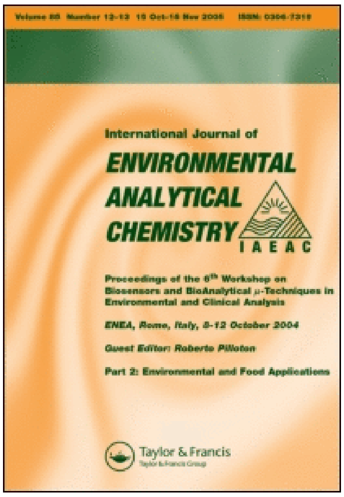

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Comparison of Techniques for the Analysis of Industrial Soils by Atomic Spectrometry

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COMPARISON OF TECHNIQUES FOR THE ANALYSIS OF INDUSTRIAL SOILS BY ATOMIC SPECTROMETRY

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Methods based on AAS, ICP-AES and XRFS have been developed for determination of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn in soil layers from pits excavated on a redundant industrial site. Samples were dried and sieved, and the < 2 mm fraction was ground in a ball mill prior to analysis. For ICP-AES and AAS, 1 g sub-samples were digested with *aqua regia* in a microwave oven. The dry weight detection limits of the analytes were in the range 2–25 $\mu g\ g^{-1}$ for FAAS, 0.003–0.2 $\mu g\ g^{-1}$ for ETAAS and 0.04–1.6 $\mu g\ g^{-1}$ for ICP-AES. When digests of the industrial soils were analysed, calibration with acid-matched standards gave acceptable accuracy for all the analytes, except for Cd when determined by ETAAS (30–40 % suppression). Despite lack of reference materials of industrial origin, analysis of two soil reference materials by these techniques produced concentrations that were within ± 10 % of the certified or recommended values for elements extractable with *aqua regia*. Direct standard-less analysis of a soil reference material with a portable x-ray fluorescence (P-XRF) analyser gave concentrations for a range of elements that were within a factor of 2 of the certified values. When the XRFS and ICP-AES methods were used to analyse the industrial soils, the concentrations obtained were similar (to within 30%) for Cu, Pb and Zn in most of the samples and for Cr, Mn and Ni in some of the samples. The concentrations of V estimated with the P-XRF analyser were 4 to 7-fold higher than those obtained by ICP-AES. The discrepancies were thought to be caused by spectral enhancement interferences in XRFS. Cadmium was not determined accurately by either ICP-AES or P-XRFS owing to spectral interferences. The work has highlighted the importance of analysing samples from across a site and at different depths, when assessing the extent of metal contamination on industrial land.

Keywords: Contaminated land; microwave assisted digestion; atomic absorption spectrometry; inductively coupled plasma atomic emission spectrometry; portable x-ray fluorescence spectrometry

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INTRODUCTION

Soils receive potentially toxic elements from both natural and a wide range of anthropogenic sources. Examples include the weathering of primary minerals, mining, fossil fuel combustion, the metallurgical, electronic and chemical industries and waste disposal[1]. The main hazards associated with release of heavy metals into the terrestrial environment include ingestion and inhalation, uptake by crops rendering them unsafe to eat, and contamination of water resources by leaching into surface and ground waters [1–3]. Inhibition of plant growth by phytotoxic metals may also occur at elevated concentrations. There is growing concern amongst industrialised nations over the risk to human health arising from contaminated land. Legislation requires that owners and sellers comply with regulations on acceptable levels of contaminants and, if necessary, steps must be taken to ensure appropriate remediation.

The assessment of contamination normally requires a site investigation (Table I)[4]. After the site's history has been established, the next step involves chemical analysis. This presents a considerable challenge when the site is industrial, rather than arable, land as the material to be sampled can vary considerably in composition and particle size.[5] Industrially-contaminated land typically contains ash, clinker, pieces of brick, refuse and spoil, together, occasionally, with some true soil (collectively known as "made ground"). Many sites cover expansive areas of land, and are heterogeneous in both vertical and horizontal directions. Consequently, selection of appropriate samples to assess contamination is a major problem. Whilst various strategies for sampling contaminated soils have been proposed [6–10], these have been mainly applied to agricultural and arable land with historical contamination ; these sites are likely to be much more homogeneous than recent, made ground. Few studies on the sampling and analysis of heterogeneous industrial land have been reported.

TABLE I Stages involved in a site investigation[4]

Stage	*Purpose*
Historical Survey	to assess if soil or groundwater at a site is likely to have become contaminated by industrial operations
Site investigation	to obtain an overall picture of the contamination present on the site by sampling and chemical analysis
Data evaluation and Risk Assessment	information from the first stages used to judge whether there is a significant risk to human activity or the environment
Review of remediation options	selection of the most appropriate and cost effective clean up procedures
Implementation	site clean up

When assessing a site for metal contamination, boreholes may be sunk or soil pits excavated to explore layers of material which can be sampled in a manner similar to soil profiling[11]. In some circumstances, this approach has the advantage that the mobility of metals through the profile may be assessed. However, because of site heterogeneity, very many pits may be required for accurate hazard assessment, and the cost of analysis for the large number of samples obtained may be prohibitive.

