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# A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land

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## Abstract

Cadmium, chromium, copper, lead, manganese, nickel, vanadium and zinc have been determined in samples of made-up ground from layers of a trial pit excavated on a recently derelict, industrially contaminated site. The pseudototal metal content of the layers was determined following a microwave-assisted digestion with aqua regia. Operational speciation was performed using the BCR three-step sequential extraction procedure. Analyses were carried out by flame or electrothermal atomic absorption spectrometry (FAAS or ETAAS). A suppressive interference ( $\sim 30\%$ ) was observed in the determination of cadmium in aqua regia digests by ETAAS, but not in  $0.11 \text{ mol l}^{-1}$  acetic acid,  $0.1 \text{ mol l}^{-1}$  hydroxylammonium chloride or  $1.0 \text{ mol l}^{-1}$  ammonium acetate extracts. Agreement between duplicate samples was acceptable (i.e. within 10%) for most elements in most layers, but some large discrepancies were apparent, especially for lead. The amount of metal extracted in the sequential procedure (i.e. Step 1+Step 2+Step 3+residual) did not generally agree well with pseudototal digestion. Various layers of the trial pit contained significant levels of contaminant metals, but these were not always in easily mobilized forms. For example, less than 0.2% of the lead ( $\sim 4000 \mu\text{g g}^{-1}$ ) at 65–85 cm depth was present as exchangeable or acid-soluble species. The study illustrates the importance of considering metal speciation when assessing the mobility of potentially toxic elements in industrially-contaminated land. © 1998 Elsevier Science B.V.

*Keywords:* Chemical speciation; Heavy metals; Sequential extraction; Soil; Contaminated land

## 1. Introduction

The problems of contaminated land are of increasing concern in the developed world. In England and Wales, up to 100,000 sites may be affected [1], with a

further 6000 derelict or vacant sites in Scotland [2]. Estimated clean-up cost in the Netherlands, Germany and the USA (Superfund sites) are each of the order of tens of billions of pounds sterling [3].

It is vital that analyses performed on such sites provide reliable and appropriate information, on the basis of which remediation options can be assessed. However, no dedicated procedures exist for the ana-

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lysis of recently-derelict, industrially-contaminated land, and methodology developed for the analysis of conventional soils may not always prove appropriate. Former industrial sites present considerable sampling difficulties since the contamination may be extremely heterogeneous and the site may contain large quantities of anthropogenic material (from fine ash particles, through ore, clinker and discarded catalyst, to bricks and concrete pallets). Also, many former industrial sites have been used for various manufacturing processes, often over several years, and it is rare for only one contaminant to be present. High levels of co-contaminants may give rise to unexpected interference in the determinative step of analyses performed. It is therefore important that the suitability of established analytical procedures be re-evaluated prior to use in contaminated land assessment.

In the UK, concentrations of contaminant metals and metalloids are generally compared with guideline levels issued by the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) (Table 1) [4]. An important limitation of this approach is that, for many of the elements, threshold trigger values relate to total metal concentrations. These reflect only the maximum amount of contamination present and give no indication of likely environmental impact since they provide no information on potential environmental mobility or bioavailability-considerations which are of prime concern to site assessors and engineers.

Chemical speciation strongly influences the mobility of metals in soil. However, whilst methods for determination of true species (i.e. specific compounds or elements in a particular oxidation state [5]) are now

available for various trace elements in aqueous systems, methodology for speciation in solids is less well developed. Direct methods for determination of solid-state speciation are generally of insufficient sensitivity for environmental trace analysis (e.g. NMR spectroscopy) or require very specialized equipment (e.g. EXAFS) [6]. Operational methods of speciation, such as the use of single or sequential extraction are thus commonly applied.

A number of investigators have highlighted pitfalls in the use of sequential extraction [7], the most serious of which appear to be the poor selectivity of the reagents used [8–10] and post-extraction re-adsorption of released metals [9,11] (although the latter may be less important at trace levels in real samples [12]). These limitations mean that sequential extraction cannot be used to determine specific geochemical associations, but the approach is still of value in the assessment of land contamination. Sequential extraction can be used to give an indication of the amounts of metals in various “reservoirs” which could be mobilized by changes in soil chemistry (notably pH or Eh) [13].

A large number of sequential extraction procedures have been developed (see, for example, [14] and references therein) many of which are variants on that of Tessier et al. [15]. As part of a recent attempt to harmonize methodology for leaching/extraction tests throughout the European Community [16], the BCR (now the Standards, Measurement and Testing Programme) has developed a three-stage, sequential extraction protocol [17] in which metals are divided into acid soluble/exchangeable, reducible and oxidizable fractions. The method has proved reproducible and gave good recoveries with respect to acid dissolu-

Table 1  
ICRCL threshold trigger values ( $\mu\text{g g}^{-1}$ ) [4]

|   | As | Cd | Cr*       | Cu  | Hg | Ni | Pb   | Zn  |
|---|----|----|-----------|-----|----|----|------|-----|
| a | 10 | 3  | 600 (25)  |     | 1  |    | 500  |     |
| b | 40 | 15 | 1000 (25) |     | 20 |    | 2000 |     |
| d |    |    |           | 130 |    | 70 |      | 300 |
| e |    |    |           | 50  |    | 20 |      | 130 |

a – Domestic gardens and allotments.

b – Parks, playing areas, open spaces.

d – Any uses where plants grow.

e – Any uses where plants grow, determined by extraction with  $0.05 \text{ mol l}^{-1}$  EDTA.

