

A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials

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Abstract A comprehensive review of the single and sequential extraction schemes for metal fractionation in environmental samples such as soil and industrially contaminated soils, sewage sludge and sludge amended soils, road dust and run off, waste and miscellaneous materials along with other approaches of sequential extraction methods are being presented. A discussion on the application of chemometric methods in sequential extraction analysis is also being given. The study of single and sequential extraction methods for various reference materials are also being looked into. The review covers several aspects of the single and sequential extraction methodologies. The use of each reagents involved in these schemes are also discussed briefly. Finally the present upto date information by different workers in various fields of environmental geochemistry along with the possible future developments are also being outlined.

Keywords Chemometric methods · Reference materials · Road dust and run off · Sequential extraction procedures · Sewage sludge and sludge amended soil · Single extractants · Soil and contaminated soil · Trace elements

1 Introduction

The biohazard in soils is attributable to several heavy metals and metalloids and often been assessed by determination of their total soil contents and national guidelines based on such total contents are currently in use in various countries. Total soil contents, however, reflect the geological origins of soils as well as the anthropogenic inputs such as pollutants from industrial processes and are poor indicators of mobility or bioavailability. A more relevant assessment of the contents of elemental contamination in the environmental context can be made by measuring the “pseudototal” element contents of a soil by the analysis of strong acid or aqua regia digests of soils. Pseudototal soil contents give an assessment, therefore, of the maximum potentially soluble or mobile contents of metals and, in the case of environmental metal contaminants, usually not bound in silicates, a measure of the maximum potential hazard that could occur in long term or in extreme environmental regimes.

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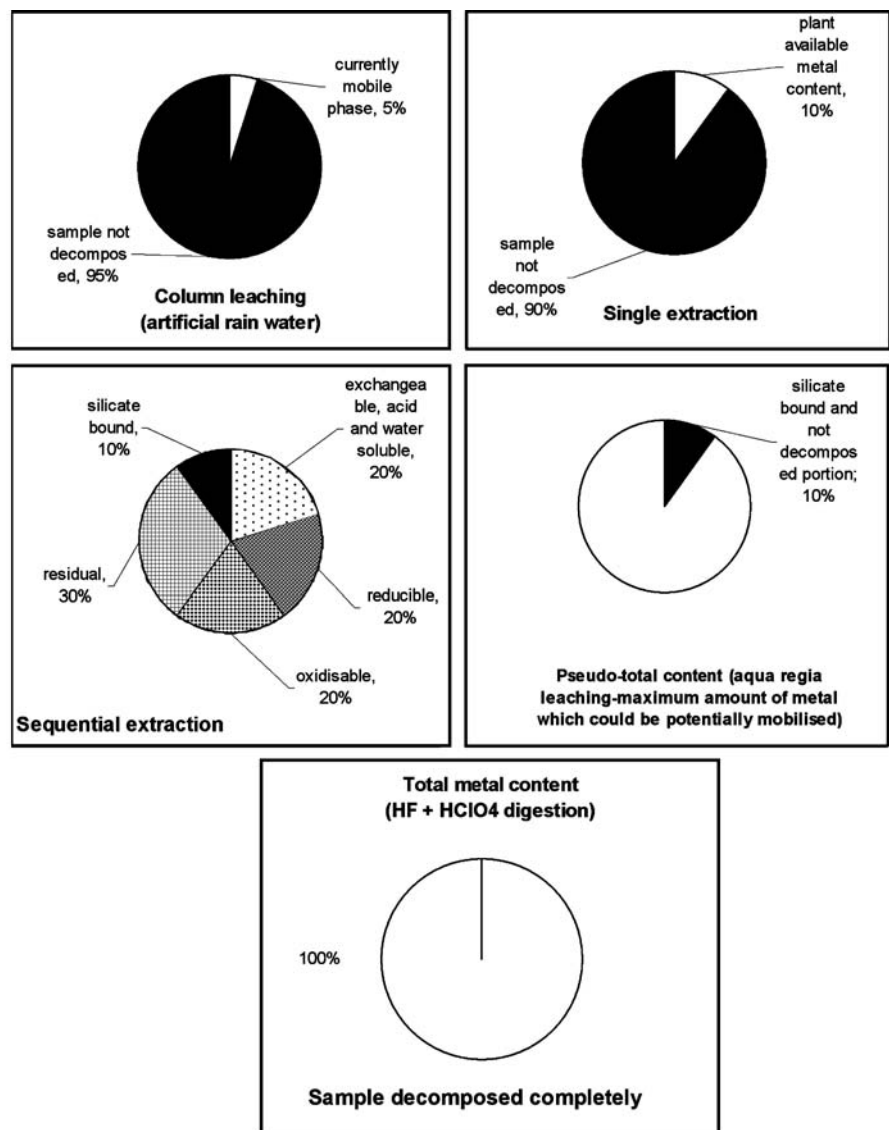
But selective extraction methods have been used to target element species in soil, or elements bound to, or associated with, particular soil phases or compounds. Examples include the use of extractants to release, metals on exchange sites, or metals bound or associated with soil organic matter etc. Thus, undoubtedly selective extraction methods can assess the amounts of mobile or potentially mobile species which in turn may correlate with plant-available contents under certain environmental or agricultural conditions.

For heavy metals and other potentially toxic elements, selective extraction methods are not only useful for the assessment of the mobile and potentially mobile species, for the plant availability etc., but the data also has been highly useful in the land use assessment.

A schematic diagram of the different approaches to the determination of heavy metals in soil is shown in Fig. 1.

Single and sequential extraction methods are also used in more fundamental studies such as : to elucidate

Fig. 1 Different approaches applied in general to the determination of heavy metals in soil (% values shown above are only tentative as they are metal and matrix dependent)



the soil chemistry, to assess the structure and composition of soil components and to improve understanding of the processes in the soil that control the mobilization and retention of nutrient and toxic elements as well as to illuminate their transport mechanisms.

Both single and sequential extraction methods are of major interest to the environmental scientist particularly in the study of the fate of environmental pollutants. Many of the extractants intended to target particular phase are also used in functional studies. The specificity of many of these reagents can be improved by combining a series of them in a sequential extraction scheme in which the residue from a first extraction is used as the material for a second extraction and so on through a number of stages. The soil phase attacked by each extracting reagent is thus restricted by the preceding extraction in the series and is thereby made more specific. Even if, all these procedures are operationally defined, they provide useful information.

Before going into the detailed discussion of the single and sequential extraction procedures a brief particulars on the methods of sample collection and the pretreatment are important so that proper sample has been collected for the analysis. Hence the details are given below.

2 Methods of Sample Collection and Pretreatment

2.1 Sample Collection

The procedure of sample collection mainly depends on the nature of the investigation. In an agricultural context where environmental contamination has occurred in a horizontal homogeneous way, e.g. by aerial deposition or fertilizer treatment, some 20–25 “sample units” for an area of 1–2 ha of arable soil are taken to plough depth (25 cm approx.) by auger at intervals along a W-shaped track or alternatively from 20–25 approximately equal squares covering the area.

For permanent pasture or grassland a sampling depth of 10 cm is appropriate. These sampling units are combined to provide for the laboratory a bulk sample, in a polyethylene bag, of some 1–2 kg field-moist soil.

On land contaminated by industrial activities first a systematic survey is made of samples from a grid of 50 m² at a fixed depth of 50 cm. These samples are inspected and the results of this preliminary study act as a guide to further sampling and analysis. Moreover, sampling at a fixed depth will not be useful where the

site has been subject to landfill (Fortunati et al. 1994) or as is often the case on industrial sites, has been built up by deposits of fill material itself contaminated. Rubio and Ure (1993) suggested an alternative strategy of judgment sampling which makes use of historical and anecdotal information to choose relevant sampling locations. These can then be sampled at the surface of the soil or profile samples taken from a soil pit dug to a depth of at least 1 m. As land from industrial sites often is essentially made-up ground, the samples are only nominally soils and the profile samples cannot be categorised into the usual horizons of natural soils. Examination of the soil profile can, however, identify distinct layers with distinguishable visual, olfactory or textual characteristics. Sampling of such identified layers down the soil profile can not only establish the vertical distribution of a contaminant but identify a particular profile layer material as a source of contamination (Davidson et al. 1998).

Rubio and Ure (1993) had also furnished excellent information on different aspects of sampling (a) Sample contamination using inappropriate materials, containers and tools as well as the possibility of losses of analyte during sample handling (b) Minimum sample weight criteria for representative sampling of dry soils in the field (c) Use of traps and continuous flow centrifugation methods for sediments and bottom sediments collection by grabs or cores and their comparison (d) Drying and storage temperatures to be controlled to minimize any significant changes in the metal species (e) Preservation of samples in an inert atmosphere or by irradiation and (f) Difficulties of establishing definitive protocols for sampling and sample pretreatment along with the need for selecting the appropriate technique in each particular case.

In a nutshell, it can be concluded that, there is a clear possibility of obtaining biased results when sampling only once. Distinction should also be made between sampling of (1) natural, agricultural, grassland, forest, or moorland soil where to some extent element distribution and speciation can be regarded as homogeneous and (2) industrially contaminated soils will usually have an element distribution and speciation that is heterogeneous not only over the surface area but also with depth. In the first case, representative samples of the area top soils may be required. In the second case, statistical sampling may be desirable but will often be uneconomical, and the so-called judgmental sampling using selected pit sampling of soil profiles may be required.

Filgueris et al. (2002) and Hlavay et al. (2004) have discussed in depth the various procedures to be followed for the sampling of different materials and the readers can refer these documents for the full particulars regarding sampling methodologies.

2.2 Sample Pretreatment

Ideally, sample pretreatment should not disturb the original metal distribution and keep it during storage prior to application of sequential extraction.

Drying seems to accelerate the crystallization of solids such as Fe–Mn oxides and promotes Fe, Mn and S oxidation, causing an increase in metals bound to Fe and Mn oxyhydroxides to the detriment of more labile phases made up of the exchangeable and carbonatic fractions (Bordas and Bourg 1998). However, the difficulties of storing field moist soils at temperatures low enough to minimise changes in soil nature with time, produced by microbiological action, or by chemical transformations due, for example, to oxidation or reduction and to prevent losses of volatile species, all make the use of moist soils only justifiable in limited special cases. Furthermore, not only are homogenisation and sub sampling of such wet soil difficult but, in consequence, representative sub samples of less than about 100 g are difficult to achieve. In addition this last limitation makes the preparation of certified reference materials with such large minimal sample weights difficult if not impracticable (Ure 1994). Hence in practice, in most soil laboratories, generally soil is dried before analysis. As further advantages, extractable metal contents are temporally stable in dried samples over periods of months, even years which is a necessary requirement for preparation of soil and sediment reference materials.

When drying the soil would entail a loss of essential information it is preferable to make use of the soil solution it self obtained, for example, by centrifugation or displacement rather than trying to use field moist soils (Ure 1996). Drying of the samples should be carried out at <30°C because soils stored over a 12-month period at 40°C showed small but significant increases in acetic acid extractable Cu, Cr but not for Cd, Ni, Pb and Zn (Rauret et al. 2000a).

Bearing in mind that no method of sample pretreatment preserves the speciation intact, metal extractability should at least be affected to a similar extent for the metals of interest. This is far from being

the rule since metals such as Pb and Cd differed in their response to several pre-treatments (Davidson et al. 1999b). Quevauviller et al. (1993) concluded that sequential extraction should be applied to wet, sieved sediment immediately after sampling so that environmentally relevant information is obtained. It is clear that the last recommendation cannot always be followed. In a comparison of several pre-treatment methods such as freeze-drying, air-drying and oven-drying at 105°C, (Bordas and Bourg 1998) it was found that Cd, Cu and Pb were the metals most sensitive to pre-treatments, freeze-drying and air-drying being the least disturbing procedures. Davidson et al. (1999a) found in a study with industrially-contaminated soil for assessment of variability sources that repeatability was higher for air-dried samples than for field-moist soils, but larger amount of metals were extracted, suggesting alterations in the metal distribution during drying.

After drying, sieving is necessary to obtain the appropriate particle size distribution. This operation should be made with nylon sieves in order to avoid metal contamination. The smaller particle size used in sediments (<63 µm) in comparison with soils (<2 mm) means that the representative sub-sample used for extraction can be much smaller (i.e. 0.5–2 g for sediments vs. 5–20 g for soils).

Another aspect to be considered is the need for remixing before extraction. The influence of the manual remixing procedure to avoid segregation of particles in the bottle and the grinding of the solid sample has been studied for soils (Clevenger 1990). The stability of the soils was generally independent of the particle size distribution, but the metal extractability was affected by grinding, so rehomogenisation merely by manual shaking was recommended. Sahuquillo and Rauret (2003) covered several aspects of the sample pretreatment for sequential extraction procedures and the readers can refer the document for full particulars.

Once the extracts are separated from the solid material, acidification is recommended to guarantee a better conservation (Whalley and Grant 1994; Ianni et al. 2001).

Regarding sewage sludge, thermal treatment at 180°C was seen to benefit its use as soil fertilizer since on the one hand metal leaching is decreased and, on the other hand, losses of organic matter are negligible, thereby keeping its usefulness as organic amendment (Obrador et al. 2001).

Detailed guidelines on long and short term storage of soil samples had been brought by International Organization for Standardization (ISO 18512 2006) and the readers may refer the document for details. However as a conclusion, sample storage seems to be generally less critical to the analysis of extractable metal fractions than air-drying, but it is likely to enhance the effects of air-drying in the case of redox sensitive elements.