Traditionally, techniques based on atomic spectrometry have been used for the determination of metals in soils and related materials. Solubilisation of the analytes, generally, is required for AAS and AES and most of the standard protocols involve the reflux of samples in the presence of strong acids such as *aqua regia* [12–15]. However, despite the introduction of microwave assisted heating, sample digestion is generally the slowest step in the analysis procedure.[16] X-ray fluorescence spectrometry (XRFS) may be used to analyse soils directly or with minimum sample preparation (e.g. drying and grinding) [17–20]. In particular, the development of portable energy dispersive XRF instruments has provided the opportunity for on-site analysis. [21–23] The accuracy of the concentrations obtained depends on the suitability of the stored calibration data sets and response functions. Potts *et al.* [22] evaluated a field-portable XRF instrument by analysis of silicate-based reference materials. Good agreement with certified concentrations (recoveries of 63–108 %) was achieved for a range of elements when the appropriate calibration algorithm was used. The agreement was improved further by application of correction factors to account for calibration bias. Puls *et al.* [23] used a different P-XRF spectrometer to determine Cr in contaminated soil. The XRF results were 2–5 fold lower than concentrations determined by ICP-AES and the under-determination was attributed to a poor choice of calibration samples.

Other workers have compared ICP-AES and laboratory-based XRFS for analysis of contaminated soils. Wilson *et al.* [20] reported that XRFS consistently gave higher concentrations of Cu, Ni and Zn than the values obtained by ICP-AES, when samples from a landfill site were analysed. However, the differences were considered to be minor and each set of results led to the same conclusion regarding categorisation of the contamination status of the site. Duane *et al.* [18] evaluated the performance of a mobile laboratory equipped with ICP-MS, by comparing the results obtained for samples from the site of a disused mine with concentrations determined with laboratory-based ICP-AES, ETAAS and XRFS. XRFS was better for screening heavily contaminated soils, but for medium to lower concentrations, ICP-MS was regarded as superior, owing to its extensive linear working range, despite requiring digestion of finely ground samples.

A useful application of field-portable XRF instrumentation in the analysis of industrial land is likely to be the screening of samples prior to full quantitative determination of metals by laboratory-based techniques. As previously indicated, few studies have been conducted to assess the accuracy of results when a P-XRF spectrometer is used to analyse samples from pits on heterogeneous industrial land. In the present study, materials sampled from two pits excavated on a site formerly used for chemical manufacture were pre-treated, microwave digested in *aqua regia* and analysed for Cd, Cr, Cu, Mn, Ni, Pb, V and Zn by FAAS, ETAAS and ICP-AES. The digestion procedure was validated using two reference materials with known concentrations of metals extractable by *aqua regia*. The finely ground material was also analysed by a P-XRF instrument. As the samples were variable in composition and considering the current lack of reference materials for industrial land, no attempt was made to match exactly the stored calibration algorithm to the sample matrices, nor apply correction factors for calibration bias. Both of these procedures would be impractical when screening many samples of different composition, and perhaps unnecessary if only semi-quantitative data were required for preliminary assessment. The concentrations determined by XRFS were compared with those obtained by analysis of HF and *aqua regia* digests of the samples using the other techniques.

EXPERIMENTAL

Sampling

Material typical of industrially-contaminated land was obtained from pits (depth 1–1.5 m) excavated on a former chemical manufacturing site, using a mechanical digger. The pits were approximately 100 m apart. Several layers of material were present in each pit (Table II) varying in thickness, colour and composition. Samples were removed from each layer using a trowel and tray and transferred to labelled polyethylene bags.

In the laboratory, the samples were dried for 48 hours on aluminium trays lined with greaseproof paper at 30 °C, then bottled and stored in a chest freezer at −18°C. Prior to analysis, the samples were sieved using nylon mesh to obtain the < 2 mm diameter fraction. This was coned and quartered to obtain a homogeneous sub-sample of 10–20 g which was finely ground to a powder in an agate ball mill, to provide a specimen for analysis.

It is possible that the particles > 2 mm contained significant levels of metal contaminants, owing to the unusual nature of the soil sampled. These were therefore retained for separate study whilst, for the present work, only the < 2 mm fraction was characterised further. Sub-samples of the material were heated in silica crucibles to constant weight, at 105 and 450 °C, to obtain the moisture content and loss on ignition (LOI), respectively. The percentage distribution of sand, silt and clay in the < 2 mm fraction of the samples was determined using the Bouycous method [24]. The data are shown in Table II together with pit descriptions.

TABLE IIa Description of the horizons sampled from trial pit 1

Layer (cm)	*Description*	*Moisture content (%)*	*Loss on ignition (%)*	*Sand (%)*	*Silt (%)*	*Clay (%)*
2–13	top soil and clinker; sandy loam to silt loam; loose stones; few fibrous roots	1.9	6.0	76.4	21.6	2.0
18–28	made up ground dominamd by clinker and pockets of finer yellow and grey ash	1.7	5.3	76.4	21.6	2.0
35–45	made ground dominated by clinker; greyish brown; coarser with higher proportion of larger fragments than in 18–28 cm layer	1.8	5.7	86.6	11.4	2.0
47–50	fine ash ; black, stone or clinker free; very compact, probably sufficient to impede downward percolation of water	3.5	6.9	71.8	22.0	6.2
60–85	made ground ; extremely mixed layer with high proportion of broken and complete bricks ; varaible interstital material probably a mixture of ash and clinker	2.9	7.4	47.2	40.4	12.4

TABLE IIb Description of the horizons sampled from trial pit 2

Layer (cm)	*Description*	*Moisture content (%)*	*Loss on ignition (%)*	*Sand (%)*	*Silt (%)*	*Clay (%)*
0–10	concrete road (not sampled)	-	-	-	-	-
10–20	mixed horizon of topsoil, ash and clinker ; evidence of white ash material in pockets	1.6	24.2	76.4	17.5	6.1
25–30	black, stone free, relatively compact	6.0	22.6	60.6	37.2	2.1
35–45 and 55–64	clinker of variable size dominated with inliers of fine ash ; dark reddish brown	4.5 4.7	11.8 12.6	52.9 50.7	47.1 47.2	0.0 2.1
75–84	made ground ; mainly fine ash with some clinker	2.6	20.1	75.2	18.7	6.2
85–91	made ground; possibly glacial material *in situ*, very pale brown with reddish brown mottles	1.6	17.0	41.9	52.0	6.1
91–100	glacial material *in situ*; material appear completely gleyed	6.5	19.0	28.3	65.3	6.4