\* Values in parenthesis refer to Cr(VI) determined by extraction with  $0.1 \text{ mol l}^{-1}$  HCl at  $37.5^\circ\text{C}$ .

tion [18] but, like other schemes of this type, suffers from some non-specificity [19]. Reference materials, certified for metals extractable by the BCR procedure, are currently in preparation [20,21].

In the present work, the BCR sequential extraction scheme was applied to “made-up ground” material removed from layers of a pit on a former industrial site, in order to assess potential metal mobility. Analysis was performed by atomic absorption spectrometry (AAS), and interferences due to the unusual nature of the substrate were assessed.

## 2. Experimental

### 2.1. Apparatus

A Pye-Unicam PU 9100 flame atomic absorption spectrometer, with air-acetylene flame, was used to determine copper, manganese and zinc in digests and extracts, and a PU 9400, with nitrous oxide-acetylene flame, to determine chromium. Cadmium, chromium, lead, vanadium and concentrations of copper below the detection limit of flame AAS (FAAS), were determined by graphite furnace atomic absorption spectrometry (GFAAS), using an ATI-Unicam 939 Solaar system fitted with a PU9380 furnace autosampler and PU9390 atomizer. Contamination, possibly arising from the autosampler, meant it was not possible to determine nickel with this system, and an alternative spectrometer was used. Nickel was determined using an ATI-Unicam 929 system, with FS90 Plus autosampler and GF90 atomizer. Deuterium background correction was used for all analyses except for the determination of chromium, since the intensity of the D<sub>2</sub> lamp was too low at 357.9 nm. Part-ridged, pyrolytic graphite coated cuvettes and wall atomization

were used for chromium, copper, nickel and vanadium. Platform atomization and palladium modification (200 mg l<sup>-1</sup> Pd) were preferred for the determination of cadmium and lead. The injection volume was 20 µl (10 µl of extract+10 µl of modifier, mixed wet, for cadmium and lead). Furnace programmes were optimized (peak area measurement) for the determination of each analyte in each extractant/digest (Tables 2 and 3). Analytes were determined at the following wavelengths (nm): Cd 228.8; Cr 357.9; Cu 324.8; Pb 217.0 (261.4 for ammonium acetate extracts); Mn 279.5; Ni 232.0; V 318.5, and Zn 213.9.

A CEM MDS 2000 microwave oven (633 W) was used to aid soil digestion and a MSE Mistral 1000 bench top centrifuge to separate extractants from residues in the sequential extraction procedure. The digestion vessels were made of PTFE PFA and the centrifuge tubes were of polypropylene. All glassware and plastic containers were previously soaked overnight in 10% nitric acid and rinsed with distilled water.

### 2.2. Reagents

All reagents were obtained from Merck, Poole, Dorset, UK, except hydrogen peroxide (Puriss grade, from Fluka, Gillingham, Dorset, UK). Acetic acid, hydroxylammonium chloride and ammonium acetate were of AnalaR grade, and hydrochloric acid and nitric acid were Aristar reagents. Calibrants were reagent-matched (i.e. made up in 20% aqua regia, 0.11 mol l<sup>-1</sup> acetic acid, 0.1 mol l<sup>-1</sup> hydroxylammonium chloride or 1.0 mol l<sup>-1</sup> ammonium acetate) and were prepared by serial dilution of 1000 µg ml<sup>-1</sup> Spectrosol solutions of the appropriate elements.

Table 2  
Temperature programme for GFAAS

| Furnace programme step | Temperature (°C) | Hold time (s) | Ramp rate (°C s <sup>-1</sup> ) | Argon gas flow rate (ml min <sup>-1</sup> ) |
|------------------------|------------------|---------------|---------------------------------|---|
| 1                      | 120              | 30            | 10                              | 300   |
| 2                      | Optimum          | 30            | 50                              | 300   |
| 3                      | Optimum          | 3             | Maximum*                        | 0   |
| 4                      | 2800             | 3             | Maximum                         | 300   |

\* >2000°C s<sup>-1</sup>.

Table 3  
Optimum char and atomization temperatures for determination of analytes in extractants by GFAAS (°C)

| Extractant                         | Cadmium |         | Chromium |         | Copper |         | Lead |         | Nickel |         | Vanadium |         |
|------------------------------------|---------|---------|----------|---------|--------|---------|------|---------|--------|---------|----------|---------|
|                                    | Char    | Atomise | Char     | Atomise | Char   | Atomise | Char | Atomise | Char   | Atomise | Char     | Atomise |
| CH <sub>3</sub> COOH               | 850     | 1800    | 1400     | 2300    | 1000   | 2050    | 1300 | 2200    | 1400   | 2600    | 1500     | 2800    |
| NH <sub>2</sub> OH.HCl             | 850     | 1800    | 1400     | 2200    | 1000   | 2100    | 1000 | 2100    | 1400   | 2400    | 1500     | 2800    |
| CH <sub>3</sub> COONH <sub>4</sub> | 800     | 1600    | 1400     | 2400    | 1200   | 2000    | 1150 | 2000    | 1400   | 2400    | 1500     | 2800    |
| aqua regia                         | 500     | 1750    | 1400     | 2300    | 1200   | 2100    | 1200 | 2200    | 1400   | 2400    | 1500     | 2800    |

Furnace temperatures optimized using peak area measurements.

