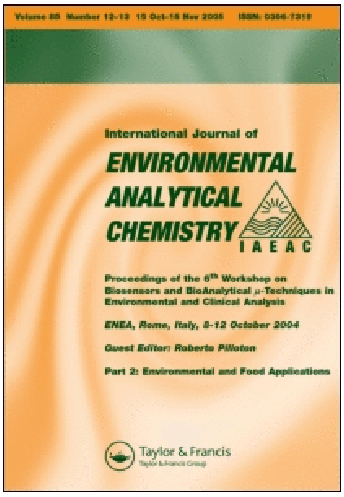

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Fractionation of lead in soils affected by smelter activities using a continuous-flow sequential extraction system

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A continuous-flow sequential extraction system was used to study the distribution of Pb, and its association with other elements (Fe, Al and Ca), in soils around a Pb smelter. Soil samples were analysed by a four-step continuous-flow sequential extraction procedure employing a modified Tessier/BCR scheme. Recoveries of Pb using the flow system (88–111%) were higher than those obtained using a conventional batch extraction system. There were also some differences in Pb distribution between fractions as determined using the two extraction systems. The most abundant fraction of Pb was extracted during the dissolution of soil oxides (Fe/Al). Extractograms (plots of concentration of elements *vs*. extractant volume/time) indicated that anthropogenic Pb was predominantly adsorbed onto Fe oxide surfaces in contaminated soils. In soil profiles, the highest amounts of Pb were found in the topsoil surface layers (0–5 cm) of the contaminated soils with only limited movement into subsurface layers.

Keywords: Continuous-flow extraction system; Elemental association; Sequential extraction; Pb; Smelter

1. Introduction

Many heavy metals are very common in industrial and domestic usage. Consequently, wastes containing heavy metals have been dispersed into the environment through their improper management and disposal. Metal smelters are important industrial point sources of heavy metals. Toxic metals emitted into the atmosphere can be re-deposited onto the land and accumulate in the soil. Moreover, the accumulated metals in soil may be taken up by plants, which could cause human health problems through the food chain. Therefore it is important to assess soil contamination in order to understand the potential adverse effects and to impose appropriate control measures.

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In most circumstances, risk assessment to human health from contamination of soils by heavy metals has usually been based on total concentrations of metals in soil. This can provide information on the degree of contamination [1]. Unfortunately, the potential risk from contaminated soil is not dependent on the total concentration of the element alone, but on the chemical reactivity of the element or the chemical species of the element of interest. The identification of chemical species or forms and their quantitative data should be used to assess the bioavailability, toxicity and environmental impact of contaminant metals. In recent years, there has been development of chemical testing procedures to measure bioavailability to plants of metals and metalloids in soil [2]. In general, sequential extraction using a series of chemicals of increasing strength is a widely used method for metal fractionation and evaluation of the potential of metal leaching [3]. The sequential extraction approach can provide detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of metals [4]. Elements extracted in the same extraction steps have been used as evidence of their chemical association (e.g. [5]). However, this may not always be absolutely correct, because elements extracted from the same phase may not have dissolved simultaneously but at different times during the same extraction step. In our previous work, we have developed a continuous-flow system for sequential extraction [6, 7], which has shown many advantages over the batch system such as speed, ease of operation, less vulnerability to variation in extraction conditions, high extraction efficiency and freedom from operational contamination. The flow system has also been proved to reduce the problem of metal readsorption and redistribution during extraction in comparison with the batch system [8]. Extractograms, i.e. plots of concentration of element extracted *vs*. subfraction number (in effect time) obtained using the system also provides kinetic information and information on solid phase elemental associations [9].

The purpose of the present study is to investigate the use of a continuous flow extraction system to determine the distribution of Pb in soils contaminated by atmospheric fallout from a metal smelter. The study compares the results obtained using the flow system with those obtained for the same soils using a traditional batch extraction system. A secondary objective was to use the extractograms obtained from the flow extraction system for interpretation of elemental associations in the various soil fractions. Results obtained from this work should help improve our understanding of the transformations of contaminant Pb at an industrially contaminated field site.

2. Materials and methods

2.1 *Soil samples*

Surface soil samples (0–5 cm) were sampled from the area surrounding a small Pb smelter located in Saraburi Province, approximately 110 km north of Bangkok, Thailand (figure 1). The smelter has been operating for the last 10 years and it is used essentially to recycle Pb from old batteries. Sampling was carried out at distances of between 0 and 2.5 km from the smelter by taking several subsamples with a trowel, and bulking from an area of approximately 0.5 m^2 at each location. Since the land surrounding the smelter has many different private owners, only parts of the area were accessible. The areas sampled were all uncultivated grassland. A preliminary

