- 147 E. Martley, B. Gulson, H. Louie, M. Wu and P. Di, *Geochem.: Explor., Environ., Anal.*, 2004, **4**, 171.
- 148 H. Ghrefat and N. Yusuf, *Chemosphere*, 2006, **65**, 2114.
- 149 N. Calace, B. M. Petronio and M. Pietroletti, *Ann. Chim. (Rome, Italy)*, 2006, **96**, 131.
- 150 Report ISO 11074:2005, *Soil quality – vocabulary*, International Standards Organization, Geneva, Switzerland, 2005.
- 151 A. D. K. Banerjee, *Environ. Pollut.*, 2003, **123**, 95.
- 152 C. Aydinalp and S. Marinova, *Pol. J. Environ. Stud.*, 2003, **12**, 629.
- 153 G. Bird, P. A. Brewer, M. G. Macklin, D. Balteanu, B. Driga, M. Serban and S. Zaharia, *Appl. Geochem.*, 2003, **18**, 1583.
- 154 M. Imperato, P. Adamo, D. Naimo, M. Arienzo, D. Stanzione and P. Violante, *Environ. Pollut.*, 2003, **124**, 247.
- 155 X. D. Cao, L. Q. Ma, M. Chen, D. W. Hardison and W. G. Harris, *Sci. Total Environ.*, 2003, **307**, 179.
- 156 A. Navas and H. Lindhorfer, *Environ. Int.*, 2003, **29**, 61.
- 157 P. Kotoky, B. J. Bora, N. K. Baruah, J. Baruah and G. C. Borah, *Chem. Speciation Bioavailability*, 2003, **15**, 115.
- 158 P. Janos, L. Herzogova, J. Rejnek and J. Hodslavska, *Talanta*, 2004, **62**, 497.
- 159 G. Renella, P. Adamo, M. R. Bianco, L. Landi, P. Violante and P. Nannipieri, *Eur. J. Soil Sci.*, 2004, **55**, 123.
- 160 I. Ahumada, P. Escudero, M. A. Carrasco, G. Castillo, L. Ascar and E. Fuentes, *J. Environ. Monit.*, 2004, **6**, 327.
- 161 A. Guevara-Riba, A. Sahuquillo, R. Rubio and G. Rauret, *Sci. Total Environ.*, 2004, **321**, 241.
- 162 K. Ellass, A. Laachach and M. Azzi, *Ann. Chim. (Rome, Italy)*, 2004, **94**, 325.
- 163 F. Liu, H. G. Liu, Q. F. Yu and Y. F. Nie, *J. Environ. Sci. (China)*, 2004, **16**, 885.
- 164 E. Margui, V. Salvado, I. Queralt and M. Hidalgo, *Anal. Chim. Acta*, 2004, **524**, 151.
- 165 S. Yu, Z. L. He, C. Y. Huang, G. C. Chen and D. V. Calvert, *Geoderma*, 2004, **123**, 163.
- 166 Q. J. Song and G. M. Greenway, *J. Environ. Monit.*, 2004, **6**, 31.
- 167 A. Giacalone, A. Gianguzza, S. Orecchio, D. Piazzese, G. Dongarra, S. Sciarrino and D. Varrica, *Chem. Speciation Bioavailability*, 2005, **17**, 83.
- 168 S. Esakku, A. Selvam, K. Joseph and K. Palanivelu, *Chem. Speciation Bioavailability*, 2005, **17**, 95.
- 169 F. Liu, J. G. Liu, Q. F. Yu, Y. Y. Jin and Y. F. Nie, *J. Environ. Sci. Health, Part A*, 2005, **40**, 1975.
- 170 J. Virkutyte, E. van Hullebusch, M. Sillanpaa and P. Lens, *Environ. Pollut.*, 2005, **138**, 517.
- 171 D. Wiechula, K. Loska and I. Korus, *Water, Air, Soil Pollut.*, 2005, **164**, 315.
- 172 P. K. Lee, Y. H. Yu, S. T. Yun and B. Mayer, *Chemosphere*, 2005, **60**, 672.
- 173 E. Remon, J. L. Bouchardon, B. Cornier, B. Guy, J. C. Leclerc and O. Faure, *Environ. Pollut.*, 2005, **137**, 316.
- 174 T. Becquer, J. Dai, U. Quantin and P. Lavelle, *Soil Biol. Biochem.*, 2005, **37**, 1564.
- 175 A. S. Joksic, S. A. Katz, M. Horvat and R. Milacic, *Water, Air, Soil Pollut.*, 2005, **162**, 265.
- 176 S. Amir, M. Hafidi, G. Merlina and J. C. Revel, *Chemosphere*, 2005, **59**, 801.
- 177 A. Navas and H. Lindhorfer, *Soil. Sediment Contam.*, 2005, **14**, 249.
- 178 G. Glosinska, T. Sobczynski, L. Boszke, K. Bierla and J. Siepak, *Pol. J. Environ. Stud.*, 2005, **14**, 305.
- 179 C. Wang, X. Hu, M. L. Chen and Y. H. Wu, *J. Hazard. Mater.*, 2005, **119**, 245.
- 180 K. M. Banat, F. M. Howari and A. A. Al-Hamad, *Environ. Res.*, 2005, **97**, 258.
- 181 G. Bird, P. A. Brewer, M. G. Macklin, M. Serban, D. Balteanu and B. Driga, *J. Geochem. Explor.*, 2005, **86**, 26.
- 182 Z. Y. Hseu, *Chemosphere*, 2006, **63**, 762.
- 183 S. Audry, G. Blanc, J. Schafer, G. Chaillou and S. Robert, *Geochim. Cosmochim. Acta*, 2006, **70**, 2264.
- 184 Q. J. Song and G. M. Greenway, *Int. J. Environ. Anal. Chem.*, 2006, **86**, 359.
- 185 I. Walter, F. Martinez and V. Cala, *Environ. Pollut.*, 2006, **139**, 507.
- 186 V. Saenz, J. Blasco and A. Gomez-Parra, *Environ. Toxicol. Chem.*, 2003, **22**, 2833.
- 187 J. Ciba, M. Zolotajkin, J. Kluczka, K. Loska and J. Cebula, *Waste Manage. (Amsterdam, Neth.)*, 2003, **23**, 897.
- 188 S. Lee, J. W. Moon and H. S. Moon, *Environ. Geochem. Health*, 2003, **25**, 433.
- 189 M. Yaman and S. Bakirdere, *Microchim. Acta*, 2003, **141**, 47.
- 190 C. G. Yuan, J. B. Shi, B. He, J. F. Liu, L. N. Liang and G. B. Jiang, *Environ. Int.*, 2004, **30**, 769.
- 191 M. C. Z. Moturi, M. Rawat and V. Subramanian, *Environ. Monit. Assess.*, 2004, **95**, 183.
- 192 A. V. Filgueiras, I. Lavilla and C. Bendicho, *Sci. Total Environ.*, 2004, **330**, 115.
- 193 P. Adamo, M. Arienzo, M. Imperato, D. Naimo, G. Nardi and D. Stanzione, *Chemosphere*, 2005, **61**, 800.
- 194 D. Relic, D. Dordevic, A. Popovic and T. Blagojevic, *Environ. Int.*, 2005, **31**, 661.
- 195 M. A. Okbah, M. A. Shata and M. A. Shridah, *Chem. Ecol.*, 2005, **21**, 23.
- 196 A. Bielicka, I. Bojanowska and A. Wisniewski, *Pol. J. Environ. Stud.*, 2005, **14**, 145.
- 197 B. Walna, J. Siepak, S. Drzymala and T. Sobczynski, *Pol. J. Environ. Stud.*, 2005, **14**, 243.