## 2.3. Procedures

### 2.3.1. Sampling and sample pre-treatment

A trial pit was excavated on a disused industrial site in NW England. Over forty different industrial processes had operated on the site, which had been in continuous use for chemical manufacturing since 1847 [22]. The samples were removed from a number of visually distinct, sub-surface layers (Table 4). These were bagged, labelled and returned to the laboratory where they were coned and quartered to give ~100 g sub-samples. Larger objects (including stones, pieces of brick, concrete and cinders) were removed and the remaining material was air-dried at <30°C under local exhaust ventilation to remove hazardous volatile components released, then sieved through a 1 mm nylon

mesh. The air-dried samples were then coned and quartered again (to ~20 g) and two, 3 g, sub-samples were removed for sequential extraction and three, 1 g, sub-samples for microwave-assisted digestion.

### 2.3.2. Microwave-assisted digestion

Pseudototal metal content was determined by digestion with aqua regia. Vessels containing 1 g of the made-up ground material and 20 ml of acid were heated at full power to a pressure of 120 psi, for 10 min. Digests were filtered through Whatman No. 541 filter paper into 100 ml volumetric flasks. The digestion vessels were then rinsed with distilled water. The washings were also filtered into the flasks. Each filtrate was made up to the mark with further distilled water, to give a final sample solution containing 20%

Table 4  
Characteristics of material from layers of the trial pit

| Layer | Depth (cm) | Sampling depth (cm) | Description <sup>a</sup>  | Moisture (%) <sup>b</sup> | Loss on ignition (%) <sup>c</sup> | Sand (%) <sup>d</sup> | Silt (%) <sup>d</sup> | Clay (%) <sup>d</sup> |
|-------|------------|---------------------|---|---------------------------|-----------------------------------|-----------------------|-----------------------|-----------------------|
| 1     | 0–15       | 2–13                | Mixture of topsoil and clinker 10 YR 3/2 very dark brown                                      | 1.9                       | 22.7                              | 76.4                  | 21.6                  | 2.0                   |
| 2     | 15–33      | 18–28               | Made-up ground dominated by clinker and pockets of finer ash 10 YR 4/1 dark grey              | 1.6                       | 20.2                              | 76.4                  | 21.6                  | 2.0                   |
| 3     | 33–47      | 35–45               | Made-up ground dominated by clinker 10 YR 5/2 greyish brown                                   | 1.8                       | 21.4                              | 86.6                  | 11.4                  | 2.0                   |
| 4     | 47–50      | 47–50               | Fine ash 10 YR 2/1 black  | 3.5                       | 27.2                              | 71.8                  | 22.0                  | 6.2                   |
| 5     | 50–100     | 60–85               | Made-up ground; extremely variable mixture of ash and clinker with broken and complete bricks | 2.9                       | 18.9                              | 47.2                  | 40.4                  | 12.4                  |

<sup>a</sup> Colour was determined according to the Munsell soil classification system [23].

<sup>b</sup> Determined by drying to constant weight at 105°C.

<sup>c</sup> Determined by ashing to constant weight at 450°C.

<sup>d</sup> Particle size distribution (of the <2 mm fraction) was determined by the Bouyous method [24].

Table 5  
BCR three-stage sequential extraction scheme

| Extraction step | Reagent(s)   | Nominal target phase(s)                        |
|-----------------|--|--|
| 1               | CH <sub>3</sub> COOH (0.11 mol l <sup>-1</sup> )   | Soil solution, carbonates, exchangeable metals |
| 2               | NH <sub>2</sub> OH.HCl (0.1 mol l <sup>-1</sup> at pH 2)   | Iron/manganese oxyhydroxides                   |
| 3               | H <sub>2</sub> O <sub>2</sub> (8.8 mol l <sup>-1</sup> ) then CH <sub>3</sub> COONH <sub>4</sub><br>(1.0 mol l <sup>-1</sup> ) at pH 2 | Organic matter and sulfides                    |
| (Residual)*     | aqua regia   | Remaining, non-silicate bound metals           |

\* Digestion of the residual material is not a specification of the BCR protocol.

(v/v) aqua regia. Residual material remaining after Stage 3 of the sequential extraction was digested similarly, using 20 ml of aqua regia. No detectable contamination was found when blank vessels (containing acid but no sample) were processed

### 2.3.3. Sequential extraction

Sequential extraction was performed using the three-stage procedure recommended by BCR (Table 5) [17], except that a 3 g sample was used instead of 1 g (to improve representativeness), and extraction was performed by shaking at 40 rpm because a shaker operating at 30 rpm was not available. Extractant volumes were also increased to maintain a constant solid: solution ratio, since it is known that this can affect the results obtained [25].

*Step One:* A 120 ml volume of acetic acid (0.11 mol l<sup>-1</sup>) was added to 3 g of dry "soil" in a 250 ml polypropylene wide-mouthed bottle. The bottle was shaken for 16 h (overnight) at ambient temperature (20°C) on an end-over-end mechanical shaker operating at ~40 rpm. The extract was separated from the solid residue by centrifugation (4000 rpm) and decanted into a polyethylene container and stored at 4°C for analysis. The residue was washed with 60 ml of distilled water by shaking for 15 min, centrifuged and the washings discarded.

*Step Two:* The residue from Step One was slurred with a portion of a 120 ml volume of hydroxylammonium chloride (0.1 mol l<sup>-1</sup>, adjusted to pH 2 with nitric acid) and transferred quantitatively back to the wide-mouthed bottle, where the remainder of the reagent was added. The extraction procedure was then performed as described above.