3 Extractants for Assessing the Easily Leachable or Potentially Leachable Trace Element Contents of Soils and Other Related Materials

The use of chemical extractants for the assessment or prediction of agricultural crop plant contents, plant growth or health and the estimation of the likelihood of plant or animal (consuming the fodder plant) deficiency or toxicity has been a major topic of study in agricultural laboratories for almost half a century, therefore exists a large body of information on soil extractants for these purposes and for which plant contents and soil extractable contents are correlated and the methods validated over several years for different crops and different soil types. The extractants developed are not universal reagents, but remain, to varying degrees, soil and crop specific.

Table 1 lists some of the extractants used for assessing plant-available element contents in an agricultural context. It is also important to note that, the validity of these extractants as measures of plant availability is much less well established in the case of industrial polluted soils where concentrations observed are well in excess of normal soil contents hence correlations are relatively unsubstantiated in those cases.

3.1 Single Extractants

In recent years the assessment of the mobile fractions of heavy metals in soils, as an indication of potential risk of toxic species entering the biosphere and the possible negative effects on ground water quality and their availability to plants and the need to evaluate the environmental impact has been a major topic of investigation all over the world as the number of contamination sites are increasing. One of the approaches most widely used to study metal mobility in soils is the use of single extraction procedures using unbuffered salt solutions that can be considered

as good models for simulating raining and flooding events. Several studies have demonstrated the suitability of these extraction procedures for the prediction of plant uptake in soils (Menzies et al. 2007 and the references therein). While many of the extractants listed in Table 1 have been applied to various heavy metal assignment, the principal extraction reagents now favored are the weak salt solutions of calcium chloride, sodium nitrate and ammonium nitrate. They are also called as unbuffered mild extractants or neutral salt solutions and a more productive approximation to the soil solution in a better buffered state is obtained by extraction with weak neutral salt solutions and presently 0.01 M calcium chloride has been recommended in The Netherlands (Houba et al. 1996) and 0.1 M sodium nitrate in Switzerland (Hani and Gupta 1986) and 1 M ammonium nitrate in Germany (DINV 19730 1995) as a standard national protocols.

Single extractants can also be considered in their role of releasing elements from particular soil phases with which they are bound or associated. Extractants can be classified according to these soil phases or binding types and many of the extractants listed in Table 2 can be regarded in this light. The classification of extractants in this way is extremely useful in the study of soil chemistry and in elucidating the mechanisms of metal binding, transformation or release in soils. Unfortunately most available extractants are less specific than desired. More than one target site may be attacked or the release from the target site be less than complete. Table 2 lists only some typical single extractants with their ideal target species, but, in view of the limitations noted above, they are best regarded as extractants whose extracted phases are operationally defined i.e., by the procedure used to isolate them. Despite these limitations, which should always be borne in mind when interpreting results, the concept of a single extractant releasing element species or elements associated with a particular soil phase is still a useful one and constitutes one of the few tools available for assessing the binding and mobilisation of elements in soils.

3.2 Reagents and Targeted Phases

To understand more intricately the several reactions and mechanisms involved between the various reagents and the different phases, the fraction associated with each soil phase (or element binding type)

Table 1 Examples of extractants for assessing plant-available trace element contents of soils (few selected examples)

Extractant	Elements	Reference
Water	Cd, Cu, Zn	Mahler et al. (1980)
	As	Szakova et al. (2001b)
	Zn, Y, La, Al, Cu, Cd	Takeda et al. (2006)
Boil/reflux water	B	Mahler et al. (1984)
	B	Chaudhary and Shukla (2004)
Boil/reflux water+0.01 M CaCl ₂	B	Sterckeman et al. (1996)
	B	Chaudhary and Shukla (2004)
Water, microwave heat; 0.125% BaCl ₂ solution	B	De Abreu et al. (1994)
0.5 M NH ₄ CH ₃ COO+0.02 M EDTA	Cu, Fe, Mn, Zn	Sauerbeck and Styperek (1985)
1 M NH ₄ CH ₃ COO+0.01 M EDTA, pH 7	Cu, Mn, Zn	Sterckeman et al. (1996)
1 M NH ₄ CH ₃ COO, HCl, EDTA, HNO ₃	Ca, Mn, Pb	Gronflaten and Steinnes (2005)
1 M NH ₄ CH ₃ COO	Zn, Y, La, Al, Cu, Cd	Takeda et al. (2006)
0.05 M (NH ₄) ₂ SO ₄	As	Szakova et al. (2001b)
1 M NH ₄ NO ₃	Ni	Merkel (1996)
1 M NH ₄ NO ₃	Cd, Tl	Gryschko et al. (2005)
1 M NH ₄ NO ₃	Ca, Mn, Pb	Gronflaten and Steinnes (2005)
1 M NH ₄ NO ₃	Al, Zn, Mo, Ba, Cd, Se, Sr, Cu, Pb, Ni, Hg, Cr, As	Rekasi and Filep (2006)
1 M NH ₄ NO ₃	Zn, Y, La, Al, Cu, Cd	Takeda et al. (2006)
1 M NH ₄ NO ₃	Cu	Gupta and Sinha (2006a)
0.1 M NaNO ₃	Zn, Cu, Cd, Ni, Pb	Gupta and Aten (1993)
0.05 M and 0.1 M CaCl ₂	Cd, Zn	Sauerbeck and Styperek (1985)
0.1 M CaCl ₂	Zn, Cd	Smilde et al. (1992)
0.01 M CaCl ₂	Cd	Novozamsky et al. (1993)
0.1 M CaCl ₂	Cd	Merkel (1996)
0.01 M and 0.05 M CaCl ₂	Cd	Andrewes et al. (1996)
0.01 M CaCl ₂	As	Szakova et al. (2001b)
0.01 M CaCl ₂	Pb, Mn	Gupta and Sinha (2006a)
0.01 M CaCl ₂	Zn, Y, La, Al, Cu, Cd	Takeda et al. (2006)
0.01 M CaCl ₂ /0.005 M DTPA	Cu, Zn	Merkel (1996)
0.1 M Ca(NO ₃) ₂	Pb	Ji-tao et al. (2006)
0.005 M DTPA+0.1 M Triethanol amine+ 0.01 M CaCl ₂ , pH 7	Cu, Fe, Mn, Zn	Sterckeman et al. (1996)
0.005 M DTPA	Fe, Zn, Ni	Gupta and Sinha (2006a)
0.005 M DTPA	Cd, Pb	Wang et al. (2006)
1 M EDTA pH 6	Cd, Cu, Ni	Clayton and Tiller (1979)
0.05 M EDTA	Ca, Mn, Pb	Gronflaten and Steinnes (2005)
0.05 M EDTA	Cd, Zn, Cu	Guo et al. (2006)
0.4 M CH ₃ COOH	Zn, Co	Houba et al. (1996)
0.43 M HNO ₃	Cu	Houba et al. (1996)
HNO ₃ concentrated	Ca, Mn, Pb	Gronflaten and Steinnes (2005)
0.01 M HNO ₃	Zn, Y, La, Al, Cu, Cd	Takeda et al. (2006)
Low-mol-wt.organicacids (LMWOAs)	La, Ce, Pr, Nd	Wang et al. (2004)

have been considered individually and the reagents used to extract them are discussed in a more detailed way hereunder. Excellent and very exhaustive information had also been provided by Pickering (1986), Ure and Davidson (2001), Gleyzes et al. (2002a) which can be consulted for more details.

3.2.1 The Soil Solution

The water-soluble metals can be determined from the saturation paste extract of a soil or by extracting soil with deionised water at a certain soil–water ratio. (Svete et al. 2000).

Table 2 Examples of extractants or isolation procedures and the corresponding phases (few selected examples)

Phase extracted or isolated	Extractant or isolation method	Reference
Water-soluble	Water	Svete et al. (2000)
	Hot water	Sterckeman et al. (1996)
Soil solution	0.01M potassium nitrate	Sauve et al. (1997)
	Centrifugation	Linehan et al. (1985)
	Displacement	Sanders (1983)
	Dialysis	Lee and Zheng (1994)
	Filtration	Filgueiras et al. (2002)
Exchangeable	Ultrafiltration	Wang and Benoit (1996)
	1 M potassium chloride	Grove et al. (1982)
	0.01–0.5 M calcium chloride	Schramel et al. (2000)
	0.5–1 M magnesium chloride	Tessier et al. (1979)
	0.2 M potassium nitrate	Grove et al. (1982)
		Gupta et al. (1990)
	0.1–0.5 M calcium nitrate	Boruvka et al. (1997)
		Ji-tao et al. (2006)
	1 M ammonium nitrate	Symeonides and McRae (1977); Schramel et al. (2000); Gryschko et al. (2005)
	1 M ammonium acetate	Del Castilho and Rix (1993); Sager (1999); Takeda et al. (2006)
	0.43 M acetic acid	Ure (1996)
	0.1 M Barium chloride	Nageswara Rao (2005)
	1 M Ammonium chloride	Grove et al. (1982); Krishnamurthi et al. (1995); Guo et al. (2006)
	0.5 M Magnesium nitrate	Gommy et al. (1998); Parat et al. (2003)
	0.2 M Aluminum chloride	Hughes and Noble (1991)
0.4 M Lithium chloride	Sager (1999)	
0.1 M Strontium chloride	Moral et al. (2002)	
0.1 M Sodium nitrate	Gupta and Aten (1993); Pueyo et al. (2004)	
Less readily exchangeable (specifically sorbed)	0.5 M acetic acid	McLaren et al. (1986)
	0.125 M copper acetate	Soon and Bates (1982)
	0.05 M lead nitrate	Miller et al. (1986)
	1 M ammonium acetate or 1 M NH ₄ NO ₃ at pH6	Zeien and Bruemmer (1991)
	0.1 M sodium pyrophosphate	Hall et al. (1996a); Boruvka et al. (1997)
Organically bound	0.1 M Potassium pyrophos-phate	Miller (1986)
	0.1/0.7 M sodium hypochlorite	Shuman (1983); Parat et al. (2003)
	0.4 M EDTA	McLaren et al. (1986)
	Hydrogen peroxide/nitric acid/sodium acetate	Tessier et al. (1979); Parat et al. (2003)
	Sodium dodecyl sulfate in NaHCO ₃ mixed with an organic compound	Batley (1989)
Carbonate-bound	0.1 M acetic acid	Arunachalam et al. (1996)
	0.5 M acetic acid	McLaren et al. (1986)
	1 M acetic acid	Barona et al. (1995)
	1 M Sodium acetate and acetic acid at pH 5	Foerstner et al. (1981); Krishnamurthi et al. (1995); Ure (1996)
	0.05 M EDTA	McGrath (1996)
Manganese oxide-sorbed	0.1 M hydroxylamine hydrochloride	Miller et al. (1986)
Iron oxide-sorbed	Dithionite/citrate/bicarbonate At pH 7.3	Mehra and Jackson (1960); Pickering (1986)

Table 2 (continued)

Phase extracted or isolated	Extractant or isolation method	Reference
	0.1 M Hydroxylamine hydrochloride 0.1 M Oxalate	Miller et al. (1986) McKeague and Day (1966); Bibak et al. (1994)
Residual (non-silicate-bound)	Nitric acid Aqua regia	Gupta et al. (1996) ISO 11466 (1995)
Mineral lattice	Nitric/hydrofluoric/perchloric	Parat et al. (2003)

This phase contains the water soluble species made up of free ions and ions complexed with soluble organic matter and other constituents. It constitutes the most mobile and potentially the most available metal and metalloid species. The concentration of trace element nutrients or pollutants in the soil solution is very low and only accessible to the most sensitive analytical techniques. This phase can be isolated by centrifugation (Linehan et al. 1985), displacement (Campbell et al. 1988; Sanders 1983), filtration (Brummer 1986), ultrafiltration (Wang and Benoit 1996) or dialysis etc., (Lee and Zheng 1994; Ure and Davidson 2001).

3.2.2 Exchangeable/Non-specifically Sorbed Fraction

This fraction includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes etc. Changes in the ionic composition, influencing adsorption–desorption reactions, or lowering of pH could cause remobilisation of metals from this fraction. (Krishnamurti et al. 1995; Arunachalam et al. 1996; Narwal et al. 1999; Ahnstrom and Parker 2001). Exchangeable metal ions are a measure of those trace metals which are released most readily into the environment. Metals corresponding to the exchangeable fraction usually represent a small portion of the total metal content in soil, sewage sludges, and sediments and can be replaced by neutral salts (Rauret 1998). Thus, this fraction generally accounted for less than 2% of the total metals in soil present, the exceptions to this were the macro-elements, K, Ca and Mn (Emmerson et al. 2000).

Readily exchangeable fraction, also described as non-specifically adsorbed fraction, can be released by the action of cations such as K, Ca, Mg or (NH₄) displacing metals weakly bound electrostatically on

organic or inorganic sites. These cations have been widely employed for this purpose, generally at relatively high concentrations (Beckett 1989, pp.143–176). Examples are tabulated in Table 2. Neutral salts of strong acids and bases have the advantage that they do not affect the pH at the exchange sites, nor do they attack silicate or oxyhydroxide phases. Ammonium salts of strong acids, such as NH₄Cl or NH₄NO₃, however, can lower the pH and encourage the hydrolysis of clays. Salts of weak acids, such as acetates, can, conversely, increase the pH with possible precipitation of metal hydroxides – an effect countered, however, by the complexation of metals by acetate. This complexation also inhibits the readsorption of released metals (Gomez-Ariza et al. 2000).

