

Sequential extraction of soils for multielement analysis by ICP–AES

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Abstract

Realistic environmental interpretation of soil contamination depends on an understanding of how metals are bound to the various phases in the soil. A five-step sequential chemical extraction scheme, originally designed for sediment analysis by flame atomic adsorption spectroscopy (FAAS), has been developed for the multielement analysis of soils by inductively coupled plasma–atomic emission spectrometry (ICP–AES). Each of the chemical fractions is operationally defined as follows: (1) exchangeable; (2) bound to carbonates or specifically adsorbed; (3) bound to Fe–Mn-oxides; (4) bound to organic matter and sulphides; and (5) residual. The number of elements determined by ICP–AES has been extended to fifteen (Be, Ca, Co, Cr, Cu, Fe, K, Li, Mn, Ni, P, Pb, Ti, V, Zn), which include most of the major elements, thereby increasing the potential of the sequential extraction method by enabling broader studies of geochemical associations in soils. The precision was estimated to be $\sim 5\%$ (2σ) for each extraction step. The overall recovery rates of international reference materials were between 85 and 110% for most elements, with an average of 92%. There is good agreement between the results for the international reference material (USGS MAG-1) in each extraction step and published values. A wide range of soil reference materials, including SO-1–SO-4 and BCR141–BCR143, were also analysed for future comparison. The application of the method to soils contaminated by past mining and smelting activities showed distinctive partitioning patterns of heavy metals from the two sources. The multielement measurements gave useful information to assist in the interpretation of the possible geochemical forms and sources of the trace elements in soils.

1. Introduction

Most studies dealing with particulate metals in sediment, soil and water systems are concerned with total metal concentrations. Relatively few attempts have been made to evaluate the speciation of metals in particulate form (i.e. the partitioning among the various forms in which they might exist). Metals in soils may be present in several different geochemical phases that act as reservoirs or sinks of trace elements in the envi-

ronment (Jenne, 1977; Kramer and Allen, 1988). These phases include the following broad categories: exchangeable; specifically adsorbed; carbonate; Fe- and Mn-oxides; organic matter; and mineral lattice. All of these may occur in a variety of structural forms (Tessier et al., 1979; Beckett, 1988). It is now recognised that the quantification of the chemical forms of metals in soils is essential for estimating the mobility and bioavailability of the metals in the environment (Leschber et al., 1985; Broekaert et al., 1990).

One approach to the analytical determination of the distribution of metals among these physicochemical

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phases has been made by phase-selective chemical extractions involving single or multiple extracting reagents. Multi-step sequential extraction schemes appear to be of greater value than a single extractant, providing more detailed information of possible metal chemical forms in the soil (Tessier et al., 1979; Pickering, 1986). The reagents utilised in the sequential extraction have been chosen on the basis of their supposed selectivity and specificity towards particular physicochemical forms, although variations in reagent strength, volume and extraction time between schemes are apparent.

Many different sequential extraction procedures have been developed for partitioning trace elements in sediments, soils and sludges (Tessier et al., 1979; Lake et al., 1984; Shuman, 1985). In particular, the protocol of Tessier et al. (1979) has been thoroughly researched and rigorously tested (Tessier et al., 1979; Valin and Morse, 1982; Rapin and Förstner, 1983; Martin et al., 1987; Kim and Fergusson, 1991). This method is now widely applied in sediment and soil studies by many investigators (i.e. Harrison et al., 1981; Hickey and Kittrick, 1984; Förstner, 1985; Xian, 1989; Clevenger, 1990). However, the limitations of this sequential extraction method have been addressed by several researchers (Jouanneau et al., 1983; Khebonian and Bauer, 1987; Bermond, 1992). These limitations include the technical difficulties associated with achieving complete and selective dissolution and recovery of trace metals from those geochemical phases in soils and sediments, for example, the overlap of chemical reagents and re-adsorption of trace metals during extraction. Despite these inherent limitations, the sequential extraction scheme is still a very useful method for characterising solid-phase associated trace metals in soils and sediments (Belzile et al., 1989; Kim and Fergusson, 1991).

Although the procedure of Tessier et al. (1979) has been widely used in many soil and sediment studies, the accuracy and precision of the techniques used in each study have rarely been estimated. Comparability of the results produced by different authors is therefore problematical. Furthermore, the analysis of the extraction solutions using flame atomic absorption spectrophotometry (FAAS) is only appropriate for the determination of a relatively small number of elements. The investigation of soil contamination frequently requires the analysis of substantial numbers of samples for a large suite of elements. The method described

below has been developed to enable large batches of samples to be processed rapidly, whilst maintaining acceptable accuracy and precision for environmental interpretation. Moreover, the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES) to analyse the extractant solutions for some 15 elements has increased the productivity of the sequential extraction method and enabled a broader study of the geochemical associations in soils.

2. Experimental

Analar[®]-grade chemicals and deionised water (DIW, conductivity > 1 M Ω cm) were used throughout the study. All pipettes, tubes and containers were washed with a detergent (Decon[®]), then soaked for 24 hr in 2% nitric acid (HNO₃) solution and rinsed repeatedly with DIW. The soil samples were dried at 25°C in a filtered air drying cabinet for 3 days. These samples were then sieved through a 2-mm sieve and milled in an agate pot to a fine powder (< 170 μ m). International reference materials were selected, these included: MAG-1 (U.S. Geological Survey, U.S.A.; USGS); SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Material Project, Canada; CCRMP); and BCR-141, BCR-142 and BCR-143 (Community Bureau of Reference, Belgium; BCR). Descriptions of these reference materials have been given by Potts et al. (1992). All the test materials were dried at 105°C overnight before use. The reference materials, duplicates of samples and reagent blanks were distributed at random throughout the whole extraction procedure to make the most realistic assessments of data quality (Ramsey et al., 1987).

2.1. Extraction steps

The sequential extraction scheme was developed from that of Tessier et al. (1979), and retains the same terminology. The extraction was carried out progressively on an initial weight of 1.000 g of test material. The extractants and operationally defined chemical fractions were as follows:

(1) Fraction 1: exchangeable — sample extracted with 8 ml of 0.5 M magnesium chloride (MgCl₂) at pH 7.0 for 20 min, with continuous agitation, at room temperature.