*Step Three:* A 30 ml volume of hydrogen peroxide (8.8 mol l<sup>-1</sup>) was added in small aliquots to the resi-

due from Step Two. The centrifuge tube was covered with a watch glass and the contents digested at room temperature for 1 h with occasional manual shaking. Digestion was continued by heating the tube to 85°C in a water bath for 1 h. The watch glass was removed and the tube contents evaporated to a small volume (1–2 ml). A second 30 ml aliquot of hydrogen peroxide was added and the digestion procedure repeated. The cool, moist residue was then returned to the 250 ml bottle and 150 ml of ammonium acetate (1.0 mol l<sup>-1</sup>, adjusted to pH 2 with nitric acid) was added. The sample was shaken, centrifuged and the extract separated as described in Step One. The solid residue was retained for microwave digestion.

Reagent blanks were negligible and no detectable contamination was found when aliquots of the sequential extraction reagents were processed and analyzed with the samples. Detection limits (three times the standard deviation of the blank, for  $n=3$ , divided by the slope of the calibration graph) are given in Table 6.

Table 6  
Detection limits for analytes in sequential extraction reagents and 20% aqua regia (µg g<sup>-1</sup>)

| Analyte | Acetic acid | Hydroxylammonium chloride | Ammonium acetate | Aqua regia |
|---------|-------------|---------------------------|------------------|------------|
| Cd      | 0.002       | 0.002                     | 0.003            | 0.005      |
| Cr      | 0.10        | 0.076                     | 0.05             | 5.1*       |
| Cu      | 0.02        | 0.024                     | 0.17             | 1.3*       |
| Pb      | 0.003       | 0.001                     | 0.001            | 3.3*       |
| Mn      | 0.40*       | 1.2*                      | 2.0*             | 1.0*       |
| Ni      | 0.32        | 0.33                      | 0.07             | 0.25       |
| V       | 0.024       | 0.06                      | 0.18             | 0.20       |
| Zn      | 0.16*       | 0.16*                     | 0.25*            | 0.7*       |

\* FAAS (all other values are GFAAS).

### 3. Results and discussion

#### 3.1. Interference effects

Matrix interferences were investigated by use of a single-point standard addition to extracts and digests. The amount of analyte added was approximately equivalent to that already present in the sample. No significant interference (i.e.  $100 \pm 10\%$  recovery of the added standard) was observed in the determination of chromium, copper, manganese, nickel, vanadium and zinc, but signal suppression occurred for both cadmium and lead, especially for cadmium in the residual phase and the pseudototal digest (Table 7). A high background signal was also apparent for cadmium in these solutions. This could be alleviated if the palladium modifier was not used, but a  $\sim 30\%$  suppression, which had been observed previously for industrial made-up ground, but not for digests of reference soils [26], remained. All results presented for lead and cadmium were therefore corrected as follows:

$$C_A = [C_S/A_S] \times A_A$$

where  $C_A$  is the concentration of the analyte in the

sample,  $C_S$  is the concentration of an added standard solution A is the blank-corrected absorbance.

#### 3.2. Determination of pseudototal metal content by aqua regia digestion

The aqua regia-soluble, metal contents of the layers of the trial pit are presented in Table 8. Poor reproducibility (relative standard deviation,  $RSD > 20\%$ ,  $n=3$ ) was obtained for some elements in some layers. This was less apparent for the surface horizon, which contained the highest proportion of true soil. Analyte levels were well above the detection limits (except, perhaps, for lead in Layer 3, see Table 6) and sample heterogeneity is the most likely source of the variability observed.

Cadmium levels were slightly higher than typically found in agricultural soil ( $0.2\text{--}1 \mu\text{g g}^{-1}$  [27]), and exceeded the ICRL trigger for domestic gardens and allotments in Layers 1 (2–13 cm) and 4 (47–50 cm). No anthropogenic enhancement of chromium, however, was apparent. Concentrations were within or below the typical “background” range ( $70\text{--}100 \mu\text{g g}^{-1}$  [27]). Concentrations of the phytotoxic elements copper, nickel and zinc, were greater than the

Table 7  
Recoveries of cadmium and lead standard solutions added to extracts and digests (%)

| Layer (cm) | Cadmium |        |        |          | Lead   |        |        |          |
|------------|---------|--------|--------|----------|--------|--------|--------|----------|
|            | Step 1  | Step 2 | Step 3 | Residual | Step 1 | Step 2 | Step 3 | Residual |
| 2–13       | 68      | 82     | 70     | 42 (65)  | 72     | 75     | 78     | 80       |
| 18–28      | 70      | 81     | 72     | 45 (68)  | 70     | 78     | 71     | 82       |
| 35–45      | 72      | 78     | 68     | 48 (65)  | 75     | 74     | 70     | 78       |
| 47–50      | 74      | 80     | 75     | 40 (70)  | 76     | 70     | 69     | 80       |
| 60–85      | 66      | 75     | 72     | 39 (65)  | 72     | 74     | 74     | 80       |

Values in parenthesis were obtained without addition of  $\text{Pd}(\text{NO}_3)_2$  matrix modifier.

Table 8  
Concentrations of metals released by pseudototal digestion ( $\mu\text{g g}^{-1}$  dry weight)

| Layer (cm) | Cadmium | Chromium | Copper    | Lead       | Manganese  | Nickel    | Vanadium  | Zinc       |
|------------|---------|----------|-----------|------------|------------|-----------|-----------|------------|
| 2–13       | 3.1     | 68 (7.6) | 498 (4.0) | 523 (7.6)  | 714 (6.3)  | 38 (5.8)  | 163 (6.1) | 701 (3.6)  |
| 18–28      | 1.8     | 47 (17)  | 299 (13)  | 340 (29)   | 390 (4.6)  | 68 (12)   | 152 (7.2) | 459 (7.6)  |
| 35–45      | 1.9     | 68 (6.0) | 358 (11)  | 48 (38)    | 746 (12)   | 164 (11)  | 250 (13)  | 136 (12)   |
| 47–50      | 4.5     | 34 (8.8) | 817 (2.2) | 1440 (1.0) | 1316 (2.4) | 145 (4.9) | 85 (29)   | 1729 (3.0) |
| 60–85      | 2.8     | 75 (8.1) | 745 (20)  | 4022 (23)  | 4776 (2.1) | 57 (3.9)  | 86 (35)   | 1291 (27)  |

Values in parenthesis are % RSD, for  $n=3$  specimens.