3.2.3 Specifically Sorbed Fraction

Less readily exchangeable fraction, bound by covalent forces, i.e. specifically sorbed species, are not easily displaced by major cations such as K or Ca, but require the hydrogen ion or a “soft” cation such as Pb (I) or Cu (I) to displace them from organic or inorganic sites. Magnesium salts have been reported to have a somewhat stronger displacing action than those of calcium in the case of sorbed Co and Zn (Tessier et al. 1979). Hydrogen ion in the form of 0.5 M acetic acid has been used in non-calcareous soils for copper (Berrow and Mitchell 1980) and for cobalt sorbed on iron oxyhydroxide sites (McLaren et al. 1986). Acetic acid lacks specificity in that it partly attacks carbonate and silicate phases (Rapin and Forstner 1983).

Copper acetate (0.125 M) has been used to displace metals sorbed on organic matter and on oxyhydroxides of iron (Soon and Bates 1982), while 0.05 M lead nitrate released specifically bound copper (Miller et al. 1986).

3.2.4 Organically Complexed Metal Fraction

The trace metals may be associated through complexation or bioaccumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles. Organic substances exhibit a high degree of selectivity for divalent ions compared to monovalent ions and in aquatic systems, the probable order of binding strength for metal ions onto organic matter being $Hg > Cu > Pb > Zn > Ni > Co$ (Filgueiras et al. 2002). Metallic pollutants associated with oxidizable phases are assumed to remain in the soil for longer periods but may be mobilised by decomposition processes (Kennedy et al. 1997). Degradation of organic matter under oxidising conditions can lead to a release of soluble trace metals bound to this component. Amounts of trace metals bound to sulfides might be extracted during this step (Marin et al. 1997). The organic fraction released in the oxidizable step is not considered very mobile or available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow manner (Filgueiras et al. 2002).

The most widely used procedure involves the oxidation of organic material by hydrogen peroxide with a subsequent extraction with ammonium acetate to prevent re-adsorption or precipitation of released metals. A detailed procedural protocol for this method has been published by Ure et al. (1995). In some cases formation of oxalate can occur during oxidation with hydrogen peroxide (Harada and Inoko 1977) and this can attack iron and manganese oxyhydroxides and release metals sorbed on clays (Ure and Davidson 2001). H_2O_2 – ammonium citrate does not completely leach metals associated with sulfides. Other oxidising reagents, such as H_2O_2 /ascorbic acid or $HNO_3 + HCl$ are used which can dissolve sulfides with enhanced selectivity, but, on the other hand, silicates are attacked to some extent (Klock et al. 1986).

Oxidation with alkaline sodium hypochlorite has also been recommended (Shuman 1983) although the fraction of organically bound metals released showed considerable variability in different soil horizons (Papp et al. 1991).

An alternative approach uses sodium or potassium pyrophosphate (0.1 M at pH 10) to disperse colloidal organic material by complexing the flocculating Ca, Al or Fe cations. This reagent is more selective for the easily soluble organic fraction i.e., metals associated

with humic and fulvic acids. Minimal degradation of Mn and Fe oxides and silicates have been indicated for hypochlorite (Hall et al. 1996b; Hall and Pelchat 1999; Neel et al. 2007; Iwegbue et al. 2007).

Complexing extractants such as EDTA or DTPA can, by virtue of their strong complexing ability, displace metals from insoluble organic or organometallic complexes in addition to those sorbed on inorganic soil components (Berrow and Mitchell 1980; Ure and Davidson 2001).

Non-oxidising reagents have also been attempted for extraction of metals associated with organic matter such as sodium dodecyl sulfate in $NaHCO_3$ mixed with an organic compound such as diaminemethane, *N,N*-dimethyl formamide, dimethylsulfoxide, etc. (Batley 1989).

3.2.5 The Carbonate Phase

Carbonate can be an important adsorbent for many metals when organic matter and Fe–Mn oxides are less abundant in the aquatic system (Stone and Droppo 1996). The carbonate form is a loosely bound phase and liable to change with environmental conditions. This phase is susceptible to changes in pH, being generally targeted by use of a mild acid. The time required for complete solubilisation of carbonates depend on several factors such as particle size of the solid, type and amount of carbonate in the sample, etc (Beck et al. 2001).

The most common reagent for the extraction of trace metals from carbonate phases in soil is 1 M sodium acetate acidified to pH 5 with acetic acid. Carbonate phases effectively attacked include dolomite, but the presence of acetic acid also promotes the release of metals specifically sorbed on inorganic and organic substrates (Tessier et al. 1979; Ahnstrom and Parker 1999).

3.2.6 The Fraction Associated with Hydrous Oxides of Iron and Manganese

Hydrous oxides of manganese and iron are extracted together and are the well known “sinks” in the surface environment for heavy metals. Scavenging by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: coprecipitation; adsorption; surface complex forma-

tion; ion exchange; and penetration of the lattice (Hall et al. 1996a).

The amorphous oxyhydroxides of iron and manganese strongly sorb trace elements, initially in exchangeable forms, but increasingly with time are transformed to less mobile, specifically adsorbed forms. Acidified hydroxylamine hydrochloride 0.1 M releases metals mainly from amorphous manganese oxide phases with little attack on iron oxide phases (Shuman 1982). Increasing the hydroxylamine hydrochloride concentration to 0.5 M (Sahuquillo et al. 1999) and decreasing the pH from 2 to 1.5 (Chao 1972; Sahuquillo et al. 1999) provides effective attack on the iron oxide phases while still releasing metals from manganese oxide phases.

Sodium dithionate has been used in combination with sodium citrate and sodium bicarbonate in a range of concentrations (Beckett 1989, pp.163–164) and usually at pHs between 5.8 and 7.3 for the reduction of both crystalline and amorphous iron oxide phases and release of sorbed trace metals (McKeague and Day 1966). It is little used for heavy metal studies because of contamination of the dithionite with zinc and the possibility of precipitation of metal sulfides (Gibson and Farmer 1986). Additionally, this reagent easily attacks silicates (Rozenon and Heller 1978). The ascorbic acid/ammonium oxalate reagent offers several advantages over the previous reagent, since it can be achieved with a high purity degree, and does not attack silicates (Shuman 1982; Bibak et al. 1994).

Although acid (pH 3) ammonium oxalate has been widely used to dissolve iron and aluminium oxides and release bound trace metals, nevertheless, leaching of metals associated with organic matter is likely to occur as a result of the complexing capacity of oxalate (Slavek et al. 1982) and further, the extraction is sensitive to light and particularly to ultraviolet light (Endredy 1963). Schwertmann (1964) showed that in the dark the amorphous iron oxides were mainly attacked and under ultraviolet illumination the crystalline phases were dissolved as effectively as the dithionate reagent. Heavy metals are released, with the exception of lead and cadmium whose oxalates are poorly soluble and which coprecipitate with calcium oxalate (Chao and Zhou 1983). The use of oxalic acid at the lower pH of 2.5 improved the performance relative to acid ammonium oxalate in that Cd was almost unaffected although lead was partially lost by precipitation (Sahuquillo et al. 1999).

3.2.7 Strong Acid-extractable Fraction: Pseudototal Trace Element Contents

Digestion in strong acids such as nitric acid, hydrochloric acid or mixture such as aqua regia that do not dissolve the silicate matrix can give an estimate of the maximum amounts of elements that are potentially mobilisable with changing environmental conditions. It is therefore a useful tool in the assessment of the long-term potential risk of heavy or toxic metals entering the biosphere. Such reagents do not mobilise trace elements from geological, silicate parent materials but dissolve metal pollutants which largely enter the soil environment in non-silicate-bound forms. The terms pseudototal analysis and pseudototal contents are useful in expressing the environmental role of such strong acid digestion procedures. Aqua regia digestion is now a well-used procedure (ISO 11466 (1995)) with a legal status in some European countries and has been used as a reference procedure in the preparation of soil and sediment reference materials certified for extractable contents by the European Community of Bureau of Reference (BCR), now the Standards, Measurement and Testing Program (SM&T).

4 Other Selective Extraction Methods

Extraction procedures have also been developed for the determination of the anionic species in soils of elements such as sulfur which are important as binding sites for metals as well as for its own mobility and availability (Cordos et al. 1995). The important biosignificant element selenium has similarly received attention along with Cr, Pt, Tl for their estimation in the soil solution or soil extracts (Blaylock and James 1993; Seby et al. 1997; Zbiral et al. 2002). Review by Gleyzes et al. (2002a) provides an excellent information on the extraction of anionic species of As, Se, Cr etc. Recent review by Smichowski et al. (2005) also furnishes a detailed account of metal fractionation of atmospheric aerosols using various sequential chemical extraction procedures.

5 Sequential Extraction Methods

Sequential extraction involves treatment of a sample of soil or sediment with a series of reagents in order to partition the trace element content.

The principal advantage claimed for sequential extraction over the use of single extractants is that the phase specificity is improved. This occurs because each reagent has a different chemical nature (e.g. a dilute acid, reducing or oxidising agent) and the steps are performed roughly in order of increasing “vigour.” Hence, in a typical procedure, the first species to be isolated are those already in the soil solution or sediment pore water, perhaps together with those loosely attached at cation-exchange sites in the matrix. This is generally followed by stepwise attack on the carbonate phase, iron and manganese oxyhydroxides and organic matter. Finally, more refractory soil components, sometimes including the primary silicates, may be dissolved. With the use of additional reagents, the mineralogical phases may be further subdivided: for example, many procedures involve separate attacks on the more labile, amorphous iron oxyhydroxides and the more refractory, crystalline forms etc.

Although there are several sequential extraction procedures in the literature the Tessier scheme and the BCR scheme are usually the most adopted methods by various workers. Hence the brief details of these two methods are given in Tables 3 and 4 respectively.

The BCR sequential extraction scheme which was originally developed for the analysis of heavy metals in sediments, has been standardized and reference materials are available and has been successfully applied to a variety of matrices, including calcareous soils (Alvarez et al. 2006), contaminated soils (Pueyo et al. 2003), road side soils (Yusuf 2006), industrially contaminated soils (Van Herreweghe et al. 2003), sewage sludge (Lihareva et al. 2006), Sludge amended soil (Rauret et al. 2000a), fly ash (Smeda and Zyrnicki 2002), mining waste (Margui et al. 2006) etc.

6 Quality Control of the Extraction Data

The usefulness of a certified reference material (CRM) for validation of analytical methodology depends critically on how well the certified values are established and special difficulties exist when the species to be determined are isolated via an operationally-defined procedure (Sahuquillo et al. 1999). The Community Bureau of Reference (BCR, now the Standards, Measurements and Testing Programme), being aware of this drawback, has undertaken in the past few years a series of inter-laboratory studies leading to certification of extractable contents of several metals according to a common three-stage sequential extraction scheme i.e., BCR SES (Ure et al. 1993; Quevauviller et al. 1997b; Rauret et al. 2000a) and single extractions with EDTA and acetic acid (Quevauviller et al. 1997a, c). So far, the results of these studies have conducted to the certification of two sediments (CRMs BCR 601 and 701) using the BCR SES (original and modified) and sewage sludge amended and calcareous soils (CRMs BCR 483, 484, 600 and 700) using single extraction with EDTA and acetic acid. Indicative values for extractable metal contents from CRM BCR 483 upon application of the modified BCR SES have also been published (Rauret et al. 2000b). Samples which are the candidates for reference materials to be certified for extractable metal contents are firstly characterized through homogeneity tests (i.e. comparison of between-bottle and within bottle precision) and stability studies (i.e. by studying the extractable metal contents for bottles kept at -20, +20 and +40°C during a period of 12 months). Marin et al. (1997) concluded their study saying that the sequential extraction scheme recommended by BCR is sufficiently repeatable and

Table 3 Operating conditions required in the Tessier sequential extraction procedure ^a [Tessier et al. (1979)]

Stage	Fraction	Reagent	Experimental conditions
1	Exchangeable	8 ml of 1 mol l ⁻¹ MgCl ₂ (pH 7)	1 h at 25°C
2	Associated with carbonates	8 ml of 1 mol l ⁻¹ NaOAc (pH 5 with acetic acid)	5 h at 25°C
3	Associated with Fe–Mn oxides	20 ml of NH ₂ OH·HCl, 0.04 mol l ⁻¹ in 25% w/v HOAc (pH~2)	6 h at 96°C
4	Associated with organic matter	3 ml of 0.02 mol l ⁻¹ HNO ₃ /5 ml of 30% m/v H ₂ O ₂	2 h at 85°C
		+3 ml of 30% m/v H ₂ O ₂	3 h at 85°C
		+5 ml of 3.2 mol l ⁻¹ NH ₄ Oac	30 min at 25°C

^a For 1 g sample

Table 4 The BCR (Community Bureau of Reference, now the Standards, Measurement and Testing Program (SM&T) optimized sequential extraction procedure^a [Rauret et al. (1999)]

Step number	Extractant	Fraction	Nominal target phase (s)	Experimental conditions
1	40 ml of 0.11 mol l ⁻¹ acetic acid solution	Exchangeable, acid-and water-soluble	Soil solution, exchangeable cations, carbonates	Room temperature, 16 h, constant shaking
2	40 ml of 0.5 mol l ⁻¹ hydroxyl amine hydrochloride solution at pH 1.5 (with nitric acid)	Reducible	Iron and manganese oxyhydroxides	Room temperature, 16 h, constant shaking
3	10 ml of 30% w/v H ₂ O ₂ 10 ml of 30% w/v H ₂ O ₂ 50 ml of 1 mol l ⁻¹ then 1 M ammonium acetate at pH 2	Oxidisable	Organic matter and sulfides	Room temperature, 1 h, occasional agitation +85°C, 1 h 85°C, 1 h, Reduce the volume to a few ml Room temperature, 16 h, constant shaking
4	Aqua regia ^b	Residual	Non-silicate minerals	ISO 11466 (1995) method adopted

^a For 1 g sample

^b Recommended, to allow comparison for quality control purposes of sequential extraction (Σ =Step 1+step 2+Step 3+Residual) with results obtained by a separate aqua regia digestion of original material.

reproducible to be applied to metal distribution studies, but also advised that care must be taken when this procedure is applied to soil and sediments with extremely different chemical compositions. For example, Sulkowski and Hirner (2006) discussed in detail the problems associated with the sequential extraction of high carbonate content soils.