Table 1
Instrumental operating conditions

ICP–AES instrument	Applied Research Laboratories [®] , ARL 34000C, 1-m vacuum polychrometer with PDP [®] 11/04 computer
Forward power	1.25 kW at 27 MHz
Reflected power	< 10 W
Viewing height	4.0-mm square window centred 14 mm above the load coil
Torch	Fassel [®] type
Gas flow-rate:	
coolant	12.0 l min ⁻¹
auxiliary	0.4 l min ⁻¹
injector	1.0 l min ⁻¹
Spray chamber	Scott [®] double-pass type
Nebuliser	Concentric glass (Meinhard [®] TR-30-3A)
Solution uptake rate	1.0 ml min ⁻¹ (unpumped)
Uptake tube	310 × 0.5-mm i.d. polyethylene
Nebuliser tip wash	0.5 ml of de-ionised water containing 1% v/v Photo-flo [®] between sample solutions
Pre-flush, integration time	20 s and 3 × 5 s

(2) Fraction 2: bound to carbonate and specifically adsorbed — residue from step (1) leached for 5 hr with 8 ml of 1 M sodium acetate (NaOAc; adjusted to pH

Table 2
The instrumental detection limits (2 σ) for individual elements in each extraction step ($\mu\text{g g}^{-1}$)

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
D.F. ^c	20	80	13.33	13.33	25	
Be	0.004	0.016	0.003	0.003	0.005	0.018
Ca	1.00	4.00	0.67	0.67	1.25	4.41
Co	0.10	0.40	0.07	0.07	0.13	0.44
Cr	0.10	0.40	0.07	0.07	0.13	0.44
Cu	0.10	0.40	0.07	0.07	0.13	0.44
Fe	0.40	1.60	0.27	0.27	0.50	1.76
K	1.00	4.00	0.67	0.67	1.25	4.41
Li	0.10	0.40	0.07	0.07	0.13	0.44
Mn	0.20	0.80	0.13	0.13	0.25	0.88
Ni	0.20	0.80	0.13	0.13	0.25	0.88
P	1.00	4.00	0.67	0.67	1.25	4.41
Pb	1.00	4.00	0.67	0.67	1.25	4.41
Ti	0.10	0.40	0.07	0.07	0.13	0.44
V	0.10	0.40	0.07	0.07	0.13	0.44
Zn	0.20	0.80	0.13	0.13	0.25	0.88

^aFollowing the sequential extraction steps described in the text: step (1), exchangeable fraction; step (2), fraction bound to carbonate and specifically adsorbed; etc.

^bSum represents the detection limit for the five fraction estimated from:

$$DL_{\text{Sum}}^2 = DL_{\text{step1}}^2 + DL_{\text{step2}}^2 + \dots + DL_{\text{step5}}^2$$

^cD.F. = dilution factor for each step (ml g^{-1}).

5.0 with acetic acid, HOAc) at room temperature. Continuous agitation was maintained during the extraction.

(3) Fraction 3: bound to Fe–Mn-oxides — residue from step (2) was extracted with 20 ml of 0.04 M hydroxylammonium hydrochloride ($\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$) in 25% (v/v) HOAc for 6 hr. The extraction was performed at 96°C with occasional agitation. After extraction, the extract solutions were diluted to 20 ml with DIW and subjected to continuous agitation for 10 min.

(4) Fraction 4: bound to organic matter and sulphide — to the residue from step (3), 3 ml of 0.02 M HNO_3 and 5 ml of 30% hydrogen peroxide (H_2O_2 ; adjusted to pH 2.0 with HNO_3) were added. The sample was heated progressively to 85°C, and maintained at this temperature for 2 hr with occasional agitation. A second 3-ml aliquot of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3) was then added, and the mixture was heated again at 85°C for 3 hr with intermittent agitation. After cooling, 5 ml of 3.2 M ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3 were added, followed by dilution to a final volume of 20 ml with DIW. The tubes were then continuously agitated for 30 min.

(5) Fraction 5: residual phase — residue from step (4) was digested with 4 ml concentrated HNO_3 (70% w/w), 3 ml perchloric acid (HClO_4 , 60% w/w) and 15 ml hydrofluoric acid (HF, 40% w/w) to dryness using the following heating regime: 90°C for 6 hr, 120°C for 10 hr and 190°C for 6 hr. The remaining material was then taken up in 5 ml of 5 M HCl at 70°C for 1 hr, and diluted to 25 ml with DIW.

The extractions (except the last HF– HClO_4 – HNO_3 step) were conducted in 50-ml polysulphone centrifuge

Table 3
The sequential extraction results ($\mu\text{g g}^{-1}$) for USGS MAG-1

Element		Extraction step ^a					Sum ^b
		(1)	(2)	(3)	(4)	(5)	
Co	A	<0.8	<0.8	4.0 ± 0.4	1.9 ± 0.2	14.1 ± 1.6	20.4 ± 2.2
	B	<0.2	<0.8	3.3 ± 0.3	1.8 ± 0.1	14.1 ± 0.4	19.2 ± 1.0
Cu	A	0.3 ± 0.2	<0.4	<0.4	7.2 ± 1.4	19.8 ± 3.4	27.1 ± 2.4
	B	0.6 ± 0.1	<0.4	<0.1	2.9 ± 0.5 ^c	24.3 ± 0.4 ^c	26.7 ± 1.2
Fe	A	<0.4	7.8 ± 1.6	3,460 ± 360	1,300 ± 520	41,000 ± 2,400	45,800 ± 2,400
	B	7.11 ± 15 ^c	13.2 ± 4.7 ^c	2,020 ± 230 ^c	980 ± 230	36,700 ± 400 ^c	39,700 ± 970 ^c
Mn	A	53.0 ± 11.0	72.0 ± 13.0	135 ± 7	31 ± 18	375 ± 26	670 ± 24
	B	60.5 ± 6.2	68.7 ± 4.6	125 ± 8	41 ± 3	405 ± 30	700 ± 31
Ni	A	<0.8	2.6 ± 1.6	10.5 ± 1.8	5.8 ± 1.0	34.6 ± 8.0	53.5 ± 5.6
	B	0.4 ± 0.2	1.2 ± 0.3	7.8 ± 1.1 ^c	7.1 ± 0.2	31.6 ± 0.2	48.6 ± 2.2
Pb	A	<0.8	4.6 ± 1.0	4.2 ± 0.8	2.5 ± 2.0	12.6 ± 3.0	23.8 ± 1.4
	B	<1.0	<4.0	3.4 ± 0.7	2.6 ± 0.9	15.7 ± 16 ^c	25.4 ± 16 ^c
Zn	A	<0.2	2.2 ± 0.8	24.5 ± 2.0	13.1 ± 4.2	90.2 ± 4.6	130 ± 4.4
	B	<0.2	1.8 ± 0.5	16.2 ± 3.0 ^c	6.9 ± 2.5	86.9 ± 6.0	111 ± 1.5 ^c

A = calculated from Tessier et al. (1979), mean value and $2 \times$ standard deviation for four replicate determinations; B = this study, mean value and $2 \times$ standard deviation for three determinations in different batches.