Microwave Assisted Digestion

A CEM MDS 2000 microwave oven rated at 630 W, with programmable power and time settings, was used to aid digestion. Approximately 1 g of milled soil was accurately weighed into each microwave digestion vessel and, for *aqua regia* digestion, 15 ml hydrochloric acid and 5 ml nitric acid were added Alternatively, 15 ml HF was used to achieve more efficient digestion of silicate material. When the maximum number of twelve vessels was used, samples were heated at full power and maintained at a pressure of 120 psi for 20 minutes. For each bomb not used, 5% was deducted from the total power. After cooling, the carousel holding the sample vessels was removed from the oven and placed in a fume cupboard, whereupon the vessels were vented. The digests were filtered through Whatman No 541 ashless filter paper, washed and made up to a final volume of 100 ml with 5% (V / V) nitric acid. Blank solutions were prepared by adding appropriate volumes of the acids to further digestion vessels and processing these along with the soil samples.

Instrumentation

Philips PU9100 and PU9400 instruments were used for analysis by FAAS. The optimised conditions are given in Table III. A Unicam Solaar 939 spectrometer, PU9390 electrothermal atomizer, and PU9380 furnace autosampler were used for analysis by ETAAS. A continuum (deuterium) lamp method of background correction was applied. Pyrolytic-graphite coated part-ridged tubes were used either with or without a pyrolytic-graphite platform, depending on the volatility of the analyte. The drying temperature was 150 °C with a ramp rate of 10 °C s^{-1} and a hold time of 20 s (or 30 s if a platform was used). For the char stage, the ramp rate was 150 °C s^{-1} and the hold time 20 s. The injection volume was 20 µl and the optimised char and atomization temperatures are given in Table III.

For both FAAS and ETAAS, absorbance measurements were made in triplicate for each standard and sample solution. Detection limits obtained for the analytes are given in Table IV. The values are based on 3 times the standard deviation of the element concentration in an acid matched blank solution analysed 10 times and correspond to 1 g of dry weight soil digested and diluted to 100 ml. No appreciable difference was found between absorbance signals measured for the procedural blank and the acid matched blank used for calibration, for any of the metals. The concentrations of metals present in the material were, in general, far higher (10–500 fold) than the measured detection limits.

TABLE III Optimum operating conditions for analysis of the analyte elements by AAS

		Optimum conditions for analysis by FAAS		*Optimum conditions for analysis by ETAAS*	
Metal	*Wavelength (nm)*	*Burner height*	*Fuel flow*	*Char temperature (°C)*	*Atomization temperature (°C)*
Cd	228.8	4	22	600	1400
Cr	357.9	6	4.4	1500	2800
Cu	324.8	4	22	1500	2500
Mn	279.5	4	24	1100	2600
Ni	341.5	4	24	1200	2400
Pb	283.5	4	22	900	1800
V	213.9	8	4.3	1500	2800
Zn	318.5	4	21	1000	1500

PU9100 (air-acetylene) used for all metals by FAAS, except vanadium and chromium, which were determined using the PU9400 (nitrous oxide-acetylene).

measurement time for determination by FAAS was 3 s, except for vanadium and chromium, which required 4 s.

for determination by ETAAS, part-ridged tubes were used for atomization of Cr, Mn, Ni and V, with a measurement time of 3 s; for Cd, Cu, Pb and Zn, atomization was from a platform, with a measurement time of 5 s.

TABLE IV Detection limits (in μg g^{-1} dry weight soil) for metals in soil by FAAS, ETAAS and ICP-AES

Metal	*FAAS*	*ETAAS*	*ICP-AES*
Cd	6.3	0.01	0.2
Cr	4.2	0.07	0.81
Cu	7.3	0.04	0.12
Mn	3.9	0.09	0.04
Ni	25.0	-	1.6
Pb	13.0	0.10	1.4
V	20.0	0.20	0.2
Zn	1.9	2.5×10^{-3}	0.67

detection limit based on 3 × standard deviation of a blank analysed 10 times, for digestion of 1.0 g dry weight soil and a final sample volume of 100 ml.

spectral lines used for determination by ICP-AES were :

Cd - 226.502nm (II); Cr - 357.869 nm (I); Cu - 324.754 nm (I); Mn - 257.610 nm (II); Ni - 352.454 nm (I); Pb - 220.353 nm (II); V - 309.311 nm (II) and Zn - 213.856 nm (II), where (I), (II) represent atom and ion lines, respectively.

Soil solutions were also analysed by ICP-AES using a Varian Liberty instrument, which employs a solid state RF generator operating at a frequency of 40.68 MHz. A dual channel 10-roller peristaltic pump was used to deliver solutions to a pneumatic concentric glass nebuliser and Sturman-Masters type of spray chamber. A compromise set of operating parameters was used (Table V) and under these conditions, the detection limits given in Table IV were obtained for sequential determinations. The detection limits were calculated as defined above.