The sediments certified so far for extractable metal content (i.e. CRMs 601 and 701) were homogeneous at 1 g mass level, the mass used for sequential extraction. It should be stressed that certified materials are subjected to exhaustive mixing, homogenisation and sieving operations including in some cases further coning and quartering so that the sample size is conveniently diminished before bottling. Pre-treatment of real samples for determination of extractable metals is usually less stringent, and hence extraction results could be affected by non-homogeneity in a larger extent. In spite of the efforts made towards certification of soil and sediments for sequential extraction, unacceptable spread of results were observed in some cases and indicative values instead of certified ones have been provided (Quevauviller 1998a). Evidently, the operationally defined character of SES means that conditions established must be strictly followed if a

good agreement has to be obtained between fractionation results from different labs. This includes consideration of the type of mechanical shaker and extraction vessel and the method of separating the extract from the soil residue used etc.

Thus, the effects of the shaker type and speed and room temperature have been thoroughly discussed (Quevauviller 1998b). The effect of the shaking speed has been found to be more significant as well as the type of shaker, and speed should be adjusted so that the mixture is maintained in suspension during extraction. The temperature of extraction should be kept constant at 20±2°C. In conclusion, close control of the conditions of extraction are necessary so that reproducible and reliable extractable contents of soils or sediments can be obtained.

The ISO protocol (11466) for aqua regia leaching has been adapted for extraction of metals in the residue from the third stage of the BCR scheme as well as for the original sample as an internal check on the sequential extraction (Rauret et al. 2000a). Finally, in many inter-laboratory studies, most of the errors detected were due to the calibration of the method rather than to the application of the extraction scheme (Lopez-Sanchez et al. 1998). Rauret et al. (2000a)

also gave a detailed account of specific recommendations for metal determination in extracts by commonly used techniques such as ICP-OES and ETAAS etc.

Given the importance of validation for accuracy assessment, additional reference materials comprising different types of soil, sediments, sewage sludge, particulate matter etc., with certified extractable metal contents are urgently needed for quality control. But due to the non availability of sufficient reference materials in this area has prompted many workers to apply sequential extraction procedures to other reference soils and sediments which have been certified for total metal contents, in an attempt to provide interim data, useful in method validation.

Some workers (Pueyo et al. 2005) had given action limits for aqua regia and CaCl_2 extraction procedures for a contaminated soil sample so that those samples can also be used as quality control materials (QCMs). Venelinov and Sahuquillo (2006) gave an excellent account of producing quality control materials to meet the shortage of certified reference materials. The QCMs can be used for the own internal use to optimize the cost of materials and as a complimentary materials and not intended for validation purposes.

Several studies of application of sequential extraction methods to different reference materials had been carried out by various workers and few selected examples are Zemberyova et al. 2006, 2007; Vasile et al. 2006; Larner et al. 2006; Matus et al. 2006; Kubova et al. 2004, 2005; Pueyo et al. 2005; Sutherland and Tack 2002, 2003; Rauret and Lopez-Sanchez 2001; Rauret et al. 1999; Ho and Evans 1997; Hall et al. 1996a, b; Li et al. 1995a, b etc.

7 Other Approaches of Extraction

A major limitation to the wide spread adoption of sequential extraction for trace element sequestration is the lengthy sample processing time (e.g. the Tessier and BCR sequential extraction schemes require an overall operation time of about 18 and 51 h, respectively). Hence, various authors have attempted to develop more rapid means of extraction, involving ultrasonic or microwave assistance and also continuous flow extraction techniques and rotating coiled columns etc. The goal of such studies

is generally to obtain performance similar to that of a well-established methods.

In general, comparing the ultrasonic bath and microwave methods, it can be stated that, from an analytical point of view, the optimal ultrasonic method gives more accurate results than the microwave method and in particular ultrasonic versions of the BCR SES showed a better performance than the Tessier ones in order to attain similar extractability as compared with the conventional SES (Perez-Cid et al. 2001, Filgueiras et al. 2002).

A continuous-flow extraction technique has been proposed by Shiowatana et al. (2001) which has the potential to be an effective and accurate method for fractionating arsenic in soil samples. Benefits of the continuous system as compared with the batch system include the removal of errors associated with repeated centrifugation, filtration and washing. Continuous-flow extraction is faster than batch extraction and is likely to minimise readsorption problems also. An interesting feature to be investigated with continuous-flow extraction is the kinetics of the leaching process of each metal and the chemical associations present.

Rotating coiled columns (RCC) earlier used in countercurrent chromatography have been successfully applied to the leaching of heavy metals from soils and sediments by Fedotov et al. (2005). The use of multistage continuous extraction in rotating coiled columns allowed the reduction of the contact time needed for the separation of each fraction as well as heating being unnecessary for sample oxidation.

Lu et al. (2003) had applied the microwave extraction procedures for the rare earth element analysis in soils using single extractants like 0.05 M EDTA, 0.1 M acetic acid, 0.1 M HCl, 0.05 M CaCl_2 . The recommended technique shortened the operational time and improved the precision and the results were generally consistent with those obtained by using conventional methods.

Acceleration of sequential or single extractions with microwaves yielded, in general, a worse performance as compared with the use of ultrasound (Perez-Cid et al. 2001; Filgueiras et al. 2002) and best results being again obtained for metal partitioning in sewage sludge. It should be noted that heating caused by microwave treatment could cause significant changes on metal extraction, mainly in the labile phases. Also, working with soils, a set of optimised conditions were

recommended for each stage according to the type of soil and the metal to be determined on applying a microwave sequential extraction procedure (Campos et al. 1998). So far, only a few studies have been carried out on acceleration of sequential extractions. Further investigations are clearly needed to assess metal extractability, redistribution and readsorption when replacing conventional treatments (i.e. magnetic stirring, conductive heating) by other involving ultrasonic or microwave energies.

Some of the useful references in this area are Buanam et al. 2006; Nakazato et al. 2006; Tongtavee et al. 2005; Sun et al. 2004, 2005; Vaesaenen and Kiljunen 2005; Chomchoei et al. 2004, 2005; Jimoh et al. 2005; Katasonova et al. 2005; Krasnodebska-Ostrega et al. 2003; Davidson and Delevoye 2001.

8 Application of Chemometric Techniques

Chemometric techniques are applied by different workers in the field of sequential extraction to improve experimental design and also to gain as much useful information as possible from experimental results.

Analysis of variance (ANOVA and MANOVA) has been used to investigate the influence of location on forms of metals in roadside soil (Nowak 1995). Multiple regression analysis has proved valuable in processing sequential extraction data to obtain information on plant availability of trace metals in soils (Qian et al. 1996; Zhang et al. 1998).

Chemometrics have also been used by some workers to overcome some of the intrinsic deficiencies of sequential extraction, such as non-specificity. Barona and Romero (1996) used principal component analysis (PCA) to establish relationships between the amounts of metals released at each stage of a sequential extraction procedure and bulk soil properties, and demonstrated that carbonates played a dominant role in governing metal partitioning in the soil studied. The same workers employed multiple regression analysis to study soil remediation. Zufiurre et al. (1998) also used PCA to confirm their interpretation of phase association and hence potential bio-availability of heavy metals in sewage sludge.

An interesting, and somewhat radical, departure from traditional extraction methodology was proposed by Cave and Wragg (1997). They demonstrated that, with an appropriate chemometric mixture reso-

lution procedure, a simple, non-specific extraction could provide information on metal binding in soil SRM 2710 similar to that obtained by a Tessier sequential extraction. The method used a central composite design, with extraction time, nitric acid concentration and sample : extractant ratio as variables, together with PCA.

Abollino et al. (2002) have used hierarchical cluster analysis (HCA) and principal component analysis (PCA) and discriminant analysis (DA) to obtain a visual representation of the data set and gain insight into the distribution of the pollutants by detecting similarities or differences which would be more difficult to identify only by looking at the tables.

Perez and Valiente (2005) in their studies on pollution trends in an abandoned mining site by utilizing sequential extraction procedure and chemometric treatment of the data employing pattern recognition techniques PCA, HCA observed interesting trends. Statistical evaluation of the results allowed in identification of groups of samples with similar characteristics and observation of correlations between variables determining the pollution trends and distribution of heavy minerals within the studied area.

Tokalioglu and Kartal (2006a) investigated the uptake of several elements by different plants growing in the three vegetable gardens by using statistical methods such as correlation analysis, PCA and cluster analysis. The chemometric treatment of the data allowed a considerable reduction in the number of variables and the detection of structure in the relationships between metals that would give information about the relation between soil and plant systems.

Stanimirova et al. (2006) suggested an advanced method of chemometric data treatment utilizing Tucker N-way method in order to evaluate the level of pollution in soil from a contaminated site because the classical two-way approaches such as PCA are not as good at revealing the complex relationships present in environmental data sets. They also suggest that in the future, applying N-way methods and particularly Tucker method will become increasingly popular when analysing data sets arranged in three-(or higher ways), which is the case for most environmental data sets.

Various other workers have used the different chemometric techniques and some of the interesting examples are of Sarbu et al. 2007; Topalovic et al. 2006; Song and Greenway 2006; Lucho-Constantino et al. 2005; Palumbo-Roe et al. 2005; Cave et al. 2004;

Tokalioglu and Kartal 2003; Santamaria-Fernandez et al. 2002, 2003; Eichfeld et al. 2002; Maiz et al. 2000.

9 Applications of Sequential and Single Extraction Procedures

The sequential extraction procedures have been applied to various types of materials like soil, industrially contaminated soil, sewage sludge and sludge amended soil, road dust and run-off, waste and miscellaneous. The full details of the methodologies adopted by several workers for different variety of samples have been furnished in Table 5 (soil), Table 6 (industrially contaminated soil), Table 7 (sewage sludge and sludge amended soil), Table 8 (road dust and run-off), and Table 9 (waste materials and miscellaneous samples), respectively.

Radionuclides is another important area where single and sequential extraction methods are widely employed. Kennedy et al. (1997), Ure and Davidson, (2001) had reviewed the various methods employed by different workers and therefore, only important applications of sequential extraction to both natural and anthropogenic nuclides are discussed in Table 10.

Finally some of the selected examples of the application of single extractant procedures to soils and other related materials have also been furnished in Table 11.

10 Concluding Remarks

It is now well established that total metal concentrations show poor correlation with either bio-availability for plants or organisms or for predicting the impact of contaminated soils (or sediments) on ground or surface water quality.

Geochemical maps of surface soils and sediments have been prepared on the basis of total concentration. These maps allow to identify “hot spots” and can be used to classify polluted sites. However, by their nature they do not provide information on the reactivity, mobility or accessibility of the metals. For instance it is well known that chromium occurs at high levels in ceratin rock types where it is largely immobile. Extension of this types of maps to include the “reactivity” of the metals as determined by a harmonized extraction schemes offer new possibilities. One can envisage maps

which show the distribution of a certain metal fraction which is linked to plant availability or leachability. With this kind of regional maps it will be possible to identify problem areas for further investigations and, in combination with soil properties, predict the impact of changing land use, large scale civil engineering activities or acid deposition on metal behaviour etc.

A recent comprehensive study by Menzies et al. (2007) regarding the evaluation of single extractants for estimation of the phytoavailable trace metals in soils, of all the extractant types examined (104 studies and 4,500 individual data points collected from earlier works), they conclude that neutral salt solutions tended to provide the best relationship between soil-extractable trace metal and plant tissue accumulation. Of the six relationships examined for neutral salts (1 M $\text{NH}_4\text{CH}_3\text{COO}$ for Cd, 1 M NH_4NO_3 for Cd, 0.1 M NaNO_3 for Zn, and 0.01 M CaCl_2 for Cd, Zn and Ni), all had R^2 values ≥ 0.50 other than the 1 M NH_4NO_3 for Cd ($R^2=0.412$). Similarly, trace metal concentrations determined by extraction using complexing agents (such as the widely used DTPA and EDTA extractants) or acid extractants (such as 0.1 M HCl) were generally poorly correlated to plant uptake. Unlike chelating extractants (such as DTPA), neutral salts remove the metal from the soil solid phase by swamping the soil with the desorbing cation (McLaughlin et al. 2000). Menzies et al. (2007) also indicate that further research is required to investigate the effectiveness of these neutral salt extractants for wide variety of soils.

Basta et al. (2005) in their excellent article concluded that caution is recommended when using only single soil extractants for the estimation of phytoavailability because they only measure metal availability (i.e., soil and residual factors) but plant physiology and rhizosphere biochemistry can alter the relationship between the extractant and plant tissue concentration. For example, rape (*Brassica napus* L.) had a concentration ratio of plant to soil of 1.7 for Cd, about 10 times greater than corn (*Zea mays* L.) (CF= 0.18) grown on the same soil treated with biosolids.

Other methods using diffusive gradients in thin films (DGT) [Nolan et al. (2005) and Nolan (2005); Song et al. (2004)] and lux-marked bacteria (Palmer et al. 1998) rhizosphere-based study by Feng et al. (2005) reported to offer good correlations with the phytoavailable trace metals but little data is currently available to adequately assess these new approaches.