ICRCL 'd' value in all layers, except nickel in Layers 1, 2 and 4. Layer 4 was particularly contaminated with copper and zinc.

Atmospheric deposition is usually an important source of lead in soil, and typical concentration ranges for rural and urban areas are 10–30 and 30–100  $\mu\text{g g}^{-1}$ , respectively [27]. In the industrial pit, however, lead was mainly located at depth, with concentrations in Layers 1 and 4 exceeding the ICRCL 'a' trigger value and Layer 5 the 'b' value (unsuitable for use as parks, playing areas or open spaces). Manganese levels were also higher at the base of the pit profile, but still within the range commonly encountered. In contrast, vanadium was slightly enhanced in the upper layers (relative to typical agricultural soil concentrations of  $\sim 90 \mu\text{g g}^{-1}$  [27]).

It is interesting to note that, for many elements, higher levels of contamination were located at depth and would not have been detected by a surface survey. Also, the highest levels of contaminants were often found in specific, narrow layers (e.g. copper and zinc at 47–50 cm). These, too, might have been overlooked if a conventional, contaminated land assessment (coring and sampling from fixed depths) had been used rather than an approach, derived from soil surveying, based on the excavation of trial pits and sampling of distinct layers.

Although it was not possible to determine whether the material was contaminated prior to use or whilst on site, the layers of made-up ground clearly contained elevated levels of various heavy metals. Sequential extraction was performed to assess the potential for mobilization of these contaminants into the aqueous phase.

### 3.3. Determination of operational speciation by sequential extraction

Duplicate specimens (A and B) of material from each layer of the trial pit were subjected to the BCR protocol, but only one result was obtained for the residual phase of Layers 1 and 4 because of over-pressure and rupture of vessels during microwave-assisted digestion.

The agreement between the two specimens was generally good (Tables 9–12). In almost two thirds of the cases, the results for equivalent extracts were

within 10% of each other, and only nineteen duplicates showed a discrepancy greater than 30%. There were some particularly large differences for cadmium and zinc in the Residual Step of Layer 3, and for chromium in Step 2 of Layer 3 and the Residual Step of Layer 5. Particularly poor overall repeatability was apparent for lead, perhaps due to the suppressive interference discussed above, or due to a particularly heterogeneous distribution of this element in the made-up ground. There is no clear explanation for the anomalously high lead concentration in the residual phase of specimen B, Layer 3, but re-analysis of the solution by inductively coupled plasma-atomic emission spectrometry confirmed the result, suggesting either contamination of the solution or the presence of unusually lead-rich particles.

An internal check was performed on the results of the sequential extraction by comparing the total amount of metals removed in the procedure with the results of the pseudototal digestion (from Table 8). The recovery of the sequential extraction was calculated as follows:

$$\text{Recovery} = \frac{[(\text{Step1} + \text{Step2} + \text{Step3} + \text{Residual}) / \text{pseudototal}] \times 100}{}$$

In a previous study of river sediment, it was possible to obtain recoveries in the range 89–111% for chromium, copper, lead, manganese, vanadium and zinc, and of 82% for nickel [28]. Other workers have reported recoveries of 80–120% (vs. the certified values for total metal content) for fifteen elements isolated from standard reference materials by a five-step sequential extraction [29].

In the present work, recoveries were exceedingly variable. Greater amounts of lead and zinc were released from all layers by the sequential extraction than by pseudototal digestion, and smaller amounts of vanadium (except in Layer 4). Since no suitable certified reference materials were available to validate either the extraction or the aqua regia digestion of contaminated made-up ground, it was not possible to determine the source of the variability.

Cadmium was released at all steps of the sequential extraction, but the more easily mobilized forms (acid exchangeable and reducible fractions) were predominant in most layers. In contrast, chromium was found almost exclusively in the residual fractions, from which release is unlikely under environmental condi-

Table 9  
Comparison of results obtained by sequential extraction and pseudototal digestion for cadmium and chromium ( $\mu\text{g g}^{-1}$  dry weight)