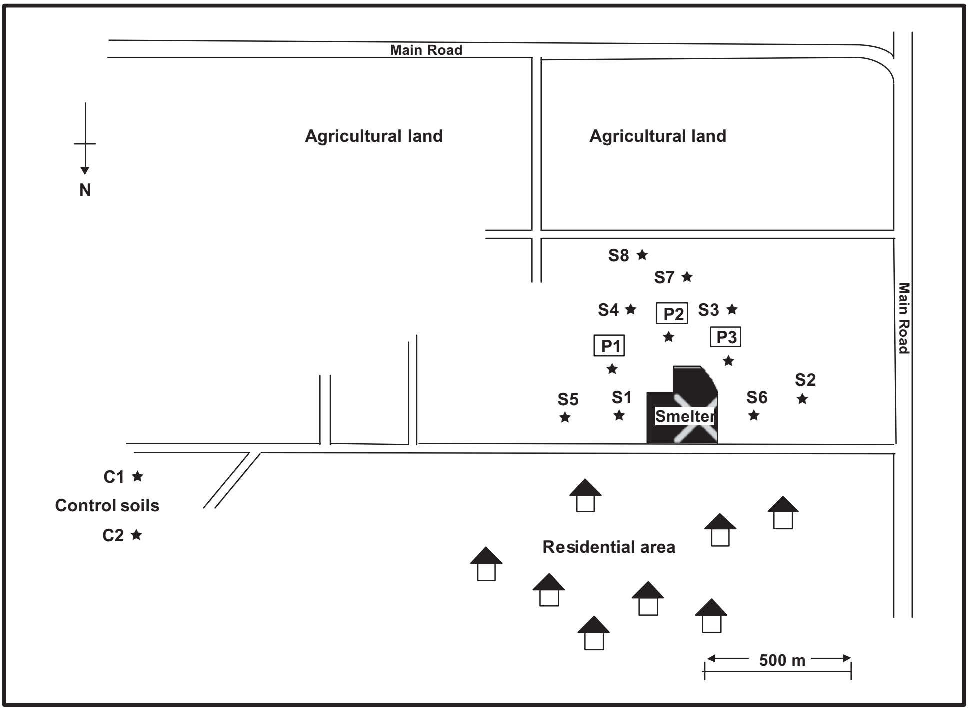


Figure 1. Map showing the sampling sites in the area adjacent to the smelter.

Table 1. General soil characteristics.

Soil	Total Pb (mg kg^{-1})	pH	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	Total Fe (%)	Total Al (%)	Total Ca (mg kg^{-1})
Control C1	21.2	5.54	21.3	56.9	21.8	2.23	5.1	1.8	2844
Soil S1	69.9	6.51	20.5	63.6	15.9	2.89	7.6	1.2	3282
Soil S2	99.2	6.17	24.6	61.9	13.5	1.47	4.7	0.8	2259
Soil S3	143.0	5.91	17.1	65.1	17.8	1.81	3.3	1.1	1875
Soil S4	246.6	5.73	20.5	61.4	18.1	2.65	3.4	1.1	2251

sampling of topsoils from the site was carried out and the total concentrations of Pb in these samples were determined. The results showed that total Pb concentrations varied in the range of 20–250 mg kg^{-1} Pb. Five of the topsoil samples were then chosen for further study to represent a range from background to high concentrations of Pb (Samples C1, S1, S2, S3 and S4). Background topsoil samples were sampled at a distance of 2 km from the smelter. The chemical and physical properties of these five soils are shown in table 1. For studying the distribution of Pb with soil depth, three soil profiles were sampled at depths of 0–5 and 5–10 cm from the surface at distances of less than 200 m from the Pb smelter (locations P1, P2 and P3, figure 1). A further sample was taken from the base of each profile (20–30 cm) in the expectation that the soil at this depth would most likely be completely unaffected by the smelter emissions. Soil samples were dried at 30°C in an oven for 5 d. All the samples were then ground and sieved through a 2-mm stainless steel sieve. All soils were stored in a desiccator prior to laboratory analysis. Soil pH was measured in a water suspension using a soil/solution ratio of 1 : 2.5 after the suspensions were shaken for 24 h on a reciprocating shaker at 20°C [10]. Total carbon content was determined by a LECO CNS 2000 Analyser. Soil texture was obtained using the Malvern Laser Sizer method [11]. Total Pb, Fe, Al and Ca were determined by acid digestion as described by Kovacs *et al.* [12] followed by atomic absorption spectrophotometric detection.

2.2 *Standard reference material (SRM)*

SRM 2711 was purchased from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD). This is a moderate contaminated soil (particle size < 74 μm) from Montana. It has been prepared to achieve a high degree of homogeneity with certified total elemental concentrations provided. Hence, it is suitable for use to validate the proposed continuous-sequential extraction method. The SRM is guaranteed for homogeneity provided that analyses are performed using a minimum sample size of 250 mg.

2.3 *Preparation of standard solutions and glassware*

The chemical reagents in this work were of analytical grade. Ultra-pure water from a MilliQ water purification unit (Millipore, Bedford, MA) was used throughout this work. All glassware used was cleaned and soaked in 10% HNO_3 and rinsed with ultrapure water before use. Standard stock solutions ($1000\,mg\,L^{-1}$) were purchased from Merck, (Darmstadt, Germany) or prepared in-house from pure metals. Working standard solutions for calibration of graphite furnace atomic absorption spectrophotometry (GFAAS) measurements were prepared by diluting the stock solution with ultrapure water or with extracting reagents before use.

2.4 *Fractionation scheme*

The fractionation scheme used was based essentially on the Tessier *et al.* [13] and BCR [14] schemes but with substantial modifications to enable its use with the flow extraction system. The geochemical phase at each extraction step is operationally defined according to the reagents used as shown in table 2. The phases extracted should be considered as nominal rather than absolute chemical fractions. For step I

Table 2. Sequential fractionation procedure.

Step	Nominal fraction	Extractant	Extraction conditions (Batch method)
I	Exchangeable	0.01 M $Mg(NO_3)_2$[a]	Shaken 24 h, 25°C
II	Acid-soluble (carbonate or specifically sorbed)	0.11 M CH_3COOH[b]	Shaken 16 h, 25°C
III	Reducible (Fe/Al/Mn oxide-bound)	0.1 M $NH_2OH \cdot HCl$, pH 2[b]	Shaken 6 h, 96°C
IV	Oxidizable (organic-bound)	30% H_2O_2 : 0.02 M HNO_3 (8 : 3 v/v)[a]	Shaken 5 h, 85°C
V	Residual	$HNO_3 + H_2O_2$[c]	Acid digestion

[a] Modification from Tessier *et al.* scheme [13, 15].
[b] Modification from BCR scheme [14].
[c] Acid digestion, Kovacs *et al.* procedure [12].