- 198 S. E. Lee, J. S. Lee and H. T. Chon, in *On the Convergence of Bio-, Information-, Environmental-, Energy-, Space- and Nano-Technologies, Pts 1 and 2*, Trans Tech Publications Inc., Zurich, Switzerland, 2005, vol. 277–279, p. 438.
- 199 G. Garcia, A. L. Zanuzzi and A. Faz, *Biodegradation*, 2005, **16**, 187.
- 200 J. Sysalova and J. Szakova, *Environ. Res.*, 2006, **101**, 287.
- 201 R. Fernandez-Martinez, J. Loreda, A. Ordonez and M. I. Rucandio, *Environ. Pollut.*, 2006, **142**, 217.
- 202 E. Tokalioglu and S. Kartal, *Atmos. Environ.*, 2006, **40**, 2797.
- 203 M. Kaasalainen and M. Yli-Halla, *Environ. Pollut.*, 2003, **126**, 225.
- 204 M. Ranville, D. Rough and A. R. Flegal, *Appl. Geochem.*, 2004, **19**, 803.
- 205 C. X. Yang, Y. H. Chen, P. Peng, C. Li, X. Y. Chang and C. S. Xie, *Sci. Total Environ.*, 2005, **341**, 159.
- 206 J. S. Dube and R. Galvez-Cloutier, *J. Environ. Eng. Sci.*, 2005, **4**, 399.
- 207 F. Reith, D. C. McPhail and A. G. Christy, *J. Geochem. Explor.*, 2005, **85**, 81.
- 208 A. S. Knox, D. L. Dunn, M. H. Paller, E. A. Nelson, W. L. Specht and J. C. Seaman, *Eng. Life Sci.*, 2006, **6**, 31.
- 209 M. L. K. Rodrigues and M. L. L. Formoso, *Water, Air, Soil Pollut.*, 2006, **169**, 167.
- 210 E. Alonso, P. Villar, A. Santos and I. Aparicio, *Waste Manage. (Amsterdam, Neth.)*, 2006, **26**, 1270.
- 211 J. Morillo, J. Usero and I. Gracia, *Chemosphere*, 2004, **55**, 431.
- 212 C. Durand, V. Ruban and A. Ambles, *Environ. Technol.*, 2004, **25**, 881.
- 213 E. V. Hullebusch, F. Auvray, F. Bordas, V. Deluchat, P. M. Chazal and M. Baudu, *Environ. Technol.*, 2003, **24**, 787.
- 214 A. G. Sowder, P. M. Bertsch and P. J. Morris, *J. Environ. Qual.*, 2003, **32**, 885.
- 215 S. Olivares-Rieumont, D. de la Rosa, L. Lima, D. W. Graham, K. D'Alessandro, J. Borroto, F. Martinez and J. Sanchez, *Water Res.*, 2005, **39**, 3945.
- 216 S. X. Wang, S. Z. Zhang, X. Q. Shan and H. Z. Mu, *Sci. China, Ser. C*, 2005, **48**, 142.
- 217 C. Caplat, H. Texier, D. Barillier and C. Lelievre, *Mar. Pollut. Bull.*, 2005, **50**, 504.
- 218 G. P. Wang, J. S. Liu and J. Tang, *Wetlands*, 2004, **24**, 608.
- 219 A. van der Veen, C. Ahlers, D. W. Zachmann and K. Friese, *Acta Hydrochim. Hydrobiol.*, 2006, **34**, 214.
- 220 Y. Li, J. J. Chen, X. L. Wang, D. M. Dong and S. H. Guo, *Chem. J. Chin. Univ.*, 2006, **27**, 627.
- 221 N. K. Erzen and J. Stupar, *Acta Chim. Slov.*, 2003, **50**, 67.
- 222 J. W. Tang, G. R. Whittecar, K. H. Johansson and W. L. Daniels, *Geochem. Trans.*, 2004, **5**, 49.
- 223 W. X. Liu, X. D. Li, Z. G. Shen, D. C. Wang, O. W. H. Wai and Y. S. Li, *Environ. Pollut.*, 2003, **121**, 377.
- 224 W. De Vries, J. Curlik, A. Muranyi, B. Alloway and B. J. Groenenberg, *Ekologia (Bratislava, Slovakia)*, 2005, **24**, 152.
- 225 J. V. Garcia-Meza, A. Carrillo-Chavez and O. Morton-Bermea, *Environ. Geol.*, 2006, **49**, 437.
- 226 G. Siebielec, T. Stuczynski and R. Korzeniowska-Puculek, *Pol. J. Environ. Stud.*, 2006, **15**, 121.
- 227 N. Basta and R. Gradwohl, *J. Soil Contam.*, 2000, **9**, 149.

- 228 N. T. Basta, R. Gradwohl, K. L. Snethen and J. L. Schroder, *J. Environ. Qual.*, 2001, **30**, 1222.
- 229 P. Castaldi, G. Garau and P. Melis, *Fresenius Environ. Bull.*, 2004, **13**, 1322.
- 230 S. Tokalioglu, S. Kartal and A. Gultekin, *Int. J. Environ. Anal. Chem.*, 2006, **86**, 417.
- 231 X. D. Cao, X. R. Wang and G. W. Zhao, *Chemosphere*, 2000, **40**, 23.
- 232 G. S. R. Krishnamurti and R. Naidu, *Aust. J. Soil Res.*, 2000, **38**, 991.
- 233 Z. W. Wang, X. Q. Shan and S. Z. Zhang, *Chemosphere*, 2002, **46**, 1163.
- 234 Z. W. Wang, X. Q. Shan and S. Z. Zhang, *Commun. Soil Sci. Plant Anal.*, 2003, **34**, 1573.
- 235 H. R. Ma, X. R. Wang and C. B. Zhang, *Chem. Speciation Bioavailability*, 2003, **15**, 15.
- 236 W. S. Wang, X. Q. Shan, B. Wen and S. Z. Zhang, *Chemosphere*, 2003, **53**, 523.
- 237 P. Parkpian, S. T. Leong, P. Laortanakul and N. T. K. Phuong, *J. Environ. Sci. Health, Part A*, 2002, **37**, 1099.
- 238 T. Punshon, K. F. Gaines, P. M. Bertsch and J. Burger, *Environ. Toxicol. Chem.*, 2003, **22**, 1146.
- 239 Y. M. Luo, X. J. Jiang, L. H. Wu, J. Song, S. C. Wu, R. H. Lu and P. Christie, *Geoderma*, 2003, **115**, 113.
- 240 D. Chaudhuri, S. Tripathy, H. Veeresh, M. A. Powell and B. R. Hart, *Environ. Geol.*, 2003, **44**, 419.
- 241 V. D. Zheljazkov and P. R. Warman, *J. Environ. Qual.*, 2004, **33**, 542.
- 242 C. M. R. Almeida, A. P. Mucha and M. Vasconcelos, *Environ. Sci. Technol.*, 2004, **38**, 3112.
- 243 Y. X. Chen, J. Y. Shi, W. D. Zhang, Q. Lin and G. M. Tian, *Plant Soil*, 2004, **261**, 117.
- 244 S. Tokalioglu and S. Kartal, *Instrum. Sci. Technol.*, 2004, **32**, 387.
- 245 H. F. Li, Q. R. Wang, Y. S. Cui, Y. T. Dong and P. Christie, *Sci. Total Environ.*, 2005, **339**, 179.
- 246 A. Jamil, K. Lajtha, S. Radan, G. Ruzsa, S. Cristofor and C. Postolache, *Hydrobiology*, 1999, **392**, 143.
- 247 J. Pempkowiak, A. Sikora and E. Biernacka, *Chemosphere*, 1999, **39**, 313.