Table 5 Application of sequential extraction procedures to soil (few selected examples)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
1	Contaminated soils from U.S.A	As. Wenzel et al. SEP	The authors carry out sequential chemical extraction experiments on two contaminated soils using a simplified 4-step sequential chemical extraction procedure (SCEP) previously developed to characterize the fractionation of As for better understanding of the different leaching behavior.	Yang and Donahoe 2007
2	Agricultural soils from Jordan	Pb, Cd, As. Tessier SEP	Based on the sequential extraction procedure it is possible to suggest the sequence of metal mobility as: Cd > Pb > As.	Banat et al. 2007
3	Tropical soils from Brazil	Cu, Zn. New SEP developed	The proposed procedure provided more detailed information on metal distribution in tropical soils and better characterization of the various components of the soil matrix.	Silveira et al. 2006
4	Polluted soil from Italy	Cu, Pb, Zn, Al, Fe, La, Sc, V, Ti, Y, Cr, Mn, Ni. Tessier SEP	A sequential extraction procedure was adopted to subdivide total concentrations into 5 operational fractions with different potential toxicity. A chemometric analysis characterized similarities or behavioral differences. High availability of several potentially toxic metals showed the soil needs remediation.	Abollino et al. 2006
5	Uncontaminated calcareous soils from Central Spain	Mn, Zn. Tessier SEP, BCRSEP optimized, SE with EDTA	The EDTA extractable Mn levels were relatively high (on average 30%), but they were less in the case of Zn (on average 3.7%). Manganese was mainly released in the residual fraction when using Tessier procedure (47%) and in the reducible fraction when using BCR procedure (47%). Zinc in these soils was dominantly associated with mineral lattices.	Alvarez et al. 2006
6	Carbonate rich soil from Germany	Ca, Mg, Sr, Ba, Co, Ni, Cu, Pb, Zn. BCRSEP optimized	The influence of carbonate and other buffering substances in soils on the results of a 3-step sequential extraction procedure (BCR) used for metal fractionation was investigated.	Sulkowski and Hirner 2006
7	Soils and vegetable samples from Turkey	Cu, Fe, Co, Ni, Cd, Cr, Pb, Zn, Mn. BCRSEP optimized	The relationship between the vegetable-metal and soil-extractable metal concentrations was examined in order to evaluate the bioavailability of metals.	Tokalioglu et al. 2006a
8	Soil, stream samples from NE Scotland	Pb. BCRSEP optimized	Sequential extraction combined with isotope analysis was studied as a tool for assessing mobilization of Pb into streams at an upland catchments in NE Scotland.	Bacon et al. 2006
9	Podzolic soil near Quebec in Canada	Pb, Cr. SEP of Land et al., modified, SE 1M NH ₄ Cl	A complete sequential extraction procedure has been applied to help understanding the complex chemical speciation of Pb in forest soils. The distribution of Pb and Cr in the studied forest soils mainly reflects progressive contamination of the watershed by anthropogenic sources.	Ndzangou et al. 2006
10	Urban soils from five European cities	Cr, Cu, Fe, Mn, Ni, Pb, Zn. BCRSEP optimized	High lead concentrations were present in some soils (>500 mg kg ⁻¹) and the potential exists for remobilization under reducing conditions. No overall relationships were, however, found between analyte concentrations and land use, nor between analyte partitioning and land use.	Davidson et al. 2006

Table 5 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
11	Soils near Oak Ridge Reservation site in U.S.A	Hg. SEP of Bloom et al.,	Sequential extraction analysis showed that both sol. and bioavailable Hg fractions were relatively small proportions whereas the organic matter bound mercury fraction constituted the major form of Hg species in the sample.	Liu et al. 2006a
12	Humic iron podzol soils from Scotland	Cr, Cu, Ni, Cd, Pb, Zn. BCRSEP original	The distribution of metals between each of the extracted fractions varied not only between each metal but also between each of the three soils indicating that both metal and soil influenced the measured distribution.	Bacon et al. 2005
13	Soil from Almaden, Spain	Hg. BCRSEP optimized, CIEMAT SEP, Digiulio and Ryan SEP	There were important differences in the mercury extraction results obtained by the three procedures according to the reagents applied and the sequence of their application. These findings highlight the difficulty of setting a universal sequential extraction procedure to obtain information on metal fractions of different mobility for any soil sample, as well as the requirement for knowledge about the mineralogical and chemical characteristics of the samples.	Sanchez et al. 2005
14	Soils from Slovakia	Se. 5 step SEP, SE with $\text{KH}_2\text{PO}_4 + 2\text{HPO}_4$ (pH 7.0; P-buffer)	The sequential extraction method used allows differentiation of five forms of selenium bound in soils. The single-step extraction releases different forms of selenium: sol., adsorbed, ligand-exchangeable, and plant protein-bound. Application of the P-buffer to soils resulted in a low recovery of selenium (3–12%) when compared to the total selenium content of the respective soils.	Hagarova et al. 2005
15	Soils from Czech Republic	As, Cd, Pb, Zn. 5 SEPs#	Regardless of the studied element, the poorest results were determined for reducible and oxidizable soil fractions. The application of at least two independent procedures or modification of the extraction scheme according to element investigated and/or particular soil characteristics can also be helpful in definition of element pattern in soils in further research.	Tlustos et al. 2005
16	Agricultural soils from Japan	Se. New SEP developed	A new sequential extraction procedure was applied to 12 soil samples in order to quantify the effect of soil components on Se adsorption. The sequential extraction results showed that 80–100% of the adsorbed Se was recovered as Al-bound Se and Fe-bound Se.	Nakamaru et al. 2005
17	Unpolluted soils from southern Spain	As, Pb, Cd, Cu, Co, Cr, Zn. BCRSEP optimized	BCR and total analysis closely agreed for As, Pb and Cd. For Cu, Co, Cr and Zn the comparison of the results did not provide definitive conclusions concerning the capability of BCR in measuring total concentrations.	Fernandez et al. 2004
18	Soil sample from Cuba	Ni, Cd, Cu, Zn. Tessier SEP	The Tessier procedure was modified by taking the extracted fractions into HCl medium, with final determination by flame at. absorption spectrometry with a nonconventional nebulization system.	Alleyne et al. 2004

Table 5 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
19	Agricultural soils from Chile	Sb. New SEP developed	The proposed extraction scheme can provide information about the availability and mobility of antimony redox species in agricultural soils.	Fuentes et al. 2004b
20	Polluted soil and sediments from Morocco	Cr, Cu, Mn, Ni, Pb, Zn. BCRSEP optimized	In soils, Ni and Mn can be regarded as moderately available followed by a lower availability of Pb while Cu, Zn and Cr have a very limited availability. In sediments, a higher availability of Mn and Zn was observed followed by a lower availability of Ni and Pb, whereas, Cu and Cr, were of very limited availability.	Elass et al. 2004
21	Urban and suburban agricultural soils from China	Cd, Cr, Cu, Ni, Pb, Zn, Mn. BCRSEP optimized	Measured data indicated a low risk for surface and ground water contamination from the urban soils in the Hangzhou City.	Zhang and Wang 2003
22	Soils affected by an accidental spill in Spain	Al, Ca, Fe, Mg, Mn, As, Bi, Cd, Cu, Pb, Tl, Zn. BCRSEP optimized	The procedure was used to obtain the distribution of both the major and trace elements in 13 soils of contrasting properties with various levels of contamination and in the sludge itself. Comparison with soil–plant transfer factors, calculated in plants growing in the affected area, indicated that a relative sequence of trace element mobility was well predicted from data of the first step.	Pueyo et al. 2003
23	Soil samples of the Swiss Jura	Cd, Cu, Ni, Pb, Zn. 3 new SEPs developed each with 6 steps	Three schemes were selected and applied to three different soil samples of the Swiss Jura. The results showed that metallic trace elements extraction with ammonium oxalate are very dependant on the metal studied. The reason could be the capability of oxalate to form stable complexes with the metals considered which sometimes are only slightly soluble.	Benitez and Dubois 1999
24	Soils from Czech Republic	As, Cd, Zn. BCRSEP optimized	The influence of selected soil properties (pH, sorption capacity, organic matter, and clay-silt-sand content) on the distribution of As, Cd, and Zn was evaluated.	Szakova et al. 1999

SEP:sequential extraction procedure

SE:single extraction

BCRSEP:Community Bureau of Reference (Now the Standards Measurement & Testing Program) sequential extraction procedure

Tessier SEP:Tessier sequential extraction procedure

#BCRSEP optimized; Tessier SEP modified by Li; Zein SEP; Wenzel et al. SEP; Azcue et al. SEP

The use of different neutral salt solutions at our laboratory for the estimation of extractable elements in wide variety of soil samples indicated that the magnitude of extraction is similar for all the three commonly used reagents like 0.1 M NaNO₃, 0.01 M CaCl₂, 1 M NH₄NO₃ although in absolute terms the values obtained from 0.1 M NaNO₃ are marginally lower than 0.05 M CaCl₂ and 1 M NH₄NO₃ (Pueyo et al. 2004). This clearly indicate that any one of the above three reagents is suitable for the estimation of

phytoavailable or easily leachable metals. So efforts should be made to harmonize the single extraction protocol similar to BCR sequential scheme so that interlaboratory comparisons can be made and finally reproducible and accurate procedure can be established.

Our studies dealing with the use of complexing agents like DTPA, EDTA and strong acids like HCl for the extraction of various metals in different soil and other related materials, gave very high recoveries as reported by earlier workers (Menzies et al. 2007),

Table 6 Application of sequential extraction procedures to industrially contaminated soils (few selected examples)

Sl. no	Matrix	Elements deter-mined and method adopted	Remarks	Reference
1	Contaminated soils near copper smelter	Cu, Zn, Pb, Cd. Tessier SEP	The degree of metal contamination was assessed using an index of geo-accumulation. The order of mobility was Zn>Cd>Cu>Pb.	Hu et al. 2006
2	Mining site soils	As, Sb. Wezel et al. SEP, SE with NH ₄ NO ₃	A non-specific-sequential extraction test showed As to be strongly associated with Fe (and Al) oxyhydroxides. In the case of Sb, in addition to the crystalline Fe-oxide bound Sb the Al-silicate phase also appeared to be significant. At both sites Sb appears to be chemical more accessible than As with consistent availability despite the varied origin and host soil properties.	Gal et al. 2006
3	Mining site soil	W. BCRSEP optimized and SE with EDTA	Tungsten appears to be relatively immobile when subjected to sequential extraction but increased bioavailability is indicated when single stage extraction using EDTA is employed.	Wilson and Pyatt 2006
4	Contaminated soils from different industries	Zn, Cr, Cu, Ni, Co, Pb, Hg, Cd, As. SEP	Relatively high percentages of Zn, Cu, and Cr associated with mobile fractions, and correspondingly high concentrations of Zn, Cr, Cu, and Pb in forage grass samples and a high degree of bioavailability to humans. Human exposure assessment revealed high concentrations of Pb, Zn, and Cr in blood and urine samples from the residents of the study area showing a direct pathway and a potential for toxicological hazard due to heavy metal pollution.	Sekhar et al. 2006
5	Contaminated soils near a copper smelter	Cu, As, Pb. Several SEP and SE procedures used#	The soils showed the following order of total metal concentration: Cu>As>Pb. Single correlation analysis was applied between the amount of metal in the single extraction method and the different fractions obtained with the sequential technique. Significant positively correlations were obtained, especially for copper and lead.	Ahumada et al. 2004
6	Contaminated soil sites near copper smelter	Cd, Cr, Cu, Pb, Zn. 6 step SEP, SE with aqua regia	Based on the assumption that the mobility of metals decreases in the order of the extraction sequence, the difference in mobility amongst metals in the three soil cores measured in this study were in the order: (Cd)>Zn≈Cu>Pb>Cr. The two contaminated sites may represent potential health and environmental hazards because of their high sol. metal content and hence a site-specific investigation is required.	Martley et al. 2004
7	Highly contaminated soil & SRMs	As. BCRSEP original and two other SEPs proposed by Manful	The sequential extractions of SRMs showed that the extraction schemes based on the phosphorus-like protocol proposed by Manful gave a more refined fractionation of As than the three-step BCR scheme. The major part of arsenic was released from the heavily contaminated samples after NaOH-extraction.	Van Herreweghe et al. 2003
8	Industrial and mining site soils	As. Tessier SEP	The results reveal that the samples are highly polluted by metals and arsenic and present very peculiar matrix characteristics, such as very high iron or carbonate contents, as compared to natural soils. Arsenic appears as an element easily mobilized when the environment	Gleyzes et al. 2002b

Table 6 (continued)

Sl. no	Matrix	Elements deter-mined and method adopted	Remarks	Reference
9	Contaminated soils from the lead and zinc mining area	Cd, Pb, Zn. BCRSEP optimized	becomes more reducing and presents an elevated risk of transfer to the groundwater. The results indicate that Cd, Pb and Zn in natural soils prevails mostly in sparingly soluble fractions. In contaminated soils, Cd, Pb and Zn are distributed between the easily and sparingly soluble fractions. Due to the high total Cd, Pb and Zn concentrations in contaminated soils close to the smelter, and their high proportions in the easily soluble fraction (80% of Cd, 50% of Pb and 70% of Zn), the soil around smelters represents an environmental hazard.	Pustisek et al. 2001
10	Fe-rich industrial or mining site soils	As. Tessier SEP and SE with EDTA	Results showed that classical Tessier's scheme over-estimated residual As. A scheme specific to anionic species was also not really suitable to evaluate As distribution in Fe-rich soil. A simplified, less time consuming scheme was established, tested on diverse industrial soils, and validated on a certified sediment reference material.	Gleyzes et al. 2001
11	Soils contaminated with slag	Ag, Cu, Ni, Pb, Zn. Tessier SEP	Through additional application of sequential extraction to the pure slags as well as to the uncontaminated soil, it was shown that during the various extraction steps applied to the soil/slag mixtures substantial redistribution of the metals between the slag and soil particles can occur.	Bunzl et al. 1999
12	Industri-ally contaminated soil	Cu, Pb, Mn, Zn. BCRSEP original	Significant differences in operational speciation were obtained when the procedure was carried out independently by three different analysts. This may be due to the critical effect of pH in step 2. Reproducibility was higher for air-dried than for field-moist soils, but larger amount of metals were extracted, suggesting alterations in speciation occurred during drying.	Davidson et al. 1999b

No. 5 step SEP for Cu, Pb and 4 step SEP for As and SE With 1M HCl, 0.005M DTPA, 0.05M EDTA, 0.1M malic-citric acid.

hence they may not be suitable for phytoavailable metal contents evaluation investigations.