(exchangeable phase), which is not required in the BCR scheme, 0.01 M $Mg(NO_3)_2$ was used as the extractant. Many authors use 1 M $MgCl_2$ for this phase following the Tessier *et al.* [13] scheme. However, using a nitrate salt reduces the background absorption when determining Pb with GFAAS. The lower strength salt was used to simulate desorption of the most weakly bound ions (exchangeable) into the soil solution (e.g. [15, 16]). For Steps II and III the reagents used in the BCR sequential extraction scheme were used [14]. Step IV was modified from the Tessier *et al.* [13] scheme by using only 30% H_2O_2 : 0.02 M HNO_3 (8 : 3 v/v) because intermittent addition of NH_4OAc during extraction is not practical in the flow system. The last step (Step V) was performed using the HNO_3/H_2O_2 digestion procedure of Kovacs *et al.* [10]. Such digestions are often referred to as pseudo-total analyses [17] since they do not include metals trapped within the lattices of silicate minerals. However, true total analyses are not considered necessary for the assessment of metal-contaminated soils since only those metals potentially available for leaching and biological processes are usually of interest [18].

In the batch extraction system, the soil sample was weighed accurately into a centrifuge tube and the extractions at each step were carried out using the equilibration times as shown in table 2. A water bath was used for the extraction steps where higher temperatures were required. Centrifugation (10,000 rpm for 10 min), decantation and filtration steps (Whatman filter paper, No. 52) were used for separation of the liquid and solid phases at each step. This differs from the Tessier *et al.* [13] procedure in which supernatants were removed by pipette. In this work, the original five soil samples (C1, S1–S4) were fractionated using both batch and continuous-flow extraction systems to examine the accuracy and efficiency of these two extraction systems. The sets of samples taken from different depths (P1–P3) were fractionated using the flow extraction system only.

2.5 *Continuous-flow extraction system*

2.5.1. The extraction chamber. An extraction chamber was designed to allow containment and stirring of a weighed sample of soil. Extractants are pumped sequentially through the chamber and leach metals from the targeted phases. The chambers and covers were constructed from borosilicate glass to have a capacity of approximately 10 mL [6, 7]. The outlet of the chamber was furnished with a filter (Whatman [Maidstone, UK]) glass microfibre filter GF/B, 47-mm diameter, 1-µm particle retention). Extractant was pumped through the chamber using a peristaltic pump (Micro tube pump, MP-3N, EYELA [Tokyo Rikakikai Co., Ltd.]) at varying flow rates using tygon tubing of 2.25 mm inner diameter. Heating of the extractants in Steps III and IV was carried out by passing the extractants through a glass heating coil approximately 120 cm in length, placed in a water bath. However, because of heat loss problems, even when the glass heating coil was immersed in a thermostat water bath controlled at 95°C, the maximum temperatures achieved in the extraction chamber were between 80 and 85°C. Thus, for Step IV in particular, the temperatures used were somewhat lower than those used for the batch system (table 2).

2.5.2. Extraction procedure. A weighed sample (1.00 g) was transferred to a clean extraction chamber together with a magnetic bar. A glass microfibre filter was then placed on the outlet followed by a silicone rubber gasket, and the chamber cover was securely clamped in position. The chamber was connected to the extractant reservoir and the collector vial using tygon tubing and placed on a magnetic stirrer. The magnetic stirrer and peristaltic pump were switched on to start the extraction. The extracting reagents were continuously and sequentially pumped through the chamber. The extracts passing through the membrane filter were collected in subfractions of 10–30 mL volume intervals until all four leaching steps were completed. For most soils examined, it was found that 120–180 mL were sufficient to leach the metals completely for each step.

2.5.3. Residue digestion. Residue digestion was performed using an acid digestion method [12] on a heating block. This system was equipped with a heating program. Amounts of 0.5–1.0 g of dried soil sample or residue from the extraction chamber were transferred to digestion tubes together with 5 mL of HNO_3 (70%) and 5 mL of H_2O_2 (30%). The digestion tubes were placed on a heating block and the digestion was operated following the recommended heating program for 6 h [12]. The digest solutions were cooled to room temperature, and filtered through Whatman filter paper No. 52, were then made up to volume in a volumetric flask. Total metal concentrations were determined by both a single digestion of non-fractionated soil and by summation of extractable metals in each subfraction of the exchangeable, acid-soluble, reducible, oxidizable and residual fractions.

2.6 *Analysis of extracts and acid digests*

Lead concentrations in extracts were determined using graphite furnace atomic absorption spectrophotometry (GFAAS). The GFAAS measurements were performed with a Perkin Elmer (Norwalk, CT) Analyst 100 equipped with a deuterium background corrector and an HGA-800 heated graphite atomizer. The sample was introduced to the atomizer using an AS-72 autosampler. Flame atomic absorption (FAAS) measurements for Fe, Al and Ca were performed using a Perkin Elmer Model 3100 spectrometer equipped with deuterium background correction. Concentrations of metals were obtained by the matrix-matched standard calibration method. Working standard solutions were prepared in the same extracting reagent as the sample solutions.