^aFollowing the sequential extraction steps described in the text: step (1), exchangeable fraction; step (2), fraction bound to carbonate and specifically adsorbed; etc.

^bSum represents the sum of the five fractions

^cIndicates the results in this study that are different from the published values at 95% confidence.

tubes (28.5×104 mm) with 24-mm polypropylene sealing caps (Nalgene[®], Sybron International, Rochester, New York, U.S.A.). When continuous agitation was required, samples were shaken lengthwise on a mechanical shaker at 50 oscillations per minute with a stroke of 8 cm. Heating of the samples was operated using an aluminium heating block. Following each extraction, the mixtures were centrifuged at 2000 rpm for 20 min at room temperature. An aliquot of the supernatant was decanted into clean glass test tubes using a Gilson pipette. The aliquot used for each extraction step was 4, 1, 15 and 15 ml for steps (1), (2), (3) and (4), respectively. The remainder of the solution was discarded. Prior to the start of next extraction step, samples were shaken with 8 ml of DIW for 5 min, and the wash solution was discarded after 20-min centrifuging. The final extraction step (HF–HClO₄–HNO₃ digestion) was carried out in large PTFE (polytetrafluoroethylene) tubes (140×25 mm) after the residue had been transferred from the polysulphone tubes by repeated suspension of the residue in DIW using a

vortex mixer, and subsequent decanting of the suspension.

2.2. Matrix adjustment and analysis of extraction solutions

In order to ensure one uniform matrix for ICP–AES analysis, the different extraction matrices were digested with concentrated HNO₃. To the aliquots of extractant solutions from steps (1)–(4), 1 ml HNO₃ (concentrated, 70% w/w) was added, and then the solutions were heated to dryness on an aluminium heating block at 140°C. Care should be taken when heating the solution from extraction steps (3) and (4) because a violent reaction of HNO₃ with NH₂·OH·HCl or NH₄OAc may occur. After adding HNO₃, these extract solutions were left overnight on a heating block at 90°C, and the temperature raised slowly to 140°C and heated to dryness. The residue in the tubes was then leached with 2 ml of 5 M HCl, and made-up to final volume of 10 ml with DIW.

Table 4
Sequential extraction results ($\mu\text{g g}^{-1}$) for reference materials SO-1-4 and BC-R141-143

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
SO-1						
Be	<0.004	0.073±0.033	0.319±0.012	0.085±0.001	1.20±0.02	1.67±0.04
Ca	2,030±10	151±3	479±153	958±63	14,500±470	18,100±500
Co	0.20±0.04	0.40±0.12	7.12±0.22	1.37±0.004	15.8±0.6	24.8±0.7
Cr	<0.1	1.16±0.41	10.2±0.6	3.06±0.09	114±1	128±1
Cu	0.44±0.04	1.27±0.34	9.39±1.06	0.72±0.01	48.1±0.1	59.9±1.1
Fe	2.95±2.63	56.8±3.5	3,770±350	62.7±2.4	42,300±880	46,200±950
K	215±1	230±12	227±18	210±5	16,600±170	17,520±171
Li	0.72±0.37	<0.4	4.89±0.59	1.68±0.04	45.2±1.4	52.5±1.6
Mn	19.7±0.1	8.29±0.19	277±10	52.9±0.3	492±10	850±14
Ni	0.59±0.43	<0.8	6.04±0.62	2.47±0.18	64.0±1.3	72.9±1.5
P	<1.0	4.66±1.66	43.0±11.3	69.5±3.7	491±8	607±15
Pb	<1.0	<4.0	1.35±0.29	1.33±0.13	8.28±2.88	12.1±3.3
Ti	0.66±0.26	0.69±0.37	1.09±0.45	7.41±6.71	4,490±43	4,500±44
V	<0.1	<0.4	17.6±1.2	6.48±2.40	84.2±3.9	109±5
Zn	0.57±0.48	2.06±0.64	10.7±0.9	1.78±0.12	8.47±1.69	104±2
SO-2						
Element Extraction step ^a						
	(1)	(2)	(3)	(4)	(5)	Sum ^b
Be	0.010±0.010	0.059±0.014	0.214±0.003	0.032±0.002	1.47±0.03	1.78±0.03
Ca	39.9±3.5	43.0±4.5	176±67	56.6±13.9	17,100±1900	17,400±1900
Co	0.10±0.05	<0.40	0.82±0.01	0.10±0.02	5.63±0.20	6.92±0.28
Cr	0.06±0.03	1.03±0.03	2.58±0.03	0.72±0.03	7.34±0.25	11.7±0.3
Cu	0.38±0.12	0.71±0.03	0.25±0.03	0.76±0.01	4.31±0.16	6.42±0.20
Fe	238±35	1,390±99	8,740±170	485±235	34,900±840	45,800±900
K	46.3±2.7	101±3	57.7±2.2	19.6±9.4	23,200±66	23,500±70
Li	0.17±0.18	<0.40	0.67±0.03	1.40±0.14	11.6±0.1	12.2±0.3
Mn	4.28±0.13	11.0±1.5	75.8±1.0	1.40±0.92	567±3	659±3
Ni	0.61±0.18	<0.8	0.53±0.02	0.21±0.03	3.79±0.34	5.32±0.45
P	8.6±2.6	179±11	235±15	339±28	2,180±80	2,940±90
Pb	<1.0	<4.0	0.71±0.24	<0.7	16.6±4.6	18.2±5.4
Ti	2.68±1.81	9.41±1.80	9.48±1.50	34.3±8.9	7,490±140	7,540±140
V	<0.1	0.88±0.03	7.94±0.24	3.58±0.08	31.1±1.9	43.5±1.9
Zn	1.21±0.61	3.34±0.10	8.78±0.28	1.34±0.80	82.7±0.8	97.4±1.3