| Layer (cm) | Cadmium |            |            |            |            |                           | Chromium |            |            |           |          |                           |
|------------|---------|------------|------------|------------|------------|---------------------------|----------|------------|------------|-----------|----------|---------------------------|
|            | Step 1  | Step 2     | Step 3     | Residual   | Sum        | Recovery (%) <sup>*</sup> | Step 1   | Step 2     | Step 3     | Residual  | Sum      | Recovery (%) <sup>*</sup> |
| 2–13       | A       | 1.5 (0.3)  | 1.1 (3.0)  | 0.21 (1.4) | 0.31 (1.9) | 3.2 (1.1)                 | 103      | 0.35 (0.9) | 3.1 (1.3)  | 14 (3.2)  | 71 (0.8) | 104                       |
|            | B       | 1.4 (0.5)  | 1.1 (2.7)  | 0.16 (1.9) | 0.29 (2.4) | 3.0 (1.0)                 | 97       | 0.37 (0.3) | 3.0 (0.7)  | 13 (1.6)  | 54 (0.6) | 70 (0.5)                  |
| 18–28      | A       | 1.5 (5.0)  | 1.2 (3.1)  | 0.14 (5.0) | 0.27 (0.4) | 3.2 (2.7)                 | 178      | 0.33 (0.6) | 3.2 (5.0)  | 11 (0.9)  | 61 (1.2) | 75 (1.0)                  |
|            | B       | 1.5 (2.0)  | 1.1 (2.1)  | 0.14 (4.3) | 0.27 (0.4) | 3.0 (1.3)                 | 167      | 0.32 (3.1) | 3.1 (1.0)  | 8.7 (1.2) | 41 (0.5) | 53 (0.4)                  |
| 35–45      | A       | 0.14 (0.4) | 0.26 (3.5) | 0.05 (12)  | 0.11 (13)  | 0.56 (3.2)                | 29       | 0.25 (4.0) | 1.9 (7.9)  | 3.3 (4.5) | 44 (1.3) | 49 (1.2)                  |
|            | B       | 0.16 (0.2) | 0.27 (3.7) | 0.07 (5.4) | 0.20 (2.0) | 0.70 (1.6)                | 37       | 0.20 (1.5) | 3.8 (0.5)  | 3.2 (3.4) | 36 (0.2) | 43 (0.3)                  |
| 47–50      | A       | 2.6 (3.8)  | 2.1 (1.6)  | 0.16 (1.9) | 0.27 (1.5) | 5.1 (2.0)                 | 113      | 0.56 (2.0) | 3.7 (2.2)  | 7.8 (4.9) | 38 (0.3) | 50 (0.8)                  |
|            | B       | 2.6 (4.7)  | 2.0 (1.0)  | 0.15 (0.7) | 0.41 (1.0) | 5.0 (2.4)                 | 111      | 0.53 (4.2) | 3.8 (3.7)  | 8.1 (1.0) | 50 (0.4) | 50 (0.4)                  |
| 60–85      | A       | 0.31 (2.3) | 1.1 (0.6)  | 0.30 (4.7) | 0.43 (1.4) | 2.1 (0.9)                 | 75       | 0.09 (7.7) | 0.43 (2.3) | 8.8 (1.8) | 39 (1.0) | 48 (0.9)                  |
|            | B       | 0.33 (1.8) | 1.0 (1.3)  | 0.32 (1.9) | 0.43 (1.4) | 2.0 (0.8)                 | 71       | 0.11 (4.5) | 0.39 (5.1) | 9.8 (7.0) | 71 (0.6) | 81 (1.0)                  |

\* Recovery = [(Step 1 + Step 2 + Step 3 + Residual) / pseudototal] × 100; pseudototal concentrations from Table 8.

Values in parenthesis are %RSD, for  $n=3$  measurements; the error on the sum is the square root of the sum of the squares of the individual errors.

All cadmium determinations, and chromium determinations in extracts, were performed by GFAAS; chromium in residuals and digests was determined by FAAS.

Table 10  
Comparison of results obtained by sequential extraction and pseudototal digestion for copper and lead ( $\mu\text{g g}^{-1}$  dry weight)

| Layer (cm) | Copper |           |           |           |           |                           | Lead   |            |           |            |            |                           |
|------------|--------|-----------|-----------|-----------|-----------|---------------------------|--------|------------|-----------|------------|------------|---------------------------|
|            | Step 1 | Step 2    | Step 3    | Residual  | Sum       | Recovery (%) <sup>*</sup> | Step 1 | Step 2     | Step 3    | Residual   | Sum        | Recovery (%) <sup>*</sup> |
| 2–13       | A      | 59 (1.4)  | 71 (1.6)  | 153 (0.2) | 204 (0.5) | 488 (0.4)                 | 98     | 28 (1.9)   | 210 (7.1) | 171 (4.1)  | 639 (2.5)  | 122                       |
|            | B      | 57 (2.5)  | 71 (0.8)  | 138 (0.9) | 221 (0.5) | 471 (0.5)                 | 95     | 25 (2.7)   | 184 (0.4) | 139 (1.6)  | 230 (0.6)  | 578 (0.5)                 |
| 18–28      | A      | 85 (2.4)  | 104 (2.1) | 119 (0.6) | 178 (0.6) | 529 (0.6)                 | 177    | 28 (2.1)   | 189 (2.7) | 64 (2.5)   | 247 (0.3)  | 528 (1.0)                 |
|            | B      | 84 (1.4)  | 101 (2.6) | 112 (1.4) | 183 (0.3) | 476 (0.7)                 | 159    | 26 (3.8)   | 171 (3.2) | 69 (1.7)   | 218 (0.6)  | 484 (1.8)                 |
| 35–45      | A      | 22 (3.9)  | 41 (1.5)  | 93 (1.1)  | 235 (0.7) | 337 (0.5)                 | 94     | 3.2 (5.9)  | 5.4 (3.9) | 6.8 (9.7)  | 50 (0.8)   | 66 (8.8)                  |
|            | B      | 22 (3.9)  | 41 (1.5)  | 88 (1.0)  | 261 (1.2) | 386 (0.6)                 | 108    | 2.1 (3.4)  | 5.8 (2.2) | 4.6 (2.4)  | 741 (1.0)  | 754 (1.0)                 |
| 47–50      | A      | 162 (0.4) | 216 (5.1) | 224 (0.4) | 863 (1.3) | 863 (1.3)                 | 106    | 62 (0.8)   | 386 (4.7) | 341 (1.3)  | 1020 (0.5) | 1810 (1.1)                |
|            | B      | 160 (1.0) | 215 (2.1) | 219 (0.9) | 303 (1.3) | 855 (0.7)                 | 105    | 88 (3.2)   | 636 (5.2) | 204 (1.1)  | 1949 (1.7) | 126                       |
| 60–85      | A      | 7.7 (0.5) | 1.3 (6.2) | 343 (1.0) | 337 (1.2) | 654 (0.8)                 | 80     | 0.77 (3.9) | 5.3 (2.4) | 2828 (0.5) | 5976 (0.4) | 149                       |
|            | B      | 7.9 (7.0) | 1.8 (1.7) | 413 (2.3) | 337 (1.2) | 759 (1.3)                 | 102    | 0.68 (4.4) | 3.7 (2.0) | 2752 (1.4) | 5958 (0.7) | 148                       |