3. Results and discussion

3.1 *Validation of the continuous-flow sequential extraction system using a standard reference material*

We initially evaluated the proposed continuous-flow sequential extraction system by carrying out a sequential extraction of 0.25 g of NIST standard reference material (SRM 2711). The resulting analytical data are shown in table 3. The sums of each element determined (Pb, Fe, Al and Ca) found in all fractions (I + II + III + IV + Residue) were compared with the reference values of acid leaching data provided by NIST. It was found that they agreed reasonably well within the range of reference values provided indicating that the extraction data obtained from the continuous-flow extraction system are reliable.

Table 3. Comparison of analytical results for summation of elemental concentrations determined using the continuous-flow sequential extraction system for SRM 2711 ($\mathrm{mg\,kg^{-1}} \pm$ s.d., $n = 3$).

Element	Step I	Step II	Step III	Step IV	Residue	Sum of fractions	Leached value[a]	Certified value[b]
Pb	3.7 ± 0.5	309 ± 9	710 ± 90	23 ± 8	91 ± 17	1138 ± 56	930–1500	1162 ± 31
Fe	ND	228 ± 12	964 ± 119	123 ± 10	14860 ± 460	16170 ± 460	17000–26000	28900 ± 600
Al	ND	ND	1290 ± 107	160 ± 18	20660 ± 550	22100 ± 430	12000–23000	28800 ± 800
Ca	3970 ± 90	11920 ± 700	3820 ± 140	25 ± 4	89 ± 13	19820 ± 660	20000–25000	65300 ± 900

ND = non-detectable.

[a] Acid leaching values for SRM 2711 provided by NIST.

[b] Certified values for total concentrations of SRM 2711 provided by NIST.

3.2 Comparison of Pb fractionation obtained using continuous-flow and batch sequential extraction techniques

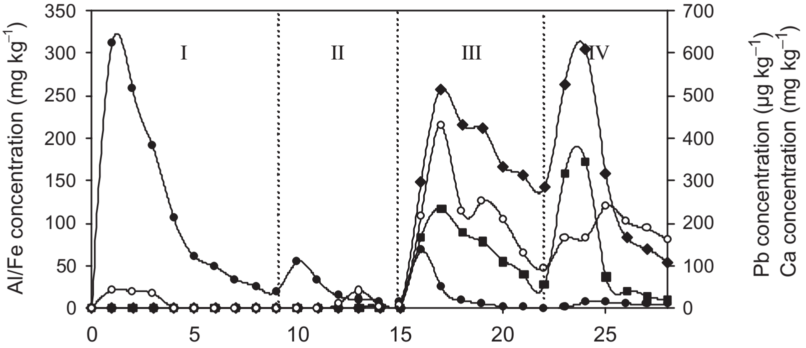
Table 4 compares the distribution of Pb in soils obtained using the flow system and a conventional batch method. In the flow system, the amounts of Pb in each individual phase were obtained by summation of the amounts in all subfractions of each step. In general, the flow system gave better recoveries of Pb compared to the batch system for all samples analysed. The summation of Pb fractions obtained using the flow method also showed good agreement with the total concentrations from a single total analysis. The recoveries in the batch system were poorer, probably as a result of losing particulate matter at each stage during centrifugation and filtration. However, the flow extraction is a closed system, which effectively solves this problem. The precision (repeatability) of the flow system appears to be slightly lower than for the batch system (see standard deviations in table 4). This is probably due to the summation of data from several subfractions for each fraction in the flow system.

Although the overall recoveries of Pb was higher using the flow system, in the first two exchangeable and acid soluble phases, the amounts of Pb extracted using the flow system were lower than those obtained using the batch system. Lead is very strongly sorbed onto soil and the flow rate of extractant at 3–5 mL min^{-1} (calculated as approximately 0.5 h total contact time) may have been too fast to allow adequate equilibration between solution and solid phases. In contrast, in the batch system, equilibration was carried out for 16 or 24 h for these fractions (table 2). In addition, although not significant in terms of overall recoveries, the Pb concentrations in subfractions of Steps I and II were often near or below detection limits. For the soil oxides (Fe/Al); extraction step, the amounts of Pb extracted using the flow system were higher than those obtained using the batch system. Conversely in the following step (oxidizable), the amounts of Pb extracted using the flow system were lower than those obtained using the batch system. These observations can be explained by the readsorption of Pb in the batch system. Chomchoei *et al.* [8] have investigated and compared the readsorption process in both batch and flow systems. For Pb, their results clearly showed that for the conventional batch system, there was significant readsorption in both the reducible and oxidizable steps. Some Pb extracted in the reducible phase was readsorbed and could be dissolved in the next step; the oxidizable phase. Hence the batch system tends to underestimate the Pb associated with the Fe/Al oxides and overestimates the Pb associated with the oxidizable fraction. In contrast, readsorption is not observed for the continuous-flow extraction system [8]. Little readsorption occurs in the flow system because the extracted Pb is gradually removed from the system in the flowing extractant before it can be readsorbed on the solid phase. According to the results of the present work, the amount of Pb in the reducible step appears to be more completely dissolved and removed in the flow system. It can be observed from the extractograms (figure 2) that the concentration of Pb approaches the baseline towards the end of the reducible step. However, this is not the case for the oxidizable step, which normally takes a longer time to complete because of clogging of the filter paper by dispersed soil. This is often found in the flow extraction for this step because the oxidizable phase is often complex and the extraction temperature achievable is not high enough for rapid dissolution of organic matter in this phase. The concentration of some elements remained well above the baseline when the extraction (Step IV) was discontinued. This also suggests an additional reason