Table 4 (continued)

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
SO-3						
Be	<0.004	0.048 ± 0.029	0.111 ± 0.004	0.006 ± 0.007	0.564 ± 0.036	0.731 ± 0.048
Ca	871 ± 27	54,500 ± 760	60,000 ± 1660	6,630 ± 350	6,020 ± 1020	128,000 ± 2,120
Co	<0.1	0.47 ± 0.14	1.40 ± 0.06	<0.07	3.24 ± 0.18	5.13 ± 0.24
Cr	<0.1	0.92 ± 0.36	2.67 ± 0.22	0.45 ± 0.10	19.5 ± 1.0	23.5 ± 1.1
Cu	0.30 ± 0.03	1.05 ± 0.03	1.91 ± 0.68	1.44 ± 0.25	10.2 ± 1.1	14.9 ± 1.3
Fe	2.84 ± 1.43	78.4 ± 1.2	1,760 ± 65	15.1 ± 1.5	11,800 ± 860	13,700 ± 860
K	177 ± 7	199 ± 15	178 ± 9	33.2 ± 1.5	10,100 ± 710	10,670 ± 710
Li	0.15 ± 0.29	<0.4	1.23 ± 0.03	0.09 ± 0.15	8.61 ± 1.26	9.81 ± 1.46
Mn	<0.2	166 ± 3	177 ± 6	4.90 ± 0.48	139 ± 12	487 ± 14
Ni	<0.2	<0.8	1.51 ± 0.02	<0.13	7.48 ± 0.37	9.71 ± 0.74
P	<1.0	10.2 ± 17.6	20.6 ± 3.4	134 ± 22	288 ± 7	452 ± 29
Pb	<1.0	<4.0	1.41 ± 0.07	<0.67	5.13 ± 0.10	6.54 ± 1.94
Ti	0.38 ± 0.14	6.67 ± 0.63	3.33 ± 0.26	11.1 ± 0.8	1,840 ± 90	1,860 ± 90
V	<0.1	<0.4	2.90 ± 0.12	0.61 ± 0.06	24.9 ± 4.0	28.4 ± 4.0
Zn	<0.2	4.36 ± 0.35	7.60 ± 0.72	<0.13	26.1 ± 1.9	38.2 ± 2.0
SO-4						
Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
Be	<0.004	0.025 ± 0.030	0.202 ± 0.001	0.099 ± 0.0005	0.811 ± 0.022	1.14 ± 0.04
Ca	4,140 ± 90	720 ± 47	623 ± 1	417 ± 19	4,590 ± 1370	10,500 ± 1,380
Co	<0.1	<0.4	3.86 ± 0.06	1.13 ± 0.03	4.44 ± 0.28	9.68 ± 0.31
Cr	<0.1	0.66 ± 0.01	1.23 ± 0.01	4.08 ± 0.004	45.5 ± 1.9	51.3 ± 1.9
Cu	0.32 ± 0.09	0.44 ± 0.52	0.09 ± 0.01	0.36 ± 0.09	19.8 ± 0.4	21.0 ± 0.7
Fe	6.61 ± 0.59	18.4 ± 7.9	1,990 ± 20	1,190 ± 10	18,350 ± 530	21,550 ± 530
K	311 ± 1	191 ± 26	182 ± 4	128 ± 1	15,200 ± 300	16,020 ± 300
Li	<0.1	<0.4	1.22 ± 0.05	0.75 ± 0.06	17.6 ± 0.5	19.4 ± 0.7
Mn	46.4 ± 0.1	49.7 ± 3.5	351 ± 2	59.5 ± 1.1	122 ± 7	628 ± 8
Ni	<0.2	<0.8	4.28 ± 0.14	6.13 ± 0.01	11.7 ± 0.9	22.5 ± 0.9
P	4.36 ± 0.84	25.0 ± 4.3	33.8 ± 4.3	295 ± 17	549 ± 31	908 ± 36
Pb	<1.0	<4.0	<0.67	2.37 ± 0.11	11.2 ± 2.2	13.2 ± 2.8
Ti	0.95 ± 0.03	1.23 ± 1.47	0.41 ± 0.23	40.6 ± 0.2	3,060 ± 43	3,100 ± 43
V	<0.1	<0.4	3.08 ± 0.002	6.46 ± 0.06	61.3 ± 2.2	71.1 ± 2.2
Zn	0.34 ± 0.30	1.52 ± 0.75	12.4 ± 0.7	2.57 ± 0.07	62.0 ± 4.4	78.8 ± 4.5

BCR-141

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
Be	0.006 ± 0.003	0.075 ± 0.015	0.493 ± 0.007	0.129 ± 0.003	1.07 ± 0.02	1.77 ± 0.02
Ca	5,780 ± 20	53,000 ± 430	44,400 ± 450	4,260 ± 110	2,780 ± 170	110,200 ± 650
Co	<0.1	1.40 ± 0.02	2.58 ± 0.07	0.22 ± 0.07	4.80 ± 0.10	9.00 ± 0.40
Cr	<0.1	0.79 ± 0.13	3.44 ± 0.002	3.98 ± 0.18	60.3 ± 0.3	68.5 ± 0.4
Cu	0.67 ± 0.06	0.73 ± 0.07	1.06 ± 0.01	1.40 ± 0.07	28.1 ± 0.03	32.0 ± 0.1
Fe	4.69 ± 2.36	7.45 ± 0.15	1,370 ± 20	296 ± 4	21,200 ± 130	22,900 ± 140
K	405 ± 7	187 ± 11	141 ± 2	58.2 ± 1.1	11,400 ± 60	12,200 ± 60
Li	<0.1	<0.4	1.24 ± 0.07	0.54 ± 0.05	33.2 ± 0.4	34.4 ± 0.7
Mn	16.6 ± 0.1	189 ± 1	196 ± 4	14.0 ± 0.4	93.6 ± 1.7	509 ± 4
Ni	<0.2	1.06 ± 0.17	4.53 ± 0.17	2.73 ± 0.05	20.3 ± 0.2	28.5 ± 0.3
P	9.28 ± 0.03	4.63 ± 1.93	73.6 ± 4.6	167 ± 4	384 ± 4	639 ± 7
Pb	<1.0	<4.0	7.72 ± 0.54	2.82 ± 0.11	22.4 ± 9.5	31.4 ± 9.7
Ti	1.04 ± 0.05	5.97 ± 0.03	2.33 ± 0.004	14.2 ± 0.3	2,740 ± 10	2,770 ± 10
V	<0.1	<0.4	3.62 ± 0.01	2.96 ± 0.10	59.9 ± 1.1	66.4 ± 1.1
Zn	<0.2	3.23 ± 0.03	8.18 ± 0.83	0.29 ± 0.03	52.9 ± 0.1	64.6 ± 0.8