\* Recovery = [(Step 1 + Step 2 + Step 3 + Residual) / pseudototal] × 100; pseudototal concentrations from Table 8.

Values in parenthesis are %RSD, for  $n=3$  measurements; the error on the sum is the square root of the sum of the squares of the individual errors.

All copper determinations, and lead determinations in residuals and digests, were performed by FAAS; lead was determined in extracts by GFAAS.



Table 11  
Comparison of results obtained by sequential extraction and pseudototal digestion for manganese and nickel ( $\mu\text{g g}^{-1}$  dry weight)

| Layer (cm) | Manganese |           |            |           |            |                           | Nickel     |            |           |           |           |                           |
|------------|-----------|-----------|------------|-----------|------------|---------------------------|------------|------------|-----------|-----------|-----------|---------------------------|
|            | Step 1    | Step 2    | Step 3     | Residual  | Sum        | Recovery (%) <sup>*</sup> | Step 1     | Step 2     | Step 3    | Residual  | Sum       | Recovery (%) <sup>*</sup> |
| 2–13       | A         | 74 (0.4)  | 134 (3.7)  | 22 (5.0)  | 685 (0.8)  | 96                        | 7.9 (1.9)  | 7.1 (2.0)  | 6.8 (0.9) |           | 139 (0.8) | 366                       |
|            | B         | 75 (1.3)  | 150 (0.2)  | 19 (2.7)  | 455 (0.3)  | 98                        | 8.6 (0.2)  | 6.1 (0.2)  | 5.9 (3.2) | 117 (0.9) | 137 (0.8) | 360                       |
| 18–28      | A         | 36 (0.8)  | 58 (0.9)   | 11 (4.6)  | 466 (0.4)  | 146                       | 3.9 (3.3)  | 4.4 (0.15) | 4.2 (3.1) | 141 (0.3) | 154 (0.3) | 226                       |
|            | B         | 31 (0.9)  | 58 (1.4)   | 13 (8.5)  | 441 (0.4)  | 139                       | 3.6 (3.9)  | 4.3 (0.11) | 4.4 (2.3) | 110 (0.1) | 122 (0.2) | 179                       |
| 35–45      | A         | 19 (4.5)  | 35 (2.9)   | 16 (8.1)  | 688 (0.4)  | 102                       | 0.72 (0.6) | 1.4 (1.4)  | 2.2 (2.3) | 161 (0.4) | 165 (0.4) | 101                       |
|            | B         | 15 (5.0)  | 33 (0.9)   | 15 (8.0)  | 530 (0.2)  | 71                        | 0.68 (2.6) | 1.2 (2.5)  | 2.5 (4.8) | 101 (0.4) | 106 (0.4) | 65                        |
| 47–50      | A         | 137 (0.8) | 881 (2.8)  | 19 (1.5)  | 473 (0.2)  | 115                       | 1.5 (7.3)  | 20 (0.8)   | 8.8 (1.2) | 89 (0.4)  | 133 (0.9) | 92                        |
|            | B         | 135 (0.7) | 947 (0.9)  | 18 (3.2)  | 1573 (0.6) | 120                       | 1.4 (3.4)  | 18 (2.1)   | 9.5 (5.7) |           | 131 (0.6) | 90                        |
| 60–85      | A         | 77 (0.7)  | 2893 (0.9) | 502 (1.8) | 1102 (0.1) | 96                        | 3.2 (7.2)  | 15 (2.3)   | 15 (4.5)  | 35 (0.5)  | 67 (1.2)  | 118                       |
|            | B         | 80 (0.7)  | 2916 (1.1) | 545 (0.9) | 1129 (0.2) | 98                        | 2.9 (4.5)  | 1.4 (2.4)  | 17 (3.6)  | 37 (0.3)  | 71 (1.0)  | 125                       |

\* Recovery = [(Step 1 + Step 2 + Step 3 + Residual) / pseudototal] × 100; pseudototal concentrations from Table 8.