TABLE V Plasma conditions for the analysis of soil digests by ICP-AES with a Varian Liberty spectrometer

Observation height (mm)	8
Forward power (kW)	1
Plasma gas flow rate (l min^{-1})	13.5
Auxiliary gas flow rate (l min^{-1})	1.5
Carrier gas rate (l min^{-1})	1.0
Pump speed (rpm)	10
Nebuliser type	pneumatic concentric nebuliser
Stabilisation time (s)	15
Sample delay (s)	15
Number of replicate measurements	5

A Spectrace TN-9000 XRF instrument was used for direct analysis of the milled soils. This is a lightweight, energy dispersive device which incorporates a mercuric iodide detector (resolution about 250 eV) and three radio-nuclide sources (^{55}Fe, ^{109}Cd and ^{241}Am) [21]. The instrument is supplied with pre-calibrated analysis packages, based on the Fundamental Parameter method. For this to operate accurately, certain assumptions must be made about any undetermined elements (low atomic number) that are present. For example, in the analysis of soils, SiO_2 is assumed to be a major component. To analyse the powdered samples, a specimen was placed in a cup, covered with a 6 μm thick polypropylene film and the analyser head held firmly against the film for a pre-set measurement time (typically 100 s). Results were calculated by the instrument from the fluorescence response and the concentrations provided in units of μg g^{-1} dry weight soil. Potts *et al.* [22] demonstrated that accurate analysis of silicate-based reference materials could be achieved with the TN-9000 if appropriate Fundamental Parameters co-efficients were calculated and used with the calibration algorithm. This approach is not as simple to apply when analysing industrial land of the type described in Table II, however, owing to the variability of the sample material and the lack of suitable reference materials with which to effect a more sample-specific calibration. In this study, therefore, the TN-9000 was operated more in a semi-quantitative mode to assess the accuracy of the concentrations obtained when a general soils analysis algorithm, supplied by the manufacturer, was used for calibration.

Reagents and Reference Materials

Metal standard solutions were prepared from 1000 μg ml^{-1} Spectrosol stock solutions (Merck, Poole, Dorset, UK). Working standards were prepared by appropriate dilution of stock solutions with 5% nitric acid. Nitric acid and hydrochloric acids were of Aristar grade and were obtained from Merck. Distilled water was used for all dilutions. All the standard solutions were matched to the acid content of the sample solutions. For example, for the analysis of 100 ml sample digests, the standard solutions contained 15 ml hydrochloric acid, 5 ml nitric acid and 80 ml of 5% (V / V) nitric acid.

To evaluate the digestion procedure, two reference materials from the Commission of the European Communities, Community Bureau of Reference (BCR) were digested with *aqua regia.* Few reference materials are available with certified *aqua regia* soluble metal concentrations and none are similar to the material under study. CRM143 and CRM143R are sewage sludge amended soils with certified or non-certified concentrations of Cd, Cr, Cu, Mn, Pb and Zn, extractable by *aqua regia.* A yellow-red soil reference material, GBW 07406, obtained from the Institute of Geophysical Exploration, China was used as part of the semi-quantitative assessment of the TN-9000 XRF instrument. The reference material was analysed to give a general indication of the accuracy of the semi-quantitative XRF procedure, for elements over a range of atomic numbers, including some of the analytes in the study. In the absence of appropriate reference materials for industrial land, the best means of assessing the accuracy of the XRF results was considered to be a comparison of the analyte concentrations with values obtained by the alternative techniques, where validation of the methods was easier to achieve.

RESULTS AND DISCUSSION

Evaluation of Methods

Digestion of CRM 143 and CRM 143R was performed in triplicate and solutions were analysed by FAAS and ICP-AES, respectively, using acid-matched standard solutions for calibration. The results in Table VI indicate that there is good agreement between the derived and certified / non-certified concentrations, with recoveries in the range 90–107% for both reference materials. The precision was also satisfactory, with RSD values generally less than 5%. As the reference materials were not necessarily typical of the soils from an industrial site and considering the variability in the pit horizons indicated in Table II, the AAS procedures were assessed further by adding a known concentration of the analytes to the digests of soil from one of the pits i.e. a "spike" was added. Analysis of the solutions before and after the analyte addition allowed calculation of a percentage recovery relative to the response of the standard, based on the absorbance signals as follows :

$$\%\,\text{recovery} = \frac{\text{Spike - Sample}}{\text{Standard}} \times 100$$

TABLE VI Certified and experimentally derived concentrations of metals in two reference materials after microwave digestion with aqua regia and analysis by AAS or ICP-AES

Metal	*CRM 143R*[#]		*CRM 143*[*]	
	Measured concentration ($\mu g\ g^{-1}$ DW soil)	*Certified value ($\mu g\ g^{-1}$ DW soil)*	*Measured concentration ($\mu g\ g^{-1}$ DW soil)*	*Recommended value ($\mu g\ g^{-1}$ DW soil)*
cadmium	70.7 ± 0.7	72.0 ± 1.8	32.5 ± 0.4	31.5
chromium	383 ± 11.7	426.0 ± 12	198.5 ± 5.0	208
copper	NA	NA	238.8 ± 2.2	236
manganese	858 ± 5.3	858 ± 11	941.7 ± 7.7	935
nickel	288 ± 5.3	296 ± 4	NA	NA
lead	180 ± 1.4	174 ± 5	1401 ± 16,1	1317
zinc	1061 ± 11.6	1063 ± 16	1262 ± 27.8	1301

No certified / recommended concentrations are available for V.

± value represents the overall standard deviation for digestion (n=3) and analysis (n=5) of each sample (i.e. $\Sigma n = 15$).

[#] analysed by ICP-AES. [*] analysed by FAAS.

The analytes were added at a level that increased the apparent concentration of the element in the digest by a factor of 0.5–1 fold. The results in Table VII show that only Cd exhibited significant suppressive interferences (reduction in signal of between 26 – 38 %). Hence, the method of standard additions was used to determine Cd in the industrial soils by ETAAS, whereas direct calibration with acid-matched standard solutions was considered suitable for the other elements. The concentrations of the elements determined by AAS are given in Table VIII along with results obtained when separate digests of the soils were analysed by ICP-AES, using direct calibration as above. Typical instrumental precision for the analysis of standard or sample solutions was in the range 0.1–3%. The standard deviation values quoted in Table VIII represent a combined estimate of the method precision and were typically found to be less than 5%.