BCR-142

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
Be	0.005	0.057	0.364	0.096	1.07	1.59
Ca	3,500	21,500	4,050	431	3,640	33,200
Co	<0.1	0.65	2.81	0.56	4.53	8.57
Cr	<0.1	1.08	4.22	5.74	57.3	68.3
Cu	0.58	1.68	2.59	5.61	17.6	28.0
Fe	1.94	19.7	2,680	441	15,700	18,900
K	98.8	104	96.9	46.8	18,800	19,200
Li	<0.1	<0.4	1.45	0.76	27.8	29.8
Mn	11.3	156	268	22.3	137	595
Ni	<0.2	1.50	7.02	3.18	16.7	28.3
P	4.4	29.1	142	175	586	936
Pb	<1.0	<4.0	7.74	5.61	37.2	52.2
Ti	0.71	3.44	0.85	20.9	3,410	3,430
V	<0.1	<0.4	6.79	4.04	36.7	47.6
Zn	<0.2	8.89	24.8	3.5	40.8	78.1

Table 4 (continued)

BCR-143

Element	Extraction step ^a					Sum ^b
	(1)	(2)	(3)	(4)	(5)	
Be	<0.004	0.002	0.219	0.099	1.18	1.51
Ca	5,040	14,300	21,200	6,380	7,450	54,300
Co	<0.1	0.54	3.75	0.51	6.58	11.4
Cr	0.35	2.35	25.2	59.8	108	196
Cu	3.24	15.7	13.1	100	81.6	213
Fe	19.7	7.91	1,410	259	22,200	23,900
K	292	163	207	78.2	10,400	11,100
Li	<0.1	<0.4	1.28	<0.07	35.1	35.7
Mn	26.6	165	511	27.0	189	919
Ni	1.17	7.26	25.6	6.21	43.7	84.0
P	29.7	189	357	890	1,920	3,380
Pb	2.31	185	371	186	364	1,110
Ti	1.32	2.58	1.89	1.30	3,640	3,650
V	<0.1	<0.4	7.65	6.99	57.8	72.9
Zn	16.0	319	440	59.2	164	998

Quoted errors are 2σ standard deviations ($n = 2$); values with no errors are single determinations.

^aFollowing the sequential extraction steps described in the text: step (1), exchangeable fraction; step (2), fraction bound to carbonate and specifically adsorbed; etc.

^bSum of the five fractions.

Table 5
Comparison of the sum concentrations ($\mu\text{g g}^{-1}$) of the five fractions with the certified total values for reference materials, SO-1–4 and BCR-141–143

Element	SO-1			SO-2			SO-3			SO-4		
	Σ	CV	R	Σ	CV	R	Σ	CV	R	Σ	CV	R
Ca	1.81	1.79	101%	1.74	1.96	88.8%	12.8	14.6	87.7%	1.05	1.10	95.5%
Fe	4.62	6.00	77.0%	4.58	5.56	82.4%	1.37	1.52	90.1%	2.16	2.37	91.1%
K	1.75	2.68	65.3%	2.35	2.45	95.9%	1.07	1.16	92.2%	1.60	1.55	103%
Mn	0.085	0.089	95.5%	0.066	0.072	91.7%	0.049	0.052	94.2%	0.063	0.060	105%
P	0.061	(0.062)	98.4%	0.29	0.30	96.7%	0.045	0.048	93.8%	0.091	(0.090)	101%
Ti	0.45	0.53	84.9%	0.75	0.86	87.2%	0.19	0.20	95.0%	0.31	0.34	91.1%

	BCR-141			BCR-142			BCR-143		
	Σ	CV	R	Σ	CV	R	Σ	CV	R
Cu	32.0 ± 0.1	32.6 ± 1.4	98.1%	28.0	27.5 ± 0.6	102%	213.7	236.5 ± 8.2	90.4%
Ni	28.5 ± 0.3	(30.9)	92.2%	28.3	29.2 ± 2.5	97.0%	84.0	99.5 ± 5.5	84.4%
Pb	31.4 ± 9.7	29.4 ± 2.6	107%	52.2	37.8 ± 1.5	138%	1,110	1,333 ± 39	83.1%
Zn	64.6 ± 0.8	81.3 ± 3.7	80.0%	78.1	92.4 ± 4.4	84.5%	998	1,272 ± 30	78.5%

Σ = mean sum concentration of the five fractions with $\pm 2\sigma$ ($n=2$); CV = certified or suggested (in parentheses) total concentration with 95% confidence interval; R = recovery rate which is calculated from the sum concentration of the five fractions and the certified value.

Multielement analysis was performed by ICP–AES under the operating conditions given in Table 1 (Ramsey and Thompson, 1987). The calibration scheme was based on that described by Thompson and Walsh (1989) with a matrix of 1 M HCl and approximate matrix matching at 2000 $\mu\text{g g}^{-1}$ Na in the trace-element calibration solutions. Calibration solutions were

also run and at regular intervals throughout each batch and at the end of the analysis, to compensate for drift.

3. Results and discussion

3.1. Instrumental detection limits

The instrumental detection limits were calculated as twice the standard deviation of 11 repeated determinations of a blank solution (1 M HCl), and reported in the same concentrations ($\mu\text{g g}^{-1}$) as those for the soil samples (Table 2). Detection limits for each element vary between the five extraction steps because of the different dilution factors at each step. The detection limits determined using ICP–AES in this study are generally better than those achieved by FAAS analysis of sequential extraction solutions, as used in the method of Tessier et al. (1979). These detection limits are considered acceptable for general analysis in environmental studies.