- 248 C. K. Yap, A. Ismail, S. G. Tan and H. Omar, *Environ. Int.*, 2002, **28**, 117.
- 249 A. S. Hursthouse, J. M. Matthews, J. E. Figures, P. Iqbal-Zahid, I. M. Davies and D. H. Vaughan, *Environ. Geochem. Health*, 2003, **25**, 171.
- 250 K. C. Sekhar, N. S. Chary, C. T. Kamala, D. S. S. Raj and A. S. Rao, *Environ. Int.*, 2004, **29**, 1001.
- 251 G. Du Laing, N. Bogaert, F. M. G. Tack, M. G. Verloo and F. Hendrickx, *Sci. Total Environ.*, 2002, **289**, 71.
- 252 C. J. Langdon, T. G. Pearce, A. A. Meharg and K. T. Semple, *Environ. Toxicol. Chem.*, 2001, **20**, 2336.
- 253 G. Maddocks, A. Reichelt-Brushett, D. McConchie and J. Vangronsveld, *Environ. Toxicol. Chem.*, 2005, **24**, 554.
- 254 S. Brown, R. L. Chaney, J. G. Hallfrisch and Q. Xue, *J. Environ. Qual.*, 2003, **32**, 100.
- 255 D. R. Leece, G. K. C. Low, M. S. Warne, T. M. Manning, J. C. Chapman and K. Koop, *Commun. Soil Sci. Plant Anal.*, 2000, **31**, 2185.
- 256 G. S. R. Krishnamurti and R. Naidu, *Environ. Sci. Technol.*, 2002, **36**, 2645.
- 257 J. Mendoza, T. Garrido, G. Castillo and N. San Martin, *Chemosphere*, 2006, **65**, 2304.
- 258 D. Lestan, H. Grcman, M. Zupan and N. Bacac, *Soil. Sediment Contam.*, 2003, **12**, 507.
- 259 M. Pueyo, J. Sastre, E. Hernandez, M. Vidal, J. F. López-Sánchez and G. Rauret, *J. Environ. Qual.*, 2003, **32**, 2054.
- 260 J. M. Alvarez and M. I. Rico, *J. Agric. Food Chem.*, 2003, **51**, 5760.
- 261 Q. W. Yang, W. S. Shu, J. W. Qiu, H. B. Wang and C. Y. Lan, *Environ. Int.*, 2004, **30**, 883.
- 262 A. Obrador, J. Novillo and J. M. Alvarez, *Soil Sci. Soc. Am. J.*, 2003, **67**, 564.
- 263 Y. H. Xu and D. Y. Zhao, *Environ. Sci. Technol.*, 2005, **39**, 2369.
- 264 M. R. Borges and E. L. M. Coutinho, *Rev. Bras. Cienc. Solo*, 2004, **28**, 543.
- 265 E. I. Bertoincini, M. E. Mattiazzo and R. Rossetto, *J. Plant Nutr.*, 2004, **27**, 1243.
- 266 P. Bhattacharyya, A. Chakraborty, K. Chakrabarti, S. Tripathy and M. A. Powell, *Environ. Geol.*, 2006, **49**, 1064.
- 267 E. M. Andre, M. C. P. Cruz, M. E. Ferreira and L. A. S. Palma, *Rev. Bras. Cienc. Solo*, 2003, **27**, 451.
- 268 F. Pedra, H. Domingues, A. B. Ribeiro, A. Polo and O. Monteiro, *Environ. Technol.*, 2006, **27**, 1357.
- 269 W. Geebelen, D. C. Adriano, D. van der Lelie, M. Mench, R. Carleer, H. Clijsters and J. Vangronsveld, *Plant Soil*, 2003, **249**, 217.
- 270 P. Peltola, A. Ivask, M. Astrom and M. Virta, *Sci. Total Environ.*, 2005, **350**, 194.
- 271 Z. A. S. Ahnstrom and D. R. Parker, *Environ. Sci. Technol.*, 2001, **35**, 121.
- 272 X. Y. Tang, Y. G. Zhu, Y. S. Cui, J. Duan and L. Tang, *Environ. Int.*, 2006, **32**, 682.
- 273 S. J. Sun, J. Xu, S. G. Dai and X. Han, *Biomed. Environ. Sci.*, 2006, **19**, 409.
- 274 H. Zhong and W. X. Wang, *Environ. Sci. Technol.*, 2006, **40**, 3794.
- 275 M. O. Mbila, M. L. Thompson, J. S. C. Mbagwu and D. A. Laird, *J. Environ. Qual.*, 2001, **30**, 1667.
- 276 I. Ahumada, P. Escudero, L. Ascar, J. Mendoza and P. Richter, *Commun. Soil Sci. Plant Anal.*, 2004, **35**, 1615.
- 277 Z. Y. Hseu, *Soil Sci.*, 2006, **171**, 341.
- 278 C. Brunori, C. Cremisini, L. D'Annibale, P. Massanisso and V. Pinto, *Anal. Bioanal. Chem.*, 2005, **381**, 1347.
- 279 A. M. Moreno, L. Perez and J. G. Parra, *Chem. Speciation Bioavailability*, 2005, **17**, 11.
- 280 B. P. Cid, M. D. Gonzalez and E. F. Gomez, *Analyst*, 2002, **127**, 681.
- 281 O. Abollino, M. Aceto, M. Malandrino, E. Mentasti, C. Sarzanini and F. Petrella, *Chemosphere*, 2002, **49**, 545.
- 282 M. Ramirez, S. Massolo, R. Frache and J. A. Correa, *Mar. Pollut. Bull.*, 2005, **50**, 62.
- 283 S. R. Cook and A. Parker, *Water, Air, Soil Pollut.*, 2006, **170**, 95.
- 284 S. Audry, G. Blanc and J. Schafer, *Sci. Total Environ.*, 2006, **363**, 216.
- 285 H. B. Jung, S. T. Yun, B. Mayer, S. O. Kim, S. S. Park and P. K. Lee, *Environ. Geol.*, 2005, **48**, 437.
- 286 S. O. Ndzangou, M. Richer-LaFleche and D. Houle, *Appl. Geochem.*, 2006, **21**, 2135.
- 287 S. I. Korfali and B. E. Davies, *Adv. Environ. Res.*, 2004, **8**, 599.
- 288 S. I. Korfali and B. E. Davies, *Environ. Geochem. Health*, 2005, **27**, 385.
- 289 E. Galan, J. L. Gomez-Ariza, I. Gonzalez, J. C. Fernandez-Caliani, E. Morales and I. Giraldez, *Appl. Geochem.*, 2003, **18**, 409.
- 290 C. Kraft, W. von Tumpling and D. W. Zachmann, *Acta Hydrochim. Hydrobiol.*, 2006, **34**, 257.
- 291 J. R. Brydie and D. A. Polya, *Mineral. Mag.*, 2003, **67**, 289.
- 292 M. H. D. Pestana and M. L. L. Formoso, *J. Phys. IV*, 2003, **107**, 1049.
- 293 L. J. Tsai, K. C. Yu, S. F. Chen, P. Y. Kung, C. Y. Chang and C. H. Lin, *Water Res.*, 2003, **37**, 4623.
- 294 E. Van Hullebusch, P. Chatenet, V. Deluchat, P. M. Chazal, D. Froissard, P. N. L. Lens and M. Baudu, *J. Phys. IV*, 2003, **107**, 1333.
- 295 I. Ko, Y. Y. Chang, C. H. Lee and K. W. Kim, *J. Hazard. Mater.*, 2005, **127**, 1.
- 296 S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin and B. Nowack, *Environ. Sci. Technol.*, 2004, **38**, 937.
- 297 C. Chaiyaraksa and N. Sriwiriyanuphap, *Chemosphere*, 2004, **56**, 1129.