Although the sequential extraction approach is unlikely to provide precise information on the mineral phases to which trace metals are bound, it does provide information on potential mobility of metal contaminants. Attempts to quantitatively predict phytoavailability and toxicity from sequential extraction data alone have not typically been successful (McLaughlin et al. 2000 and references therein). This is not only due to limitations of analytical fractionation or speciation techniques, but also to the complexity of the interactions between metals and biota, which needs to be taken into account when

estimating metal phytoavailability. Sequential extraction methods should be used in conjunction with plant bioassays to determine residual effects on phytoavailability. Similar conclusions had also been drawn by Iwegbue et al. (2007) in their review article on the application of various extraction schemes applied to composts and compost amended soils. They also recommend that along with chemical extraction tests bioassay tests should also be carried out, together, so that complete field test situation will emerge which can significantly help in evaluating the level of risk of heavy metals.

Further, a recent interesting study by Neel et al. (2007) indicate that compared to direct in situ

Table 7 Application of sequential extraction procedures to sewage sludge and sludge amended soils (few selected examples)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
1	Sewage sludge	Ni, Cr. Tessier SEP	Composting appeared to reduce Ni and Cr availability by stabilizing the two metals and making them more stable and less mobile.	Zheng et al. 2007
2	Composted sludge	Cu,Zn,Ni,Cd,Cr. Tessier SEP	Only the content of the total mobile fractions for Cu could be predictable from its total content. For the prediction of the total mobile fractions of Zn, Ni, Cd and Cr, the R ² value was significantly increased by the inclusion of other variables such as pH, temperature and organic matter content.	Liu et al. 2007
3	Compost, sewage sludge	Cu, Zn. BCRSEP optimized	The aim was to obtain information about their bioavailability, mobility, and toxicity, and correlation among the different soil extracted fractions.	Pedra et al. 2006
4	Sludge amended soil	Cr, Cu, Ni, Zn. BCRSEP optimized, Geological survey of CanadaSEP	Two sequential extraction procedures were applied to study Cr, Cu, Ni and Zn speciation in control soils and sludge-amended soils. Sewage sludge spreading over a 2-yr period did not have an impact on soil borne heavy metal concentrations but affected speciation of the most mobile fractions of Ni and Zn.	Doelsch et al. 2006
5	Sewage sludge & sediment	Cu, Pb, Cd, Zn. BCRSEP original	The procedure was applied to 4 sewage sludge samples and sediment, collected on selected sites before and after the effluent of urban wastewaters in a river and taken from wastewater treatment plant.	Lihareva et al. 2006
6	Different type of sludges	Cd, Cu, Fe, Mn, Ni, Zn. BCRSEP optimized, SE with DTPA	The sequential extraction of the compost showed a slight increase in Cd and Cu availability, and a decrease in the availability of Fe, Mn, Ni and Zn. Pelletization increased the availability of Ni and slightly reduced that of Cr. The dewatering sludge led to greater availability of Cr and Mn but reduced the concentration of Cd. The three different sludges also affected seed germination and root elongation in different ways.	Walter et al. 2006
7	Sludge amended agricultural soils	Zn. Tessier SEP, SE with DTPA	A positive and significant correlation ($r^2=0.96$) was found between the Zn concentrations extracted with DTPA and sum of F1 and carbonate-bound (F2) fractions in the sequential extractions. The concentrations of Zn extracted with DTPA were strongly correlated with the concentrations of Zn in the shoots of Chinese cabbages, indicating that F1 F2 in the sequential extractions was reliable for predicting Zn bioavailability to Chinese cabbage in the biosolid-treated soils.	Hseu 2006
8	Sludge amended soils	Cd, Cu, Pb, Zn. 2 SEPS. BCRSEP optimized and a new SEP	Significantly increased amounts of extractable metals (Cd, Cu, Pb and Zn) were evident in the sludge-amended soils compared to control soil by all extraction schemes; however, the amounts of metals extracted by each step were strongly dependent on the order of extraction, the type of reagents and the nature of the individual metals.	Kim and McBride 2006
9	Sewage sludge and BCR 483	Cu, Cd, Cr, Pb, Ni, Zn. BCRSEP optimized	The results of the partitioning study of untreated industrial wastewater sewage sludge indicate that more easily mobilized forms (acid exchangeable) were predominant for Cd and Zn, in contrast, the largest	Kazi et al. 2006

Table 7 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
10	Sewage sludge	Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn. 3 SEPs, SE with 3 reagents	amount of Pb and Cr was associated with the Fe/Mn oxide and organic matter/sulfide fractions. Metals speciation by Tessier et al. (1979), and Rudd et al. (1988), and a procedure recommended by BCR as well as analysis of chemical forms of metals, were carried out. Preparative extraction of metals from the sewage sludge using sodium salt of EDTA (Na), sodium pyrophosphate (V), and ammonia water was also investigated. As far as the examined leaching agents are concerned, EDTA-Na appeared to be the best.	Turek et al. 2005
11	Different type of sludges	Cd, Cr, Cu, Fe, Ni, Pb, Zn. BCRSEP optimized, SE with water and DTPA	The stabilization treatment undergone by the sludges strongly influenced the heavy metal distribution and the phases to which they were associated and their bioavailability level. The DTPA extraction procedure is cheap and easy to perform and the obtained results are similar to those obtained with the sequential procedure.	Fuentes et al. 2004a
12	Sewage sludge and CRM 483	Cu, Cr, Ni, Pb, Zn. Tessier SEP, SE with EDTA, Acetic acid	The results obtained with these samples for Cu, Cr, Ni, Pb and Zn using the Tessier method were compared with those supplied by the two single extraction procedures employed. In addition, the Tessier method was also applied to a reference material, CRM 483, and these results were also compared with the certified EDTA and acetic acid values for this sample.	Perez-Cid et al. 2002
13	Sewage sludge	Zn, Cd, Cu, Ni, Pb, Cr. Zeien SEP	Eleven years after the last application the metals supplied with the sludge had moved as far as 50 cm in depth. Nine years after the last application, the binding species of heavy metals were still different compared with those in the untreated soil. The whole withdrawal of heavy metals by plants yielded <1% of the applied amounts	Schaecke et al. 2002
14	Sludge amended soil	Cd, Zn. BCRSEP optimized	The addition of sewage sludge led to significant changes in Cd and Zn separation into the main fractions. The water-soluble (plant-available) fraction correlated with pH of the soil and/or sewage sludge added to the soil. The sequential extraction procedure can reasonably elucidate the changes in element distribution in soil fractions by changing physicochemical properties of the soil.	Szakova et al. 2001a
15	Sludge amended soil and CRM 483	Cd, Cr, Cu, Ni, Pb, Zn. BCRSEP optimized, SE with EDTA and aqua regia	The paper demonstrates the CRM 483 long-term stability for EDTA and acetic acid extractable contents of Cd, Cr, Cu, Ni, Pb and Zn and gives the results (obtained in the framework of an interlab. study) for the extractable contents of the same elements in the CRM 483, following the BCR three-step sequential extraction scheme. The aqua regia extractable contents following the ISO 11466 Std. are also given. The data are given as indicative (not certified) values.	Rauret et al. 2000a
16	Sewage sludge	Cu, Cr, Ni, Pb, Zn. Tessier SEP, BCRSEP optimized	The results obtained by SEPs for Cu, Cr, Ni, Pb, and Zn were compared with those estimated from single extractions using identical operating conditions applied in each individual Tessier and BCR fraction. The total	Albores et al. 2000

Table 7 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
17	Sewage sludge	Cu, Cr, Pb, Ni, Zn. Tes-sierSEP, BCRSEP	extractable metal contents obtained by both single and sequential extractions were similar for all metals in the BCR method and for Cr, Ni, and Pb in the Tessier. Both sequential extraction schemes yielded similar performance when extraction efficiencies were compared but matrix effects caused by concomitants were less pronounced in the BCR scheme in comparison with the Tessier scheme.	Perez-Cid, et al. 1996

measurements, extractions gave meaningful estimations of the relative trace element mobility, which is of interest for phytoremediation purposes or for assessing the element phytoavailability with out costly direct plant analyses. However, they also mention that previous mineralogical analyses and the examination of the solid residues will provide crucial information for the interpretation of the extraction results. At the end they also conclude that extraction approach alone is not appropriate for long term matters such as sewage sludge risk assessment etc.

The primary importance of proper sampling protocols has also been emphasized, since the sampling error can cause erroneous results even using highly sophisticated analytical methods and instruments. It was recognised that vital information on the distribution of trace-metal fractions may be lost in some cases when (soil or sediment) samples are dried. However, drying is certainly the best compromise for achieving stability of samples and interlaboratory comparability because of the better homogeneity of dried samples. Further work is certainly recommended to determine the bestway of stabilising samples (including reference materials) so that original trace element pattern is maintained during storage, prior to application of methods such as single and sequential extraction.

Even though sequential extraction procedures provide useful information in environmental studies and an increasing number of publications have appeared over the last few years, they also have some limitations and draw backs (Kheboian and Bauer 1987; Nirel and Morel 1990; Scheckel et al. 2003).

Julian and Collado (2002) in their review of sequential chemical extraction (SCE) of heavy metals mention that the major problems in sequential chemical extraction are 1. reagent selectivity 2. operative defini-

tion of methods 3. elemental redistribution or read-sorption 4. variable experimental conditions 5. scarcity of certified reference materials 6. major difficulty to validate the existing methods 7. and the evaluation of its precision. In spite of all the above methodological problems, they indicate that, at the present time sequential extraction protocols constitute the better approach to describe the geochemical association of trace elements with different fractions of solid materials.

Sutherland and Tack (2003) has emphasized that sequential extraction procedures should always be applied with full consideration of their limitations. Unless improved procedures can be developed that can be properly standardized and provide better, more conceptually defined fractions for a range of samples, it will be difficult to select one single scheme for future use. However, the optimized BCR procedure is currently the only scheme that is harmonized and standardized, and certified reference samples are available (most recently CRM 701). This is a significant advantage and provides for a degree of comparability between researchers generally not obtainable for the other procedures presented in the literature. Having said this, it is likely that the more commonly used sequential extraction schemes (i.e. the Tessier procedure) will continue to be employed by researchers. It is paramount that researchers rigorously follow the stated procedures for a selected scheme. In addition, caution should always be exercised when interpreting the results of sequential extractions, because artifacts of the scheme not only depend on the operational conditions of the method, but also vary from element to element and between different sample types.