TABLE VII Percentage recoveries for analyte elements added to digests of soils from Pit 1 analysed by FAAS and ETAAS

Horizon (cm)	*Percentage recovery (%)*						
	Cadmium	*Chromium*	*Copper*	*Lead*	*Manganese*	*Vanadium*	*Zinc*
2–13	74	96	93	98	95	92	95
18–28	72	87	95	97	103	94	97
35–45	70	89	97	123	95	86	92
47–50	66	88	94	111	99	90	87
60–85	62	96	93	93	98	96	99

Analyses were performed using FAAS, except for cadmium, chromium and vanadium for which ETAAS was used.

Analyte additions were made at levels equivalent to about half of the concentrations given in Table VIII (see text).

A severe spectral interference by Fe at approximately 226.507 nm prevented the determination of Cd at 226.502 nm by ICP-AES. For low to medium concentrations of iron, the intensity of the line is not significant but at higher concentrations, in excess of 1000 μg ml^{-1} the intensity is high enough to interfere with measurement of the cadmium line emission. Nickel was not determined by ETAAS due to contamination from the PU9380 autosampler. Comparison of the other results in Table VIII shows that for each element there is a variable degree of agreement between the concentrations obtained with both techniques. For some horizons, the concentrations are similar to within 10 %, whereas for other samples differences of 30–40 % are apparent. No systematic differences are obvious between the sets of results for any of the analytes and none of the horizons exhibited a consistent level of interference on the determination of the elements by either technique.

TABLE VIII Concentration of elements in the soils from pit 1 after *aqua regia* digestion and analysis by ICP-AES and AAS

Horizon		*μg g^{-1} (dry weight soil)*							
		Cd#	*Cr*#	*Cu**	*Mn**	*Ni*	*Pb**	*V**	*Zn**
2–13	ICP	–	54 ± 1	464 ± 4	620 ± 10	82 ± 2	487 ± 6	106 ± 1	652 ± 8
	AAS	4 ± 0.1	68 ± 2	498 ± 3	714 ± 30	–	523 ± 9	163 ± 2	701 ± 3
18–28	ICP	–	57 ± 1	240 ± 5	404 ± 8	89 ± 2	205 ± 4	121 ± 2	363 ± 5
	AAS	2 ± 0.1	47 ± 4	297 ± 14	390 ± 28	–	262 ± 11	152 ± 8	459 ± 22
35–45	ICP	–	80 ± 2	345 ± 3	746 ± 7	142 ± 3	124 ± 2	229 ± 3	689 ± 46
	AAS	2 ± 0.1	68 ± 1	358 ± 14	746 ± 16	–	112 ± 9	250 ± 9	741 ± 14
47–50	ICP	–	61 ± 1	1043 ± 8	1358 ± 12	140 ± 4	1515 ± 11	86 ± 2	2965 ± 23
	AAS	6 ± 0.1	34 ± 1	1015 ± 69	1102 ± 16	–	1435 ± 25	85 ± 3	2713 ± 256
60–85	ICP	–	70 ± 2	705 ± 6	5373 ± 34	53 ± 2	3482 ± 24	62 ± 1	870 ± 12
	AAS	4 ± 0.1	75 ± 3	734 ± 3	6421 ± 99	–	3674 ± 109	86 ± 4	1006 ± 24

determined by ETAAS * determined by FAAS.

– Cd not determined by ICP-AES because of severe spectral interference by Fe; Ni not determined by ETAAS, owing to contamination by the autosampler.

± values for determination by ICP-AES represents the overall standard deviation for digestion (n=2) and analysis (n=5) of each sample (i.e. Σn=10).

± values for determination by AAS represents the overall standard deviation for digestion (n=3) and analysis (n=3) of each sample (i.e. Σn=9).

Overall, the validation tests indicate that the methods developed give a good estimate of the analyte concentration in the *aqua regia* digests and hence, of *aqua regia* extractable concentrations of the elements in the sampled material. As two separate samples of the material from each of the horizons of pit 1 were analysed by AAS and ICP-AES, it is likely that the differences in the elemental concentrations obtained with the two techniques are a consequence of the inhomogeneity of the material.

A general indication of the accuracy of the semi-quantitative XRF method was obtained by analysis of reference material GBW 07406. The results in Table IX show that for a range of elements, the estimated concentrations are within a factor of 2 of the certified values, including those for Cu, Mn and Zn. This suggests that the P-XRF analyser could provide adequate semi-quantitative estimation of the total concentration of contaminant elements, as part of a screening procedure.

Potts *et al.* [22] quoted detection limits for a silicate rock matrix and the manufacturer's detection limits for the Spectrace TN9000, for a 200 s count time. Both sets of detection limits, multiplied by √2 to account for the differences in the counting time used here (100 s), are given in Table X, along with the range of concentrations of the elements measured in the samples from pits 1 and 2. In general, the levels measured for most of the metals in the layers are higher than the manufacturer's detection limits.

TABLE IX Concentrations of elements in reference material GBW 07406 obtained by direct analysis with the portable XRF instrument

Element	*Concentration found** *(μg g^{-1}DW)*	*Reference value (μg g^{-1} DW)*
Mn	1779	1450 ± 32
Cu	349	390 ± 6
As	290	220 ± 7
Zn	192	96.6 ± 2.4
Sr	44	39 ± 2
Sb	49	60 ± 3
Ba	66	118 ± 6

* results for a single determination.