3.2. Analytical precision

The precision for each extraction step was estimated from analyses of soil samples in duplicate using the

Table 6
Concentrations ($\mu\text{g g}^{-1}$) of the exchangeable and total Pb in soils from mining and smelting sites, Derbyshire, U.K.

	Mining area ($n=11$)	Smelting area ($n=10$)
<i>Exchangeable Pb</i> [step (1), MgCl_2 -extractable]:		
Mean	99	1,290
Median	46	1,650
Range	8.5–401	20–2,570
σ_n	126	907
<i>Total Pb</i> (sum of the 5 steps):		
Mean	22,900	25,500
Median	13,500	10,600
Range	1,950–61,700	454–81,700
σ_n	20,400	30,700

n = number of the samples analysed; σ_n = standard deviation.

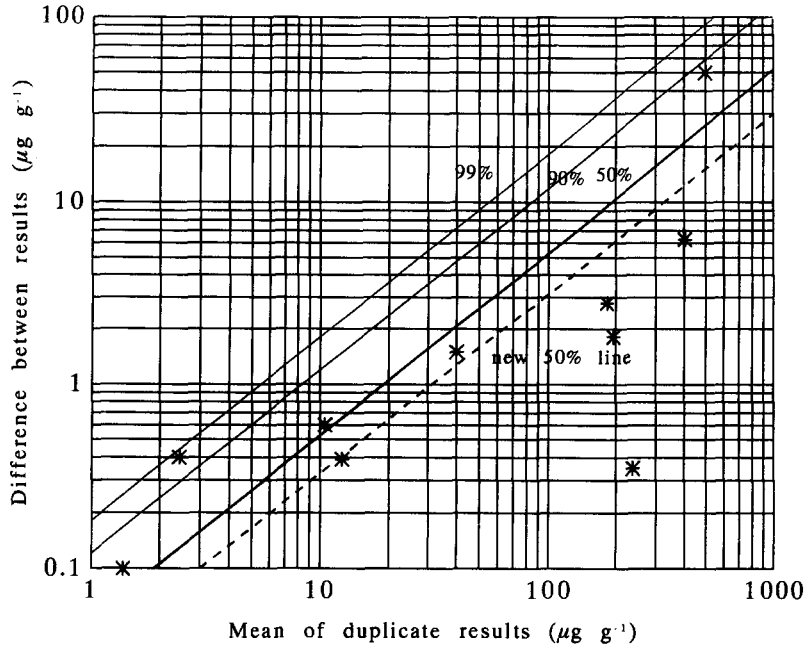


Fig. 1. Control chart for duplicate analyses of Zn at extraction step (2) with percentile lines drawn for 10% precision (i.e. 5%, 1σ). The new median line (50%) for the plotted points indicates precision of 3%, 1σ (i.e. 6%, 2σ), from its intercept with the line of 100 μg g⁻¹ mean concentration.

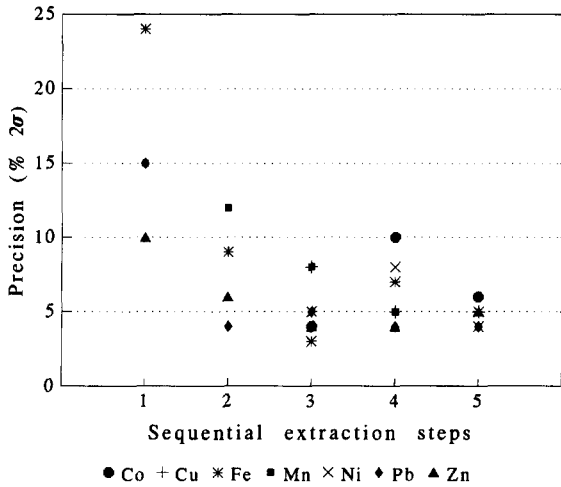


Fig. 2. Precisions calculated from duplicate analysis of Co, Cu, Fe, Mn, Ni, Pb and Zn for the five different extraction steps.

method modified from that described by Thompson and Howarth (1976). About 10% of the samples were prepared in duplicate and analysed at random positions within a batch. Using a specially designed control chart (Thompson and Howarth, 1976), it is possible to measure analytical precision by plotting the mean of duplicate results against their absolute differences (Fig. 1).

Data were assessed against a target precision of 10% using the 50%, 90% and 99% lines in the chart. A new median (50%) line was inserted parallel to the original median, bisecting the plotted points on the chart. A new precision (1σ) was estimated at the point where the new median intercepted the mean value of 100 μg g⁻¹ [in this case, ~3% (1σ) or ~6% (2σ)].

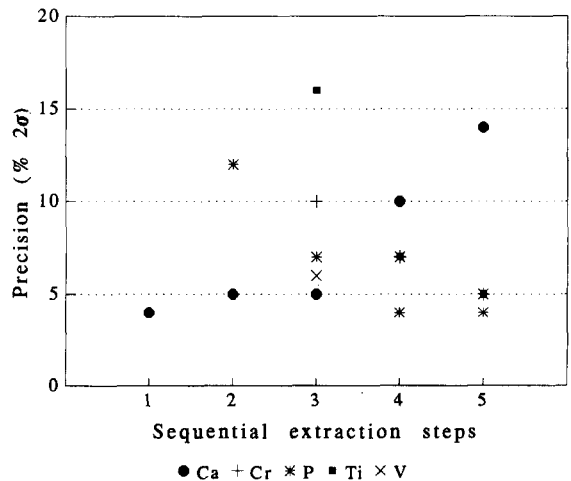


Fig. 3. Precisions calculated from duplicate analysis of Ca, Cr, P, Ti and V for the five different extraction steps.