- 298 E. E. C. de Melo, C. W. A. do Nascimento and A. C. Q. Santos, *Rev. Bras. Cienc. Solo*, 2006, **30**, 1051.
- 299 Y. G. Liu, X. H. Wang, G. M. Zeng, X. Li, C. H. Zhou, T. Fan, Y. L. Li and X. Z. Yuan, *Pedosphere*, 2006, **16**, 312.
- 300 J. G. Shi, Z. X. Yuan, S. F. Zhang, G. H. Huang, F. Dai, J. B. Li, A. Chakma, X. S. Qin and H. L. Liu, *Trans. Nonferrous Met. Soc. China*, 2004, **14**, 66.
- 301 H. Massara, C. N. Mulligan and J. Hadjinicolaou, *Soil. Sediment Contam.*, 2007, **16**, 1.
- 302 M. Vanthuyne, A. Maes and P. Cauwenberg, *Miner. Eng.*, 2003, **16**, 1131.
- 303 G. M. Nystrom, L. M. Ottosen and A. Villumsen, *J. Phys. IV*, 2003, **107**, 975.
- 304 L. M. Ottosen, K. Lepkova and M. Kubal, *J. Hazard. Mater.*, 2006, **137**, 113.
- 305 X. J. Chen, Z. M. Shen, Y. M. Lei, B. X. Ju and W. H. Wang, *Aust. J. Soil Res.*, 2006, **44**, 523.
- 306 W. Friesl, E. Lombi, O. Horak and W. W. Wenzel, *J. Plant Nutr. Soil Sci.*, 2003, **166**, 191.
- 307 S. Penilla, F. Bordas and J. C. Bollinger, *J. Colloid Interface Sci.*, 2005, **292**, 20.
- 308 F. Garrido, V. Illera and M. T. Garcia-Gonzalez, *Appl. Geochem.*, 2005, **20**, 397.
- 309 J. L. Daniels and G. P. Das, *Environ. Eng. Sci.*, 2006, **23**, 42.
- 310 J. Kumpiene, S. Ore, G. Renella, M. Mench, A. Lagerkvist and

- C. Maurice, *Environ. Pollut.*, 2006, **144**, 62.
- 311 J. Kumpiene, A. Lagerkvist and C. Maurice, *Environ. Pollut.*, 2007, **145**, 365.
- 312 J. C. Zwonitzer, G. M. Pierzynski and G. M. Hettiarachchi, *Water, Air, Soil Pollut.*, 2003, **143**, 193.
- 313 R. X. Cao, L. Q. Ma, M. Chen, S. P. Singh and W. G. Harris, *Environ. Pollut.*, 2003, **122**, 19.
- 314 M. Chen, L. Q. Ma, S. P. Singh, R. X. Cao and R. Melamed, *Adv. Environ. Res.*, 2003, **8**, 93.
- 315 S. B. Chen, Y. G. Zhu and Y. B. Ma, *J. Hazard. Mater.*, 2006, **134**, 74.
- 316 S. B. Chen, Y. G. Zhu, Y. B. Ma and G. McKay, *Environ. Pollut.*, 2006, **139**, 433.
- 317 L. J. Cajuste, L. Cajuste, C. Garcia-Osorio and J. Cruz-Diaz, *Commun. Soil Sci. Plant Anal.*, 2006, **37**, 2541.
- 318 L. S. Forsberg and S. Ledin, *Sci. Total Environ.*, 2006, **358**, 21.
- 319 R. Clemente and M. P. Bernal, *Chemosphere*, 2006, **64**, 1264.
- 320 B. P. Spalding, *Environ. Sci. Technol.*, 2001, **35**, 4327.
- 321 A. Fuentes, M. Llorens, J. Saez, M. I. Aguilar, J. F. Ortuno and V. F. Meseguer, *J. Hazard. Mater.*, 2004, **108**, 161.
- 322 B. Kim and M. B. McBride, *Environ. Pollut.*, 2006, **144**, 475.
- 323 A. R. A. Usman and A. Ghallab, *Chem. Ecol.*, 2006, **22**, 267.
- 324 R. Clemente, A. Escolar and M. P. Bernal, *Bioresour. Technol.*, 2006, **97**, 1894.
- 325 D. C. Su and J. W. C. Wong, *Environ. Int.*, 2004, **29**, 895.
- 326 C. Oliveira, N. Sobrinho and N. Mazur, *Rev. Bras. Cienc. Solo*, 2003, **27**, 171.
- 327 S. Li, R. L. Liu, M. Wang, X. B. Wang, H. Shan and H. T. Wang, *Geoderma*, 2006, **136**, 260.
- 328 M. Rajaie, N. Karimian, M. Maftoun, J. Yasrebi and M. T. Assad, *Geoderma*, 2006, **136**, 533.
- 329 M. Jalali and Z. V. Khanlari, *Soil. Sediment Contam.*, 2006, **15**, 603.
- 330 M. Antilen, N. Araya, M. Briceno and M. Escudey, *Aust. J. Soil Res.*, 2006, **44**, 619.
- 331 P. Castaldi, L. Santona and P. Melis, *Fresenius Environ. Bull.*, 2006, **15**, 1133.
- 332 M. Turek, T. Korolewicz and J. Ciba, *Soil. Sediment Contam.*, 2005, **14**, 143.
- 333 A. T. Lombardi, O. J. Garcia and W. A. N. Menezes, *World J. Microbiol. Biotechnol.*, 2006, **22**, 1013.
- 334 C. Yuan and C. H. Weng, *Chemosphere*, 2006, **65**, 88.
- 335 V. K. Tyagi, *Geosynth. Int.*, 2006, **13**, 47.
- 336 J. Y. Wang, D. S. Zhang, O. Stabnikova and J. H. Tay, *J. Hazard. Mater.*, 2005, **124**, 139.
- 337 T. Aarab, M. Smeyers, M. Remy, B. Godden and J. P. Delhay, *Waste Manage. (Amsterdam, Neth.)*, 2006, **26**, 1024.
- 338 T. T. Lim, J. H. Tay, L. C. Tan, V. Choa and C. I. Teh, *Environ. Geol.*, 2004, **47**, 1.
- 339 T. T. Lim, J. Chu and M. H. Goi, *Waste Manage. (Amsterdam, Neth.)*, 2006, **26**, 1294.
- 340 Q. Y. Huang, W. L. Chen and X. J. Guo, *Commun. Soil Sci. Plant Anal.*, 2004, **35**, 947.
- 341 S. Eich-Greatorex and L. T. Strand, *Soil Sci. Soc. Am. J.*, 2006, **70**, 778.
- 342 M. Arienzo, P. Adamo and V. Cozzolino, *Sci. Total Environ.*, 2004, **319**, 13.
- 343 S. Ishikawa, N. Ae, M. Murakami and T. Wagatsuma, *Soil Sci. Plant Nutr.*, 2006, **52**, 32.
- 344 V. U. Ultra, A. Yano, K. Iwasaki, S. Tanaka, Y. M. Kang and K. Sakurai, *Soil Sci. Plant Nutr.*, 2005, **51**, 193.
- 345 R. Santamaria-Fernandez, M. R. Cave and S. J. Hill, *J. Environ. Monit.*, 2003, **5**, 929.
- 346 Y. B. Ma and N. C. Uren, *Nutr. Cycling Agroecosyst.*, 2006, **76**, 11.
- 347 R. B. Herbert, *J. Geochem. Explor.*, 2006, **90**, 197.
- 348 B. Clozel, V. Ruban, C. Durand and P. Conil, *Appl. Geochem.*, 2006, **21**, 1781.