Comparative Analysis of Soil Horizons

Concentrations of Cr, Cu, Mn, Ni, Pb, V and Zn obtained with the P-XRFS and ICP-AES methods are given in Figures 1 (a) -(h) for samples from pit 2. Concentrations obtained by AAS were similar to those of ICP-AES and have been omitted from the figures, except for cadmium in Figure 1a. The cadmium results for ICP-AES and XRFS are not plotted owing to spectral interference of a) Fe on Cd at 226.502 nm in ICP-AES and b) a low energy emission from the Am-241 source at the Cd energy, in P-XRF.[21] As Cr, Ni and V can be associated with silicate material undigested by *aqua regia*, samples from pit 2 were also digested with HF, to permit determination of total concentrations of these elements for comparison with P-XRFS results. The concentrations obtained for Cr, Ni and V, from analysis of the HF digests, are given in Figure 1 (b), (e) and (g), respectively.

The precision (RSD) of the concentrations determined by ICP-AES was mainly in the range 3–10%. The RSD values obtained with the P-XRF analyser varied considerably as some of the analyte concentrations were close to the detection limit for this technique. For example, for the analysis of the bottom horizon of pit 2 (91–100 cm) the RSD values for Cr and Zn at 194 and 4725 μg g^{-1} were 22 and 2 %, respectively (n=10).

TABLE X Comparison of manufacturer's detection limits for the TN-9000, those derived from Potts *et al.* [22] and the range of concentrations found in material sampled from pits 1 and 2

Element	*Manufacturer's instrumental detection limit for 100 s* * *(μg g^{-1} DW)*	*Detection limits derived from Potts et al.* * *(μg g^{-1} DW)*	*Range of concentrations measured for pit 1 layers (μg g^{-1} DW)*	*Range of concentrations measured for pit 2 layers (μg g^{-1} DW)*
Cr	127	1527	150–608	< DL-702#
Cu	71	113	349–1199	< DL-1297#
Mn	283	501	1226–8728	812–13299
Ni	92	164	< DL-284#	< DL-218#
Pb	21	55	71–3780	79–1375
V	–	–	396–1326	151–893
Zn	57	89	480–3641	524–4643

* values quoted by Potts *et al.* [22] have been multiplied by √2 to account for differences in counting time used here (100 rather than 200 s).

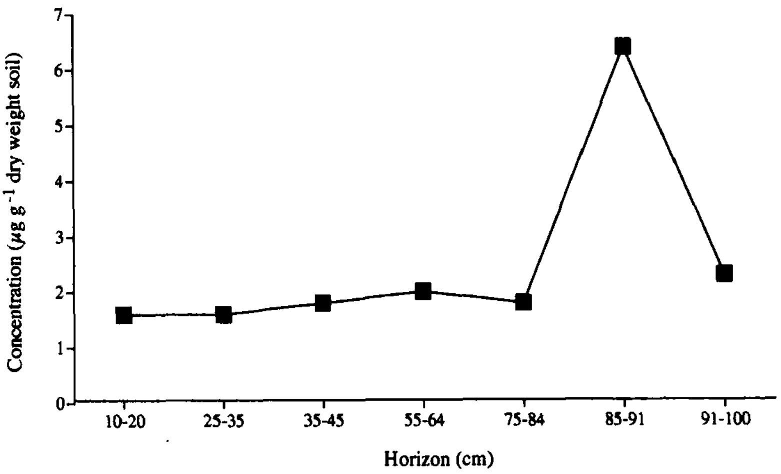
\# lowest concentration quantified for chromium in pit 2 was 173 μg g^{-1}, for copper in pit 2 was 333 μg g^{-1} and for nickel in in pits 1 and 2 were 212 and 108 μg g^{-1}, respectively.

For Cu, Pb and Zn (Figure 1 (c, (f) and (h)) the concentrations estimated with the P-XRF analyser are similar to the results obtained when the *aqua regia* digests were analysed by ICP-AES. For some horizons, the concentrations of Cr, Mn and Ni (Figure 1 (b), (d) and (e)) obtained by the two techniques are in reasonable agreement. However, for other layers, the XRF results are much higher than those determined by ICP-AES (for *aqua regia* or HF digestion), which suggests a possible spectral interference (enhancement) in the XRF measurements for these samples. In general, the concentrations of Cr and Ni in the HF digests were higher than for the *aqua regia* extracts, which is not unexpected. The element that exhibits the greatest difference in the concentrations obtained by XRFS and ICP-AES is V (Figure 1 (g)). As the concentrations of the elements in the HF digests were only slightly greater than for the *aqua regia*extracts, it is likely that either a major spectral interference affected determination of V by XRFS or that the calibration algorithm pre-programmed into the portable analyser is inappropriate for determination of V in industrial soils. It is possible that enhancement effects on V (K_α absorption edge at 0.2269 nm) were caused by fluorescent lines of Cr (K_β , 0.2085 nm), Mn (K_α, 0.2107 nm) and Fe (K_α, 0.1937 nm).

Evaluation of Soil Concentrations

In the U.K., guidance on acceptable levels of contamination for various land uses has been issued by the Government's Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) [25]. Although the location and accessibility of an industrial site can limit the possibilities for redevelopment, variations in the composition and extent of contamination across a site are also important factors to consider. In pit 1, the cadmium and lead levels equal or exceed the threshold limit values for domestic gardens and allotments (3 $\mu g\ g^{-1}$ and 500 $\mu g\ g^{-1}$, respectively) in the surface and lower horizons, whilst the 60–85 cm layer contains lead at levels which, without remediation, could prevent the re-use of the material even for parkland or playing fields [25]. Furthermore, almost all layers of pit 1 contain phytotoxic levels of copper, nickel and zinc. In pit 2, the copper and nickel concentrations in the top five horizons exceed the threshold levels for any use where plants are grown, whilst zinc is present at phytotoxic levels in all but the 55–64 cm horizon, and is well above the threshold value (300 $\mu g\ g^{-1}$) in the lowest two layers. The lead concentrations in the top four layers of pit 2 and the cadmium concentrations in the 85–91 cm layer exceed the threshold limits values for use of the soil in domestic gardens [25]. The chromium concentrations in pit 2 are well below the limit for domestic gardens (600 $\mu g\ g^{-1}$).