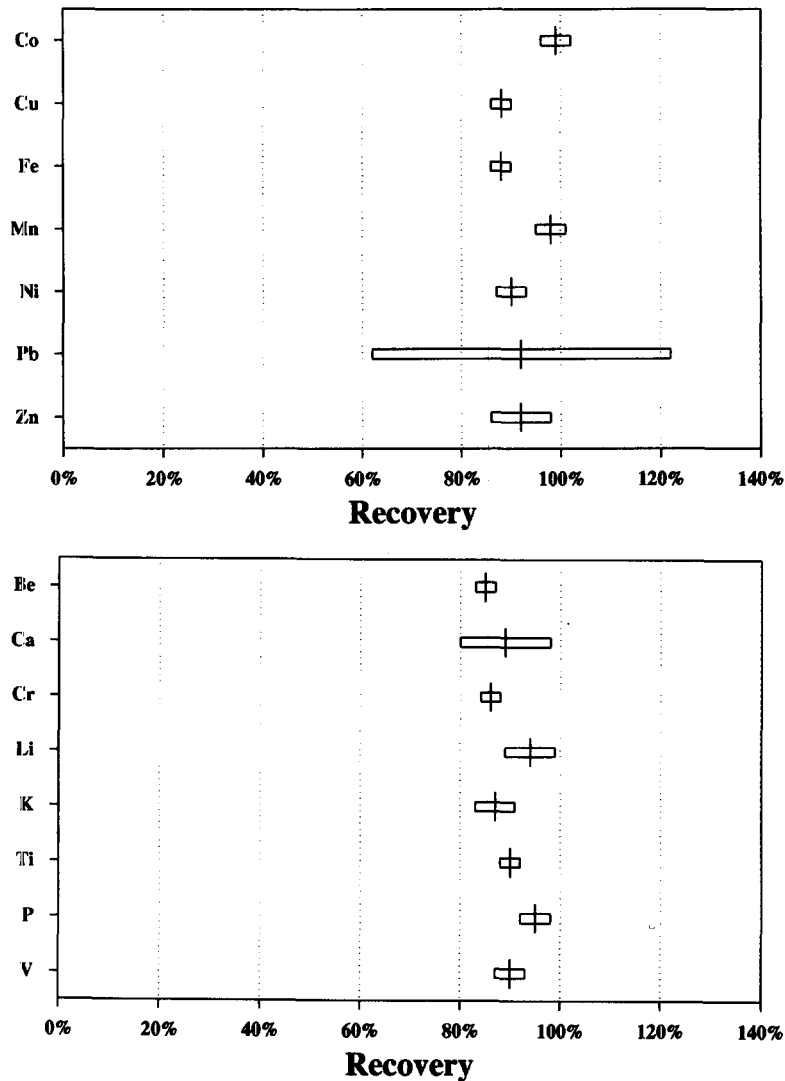


Fig. 4. Overall recovery rates for USGS reference material MAG-1 calculated from the sum concentration of the 5 extraction steps compared to the recommended value for the total concentration.

The precisions obtained by this method for elements determined at each extraction step are shown in Figs. 2 and 3. It is clear that the precision for most elements at different extraction steps is better than 10% (2σ). Most of the elements have a precision of $\sim 5\%$ in the last three extraction steps (Fig. 2). The relatively poorer precision of Fe, Mn and Pb in extraction step (1) was due to the low concentrations of these elements in the soil samples extracted by the MgCl_2 .

3.3. Accuracy of the method

The accuracy of sequential extraction methods is much more difficult to estimate than that of a total metal determination due to the many extraction steps involved. In order to assess the overall accuracy of the sequential extraction method by ICP-AES, two methods were employed here.

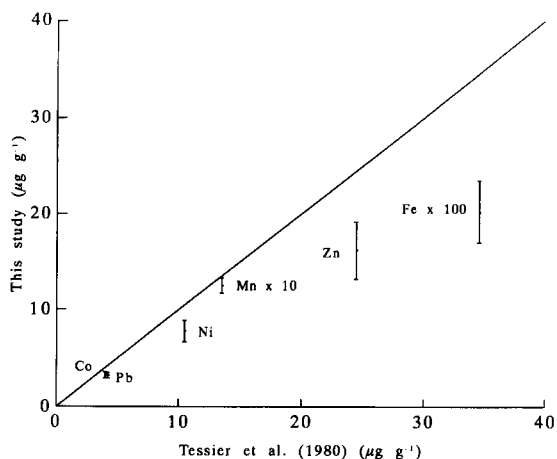


Fig. 5. Comparison with published results (Tessier et al., 1980) for USGS MAG-1 at extraction step (3). Error bars represent the mean $\pm 2\sigma$ (standard deviation).

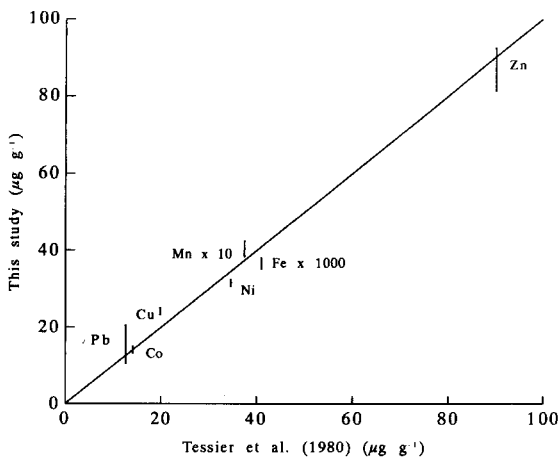


Fig. 6. Comparison with published results (Tessier et al., 1980) for USGS MAG-1 at extraction step (5). Error bars represent the mean $\pm 2\sigma$ (standard deviation).

In the first method, the sum of the concentrations from the five steps were compared with the recommended values for the total concentrations. The overall recovery rates for USGS MAG-1 for the five steps were 80–105% for all of the 15 elements determined, with an average of 92% (Fig. 4). These results were based on three observations for MAG-1 in different batches in comparison with the recommended total concentrations (Potts et al., 1992). The error bars show 95% confidence intervals for the results of the whole extraction procedure. The relative wide error bar for Pb in

Fig. 4 was due to the fact that the Pb concentrations in MAG-1 were close to the limits of detection at extraction steps (1) and (2). The recovery rates for in-house reference materials and soil samples were also $\sim 90\%$ for most of the elements determined. The high overall recovery rates clearly indicate that multielement determination on the five sequential extraction steps for soil samples can be achieved with acceptable accuracy by ICP-AES.