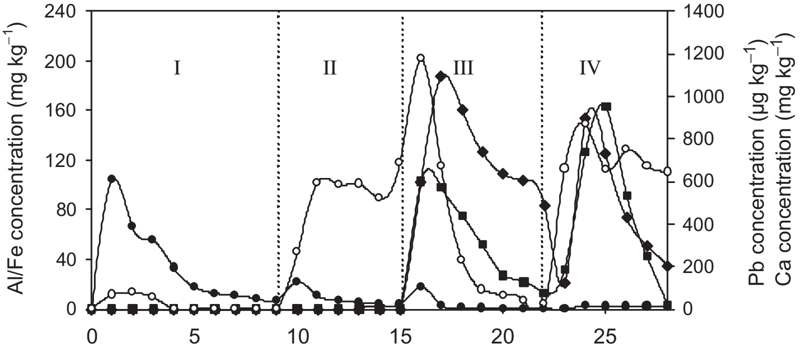
Table 4. Comparison of analytical results for batch and flow sequential extraction methods of Pb for soil samples (mg kg^{-1} ± s.d., $n = 2$).

Sample	Method	Step I	Step II	Step III	Step IV	Residue	Sum of fractions	Total
Control C1	Flow	0.11 ± 0.00	0.06 ± 0.01	11.7 ± 3.9	0.87 ± 0.25	8.77 ± 1.06	21.54 ± 3.05	20.8 ± 2.9
	Batch	0.19 ± 0.06	0.99 ± 0.17	7.44 ± 0.5	1.23 ± 0.09	4.6 ± 0.15	14.45 ± 0.30	
Soil S1	Flow	0.16 ± 0.01	0.06 ± 0.01	41.6 ± 3.1	0.78 ± 0.11	19.53 ± 3.04	62.16 ± 0.15	69.9 ± 9.0
	Batch	0.27 ± 0.07	2.21 ± 0.38	21.4 ± 1.1	5.42 ± 0.17	14.15 ± 1.43	43.36 ± 0.90	
Soil S2	Flow	0.14 ± 0.05	0.71 ± 0.10	96.8 ± 1.2	1.68 ± 0.53	11.23 ± 2.72	110.54 ± 2.19	99.2 ± 8.5
	Batch	0.25 ± 0.08	3.01 ± 0.22	54.0 ± 3.1	11.67 ± 0.29	7.30 ± 0.10	76.22 ± 1.60	
Soil S3	Flow	0.19 ± 0.10	1.73 ± 0.07	124.0 ± 0.1	1.99 ± 0.42	17.42 ± 2.86	145.29 ± 3.90	143.0 ± 2.1
	Batch	0.45 ± 0.04	3.52 ± 0.15	78.0 ± 0.2	15.89 ± 0.98	10.60 ± 0.20	108.46 ± 0.52	
Soil S4	Flow	0.03 ± 0.01	3.52 ± 0.27	229.5 ± 0.3	4.12 ± 0.09	21.81 ± 2.50	259.00 ± 2.95	246.6 ± 6.7
	Batch	0.19 ± 0.04	4.78 ± 0.83	131.2 ± 8.8	25.9 ± 0.87	18.70 ± 2.90	180.86 ± 4.70	

(a) Control soil C1



(b) Contaminated soil S4



(c) Contaminated soil P2 (0–5 cm)

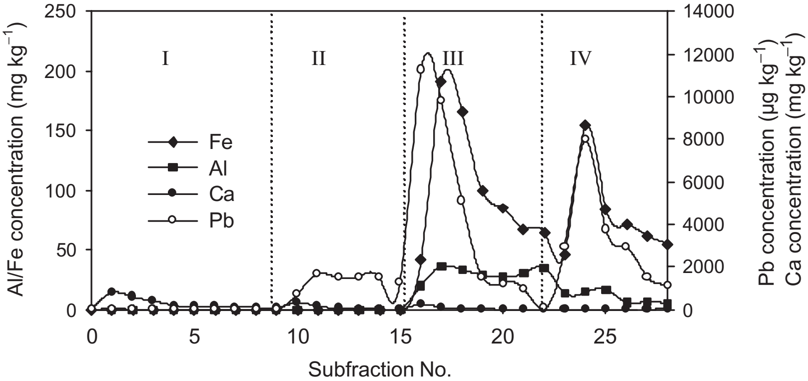


Figure 2. Extractograms obtained using the continuous-flow method for (a) control C1, (b) contaminated soil S4, and (c) contaminated soil P2 (0–5 cm). For purposes of clarity, Pb concentrations in fraction III have been scaled down by factors of 10 (C1 and P2) or 100 (S4).

why the amounts of Pb extracted in this step in the flow system are lower than those obtained in the batch system (table 4), with some of Pb in effect being carried over to the residual phase. The mean proportions of Pb present in individual fractions obtained from the both batch and flow extraction systems are shown in figure 3.

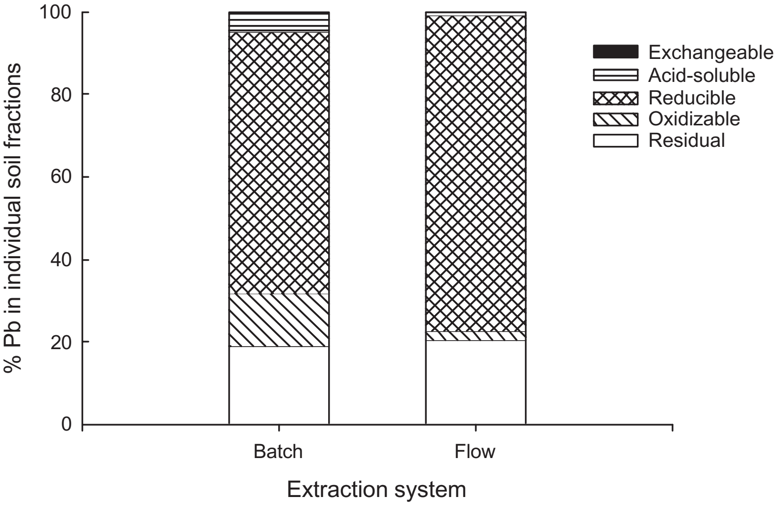


Figure 3. A comparison of mean fractional distributions of Pb in soils as determined by batch and continuous-flow methods.