- 349 K. Rasa, T. Peltovuori and H. Hartikainen, *Sci. Total Environ.*, 2006, **366**, 819.
- 350 M. E. Soltan, *Chem. Ecol.*, 2006, **22**, 359.
- 351 C. S. C. Wong, S. C. Wu, N. S. Duzgoren-Aydin, A. Aydin and M. H. Wong, *Environ. Pollut.*, 2007, **145**, 434.
- 352 J. L. Luque-Garcia and L. de Castro, *TrAC, Trends Anal. Chem.*, 2003, **22**, 41.
- 353 B. Perez-Cid, I. Lavilla and C. Bendicho, *Anal. Chim. Acta*, 1998, **360**, 35.
- 354 B. Perez-Cid, I. Lavilla and C. Bendicho, *Fresenius' J. Anal. Chem.*, 1999, **363**, 667.
- 355 B. Perez-Cid, I. Lavilla and C. Bendicho, *Int. J. Environ. Anal. Chem.*, 1999, **73**, 79.
- 356 F. S. Sun, Z. Y. Zhan, K. S. Zhang and Y. Wang, *J. Environ. Sci. (China)*, 2004, **16**, 957.
- 357 A. Vaisanen and A. Kiljunen, *Int. J. Environ. Anal. Chem.*, 2005, **85**, 1037.
- 358 C. M. Davidson and G. Delevoe, *J. Environ. Monit.*, 2001, **3**, 398.
- 359 A. Marin, A. Lopez-Gonzalez and C. Barbas, *Anal. Chim. Acta*, 2001, **442**, 305.
- 360 I. Ipolyi, C. Brunori, C. Creminini, P. Fodor, L. Macaluso and R. Morabito, *J. Environ. Monit.*, 2002, **4**, 541.
- 361 G. M. Greenway and Q. J. Song, *J. Environ. Monit.*, 2002, **4**, 950.
- 362 S. Canepari, E. Cardarelli, S. Ghighi and L. Scimonelli, *Talanta*, 2005, **66**, 1122.
- 363 B. Krasnodebska-Ostrega, M. Kaczorowska and J. Golimowski, *Microchim. Acta*, 2006, **154**, 39.
- 364 A. Vaisanen, R. Suontamo, J. Silvonen and J. Rintala, *Anal. Bioanal. Chem.*, 2002, **373**, 93.
- 365 M. Gulmini, G. Ostacoli, V. Zelano and A. Torazzo, *Analyst*, 1994, **119**, 2075.
- 366 B. Perez-Cid, I. Lavilla and C. Bendicho, *Anal. Chim. Acta*, 1999, **378**, 201.
- 367 B. Gumgum and G. Ozturk, *Chem. Speciation Bioavailability*, 2001, **13**, 25.
- 368 M. Dutta, K. Chandrasekhar, S. Dutta and A. K. Das, *At. Spectrosc.*, 2005, **26**, 137.
- 369 M. Dutta and A. K. Das, *J. Indian Chem. Soc.*, 2005, **82**, 433.
- 370 P. Pazos-Capeans, M. C. Barciela-Alonso, A. Bermejo-Barrera and P. Bermejo-Barrera, *Talanta*, 2005, **65**, 678.
- 371 M. Dutta, K. Chandrasekhar and A. K. Das, *At. Spectrosc.*, 2005, **26**, 14.
- 372 E. Campos, E. Barahona, M. Lachica and M. D. Mingorance, *Anal. Chim. Acta*, 1998, **369**, 235.
- 373 K. L. Laban and B. P. Atkin, *Int. J. Coal Geol.*, 1999, **41**, 351.
- 374 B. Perez Cid, A. Fernandez Albores, E. Fernandez Gomez and E. Falque Lopez, *Anal. Chim. Acta*, 2001, **431**, 209.
- 375 B. Perez Cid, A. Fernandez Albores, E. Fernandez Gomez and E. Falque Lopez, *Analyst*, 2001, **126**, 1304.
- 376 R. Santamaria-Fernandez, M. R. Cave and S. J. Hill, *Anal. Chim. Acta*, 2006, **557**, 344.
- 377 R. Santamaria-Fernandez, A. Moreda-Pineiro and S. J. Hill, *J. Environ. Monit.*, 2002, **4**, 330.
- 378 M. R. Cave, A. E. Milodowski and E. N. Friel, *Geochem.: Explor., Environ., Anal.*, 2004, **4**, 71.
- 379 D. Beauchemin, K. Kyser and D. Chipley, *Anal. Chem.*, 2002, **74**, 3924.
- 380 M. Jimoh, W. Frenzel and V. Muller, *Anal. Bioanal. Chem.*, 2005, **381**, 438.
- 381 R. Chomchoei, M. Miro, E. H. Hansen and J. Shiwatana, *Anal. Chem.*, 2005, **77**, 2720.
- 382 R. Chomchoei, M. Miro, E. H. Hansen and J. Shiwatana, *Anal. Chim. Acta*, 2005, **536**, 183.
- 383 P. S. Fedotov, E. Y. Savonina, R. Wennrich and B. Y. Spivakov, *Analyst*, 2006, **131**, 509.
- 384 P. S. Fedotov, R. Wennrich, H. J. Stark and B. Y. Spivakov, *J. Environ. Monit.*, 2005, **7**, 22.
- 385 P. S. Fedotov, A. G. Zavarzina, B. Y. Spivakov, R. Wennrich, J. Mattusch, K. D. C. Titze and V. V. Demin, *J. Environ. Monit.*, 2002, **4**, 318.
- 386 O. N. Katasonova, P. S. Fedotov, V. K. Karandashev and B. Y. Spivakov, *J. Anal. Chem.*, 2005, **60**, 684.
- 387 E. Y. Savonina, P. S. Fedotov and R. Wennrich, *J. Anal. Chem.*, 2006, **61**, 702.
- 388 J. Buanuam, K. Tiptanasup, J. Shiwatana, M. Miro and E. H. Hansen, *J. Environ. Monit.*, 2006, **8**, 1248.
- 389 T. Nakazato, M. Akasaka and H. Tao, *Anal. Bioanal. Chem.*, 2006, **386**, 1515.
- 390 R. Chomchoei, J. Shiwatana and P. Pongsakul, *Anal. Chim. Acta*, 2002, **472**, 147.
- 391 J. Buanuam, J. Shiwatana and P. Pongsakul, *J. Environ. Monit.*, 2005, **7**, 778.
- 392 N. Tongtavee, J. Shiwatana and R. G. McLaren, *Int. J. Environ. Anal. Chem.*, 2005, **85**, 567.
- 393 N. Tongtavee, J. Shiwatana, R. G. McLaren and J. Buanuam, *Commun. Soil Sci. Plant Anal.*, 2005, **36**, 2839.
- 394 M. Miro, E. H. Hansen, R. Chomchoei and W. Frenzel, *TrAC, Trends Anal. Chem.*, 2005, **24**, 759.
- 395 A. Barona and F. Romero, *Soil Technol.*, 1996, **8**, 303.
- 396 M. H. W. Lam, A. Y. W. Tjia, C. C. Chan, W. P. Chan and W. S. Lee, *Mar. Pollut. Bull.*, 1997, **34**, 949.
- 397 I. Stanimirova, K. Zehl, D. L. Massart, Y. V. Heyden and J. W. Einax, *Anal. Bioanal. Chem.*, 2006, **385**, 771.

- 398 C. Sarbu, K. Zehl and J. W. Einax, *Chemom. Intell. Lab. Syst.*, 2007, **86**, 121.
- 399 B. Daus and H. W. Zwanziger, *Fresenius' J. Anal. Chem.*, 1995, **352**, 444.
- 400 J. Virkanen, *Mar. Pollut. Bull.*, 1998, **36**, 729.