D'Amore et al. (2005) in their review on methods for speciation of metals in soils also reveal interesting

Table 8 Application of sequential extraction procedures to road dust and run-off (few selected examples)

Sl. no	Matrix	Elements deter-mined and method adopted	Remarks	Reference
1	Dust samples from Mexico	Ni,Cr,Zn,Cd,Co,Ba, V,Pb, Fe, Cu. SE with HNO ₃ and ultrasoni-cation	The results of this study reveal that heavy metals distribution is different in two areas of the city. The distribution of the heavy metals in dust does not seem to be controlled only by the topography of the city, but also by the location of the emission sources.	Meza-Figueroa et al. 2007
2	Road dust from Italy	Ba, Cu, Cr, Mo, Pb, Sb, Zn, Ni, V. Tessier SEP	The results indicate that the road dust samples contain non-soil-derived elements, whose primary contributors appear to be vehicular traffic and the nearby petrochemical plant. Results of sequential extraction analysis show that most metals are mainly distributed in the non-residual fractions and particularly in the organic/sulfide and Fe–Mn oxides fractions.	Manno et al. 2006
3	Urban dust from Czech Republic and SRM 1648	As, Cd, Cr, Mn, Ni, Pb, Zn, Cu, Fe. BCRSEP optimized	Work focused on toxic element concentrations in dust samples and their distribution and finding differences between two tunnel samples using the estimated mobility of trace elements, some macro-component comparisons, and further major mineralogical phases determinations.	Sysalova and Szakova 2006
4	Road side soils from Nigeria	Pb, Cu and Zn. BCRSEP optimized	Data obtained indicated that more than 50% of the metals were associated with the residual fraction, reflecting lithogenic-pedogenic control. Zinc had one-sixth of its quantity in the most mobile and/or bioavailable fraction, which is susceptible to release into solution with the decrease in pH. The amount of lead associated with the reducible fraction was significant, while an appreciable amount of copper was associated with oxidizable fraction (19%).	Yusuf 2006
5	Roadside soils from Sweden	Pb, W. 4-step SEP developed	Sequential extraction indicated that lead mainly was associated with reducible (34.4%) and oxidizable (35.4%) fractions. Tungsten was also found at high concentrations indicating a possible impact from studded tires. The multivariate technique principal component analysis (PCA) seems promising for evaluating large sequential extraction datasets.	Baekstroem et al. 2004
6	House and indoor dust samples from Turkey	Cu, Ni, Cd, Cr. BCRSEP optimized	Generally, most of the elements were found in the oxidizable and residual fractions. The total concentrations of trace metals analyzed were found in the range, for Cu: 62.4–119.8, Ni: 37.8–97.8, Cd: 2.54–4.27 and Cr: 38.7–53.5 mg/kg. The results are in agreement with the reported values in the literature.	Soylak et al. 2004
7	Road dust and road side soils from France	Pb,Cu,Cd, Zn,Ni,Cr. Various SEPs and SE are used	The profiles of total levels in the soil as a function of distance from the road edge and as a function of depth were investigated. Pb, Zn, Cu and, to a lesser extent, Cd contamination were found in samples taken on the surface and	Pagotto et al. 2001

Table 8 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
8	Road dust and soils from Hong Kong	Cd, Cu, Pb, Zn. Tessier SEP	in the immediate vicinity of the road. Soil samples appeared to exhibit little Ni and Cr pollution. Selective soil and road dust samples were also analyzed for potential chemical speciation by a sequential chemical extraction method. The chemical partitioning results show that Pb and Zn are mainly in the carbonate/adsorbed and Fe–Mn oxide phases, while Cu is largely associated with the organic and sulfide fractions. The high exchangeable Cd in urban soils and high concentration of Zn in street dusts need further investigation for their ecol. and health implications.	Li et al. 2001
9	Airborne dust from Germany	Heavy metals. 4-step SEP developed	The influence of variable extraction ratios (ratio of sample amount and vol. of extraction solvent) and the influence of intensive treatment of dust sampled by the Bergerhoff method prior to sequential extraction was within the precision of measurement of the method.	Heiser et al. 1999a
10	Road dust, House dust, Indoor dust and stream sediment samples from South Korea	Cd, Cu, Pb, Zn. Davidson et al. SEP	The Pollution Index of multi-element contamination levels in road dust is found to correlate with a calculated Urbanization and Industrialization Index. Elevated levels of Cu, Pb and Zn are also noted in house dusts near the Yusung Highway Junction and industrialized areas. A sequential extraction procedure applied to stream sediments indicates a high percentage of easily exchanged metals. The exchangeable phase of the metals may originate not from parent materials but from wastewaters and exist in an adsorbed phase on the surfaces of sediments.	Kim et al. 1998

information on the shortcomings of chemical extraction methods such as (a) As the present sequential chemical extraction methods were meant for trace metals in sediment materials, their application to heavily contaminated soils may be suspect when concentrations of the “trace” metals are no longer trace but major constituents. In this situation, the metal chemistry is no longer dominated by the other major components of the system, but is itself controlling the chemistry of other elements (b) Comparisons of sequential extractions with thermodynamic models and direct instrumental analyses are lacking (c) Application of sequential extraction methods to lead

contaminated, phosphorous amended samples results in the formation of pyromorphite [$Pb_4(PO_4)_3Cl$] during the extraction steps and hence the over – and underestimation of metal concentrations in particular steps of an extraction method could pose serious consequences in addressing risk assessments based solely on extraction results. Finally, they conclude that extraction schemes can be a useful tool in metal partitioning but always be confirmed by other methods.

The increasing number of scientific papers making reference to the so-called “BCR scheme” (referring to the sequential extraction protocol) and the single extraction procedures (in particular EDTA) illustrates

Table 9 Application of sequential extraction procedures to waste and miscellaneous materials (few selected examples)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
1	Industrial fly ash	Co, Ni. Five step SEP developed	Five step sequential extraction was carried out in order to characterize metal mobility in environmental conditions. The research involved (1) water-sol. (pH=7), (2) acid-sol. (pH=5), (3) oxide, (4) sulfide and (5) residue metal fractions.	Soco and Kalemkiewicz 2007
2	Flotation residues of a zinc and lead sulfide mine	Zn, Pb, Fe, Mn. Zein and Brummer SEP	In this study, the vertical distribution and speciation of Zn and Pb in the fine-grained flotation residues of a former sulfide ore mine in Germany were investigated to assess the inorganic weathering processes that effect the environmental risk arising from this site.	Schuwirth et al. 2007
3	Charcoal	Al, Cr, Cu, Ni, Zn, Cd, Ag, Pb. Five step SEP developed	In this study, authors test the robustness of a typical sequential extraction technique by applying it to naturally occurring charcoal that had been spiked with five different concentrations of metal ions. The method was then applied to contrasting soils mixed with this spiked charcoal.	Ma and Rate 2007
4	Sulfide tailings	Al, Mn, Cu, Zn, Ni, Pb, As. Cr, Cd. Zeien and Brummer and Das et al. SEPs	This study suggests that adding sewage sludge to the mine tailings at Aitik would not counteract the effects of the sulfide oxidation in the tailings. Furthermore, using a sequential extraction technique proved preferable to using total metal analysis in order to predict plant uptake of the elements in the tailings.	Forsberg and Ledin 2006
5	Mining waste	Pb, Zn, Cu, As, Cd. BCRSEP and SE with DTPA	BCR procedure and DTPA extraction protocol were applied in the different mining wastes in order to study Pb and Zn mobility and likely bioavailability to <i>Betula pendula</i> growing on the same mining spoils, which presents lead and zinc contents in leaves over ten times background values.	Margui et al. 2006
6	Mining waste	As, Cu. Tessier SEP and Wenzel SEP	Ten soil samples with Cu concentrations of 300–6,144 mg/kg and As concentrations of 5,512–397 15 mg/kg were sequentially extracted using two SEP. Although the total concentrations of Cu in the soils are much lower than As, Cu appears to be solubilized to a much greater extent as indicated by the higher percentage contribution of Cu in the easily mobilisable fractions.	Dybowska et al. 2005
7	Municipal solid waste	Cu, Ni, Pb, Zn, Cr, Fe, Mn, Cd. Tessier SEP	Based on the average of abs. values for the three depth levels, the bioavailability order of metals is Zn>Mn>Pb>Ni>Cu>Fe>Cr>Cd. Recovery obtained by comparing the aqua regia extracted metal content with the sum of sequentially extracted fractions was at 91–110%.	Esakku et al. 2005
8	Anaerobic granular sludge from waste water treatment plant	Co, Ni, Zn, Cu, Mn, Fe. Tessier SEP, Mossop and Davidson SEP, Stover SEP	The Stover scheme displayed a higher number of fractions which induced a poor recovery vs. the other schemes. The sequential extraction scheme recommended by Mossop and Davidson and the modified Tessier scheme gave similar trends. As a final conclusion, the modified Tessier scheme	Van Hullebusch et al. 2005

Table 9 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
9	Industrial waste water sludge & BCR 483	Cr, Pb, Ni, Cd. BCRSEP optimized	seemed the most suitable to study metal partitioning in anaerobic granular sludges. The procedure was evaluated using a certified reference material. The results from the partitioning study indicate that more easily mobilized forms (acid exchangeable) of Cd were dominant. The oxidizable fraction was dominant for all four toxic metals.	Kazi et al. 2005
10	Landfill site (operated for 50 years)	Pb, Cd, Ni, Co. Tessier SEP	Results showed that the smallest amounts of heavy metals were bound with carbonates in fraction II and in exchangeable fraction I. This fact proves their limited availability to plants, soil and water.	Rosik-Dulewska, Karwaczynska 2004
11	Waste Pb–Zn mining areas & BCR 701	Ni, Zn, Pb, Cd. BCRSEP optimized	The results indicate that more easily mobilized forms (acid exchangeable) were predominant for Cd and Zn, particularly in the sample from Cartagena. In contrast, the largest amount of Pb was associated with the Fe and Mn oxide fractions	Margui et al. 2004
12	Fly ash amended soil, tailing samples	Pb, Zn, Cd. Tessier SEP, SE with EDTA	The fly ash treatment resulted in the redn. of TCLP solubility of Pb, Zn and Cd to below the respectively regulatory limits at 5 and 10% wt./wt. fly ash addition rates in tailings and soil, respectively.	Stouraiti et al. 2002
13	Coal fly ash NBS 1633a, NIST 2709, CRM 320	Cd. BCRSEP original	The sum of the cadmium present in the individual fractions shows a good agreement with the certified value of total cadmium content. The extraction efficiency is higher than 85%. The extractable cadmium gives information about the binding forms of this element in these reference materials.	Petit and Rucandio 1999

that these procedures are now internationally recognised as reference methods for soil and sediment studies (Quevauviller 2002).

Dahlin et al. (2002a, b) in their studies indicate that sequential extraction procedures which were developed to characterise pollutant species in normal soil and sediments may be unsuitable for industrial site materials which contain larger pollutant particles, encapsulated pollutants, and / or man-made materials e.g., slags, metals and plastics. However, they mention that if employed as part of a comprehensive, site – specific characterization study, sequential extractions could be a very useful tool. This study reveals that more standardized sequential chemical extraction procedures should be developed for various types of materials to get more reliable and useful data about the different phases of the toxic metals in wide variety of materials.

Song et al. (2004) in their review of sequential extraction technology point out that this technology will develop in two new directions i.e., microwave heating-continuous flow-sequential extraction (MCSE) technology and microwave heating-ultrasonic vibrating-kinetic-parallel extraction (MUKPE) technology. SCE methods have also been utilized for the identification of the status of available nitrogen in the soil by Kodashima et al. (2005); and Bacon et al. (2006) combined SCE with isotope analysis as a tool to assess mobilization of lead into streams and several others used SCE methods for wide variety of applications.

Significant developments are being made in the application of chemometric procedures in SCE and Stanimirova et al. (2006) proposed a Tucker N – way method which can analyse data sets arranged in three – (or higher ways), which is the case for most environmental data.

Table 10 Application of sequential extraction procedures to radionuclides (few selected examples)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
1	Soil	Th. Martinez–Aguirre SEP	In this study, the sequential extraction procedure developed by Martinez–Aguirre was employed for quantification of different chemical forms of thorium in the soil. A comparison was carried out between the sequential extraction and the single extraction to evaluate the selectivity of the extractants.	Guo et al. 2007
2	Phosphogypsum samples	Ra-226, Pb-210, Th-232, U-238. H ₂ O, MgCl ₂ , NaOAc/HOAc, HNO ₃ /H ₂ O ₂ applied in sequence	The sequential extraction results show that most of the Ra and Pb are located in the iron oxide (non-CaSO ₄) fraction, and that only 13–18% of these radionuclides are distributed in the most labile fraction. It can be concluded that although all these elements are enriched in the phosphogypsum samples they are not associated with CaSO ₄ itself and therefore do not represent a threat to the surrounding aquatic environment.	Santos et al. 2006
3	Soil	U-238, Th-230, Ra-226. National Institute of Standards and Technology(NIST) SEP	A new version of a classical method was applied to study the distribution of natural radionuclides (²³⁸ U, ²³⁰ Th, and ²²⁶ Ra) in the soil fractions obtained by a sequential extraction procedure. The results confirmed that, if only non-residual fractions are considered, the sequential method applied shows a characteristic speciation pattern of these natural radionuclides in this soil matrix, i.e., the distribution of each of the three radionuclides was very similar for the two soil samples.	Blanco et al. 2005
4	Soil	U-238. Tessier SEP and M.K. Schultz's SEP	Reproducibility studies of each method and a comparison between the two sets of results were performed for uranium, thorium, and radium. The results were different for each radionuclide. Analysis of the extracted fractions was carried out by alpha spectrometry.	Blanco et al. 2004
5	Soil	Pu. Modified from Tessier SEP	Sequential extraction of Pu showed that the ion-exchangeable Pu fraction in soils was dramatically increased with DTPA treatment and decreased with time of incubation. Extractability of Pu in all fractions was not different when Pu-nitrate and Pu-citrate were applied to the same soil. More Pu was associated with the residual Pu fraction without DTPA application.	Lee et al. 2002
6	Soils	Cd-109, Zn-65. BCR SEP optimized	Using radiotracer techniques, the redistribution of Cd and Zn during sequential extraction was directly quantified.	Ho and Evans 2000
7	Mineral and organic soils	Radiostromium and radio cesium. 3 SEPs developed and used.	Three sequential extraction schemes(Common, acid, organic) were used and aging was quantified in different soils by changes in radionuclide distribution. Changes in the radionuclide exchangeable fraction over time in these soils corresponded to changes in transfer factors over a similar period.	Rigol et al. 1999

Table 10 (continued)

Sl. no	Matrix	Elements determined and method adopted	Remarks	Reference
8	Soil contaminated by slags	U-238, Ra-226, Pb-210, Ra-228. Tessier SEP	Redistribution processes of the radionuclides between the various solid constituents of the soil/slag mixtures were studied and it will be almost impossible to predict quantitatively the chemical fractionation of radionuclides in contaminated soils by investigating pure slags only.	Trautmannsheimer et al. 1998
9	Soils and sediments	Am-241, Pu-239, Pu-240, U-238. Based on Tessier and 4 other SEPs	A sequential extraction technique was developed for determining the geochemical partitioning of Am, Pu, and U in soils and sediments. Stable element analyses were combined with radiometric measurements to determine the most probable geochemical host phases of these actinides in reference sediment IAEA-135. The reproducibility of the method was quite good.	Schultz et al. 1998a
10	Soils and sediments	U-238. NIST SEP	The procedure is designed to partition a soil or sediment sample into six operationally defined fractions. The criteria for choosing optimum conditions were the maximum extraction of ^{238}U combined with a minimum dissolution of non-targeted geochemical phases.	Schultz et al. 1998b
11	Mineral and organic soils	Cs-134, Sr-85, Ag-110m 2 SEPs, one Common and second Organic developed	Both schemes were capable of distinguish the behaviour of the different radionuclides among them and also according to soil properties. Furthermore, both schemes allowed studying the time dynamics of radionuclide distributions, by means of the application of the same scheme in different times after contamination.	Vidal and Rauret 1995

Due to non availability of sufficient reference materials in this area, prompted many workers to apply SCE procedures to other reference soils and sediments which have been certified for total metal contents, in an attempt to provide interim data, useful in method validation. However, efforts should be made to develop more CRMs exclusively for single and sequential extraction procedures covering various types of materials.