Table 5. The distribution of contaminant Pb determined using the flow sequential extraction system.

	Contaminant Pb[a] (mg kg^{-1})					
Sample	Step I	Step II	Step III	Step IV	Residue	Sum
Soil S1	0.05	0.00	29.86	−0.09	10.76	40.85
Soil S2	0.03	0.65	85.05	0.81	2.46	89.00
Soil S3	0.08	1.67	112.26	1.12	8.65	123.78
Soil S4	−0.08	3.46	217.77	3.25	13.04	237.44
Mean %	0.005	0.88	87.89	0.74	10.44	
Control C1 %	0.51	0.28	54.41	4.04	40.75	

[a] Pb concentrations in fractions of control C1 have been subtracted.

Although clearly there are differences between the two systems, in both systems the highest proportion of Pb was found in the reducible fraction (60–80%), followed by the residual (10–40%), organic/sulphide bound (1–15%), acid-soluble (0.8%) and exchangeable (0.005%) fractions. However, for the following parts of this study, only the flow system has been used. This system was selected because of advantages in reducing soil loss, potential contamination and readsorption phenomena, and providing better overall Pb recoveries.

3.3 *Examination of anthropogenic Pb in the soil using the flow system*

When anthropogenic Pb is deposited and incorporated into the soil, it can be distributed and fixed by different soil phases [19]. Table 5 shows the differences in amounts of Pb (mg kg^{-1}) in individual fractions between the control and the contaminated samples (i.e. anthropogenic Pb) as determined using the flow extraction system. It can be seen that in the contaminated soils, the anthropogenic Pb is distributed between all the individual phases. However, the distribution is substantially different to that of the native soil Pb found in the control soil. Considering each fraction, there are very small proportions of contaminant Pb in the exchangeable, acid soluble phases, and oxidizable phases; 0.005, 0.883 and 0.74% respectively. Most of the contaminant Pb appears in the reducible phases (88%), with an approximate 10% in the residual fraction. This result is in agreement with earlier reports that soil oxides are important scavengers of heavy metals in soils (e.g., [20]). However, previous studies, including soils with relatively high organic matter contents, have shown that in such soils, anthropogenic Pb may occur predominantly in the oxidisable fraction [21, 22].

The above results demonstrate considerable soil pollution with Pb in the vicinity of the smelter. Our sequential extraction data also agrees with some previous studies, which have measured metal concentrations of soils affected by smelters [23–25]. Such studies have suggested that sequential extraction investigations are good tools to distinguish between contaminated and native soils. The mineral phases that hold heavy metals appear to be significantly different in the native soils compared to contaminated soils. The typically lithogenic metals Fe, Al, Ca and Pb usually occur in uncontaminated soils predominantly in the most stable fractions. Lead of anthropogenic origin has considerably higher proportions in mobile fractions and correspondingly lower proportions in residual phases.

3.4 *Lead fractionation in samples from different depths*

Data on metal fractionation of soil at different soil depths is essential for considering the processes of metal transformation, mobility and bioavailability as well as the long-term risk assessment. Total Pb concentrations in different layers of polluted soils have been measured and monitored previously [23, 24]. These studies found that Pb fractionation differed between topsoils and subsoils. Mobile Pb (exchangeable and acid soluble fractions) was high in topsoils and much lower in subsoils.

In this present study, in order to assess the vertical extent of soil contamination, topsoil and subsoil concentrations of Pb were compared using the flow sequential extraction technique (table 6). In all three profiles sampled, at a distance of 0.2 km from the emission point source, the highest concentrations of Pb were found in the topsoils, ranging from 350–450 mg kg^{-1} (table 6). However, Pb concentrations in the subsurface layers (5–10 cm and 20–30 cm) were much lower and differed from one point to another. The concentrations of Pb at a depth of 30 cm are the lowest and similar to background concentrations (ca 10–15 mg kg^{-1}). This indicates that the Pb of anthropogenic origin showed high accumulations at the soil surface and only moves slowly downward through the soil profile. The Pb fractionation data for the different depth samples are summarized in table 6. The results demonstrate that there are significant increases of anthropogenic Pb (mg kg^{-1}) in topsoil samples found in the first two most mobile fractions; the exchangeable and acid-soluble fractions. However, most anthropogenic Pb was present in the reducible fraction due to the ability of soil oxides (Fe/Al) to fix Pb. The enhancement of the available/mobile pool in the topsoil is probably responsible for the limited movement of Pb down into the deeper layers. However, most of the Pb leached from the topsoil appears to be fixed by soil oxides in the 5–10 cm layer, limiting any further movement to deeper layers. These results are similar to those reported in many previous studies [23, 24, 26]. For example, Ettler *et al.* [26] have estimated downward penetration rates of between

Table 6. Fractionation of Pb in soil profiles (mg kg^{-1} ± s.d., $n = 2$).