- 401 K. C. Yu, L. J. Tsai, S. H. Chen, D. J. Chang and S. T. Ho, *J. Environ. Sci. Health, Part A*, 2001, **36**, 1.
- 402 H. Sanei, F. Goodarzi and E. Van der Flier-Keller, *J. Environ. Monit.*, 2001, **3**, 27.
- 403 L. J. Tsai, K. C. Yu, J. S. Huang and S. T. Ho, *J. Environ. Sci. Health, Part A*, 2002, **37**, 1421.
- 404 S. Tokalioglu and S. Kartal, *Chem. Anal. (Warsaw)*, 2002, **47**, 627.
- 405 J. S. Chang, K. C. Yu, L. J. Tsai and S. T. Ho, *Water Sci. Technol.*, 1998, **38**, 159.
- 406 Z. Borovec, *Sci. Total Environ.*, 1996, **177**, 237.
- 407 L. J. Tsai, K. C. Yu, J. S. Chang and S. T. Ho, *Water Sci. Technol.*, 1998, **37**, 217.
- 408 Y. W. Wang, C. G. Yuan, X. L. Jin and G. B. Jiang, *J. Environ. Sci. (China)*, 2005, **17**, 540.
- 409 R. Zufiaurre, A. Olivar, P. Chamorro, C. Nerin and A. Callizo, *Analyst*, 1998, **123**, 255.
- 410 M. R. Cave and J. Wragg, *Analyst*, 1997, **122**, 1211.
- 411 S. Tokalioglu and S. Kartal, *Int. J. Environ. Anal. Chem.*, 2003, **83**, 935.
- 412 W. Wilcke, M. Krauss and J. Kobza, *J. Plant Nutr. Soil Sci.*, 2005, **168**, 676.
- 413 N. Teutsch, Y. Erel, L. Halicz and A. Banin, *Geochim. Cosmochim. Acta*, 2001, **65**, 2853.
- 414 J. R. Bacon, I. J. Hewitt and P. Cooper, *J. Environ. Monit.*, 2004, **6**, 766.
- 415 X. D. Li, Z. G. Shen, O. W. H. Wai and Y. S. Li, *Mar. Pollut. Bull.*, 2001, **42**, 215.
- 416 P. M. Outridge, *Water, Air, Soil Pollut.*, 2000, **118**, 179.
- 417 B. Kober, M. Wessels, A. Bollhofer and A. Mangini, *Geochim. Cosmochim. Acta*, 1999, **63**, 1293.
- 418 S. C. Wong, X. D. Li, G. Zhang, S. H. Qi and Y. S. Min, *Environ. Pollut.*, 2002, **119**, 33.
- 419 J. R. Bacon, J. G. Farmer, S. M. Dunn, M. C. Graham and S. I. Vinogradoff, *Environ. Pollut.*, 2006, **141**, 469.
- 420 A. Probst, L. Hernandez and J. L. Probst, *J. Phys. IV*, 2003, **107**, 1103.
- 421 M. Steinmann and P. Stille, *Appl. Geochem.*, 1997, **12**, 607.
- 422 S. Emmanuel and Y. Erel, *Geochim. Cosmochim. Acta*, 2002, **66**, 2517.
- 423 F. Monna, N. Clauer, T. Toulkeridis and J. R. Lancelot, *Appl. Geochem.*, 2000, **15**, 1291.
- 424 Y. Yokoo, T. Nakano, M. Nishikawa and H. Quan, *Chem. Geol.*, 2004, **204**, 45.
- 425 Y. F. Xu and F. Marcantonio, *Geochim. Cosmochim. Acta*, 2004, **68**, 2649.
- 426 S. Emmanuel, Y. Erel, A. Matthews and N. Teutsch, *Chem. Geol.*, 2005, **222**, 23.
- 427 A. Sahuquillo, G. Rauret, A. Rehnert and H. Muntau, *Anal. Chim. Acta*, 2003, **476**, 15.
- 428 S. Van Herreweghe, R. Swennen, C. Vandecasteele and V. Cappuyns, *Environ. Pollut.*, 2003, **122**, 323.
- 429 M. Mihaljevic, M. Ponavic, V. Ettler and O. Sebek, *Anal. Bioanal. Chem.*, 2003, **377**, 723.
- 430 K. A. Hudson-Edwards, S. L. Houghton and A. Osborn, *TrAC, Trends Anal. Chem.*, 2004, **23**, 745.
- 431 J. A. Jay, N. K. Blute, K. Lin, D. Senn, H. F. Hemond and J. L. Durant, *Environ. Sci. Technol.*, 2005, **39**, 9174.
- 432 R. Donahue and M. J. Hendry, *Appl. Geochem.*, 2003, **18**, 1733.
- 433 J. Y. Kim, A. P. Davis and K. W. Kim, *Environ. Sci. Technol.*, 2003, **37**, 189.
- 434 P. K. Pandey, S. Nair, A. Bhui and M. Pandey, *Curr. Sci.*, 2004, **86**, 190.
- 435 P. Bhattacharya, M. Claesson, J. Bundschuh, O. Sracek, J. Fagerberg, G. Jacks, R. A. Martin, A. D. Storniole and J. M. Thir, *Sci. Total Environ.*, 2006, **358**, 97.
- 436 Z. I. Gonzalez, M. Krachler, A. K. Cheburkin and W. Shotyck, *Environ. Sci. Technol.*, 2006, **40**, 6568.
- 437 R. X. Guo, J. L. Yang and Z. Y. Liu, *Fuel Process. Technol.*, 2004, **85**, 903.
- 438 I. Ko, J. S. Ahn, Y. S. Park and K. W. Kim, *Chem. Speciation Bioavailability*, 2003, **15**, 67.
- 439 C. Patinha, E. F. da Silva and E. C. Fonseca, *J. Geochem. Explor.*, 2004, **84**, 167.
- 440 N. Lihareva, *Microchem. J.*, 2005, **81**, 177.
- 441 J. S. Ahn, Y. S. Park, J. Y. Kim and K. W. Kim, *Environ. Geochem. Health*, 2005, **27**, 147.
- 442 J. Y. Kim, K. W. Kim, J. Ahn, I. Ko and C. H. Lee, *Environ. Geochem. Health*, 2005, **27**, 193.
- 443 A. G. Gault, D. R. Cooke, A. T. Townsend, J. M. Charnock and D. A. Polya, *Sci. Total Environ.*, 2005, **345**, 219.
- 444 M. Jang, J. S. Hwang, S. I. Choi and J. K. Park, *Chemosphere*, 2005, **60**, 344.
- 445 J. T. van Elteren, Z. Slejkovec, I. Arcon and H. J. Glass, *Environ. Pollut.*, 2006, **139**, 477.
- 446 L. Romero, H. Alonso, P. Campano, L. Fanfani, R. Cidu, C. Dadea, T. Keegan, I. Thornton and M. Farago, *Appl. Geochem.*, 2003, **18**, 1399.
- 447 M. Damris, G. A. O'Brien, W. E. Price and B. E. Chenhall, *J. Environ. Monit.*, 2005, **7**, 621.
- 448 J. U. Lee, S. W. Lee, K. W. Kim and C. H. Yoon, *Environ. Geochem. Health*, 2005, **27**, 159.
- 449 J. M. Yi, J. S. Lee and H. T. Chon, in *On the Convergence of Bio-, Information-, Environmental-, Energy-, Space- and Nano-Technologies, Pts 1 and 2*, Trans Tech Publications Inc., Zurich, Switzerland, 2005, vol. 277–279, p. 503.
- 450 J. M. Park, J. S. Lee, J. U. Lee, H. T. Chon and M. C. Jung, *J. Geochem. Explor.*, 2006, **88**, 134.