A second and potentially more rigorous method of assessing accuracy for the sequential extraction would be by the use of Certified Reference Materials (CRM's) and comparison with certified data at each extraction step. However, there are no CRM's available for the sequential extraction method, probably because there is no agreement on standard methods of extraction. However, Tessier et al. (1980) have reported sequential extraction results for Co, Ni, Cu, Pb, Zn, Fe and Mn from USGS MAG-1. The results obtained in the current study by ICP-AES can be directly compared against these published values (Table 3). There is generally good agreement between the two sets of data, especially for metal concentrations present at greater than five times the detection limits. Most of the results in this study were not significantly different

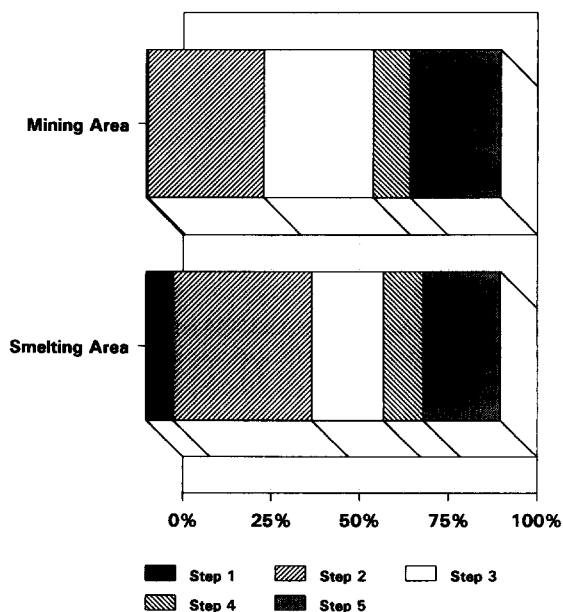


Fig. 7. Partitioning patterns of Pb in contaminated soils from the old mining and smelting areas.

from the published values given the quoted uncertainties on each value (Table 3). However, there are some marked variations of results between this study and reported data, for example, the lower values for Fe and Zn at step (3) obtained by ICP–AES (Fig. 5). This probably reflects the small systematic differences in the implementation of the extraction procedures and differential bias between the two analytical techniques. In extraction step (5), the dominant geochemical phase for most of the elements analysed, there is acceptable agreement between the results in this study and the published values (Fig. 6).

To increase the number and types of CRM's available for accuracy comparison, other certified soil materials (SO-1, SO-2, SO-3, SO-4, BCR-141, BCR-142, BCR-143) were also analysed using the proposed sequential extraction procedure. The results are summarised in Table 4, which can be used for future comparison. There is good agreement between the sum of the five fractions and the certified total concentration for these CRM's. The recovery rates for the elements with certified values are listed in Table 5.

3.4. Example of application

Having considered the analytical performance of the sequential extraction procedure, the following discussion will focus on the application of this method to soils contaminated by past mining and smelting activities to assess its suitability for this application.

Large areas of agricultural land have been contaminated by a number of metals from the historical Pb mining and smelting industries in parts of Derbyshire, U.K. (Colbourn and Thornton, 1978; Li and Thornton, 1992 and Li and Thornton, 1993). The soil contamination usually occurred over a long period but may affect crops and livestock for many years after active pollution has ceased (Thornton, 1983). Therefore, the chemical forms of these contaminant metals in soils need to be determined in order to assess the bioavailability and long-term environmental consequences of the soil contamination. Soil samples from old Pb mining and smelting sites have been subjected to the sequential chemical extraction described above. The full results of this study will be presented in another paper. The brief discussion of partitioning of Pb is given here as an example of the application of this sequential extraction method.

The exchangeable and total concentrations of Pb in soils at the old mining and smelting sites are summarised in Table 6. The total concentrations of Pb are not significantly different in the two areas. However, there are significant differences in the partitioning patterns of Pb between the soils taken from the mining area and those from the smelting areas (Fig. 7). The most important variation is the much higher exchangeable Pb in the soils at the smelting sites than that of the mining area (see Table 6 and Fig. 7). The analytical precision of this determination ($\pm 5\%$, 2σ) is more than adequate for the differentiation of these two areas, that differ by more than a factor of 10. The analytical variance in this application accounts for $< 1\%$ of the total variance within both areas, which is well within the limit of 4% (Ramsey, 1992). Any small bias that this Pb extraction may have (e.g., $\pm 7\%$ overall), will not affect the discrimination between these two patterns of Pb from the mining and smelting sources.

The major contamination sources of Pb in soils at the smelting sites were emission particulates and slag dumping. These sources contain anglesite (PbSO_4) and Pb-oxides (PbO and Pb_3O_4) which have a high solubility in the MgCl_2 extraction step (Foster and Lott, 1980; Clevenger et al., 1991). In the old mining area, however, the Pb in soils is mainly in the forms (Ford, 1976; Cotter-Howells and Thornton, 1991) of cerussite (PbCO_3), galena (PbS) and pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), which have very low solubility in the first extraction step. Therefore, the sequential extraction method demonstrates the ability to differentiate the two sources of contamination and also to infer the geochemical phases in which metals may be bound.

The bioavailability of metals in soils is thought to decrease approximately in the order of the extraction sequence, from readily available to unavailable, because the strength of extraction reagents used increases in this sequence (Harrison et al., 1981; Tessier and Campbell, 1987). Hence, the exchangeable fraction may indicate the form of the metals that are most available for plant uptake. The second step extracts metals bound to carbonate and specifically adsorbed phases, which can easily become mobile and available under conditions of lower soil pH. The remaining three fractions (Fe–Mn-oxides, organic/sulphide and residual) are generally strongly held within the soil constituents and normally unavailable to plants. From the results of the sequential extraction,

the bioavailability of Pb in soils at the smelting sites would be predicted to be higher than the Pb from the mining area.

4. Conclusions

A sequential extraction procedure modified for determination by ICP–AES can increase the number of elements determined simultaneously. One essentially uniform matrix after all five extraction steps allows a single multielement calibration of ICP–AES to be used. Multielement determinations on the five sequential extraction steps for soil samples can be achieved using this single calibration with acceptable precision and accuracy by ICP–AES. The precision of each extraction step is good with values typically $\sim 5\%$ (2σ) estimated from the analysis of duplicate samples. The overall recovery rates of USGS MAG-1 from five steps compared with the recommended total concentration values are in the range of 80–108% for most elements analysed, averaging 92%. There is acceptable comparability between the results in this study and the published values for USGS MAG-1 for each extraction step. The sequential extraction results for the reference materials (SO-1–4 and BCR-141–143) are provided for future comparison. The application of the method to contaminated soils from an old mining region demonstrates different partitioning patterns of Pb between the mining and smelting sites, and indicate the high solubility and bioavailability of Pb in the smelting areas.

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