Values in parenthesis are %RSD, for n=3 measurements; the error on the sum is the square root of the sum of the squares of the individual errors

All manganese determinations, and nickel determination in residuals and digests, were performed by FAAS; nickel was determined in extracts by GFAAS

Table 12  
Comparison of results obtained by sequential extraction and pseudototal digestion for vanadium and zinc ( $\mu\text{g g}^{-1}$  dry weight)

| Layer (cm) | Vanadium |            |           |           |           |                           | Zinc       |           |           |           |            |                           |
|------------|----------|------------|-----------|-----------|-----------|---------------------------|------------|-----------|-----------|-----------|------------|---------------------------|
|            | Step 1   | Step 2     | Step 3    | Residual  | Sum       | Recovery (%) <sup>*</sup> | Step 1     | Step 2    | Step 3    | Residual  | Sum        | Recovery (%) <sup>*</sup> |
| 2–13       | A        | 1.1 (14)   | 14 (5.9)  | 20 (3.0)  | 114 (2.5) | 70                        | 237 (1.1)  | 142 (0.9) | 106 (1.1) |           | 789 (0.4)  | 113                       |
|            | B        | 1.1 (4.5)  | 13 (0.6)  | 16 (6.0)  | 80 (3.2)  | 68                        | 225 (2.0)  | 144 (2.4) | 99 (1.0)  | 303 (0.3) | 771 (0.8)  | 110                       |
| 18–28      | A        | 0.51 (3.9) | 14 (0.3)  | 11 (0.6)  | 89 (0.2)  | 75                        | 197 (2.2)  | 136 (1.9) | 87 (1.1)  | 274 (0.5) | 694 (0.8)  | 151                       |
|            | B        | 0.51 (3.9) | 14 (1.9)  | 15 (1.1)  | 80 (1.0)  | 72                        | 182 (2.4)  | 136 (3.4) | 86 (0.8)  | 258 (0.5) | 662 (1.0)  | 144                       |
| 35–45      | A        | 0.89 (2.2) | 13 (3.5)  | 15 (0.7)  | 131 (0.2) | 64                        | 20 (2.8)   | 22 (0.6)  | 27 (2.3)  | 123 (0.4) | 193 (0.5)  | 142                       |
|            | B        | 1.1 (0.9)  | 13 (0.8)  | 13 (0.7)  | 102 (0.6) | 52                        | 20 (1.3)   | 24 (1.9)  | 32 (1.4)  | 259 (0.5) | 336 (0.4)  | 247                       |
| 47–50      | A        | 0.50 (4.0) | 12 (3.2)  | 15 (3.7)  | 78 (1.8)  | 124                       | 1097 (2.5) | 486 (0.8) | 187 (0.6) | 368 (1.0) | 2138 (1.3) | 124                       |
|            | B        | 0.34 (2.9) | 12 (3.9)  | 9.5 (3.7) | 100 (1.5) | 118                       | 993 (1.3)  | 495 (1.8) | 177 (1.3) |           | 2033 (0.8) | 118                       |
| 60–85      | A        | 0.99 (6.1) | 4.6 (9.1) | 6.2 (1.9) | 39 (0.5)  | 58                        | 170 (0.7)  | 380 (2.3) | 673 (1.9) | 436 (0.3) | 1659 (1.0) | 128                       |
|            | B        | 1.0 (9.0)  | 4.6 (3.7) | 5.2 (3.5) | 40 (1.4)  | 59                        | 172 (0.8)  | 363 (3.6) | 701 (0.9) | 454 (0.2) | 1691 (0.8) | 131                       |

\* Recovery = [(Step 1 + Step 2 + Step 3 + Residual) / pseudototal] × 100; pseudototal concentrations from Table 8.

Values in parenthesis are %RSD, for n=3 measurements; the error on the sum is the square root of the sum of the squares of the individual errors.

All vanadium determinations were performed by GFAAS and all zinc determinations by FAAS.

tions. Care must be taken, however, in interpretation of sequential extraction data for this element since, in model substrates, it was found to be extracted in Step 3 of the BCR procedure even though it was originally present in association with reducible minerals such as Goethite [18]. Nickel and vanadium were also found mainly in association with residual material, except at depth (particularly 60–85 cm) where both reducible and oxidisable forms of nickel occurred. Copper and zinc were present in all fractions, although the proportions varied down the pit profile. Layer 4 contained particularly high concentrations of labile forms of these metals. The amounts released in Step 1 of the sequential extraction alone were in excess of the ICRCL threshold trigger values for total metal content.

Manganese speciation was markedly different in the upper three, and lower two layers of the pit. Near the surface, the metal was found mainly in association with the residual fraction but, at depth, reducible species were dominant. Lead was present in various forms throughout the pit profile, but always with a significant proportion of the total in the residual phase. It is particularly interesting to note that only a small fraction (<0.2%) of the lead in the 60–85 cm layer was present as acid exchangeable or reducible species. Thus, although contamination is considerable, the forms present are relatively immobile. Contrary to what might be concluded from pseudototal digestion, the sequential extraction suggests that risk from this material (in terms of potential for transport to a receptor) may be slight and intervention unnecessary or even inadvisable since it may convert lead to more readily mobilized forms.

Comparison of the metal partitioning determined in the present work with previous studies is limited by the unusual nature of the made-up ground substrate. However, easily mobilized forms of cadmium have been reported in polluted soils [29,30] and chromium, nickel and vanadium are often associated with residual material in soils and sediment [28–30]. A predominance of residual lead has been found in sequential extraction of mine tailings, although erosion and mixing with soil appeared to promote conversion to more labile (mainly reducible) species [31]. It is possible that contamination with lead ore may explain the high concentrations of resistant forms of lead in the lower layers of the pit, but this could not be substan-

tiated as detailed historical data on the site are not available.

#### 4. Conclusions

Excavation of trial pits and analysis of distinct layers of materials found represents a better approach to contaminated land assessment than conventional, fixed depth sampling. Sequential extraction provides useful information for risk assessment since the amounts of metals mobilizable under different changes in environmental conditions can be estimated. Recently dis-used industrial sites, however, represent a particular analytical challenge. Care must be taken to assess interferences arising from typical components of made-up ground, and the limitation of certified reference materials, for either (pseudo)total analysis or sequential extraction, to contaminated agricultural soils remains a serious limitation to progress in this area.

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