- 451 M. A. Taggart, M. Carlisle, D. J. Pain, R. Williams, D. Osborn, A. Joyson and A. A. Meharg, *Sci. Total Environ.*, 2004, **323**, 137.
- 452 S. Cornu, D. Montagne and P. Conil, *C. R. Geosci.*, 2004, **336**, 1007.
- 453 V. Matera, I. Le Hecho, A. Laboudigue, P. Thomas, S. Tellier and M. Astruc, *Environ. Pollut.*, 2003, **126**, 51.
- 454 Y. Takahashi, R. Minamikawa, K. H. Hattori, K. Kurishima, N. Kihou and K. Yuita, *Environ. Sci. Technol.*, 2004, **38**, 1038.
- 455 S. Saha, K. Ghosh, I. Das and S. K. Sanyal, *J. Indian Chem. Soc.*, 2005, **82**, 364.
- 456 W. J. Liu, Y. G. Zhu, Y. Hu, P. N. Williams, A. G. Gualt, A. A. Meharg, J. M. Charnock and F. A. Smith, *Environ. Sci. Technol.*, 2006, **40**, 5730.
- 457 R. Datta, D. Sarkar, S. Sharma and K. Sand, *Sci. Total Environ.*, 2006, **372**, 39.
- 458 C. E. Renshaw, B. C. Bostick, X. H. Feng, C. K. Wong, E. S. Winston, R. Karimi, C. L. Folt and C. Y. Chen, *J. Environ. Qual.*, 2006, **35**, 61.
- 459 L. L. Embrick, K. M. Porter, A. Pendergrass and D. J. Butcher, *Microchem. J.*, 2005, **81**, 117.
- 460 E. Smith, J. Smith and R. Naidu, *Sci. Total Environ.*, 2006, **363**, 175.
- 461 D. Sarkar, R. Datta and S. Sharma, *Chemosphere*, 2005, **60**, 188.
- 462 M. I. S. Gonzaga, J. A. G. Santos and L. Q. Ma, *Environ. Pollut.*, 2006, **143**, 254.
- 463 I. Ko, C. H. Lee, K. P. Lee, S. W. Lee and K. W. Kim, *Environ. Prog.*, 2006, **25**, 39.
- 464 N. Caille, S. Swanwick, F. J. Zhao and S. P. McGrath, *Environ. Pollut.*, 2004, **132**, 113.
- 465 S. Jessen, F. Larsen, C. B. Koch and E. Arvin, *Environ. Sci. Technol.*, 2005, **39**, 8045.
- 466 T. Mrak, Z. Slejkovec and Z. Jeran, *Talanta*, 2006, **69**, 251.
- 467 F. X. Han, W. L. Kingery, H. M. Selim, P. D. Gerard, M. S. Cox and J. L. Oldham, *Sci. Total Environ.*, 2004, **320**, 51.
- 468 A. Sahuquillo, G. Rauret, M. Bianchi, A. Rehnert and H. Muntau, *Anal. Bioanal. Chem.*, 2003, **375**, 578.
- 469 N. S. Bloom, E. Preus, J. Katon and M. Hiltner, *Anal. Chim. Acta*, 2003, **479**, 233.
- 470 G. E. M. Hall and P. Pelchat, *Geochem.: Explor., Environ., Anal.*, 2005, **5**, 115.
- 471 R. Fernandez-Martinez and M. I. Rucandio, *Anal. Bioanal. Chem.*, 2003, **375**, 1089.
- 472 Y. Han, H. M. Kingston, H. M. Boylan, G. M. M. Rahman, S. Shah, R. C. Richter, D. D. Link and S. Bhandari, *Anal. Bioanal. Chem.*, 2003, **375**, 428.
- 473 C. S. Kim, N. S. Bloom, J. J. Rytuba and G. E. Brown, *Environ. Sci. Technol.*, 2003, **37**, 5102.
- 474 C. Sladek and M. S. Gustin, *Appl. Geochem.*, 2003, **18**, 567.
- 475 R. Fernandez-Martinez, J. Loreda, A. Ordenez and M. I. Rucandio, *Sci. Total Environ.*, 2005, **346**, 200.
- 476 A. J. Slowey, J. J. Rytuba and G. E. Brown, *Environ. Sci. Technol.*, 2005, **39**, 1547.
- 477 D. Koeman, M. Horvat and J. Kotnik, *J. Environ. Monit.*, 2004, **6**, 696.
- 478 C. M. Neculita, G. J. Zagury and L. Deschenes, *J. Environ. Qual.*, 2005, **34**, 255.

- 479 D. Kocman, N. S. Bloom, H. Akagi, K. Telmer, L. Hylander, V. Fajon, V. Jereb, R. Jacimovic, B. Smodis, J. R. Ikingura and M. Horvat, *J. Environ. Manage.*, 2006, **81**, 146.
- 480 G. L. Liu, J. Cabrera, M. Allen and Y. Cai, *Sci. Total Environ.*, 2006, **369**, 384.
- 481 F. X. Han, Y. Su, D. L. Monts, C. A. Waggoner and M. J. Plodinec, *Sci. Total Environ.*, 2006, **368**, 753.
- 482 G. J. Zagury, C. M. Neculita, C. Bastien and L. Deschenes, *Environ. Toxicol. Chem.*, 2006, **25**, 1138.
- 483 A. Bernaus, X. Gaona, D. van Ree and M. Valiente, *Anal. Chim. Acta*, 2006, **565**, 73.
- 484 H. B. Shi, L. N. Liang, G. B. Jiang and X. L. Jin, *Environ. Int.*, 2005, **31**, 357.
- 485 C. Trombini, D. Fabbri, M. Lombardo, I. Vassura, E. Zavoli and M. Horvat, *Cont. Shelf Res.*, 2003, **23**, 1821.
- 486 J. Beldowski and J. Pempkowiak, *Chemosphere*, 2003, **52**, 645.
- 487 L. Boszke, A. Kowalski, W. Szczucinski, G. Rachlewicz, S. Lorenc and J. Siepak, *Environ. Geol.*, 2006, **51**, 527.
- 488 Y. D. Wang, C. Stauffer, C. Keller and M. Greger, *Plant Soil*, 2005, **275**, 67.
- 489 M. T. Wright, D. R. Parker and C. Amrhein, *Environ. Sci. Technol.*, 2003, **37**, 4709.
- 490 T. R. Kulp and L. M. Pratt, *Geochim. Cosmochim. Acta*, 2004, **68**, 3687.
- 491 T. T. Lim and K. H. Goh, *Chemosphere*, 2005, **58**, 91.
- 492 C. A. P. de Leon, K. DeNicola, M. M. Bayon and J. A. Caruso, *J. Environ. Monit.*, 2003, **5**, 435.
- 493 Y. Nakamaru, K. Tagami and S. Uchida, *Chemosphere*, 2005, **58**, 1347.
- 494 M. C. Wang and H. M. Chen, *Chemosphere*, 2003, **52**, 585.
- 495 I. Hagarova, M. Zemberyova and D. Bajcan, *Chem. Pap.*, 2005, **59**, 93.
- 496 P. T. Zawislanski, S. M. Benson, R. Terberg and S. E. Borglin, *Environ. Sci. Technol.*, 2003, **37**, 2415.
- 497 M. Bujdos, A. Mul'ova, J. Kubova and J. Medved, *Environ. Geol.*, 2005, **47**, 353.
- 498 C. Lussier, V. Veiga and S. Baldwin, *Environ. Geol.*, 2003, **44**, 905.
- 499 H. R. Vongunten and P. Benes, *Radiochim. Acta*, 1995, **69**, 1.