Sample	Depth (cm)	Step I	Step II	Step III	Step IV	Residue	Sum of fractions	Total
P1	0–5	0.040 ± 0.002 (0.012)	8.36 ± 0.20 (2.63)	313.19 ± 13.26 (86.50)	2.29 ± 0.26 (0.63)	38.02 ± 10.75 (10.50)	361.8 ± 5.3	337 ± 25
	5–10	0.009 ± 0.002 (0.002)	0.73 ± 0.03 (2.29)	18.47 ± 0.12 (57.95)	1.76 ± 0.08 (5.62)	10.89 ± 1.87 (34.17)	31.87 ± 1.8	35 ± 2
	20–30	0.009 ± 0.001 (0.073)	0.11 ± 0.03 (0.903)	9.78 ± 0.56 (80.29)	0.41 ± 0.15 (3.36)	1.95 ± 0.01 (16.00)	12.18 ± 0.79	15 ± 0.5
P2	0–5	0.041 ± 0.002 (0.009)	8.02 ± 0.03 (1.809)	391.57 ± 17.81 (88.38)	20.85 ± 6.47 (4.70)	22.85 ± 5.78 (5.15)	443.3 ± 5.5	376 ± 55
	5–10	0.031 ± 0.006 (0.110)	0.63 ± 0.04 (2.26)	13.25 ± 1.45 (47.57)	1.70 ± 0.06 (6.10)	12.24 ± 1.29 (43.94)	27.85 ± 2.55	31 ± 4
	20–30	0.003 ± 0.001 (0.13)	0.07 ± 0.004 (3.07)	1.76 ± 0.01 (77.19)	0.08 ± 0.01 (3.50)	0.35 ± 0.00 (15.35)	2.28 ± 0.07	3.7 ± 0.2
P3	0–5	0.028 ± 0.006 (0.006)	6.04 ± 0.02 (1.47)	366.64 ± 11.69 (89.50)	16.29 ± 0.01 (3.97)	20.64 ± 1.23 (5.03)	409.3 ± 10.9	420 ± 45
	5–10	0.030 ± 0.001 (0.055)	0.71 ± 0.05 (1.32)	37.77 ± 0.10 (70.18)	4.18 ± 1.04 (7.76)	11.13 ± 0.18 (20.68)	53.82 ± 0.52	69 ± 1
	20–30	0.005 ± 0.001 (0.030)	0.071 ± 0.002 (0.42)	14.16 ± 0.89 (87.46)	0.18 ± 0.05 (1.11)	1.78 ± 0.30 (10.99)	16.19 ± 0.80	11 ± 0.07

Figures in parenthesis show % of total concentration in each fraction.

0.3 and 0.36 cm y^{-1} for Pb in soils surrounding a Pb smelter. On this basis, since the smelter in the current study has been operating for only 10 years, it is probably not surprising that Pb movement downwards appears to be somewhat limited.

3.5 *Chemical associations of Pb and major elements (Fe, Al and Ca) in soil fractions using extractograms*

One of the problems when using batch sequential extraction to study chemical associations is the non-absolute evidence of elemental associations. Elements extracted in the same extraction step have been used as evidence of their chemical associations. However, this may not always be absolutely correct, because elements extracted in the same extraction step may not have dissolved simultaneously but at different times during the extraction step. For the continuous-flow sequential extraction, the extractants were continuously and sequentially pumped through the chamber containing the soil samples. The extracts were collected at set volume intervals (subfractions) with time until each extraction step was completed, as indicated by the extraction profiles reaching baseline. The graphical plot of metal concentrations in subfractions *vs.* subfraction number is called an extractogram. Using overlayed extractograms for different elements, and by comparing detailed peak profiles and peak shapes, it is possible to evaluate the elemental associations in the various extracted solid phases [9, 27]. If two elements are closely associated in a particular geochemical phase, they should show similar peak shapes, and a high correlation between amounts extracted in each subfraction of the particular phase. Metals, which are not closely associated, but are leached in the same extraction step, will show peak profiles, which do not coincide with time during the extraction. As a result, the extractogram enables a detailed examination of possible associations between elements, and therefore provides an insight into the sources of elements present in each fraction.

The distribution and chemical associations of Pb and major elements in soil (Fe, Al and Ca) for a control and contaminated soils (topsoils) can be evaluated using the extractograms shown in figure 2. Variations in the Pb extraction profiles between the control and contaminated soils are most likely due to the difference between the lithogenic and anthropogenic origin of Pb particularly in the reducible phase. The extractograms for the exchangeable phase show little difference in extraction profiles of Pb between the contaminated and control soils. In the exchangeable fraction, very small amounts of Pb were found and extracted along with Ca extracted in the early stages.

Some previous studies of the Pb smelting process have reported that the Pb emission from smelters is predominantly in the form of Pb sulphates ($PbSO_4$, angelsite) [28, 29], or as a combination of Pb sulphates and chlorides ($PbCl_2$, cotunnite) [25]. Although $PbSO_4$ is less soluble than $PbCl_2$, both compounds will dissolve in the soil, and therefore the very small amounts of Pb in the exchangeable fraction found in this work may be derived from these sources. The more soluble $PbCl_2$ in particular could also be responsible for the slight downward movement of Pb observed in this study. Li and Thornton [29] also suggested that the large amounts of Ca (55%) present in the exchangeable fraction were due to the possible presence of $CaSO_4$ in the area surrounding the smelter. However, they could also be due to Ca adsorbed by the exchange complex.

In the acid soluble phase, it is difficult to see the profile of Pb present in the control soil since Pb in this particular fraction was found at very low concentrations. However, the Pb profile seems to be lagging behind the Ca profile in both the control and contaminated samples. The small amounts of Ca extracted most probably results from the low contents of $CaCO_3$ in our soil samples. The concentrations of Pb found in the contaminated soils in the acid soluble step remained relatively high with no sign of approaching the baseline. These continuous leaching signals are possibly a contribution from Pb sorbed on the surface of soil oxides. Dissolution of Fe oxide was negligible as no Fe peak was observed in this particular step.