(a) Cd



(b) Cr

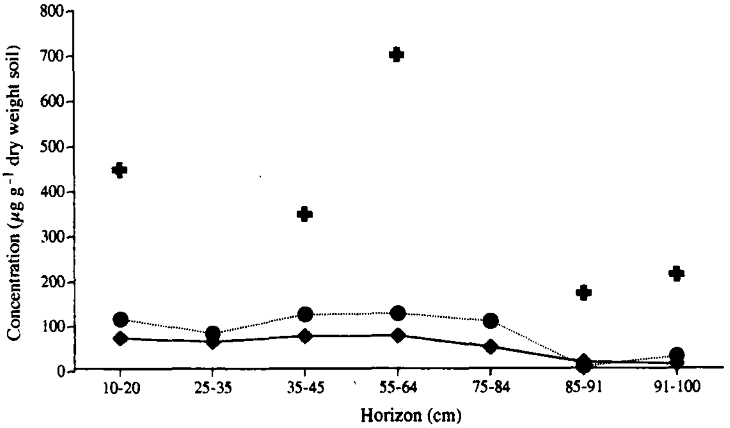
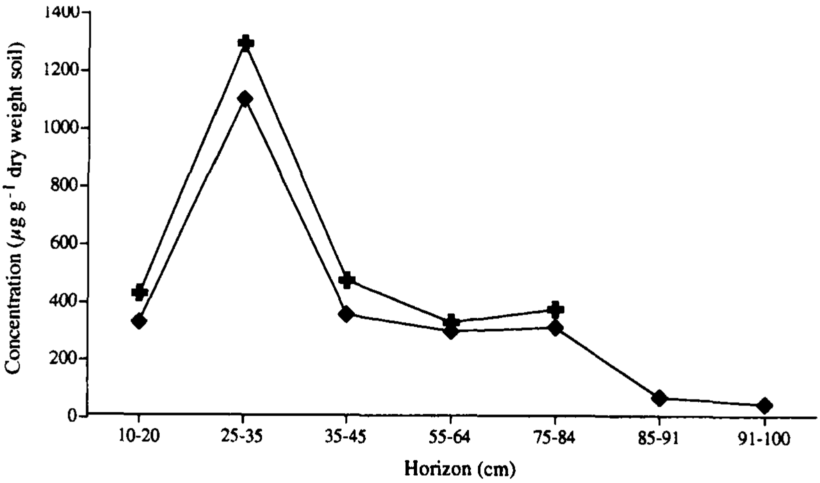


FIGURE 1 Concentrations of elements in finely ground fractions of layers in pit 2 on the industrial site, determined by ICP-AES for *aqua regia* (♦) and HF (•) digests, AAS for *aqua regia* digests (■) and P-XRF for powdered soil (+); (a) Cd, (b) Cr, (c) Cu, (d) Mn, (e) Ni, (f) Pb, (g) V and (h) Zn ; P-XRF values less than manufacturer's detection limits are omitted

(c) Cu



(d) Mn

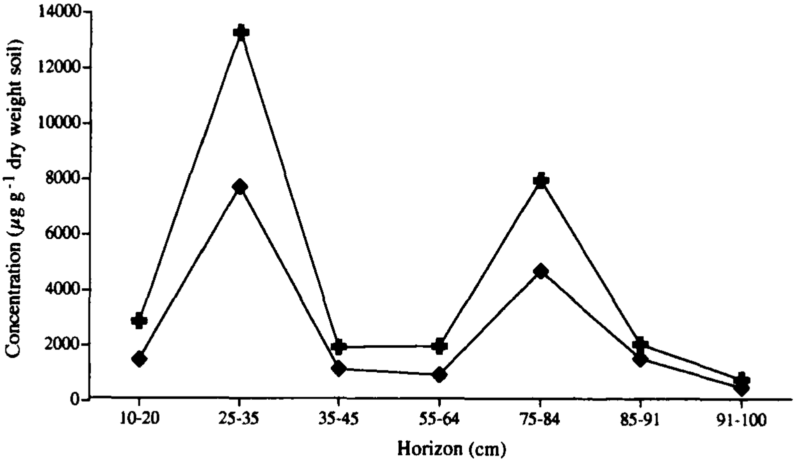
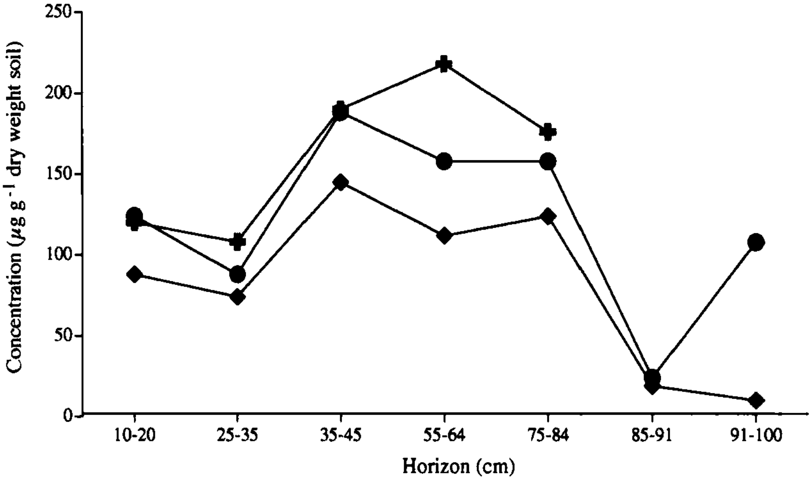