From this review, it appears that all the reagents used in the various schemes have advantages and disadvantages and there is not an ideal reagent or an ideal protocol for general use. Therefore, the choice of procedure must be related to a definite objective, taking into account the nature of the sample: sediment; soil; sludge; or, industrially-polluted soil etc. Interpretation of results must not be based on the mineralogical fraction targeted but rather on the reagent used, implying a perfect knowledge of its action on the solid

phase. A complementary approach characterising the solid residue can help in understanding the action of the reagent and the association of trace elements to the matrix. Finally, in the not-too-remote future, combination of the application of well-designed sequential extraction schemes and speciation studies of the solutions obtained will give a better view of the potential for transfer of trace elements in the environment and of the risks involved.

Finally, it may be emphasized that, some of the areas which needs more attention are (a) preparation of new reference materials with certified extractable contents (b) harmonisation of sequential extraction schemes in order to facilitate comparability of data (c) design of accelerated schemes based on the existing ones so that overall treatment times are diminished (d) development of extraction schemes specifically optimised for the characteristics of the target sample (e) implementation of on-line manifolds for performing

Table 11 Application of single extractants procedure to soil and other related materials (few selected examples)

Sl. no	Matrix	Elements determined and reagents used	Remarks	Reference
1	Soils	Cd,Zn, Ni,Cu, Pb. DTPA, EDTA, HCl, CaCl ₂ , NaNO ₃	A large data set was taken from the literature, and it would appear that neutral salt extractants (such as 0.01 M CaCl ₂ and 0.1 M NaNO ₃ provide the most useful indication of metal phytoavailability across a range of metals of interest, although further research is required.	Menzies et al. 2007
2	Domestic and industrial sludges	Pb, Hg, Cd, Zn. EDTA, Pyridine, Acetic acid	Single extraction techniques were applied to these samples with the objective of studying the leaching behavior of the metals in different sludges and also to predict their possible mobility when these wastes are disposed on the environment and landfills.	Olajire et al. 2006
3	Sewage irrigated soils	Cd, Cr, Cu, Pb, Zn. DTPA	The present study was carried out with a view to study the influence of different soil characteristics on DTPA-extractable heavy metals (Cd, Cr, Cu, Pb and Zn) in sewage-irrigated soil profiles of Allahabad region, U. P., India.	Mani and Kumar 2006
4	Contaminated Phaeozem	Cd, Pb, Cu, Zn. EDTA, NH ₄ Cl	EDTA can be regarded as an extractant for assessing the plant-available species of Cd, Cu, and Zn; NH ₄ Cl released electro-statically weakly bound metals and was used to estimate the mobile species.	Guo et al. 2006
5	Sludge amended soil	Cu, Zn. DTPA	Results obtained for DTPA-extractable metal indicated higher metal availability in sludge-amended soils.	Mendoza et al. 2006
6	Tailing soils	Pb, Zn, Cu. EDTA, HNO ₃ , CaCl ₂	The extractability of extractants for Pb and Zn was in the order EDTA>HNO ₃ >CaCl ₂ , while for Cu it was HNO ₃ >EDTA>CaCl ₂ .	Liu et al. 2006b
7	Agricultural soils	Al, Cu, Cd, U, Zn, Y, La. HNO ₃ , EDTA, NH ₄ OAc, NH ₄ NO ₃ , CaCl ₂ , H ₂ O	From agricultural fields in Aomori, Japan, 16 soil samples were collected. Elements in the samples were extracted using acids, chelating agents, neutral salt solutions and pure water. The 28 elements in the extracted solutions and plant samples were determined.	Takeda et al. 2006
8	Calcareous chernozem soil	Ba, Mo, Sr, Se, Cu, Ni, Zn, Al, Cd, Pb, Hg, Cr, As. NH ₄ NO ₃	The effect of microelement loads was studied on the mobile, mobilizable and pseudo total element concentrations of a calcareous chernozem soil in a long-term field experiment.	Rekasi and Filep 2006
9	Fly ash amended soil	Fe, Mn, Zn, Ni, Cr, Cu, Pb. DTPA, NH ₄ NO ₃ CaCl ₂	A pot experiment was carried out to study the potential of the plant of Brassica juncea for the phytoextraction of metal from fly ash amended soil and to study correlation between different pool of metals and metal accumulated in the plant to assess better extractant for plant available metals.	Gupta and Sinha 2006a
10	Tannery sludge amended soil	K, Na, Fe, Zn, Cr, Mn, Cu, Pb, Ni, Cd. EDTA, DTPA, NH ₄ NO ₃ , Na NO ₃ , CaCl ₂ .	The metal accumulation after 60 d of growth of the plant was found in the order of K>Na>Fe>Zn>Cr>Mn>Cu>Pb>Ni>Cd and its translocation was found less in upper part. The accumulation of toxic metals (Cr, Ni and Cd) in the plants was found to increase with increase in sludge ratio, in contrast, the accumulation of Pb decreased.	Gupta and Sinha 2006b
11	Humic forest soil	Ca, Mg, Mn, Cu, Zn, Pb. NH ₄ OAc, NH ₄ NO ₃ , HCl, EDTA, HNO ₃	None of the extractants was shown to be superior to the others in providing the best correlation with the elements concentrations in selected plant/plant	Gronflaten and Steinnes

Table 11 (continued)

Sl. no	Matrix	Elements determined and reagents used	Remarks	Reference
			compartments. In the case of Ca, Mn, and Pb all of the extractants including concentrated HNO ₃ provided significant correlations with at least some of the selected plant/plant compartments.	2005
12	Soil	Cd, Zn, Ni, Co, Cu, Hg, Cd. NH ₄ NO ₃ , KNO ₃ , H ₂ O	The results of soil analyses should be checked additional by plant analyses especially under conditions with a high probability for misleading results by the 1 M NH ₄ NO ₃ -extraction. Alternatively, extraction with 1 M KNO ₃ -solution can be performed to exclude the effect of metal amine complex formation.	Gryschko et al. 2005
13	Soil, sediment, rock	Al. H ₂ O, KCl, NH ₄ Cl, BaCl ₂	The single extraction agents were found to be the best for the quantitative estimation of the aluminum mobility in rocks, soils, and sediments caused by acidification of the environment. This fact was confirmed by reactive aluminum determination in the same samples.	Matus et al. 2004
14	Soils effectedwith pyritic sludge & acid waste waters	As,Cd,Cu,Pb, Zn. CaCl ₂ , EDTA, HOAc	Results from extraction tests indicated that changes of the trace element interaction over time depended on the soil pH and on the source of contamination. The acetic acid was recommended as the best test among those studied to derive conclusions about dynamics pattern because it provided significant desorption yields in most scenarios.	Sastre et al. 2004
15	Arid soils	B. Several extractants#	Greenhouse and lab. studies were undertaken to evaluate the suitability of extractants for determining the boron (B) status of arid soils of Rajasthan (India) using mustard (<i>Brassica juncea</i> L.) as a test crop. For predicting response of mustard to B application, several extractants have been tried with variable results.	Chaudhary and Shukla 2004
16	Contaminated soils & BCR CRM 483	Cd, Cu, Pb, Zn. CaCl ₂ , Na NO ₃ , NH ₄ NO ₃	The metal extraction efficiency obtained with each procedure was slightly different, and the three methods provided equivalent information while predicting the relative trace-metal mobility (Cd>Zn>Cu>Pb) in the soils studied. The 0.01 M CaCl ₂ extraction procedure was the most suitable method for performing a harmonization process.	Pueyo et al. 2004
17	Wet rhizosphere soil	La, Ce, Pr, Nd. SE with LMWOAs and BCRSEP 1&2 steps	Poor correlation was obtained between LREEs in fractions water sol., exchangeable and carbonate bound (1 step) and Fe–Mn oxide bound (2 step) of the BCR method and LREEs in apoplasm and symplasm and in intact roots. Hence, the LMWOAs extraction method is recommended for measuring the bioavailability of LREEs in soils.	Wang et al. 2004
18	Soil and plant samples	Zn, Cu, Mn. DTPA, Citirc acid	DTPA was more suitable for predicting phytoavailable Cu than citric acid. Plant Mn concentration could not be correlated to any of the extracting agents.	Lombnaes and Singh 2003
19	Volcanic soils	Co, Cu, Ni, Pb, Zn. DTPA	The DTPA-extractable metal contents, generally used as plant-available metals, are low enough and show	Bastida et al. 2003

Table 11 (continued)

Sl. no	Matrix	Elements determined and reagents used	Remarks	Reference
20	Calcareous and acidic soils	Cd, Cu, Zn. NaNO ₃ , DTPA, EDTA	the small availability of all these trace elements in regard to the total content of them. Cadmium depletion was most apparent in the acidic soil, with a significant decrease observed in the NaNO ₃ , DTPA, and EDTA-extractable fractions following <i>T. caeruleus</i> growth compared with control pots. <i>T. caeruleus</i> , and to a lesser extent <i>S. viminalis</i> , can alter the heavy metal distribution in different soil pools within 90 days.	Hammer and Keller 2002
21	Soil	As, Cd, Zn. Aqua regia, HNO ₃ , HOAc, DTPA	Solutions of acetic acid and DTPA were able to release a part of the element fraction bound in Fe/Mn oxides and organic matter of soil sample. Arsenic represents an exception because it is not released by DTPA.	Szakova et al. 2001b
22	Agricultural soils	Cu. EDTA, HOAc, CaCl ₂ , H ₂ O, NH ₄ NO ₃	After comparing the results of the different extraction procedures the environmental behaviour of copper and its risks for plants, micro-organisms and groundwater is discussed in brief.	Schramel et al. 2000
23	Andisol soil	Cd, Cu, Ni, Pb, Zn. DTPA, HCl, ADTPA.	The three phytoavailable extractants gave lower values of the oxidizable and reducible metal fractions; but, higher values of the carbonate fractions were observed.	Salas et al. 1998
24	Polluted soils	Cd,Pb, Zn,Cu. EDTA	The behaviour of the cations seems to depend heavily on an excess or a lack of EDTA. In the case of excess, concentrations of cations extracted are most of time pH-independent and in the case of lack of EDTA, amounts of extracted cations show a complex behaviour vs. pH which changes with the type of cation and with the degree of soil pollution. A competition phenomenon between minor and major cations of the soil seems to be revealed.	Ghestem and Bermond 1998
25	Marsh soils	Cd, Cu, Ni, Pb, Zn. CaCl ₂ /DTPA (CAD), CaCl ₂ , NH ₄ NO ₃ , and aqua regia,	Plant available Cu was detectable only by CAD method. The highest correlation between metal content of soil and plant was shown for Zn by CAD method, for Ni by NH ₄ NO ₃ method. The Pb values only detectable by CAD method were not regarded as plant available. The CaCl ₂ method was the best to predict contamination of wheat with Cd.	Merkel 1996
26	Humus samples	Co, Cu, Fe, Ni, Pb, Zn. Na ₄ P ₂ O ₇	Study of the contact time of 1 g of humus in 100 mL of 0.1 M Na ₄ P ₂ O ₇ solution for 30 samples revealed that the conventional 16-h duration could be decreased to 1 h (with const. agitation) without significantly lessening the amount of Co, Cu, Fe, Ni, Pb or Zn extracted.	Hall et al. 1996a

Hot CaCl₂, Hot water, Sorbitol+NH₄ OAc+BTEA, Mann-itol+NH₄OAc+TEA, NH₄OAc, Salicylic acid+NH₄OAc+TEA, Mannitol+CaCl₂

sequential extractions (f) development of single extraction methodology simultaneously so that operation procedures are simplified (g) development of small-scale extractions to minimise sample and

reagent consumption (h) application of sequential extraction for characterisation of metal mobility for different variety of environmental samples because till date, huge amount of data is available for soils and

sediments but there are limited number of applications for coal fly ash, solid waste incineration bottom ash, airborne dust, etc. (i) use of chemometric approaches for robustness testing of sequential extraction protocols, for finding relationships between soil metal fractions and plant uptake, and for characterisation of pollution sources from partitioning results in soils and sediments (j) more investigations of changes in metal mobility in soils subjected to amendment etc.

At the outset, authors experiences in the field of single and sequential chemical extractions for the past few years (Lopez-Sanchez et al. 1998, 2002; Pueyo et al. 2001a, b, 2003, 2005; Sahuquillo et al. 1999, 2002, 2003; Sahuquillo and Rauret 2003; Rauret et al. 1999, 2000a, b, 2001; Llauro et al. 2001) reveal that there are lot of advantages of these methods and still enormous scope for further research and developments in these areas because pollution sites are increasing throughout the world and there is urgent need of methods for faster, reliable and cost-effective pollution assessment so that suitable remedial measures can be taken up on priority basis at an appropriate time.

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