In the reducible and oxidizable steps, Fe and Al were found in significant amounts. The predominant fraction for Pb appeared in the reducible fraction. However, there are some significant visual differences observed in the extractograms between the control and contaminated soils. It can be seen in the extractogram of the control soil (figure 2a) that Pb does appear to dissolve at the same time as Fe and Al in the reducible fraction (Step III). This indicates a close association between Pb and soil oxides. In contrast, for the contaminated soils, the initial Pb peak was found to rise rapidly in the early part of this stage, and preceded the bulk of the Fe and Al dissolution. Data obtained using batch methods are unable to provide this type of information.

On the basis of the above patterns observed in the extractograms, it could be concluded that Pb was predominantly absorbed on the Fe/Al oxide surfaces, indicating an anthropogenic origin. The results also suggest that Fe/Al oxides are the major components of importance in fixing heavy metals in the soils at this contaminated site.

In the oxidizable fractions, the extraction step could not be carried out to completion as discussed previously. However enough data was produced to consider the chemical associations in this step. The extractograms of Pb do not show up as well-defined peaks decreasing to the baseline by the end of the fraction, and there is no clear correlation of the Pb extractograms with those Fe, Al and Ca.

The visual interpretation of elemental associations using the extractogram is strongly supported by examination of the extraction data using plots of mole ratios of Pb/Fe in the reducible phase. The mole ratio of Pb/Fe in each subfraction was plotted against subfraction number for this particular phase as shown in figure 4. It can be seen that high ratios of Pb/Fe were found in the early subfractions in contaminated soils and correspond to Pb adsorbed on the Fe oxide surfaces. According to the plots of the Pb/Fe mole ratios of the contaminated soils, the Pb/Fe mole ratios decreased with subfraction number and approached a constant value. The more highly contaminated soils show higher Pb/Fe mole ratios in the early subfractions. This mole ratio plot can be used as a tool for identification of anthropogenic origin and degree of contamination.

4. Conclusions

A continuous-flow extraction procedure was applied to contaminated soils from an area adjacent to a Pb smelter. The results obtained from this study demonstrate that the flow system was an effective and accurate method for fractionating soil Pb. The sum of Pb in all subfractions obtained using this method gave good recoveries when compared with results of total concentration obtained from total digestion.

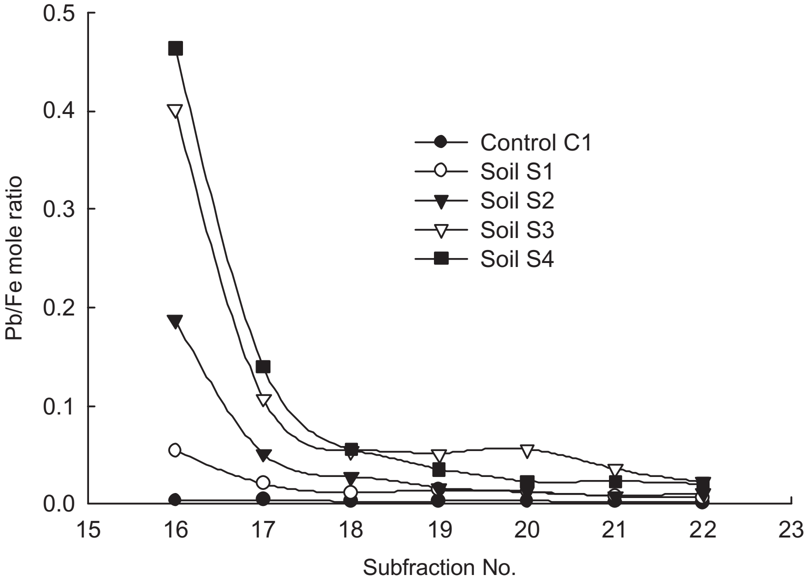


Figure 4. Pb/Fe mole ratio plots for subfractions in the reducible phases of the control and contaminated soils.

In addition, the continuous-flow system eliminates some tedious procedures, such as centrifugation and manual filtration that are required for the batch method. However, it must be recognized that the results obtained using the continuous-flow system, in terms of Pb distribution between fractions, are likely to differ to some extent from those obtained using conventional batch techniques. The reasons for this have been fully discussed above. For the soil samples examined in this study, Pb was predominantly present in the reducible and residual phases. The most predominant fractions for Fe and Al are the residual phases, followed by the reducible phases. In contrast, most Ca is in the exchangeable and residual phases.

An additional advantage of the flow system is the detailed information obtained from the extractogram. Detailed investigations using extractograms, particularly for inter-element comparisons, can clearly provide useful information not possible with the batch technique. The flow system has a high potential for evaluating elemental associations and the modes of occurrence of Pb in soil samples. The fractionation profiles/extractograms of Pb were found to depend strongly on the metal origin. For contaminated soils in this study, the extractograms have shown that Pb was predominantly adsorbed on soil oxide surfaces, especially in topsoil samples, indicating anthropogenic origin. The visual interpretation of Pb adsorption on the surface using extractograms is strongly supported by an examination of the Pb/Fe mole ratio plots. Total concentrations of anthropogenic Pb were much higher in topsoils than in subsoils. However, enhancement of Pb in the most available/mobile fractions (exchangeable and acid soluble) in the topsoil (0–5 cm) had resulted in a limited movement of Pb into the underlying soil (5–10 cm). There was no further detectable movement of Pb below this layer.

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