- 500 M. K. Schultz, W. Burnett, K. G. W. Inn and G. Smith, *J. Radioanal. Nucl. Chem.*, 1998, **234**, 251.
- 501 M. K. Schultz, K. G. W. Inn, Z. C. Lin, W. C. Burnett, G. Smith, S. R. Biegalski and J. Filliben, *Appl. Radiat. Isot.*, 1998, **49**, 1289.
- 502 M. K. Schultz, W. C. Burnett and K. G. W. Inn, *J. Environ. Radioact.*, 1998, **40**, 155.
- 503 J. A. Lucey, L. L. Vintro, D. Boust, P. I. Mitchell, A. Gouzy and L. Bowden, *J. Environ. Radioact.*, 2007, **93**, 63.
- 504 A. J. Plater, M. Ivanovich and R. E. Dugdale, *Appl. Geochem.*, 1992, **7**, 101.
- 505 A. Takeda, H. Tsukada, Y. Takaku, S. Hisamatsu and M. Nanzyo, *Sci. Total Environ.*, 2006, **367**, 924.
- 506 C. Galindo, L. Mougin, S. Fakhi, A. Nourreddine, A. Larngari and H. Hannache, *J. Environ. Radioact.*, 2007, **92**, 41.
- 507 K. Bunzl, R. Kretner, P. Schramel, M. Szeles and R. Winkler, *Geoderma*, 1995, **67**, 45.
- 508 P. Blanco, F. V. Tome and J. C. Lozano, *Appl. Radiat. Isot.*, 2004, **61**, 345.
- 509 P. Blanco, F. V. Tome and J. C. Lozano, *J. Environ. Radioact.*, 2005, **79**, 315.
- 510 M. S. Al-Masri, K. Al-Karfan, H. Khalili and M. Hassan, *J. Environ. Radioact.*, 2006, **91**, 103.
- 511 S. E. Howe, C. M. Davidson and M. McCartney, *J. Anal. At. Spectrom.*, 1999, **14**, 163.
- 512 J. L. Aguado, J. P. Bolivar and R. Garcia-Tenorio, *J. Environ. Radioact.*, 2004, **74**, 117.
- 513 A. J. G. Santos, B. P. Mazzilli, D. I. T. Favaro and P. S. C. Silva, *J. Environ. Radioact.*, 2006, **87**, 52.
- 514 M. Trautmannsheimer, P. Schramel, R. Winkler and K. Bunzl, *Environ. Sci. Technol.*, 1998, **32**, 238.
- 515 D. Desideri, L. Feduzi, A. A. Meli and C. Roselli, *J. Radioanal. Nucl. Chem.*, 2006, **267**, 551.
- 516 K. Bunzl, H. Flessa, W. Kracke and W. Schimmack, *Environ. Sci. Technol.*, 1995, **29**, 2513.
- 517 M. H. Lee, Y. Y. Yoon, S. B. Clark and S. E. Glover, *Radiochim. Acta*, 2004, **92**, 671.
- 518 M. Puhakainen, I. Riekkinen, T. Heikkinen, T. Jaakkola, E. Steinnes, K. Rissanen, M. Suomela and H. Thoring, *J. Environ. Radioact.*, 2001, **52**, 17.
- 519 P. McDonald, J. V. I. Battle, A. Bousher, A. Whittall and N. Chambers, *Sci. Total Environ.*, 2001, **267**, 109.
- 520 A. Abdelouas, B. Grambow, M. Fattahi, Y. Andres and E. Leclerc-Cessac, *Sci. Total Environ.*, 2005, **336**, 255.
- 521 A. Baumann, W. Schimmack, H. Steindl and K. Bunzl, *Radiat. Environ. Biophys.*, 1996, **35**, 229.
- 522 M. M. Vinichuk, K. J. Johanson, K. Rosen and I. Nilsson, *J. Environ. Radioact.*, 2005, **78**, 77.
- 523 M. J. Keith-Roach, K. Morris and H. Dahlgard, *Mar. Chem.*, 2003, **81**, 149.
- 524 K. S. Davies and G. Shaw, *Sci. Total Environ.*, 1993, **132**, 71.
- 525 T. Ohnuki, *J. Nucl. Sci. Technol.*, 1992, **29**, 996.
- 526 A. Rigol, M. Roig, M. Vidal and G. Rauret, *Environ. Sci. Technol.*, 1999, **33**, 887.
- 527 K. Bunzl, W. Kracke, W. Schimmack and L. Zelles, *J. Environ. Radioact.*, 1998, **39**, 55.
- 528 T. T. Vandergraaf, D. J. Drew, D. Archambault and K. V. Ticknor, *J. Contam. Hydrol.*, 1997, **26**, 83.
- 529 B. Salbu and E. Steinnes, *Analyst*, 1992, **117**, 243.
- 530 D. H. Oughton, B. Salbu, G. Riise, H. Lien, G. Ostby and A. Noren, *Analyst*, 1992, **117**, 481.
- 531 B. Salbu, D. H. Oughton, A. V. Ratnikov, T. L. Zhigareva, S. V. Kruglov, K. V. Petrov, N. V. Grebenshakikova, S. K. Firsakova, N. P. Astasheva, N. A. Loshchilov, K. Hove and P. Strand, *Health Phys.*, 1994, **67**, 518.
- 532 V. A. Poiarkov, A. N. Nazarov and N. N. Kaletnik, *J. Environ. Radioact.*, 1995, **26**, 259.
- 533 S. V. Krouglov, A. D. Kurinov and R. M. Alexakhin, *J. Environ. Radioact.*, 1998, **38**, 59.
- 534 Y. Sanada, T. Matsunaga, N. Yanase, S. Nagao, H. Amano, H. Takada and Y. Tkachenko, *Appl. Radiat. Isot.*, 2002, **56**, 751.
- 535 M. Vidal and G. Rauret, *Int. J. Environ. Anal. Chem.*, 1993, **51**, 85.
- 536 C. M. Davidson, M. D. Gibson, E. Hamilton, B. H. MacGillivray, J. Reglinski and E. Rezabal, *Chemosphere*, 2005, **58**, 793.
- 537 B. Wilson and F. B. Pyatt, *Sci. Total Environ.*, 2006, **370**, 401.
- 538 P. Matus, J. Kubova, M. Bujdos and J. Medved, *Talanta*, 2006, **70**, 996.
- 539 P. Matus, J. Kubova, M. Bujdos, V. Stresko and J. Medved, *Anal. Bioanal. Chem.*, 2004, **379**, 96.
- 540 C. A. Lucho-Constantino, F. Prieto-Garcia, L. M. Del Razo, R. Rodriguez-Vazquez and H. M. Poggi-Varaldo, *Agric. Ecosyst. Environ.*, 2005, **108**, 57.
- 541 L. Wang, N. Kubota, T. Higashi and T. Fujimura, *Soil Sci. Plant Nutr.*, 2004, **50**, 339.
- 542 J. Poledniok and F. Buhl, *Talanta*, 2003, **59**, 1.
- 543 Y. W. Chen, T. L. Deng, M. Filella and N. Belzile, *Environ. Sci. Technol.*, 2003, **37**, 1163.
- 544 E. Fuentes, H. Pinochet, M. Potin-Gautier and I. De Gregori, *J. AOAC Int.*, 2004, **87**, 60.
- 545 F. Reith and D. C. McPhail, *Geochim. Cosmochim. Acta*, 2006, **70**, 1421.
- 546 H. Al-Najar, A. Kaschl, R. Schulz and V. Romheld, *Int. J. Phytorem.*, 2005, **7**, 55.
- 547 D. Fliegel, Z. Berner, D. Eckhardt and D. Stuben, *Anal. Bioanal. Chem.*, 2004, **379**, 131.