FIGURE 1 Continued

(e) Ni



(f) Pb

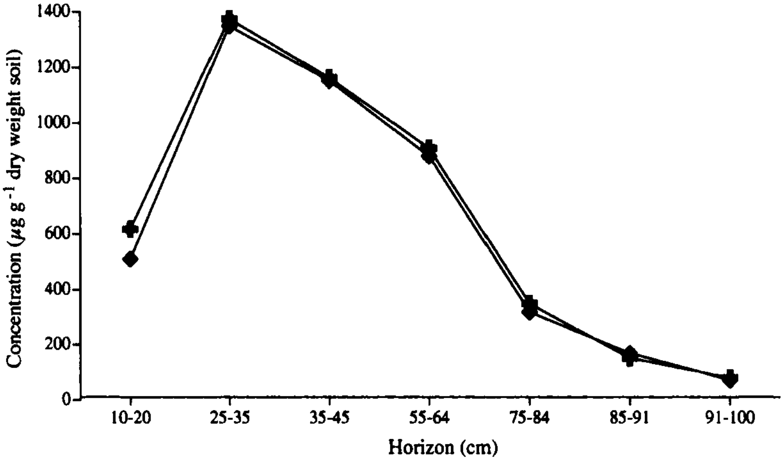
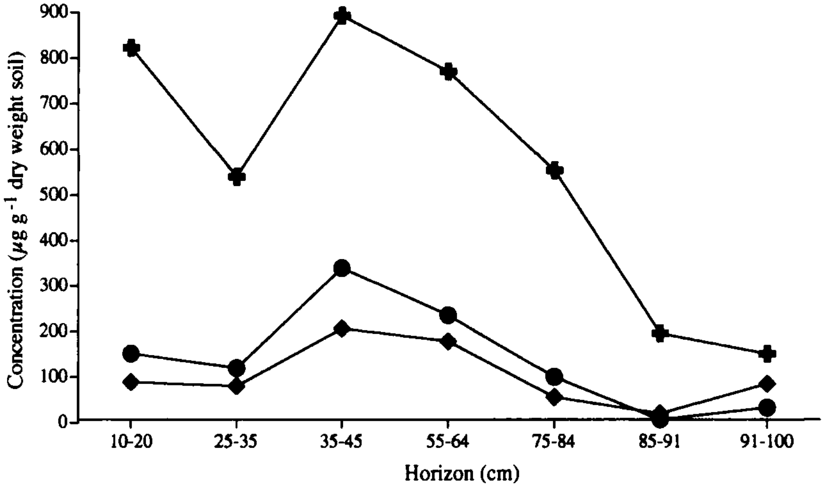


FIGURE 1 Continued

(g) V



(h) Zn

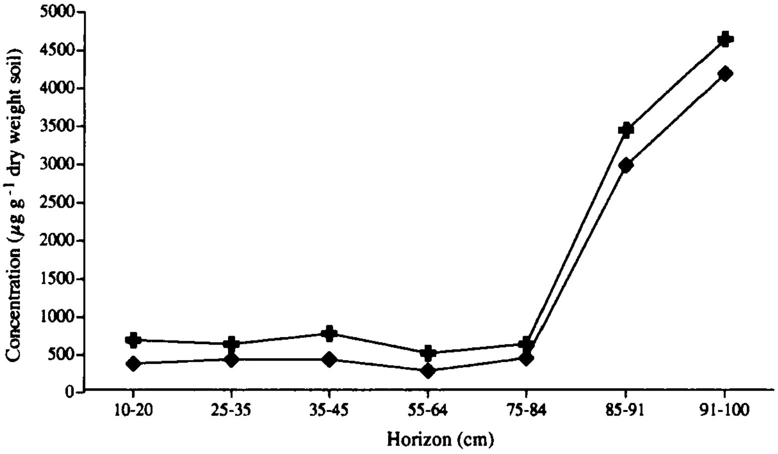


FIGURE 1 Continued

In view of the unusual nature of the made ground material, limited comparison is possible between results obtained in the present study and typical heavy metal concentrations in soil. Cadmium, nickel and vanadium levels are only slightly greater than those found in agricultural soils, but copper and zinc are significantly enhanced (typical concentrations 20–30 and 50 $\mu g\ g^{-1}$, respectively [26]). Chromium and manganese concentrations are within typical soil ranges but the lead level at depth (60–85 cm) exceeds typical values by more than an order of magnitude [26].

There are few similarities in the distributions of the metals between the layers of the two pits studied. In pit 1, there is some evidence of similar trends in concentration with depth between chromium and vanadium, copper and zinc, and manganese and lead, whilst in pit 2, the copper and manganese levels seem more clearly correlated. The highest concentrations of copper, manganese and lead occur in the lower layers of pit 1, but are closer to the surface in pit 2. The variations in metal concentrations across the site may be influenced by differences in (a) the original levels of contaminants in the made ground material deposited on the site, (b) contamination during use and (c) subsequent metal mobilities.

CONCLUSIONS

Material taken from two excavated pits on the site of a former chemical manufacturing plant was sampled, processed and analysed using three different techniques. Validation tests, including digestion and analysis of two reference materials and spike and recovery analyses performed on sample digests, indicated that the AAS and ICP-AES methods gave reasonably accurate estimates of the analyte concentrations extractable by *aqua regia*. In addition, despite not using precise algorithms specific to the type of material from the pit horizons, most concentrations determined by XRFS were within a factor of two of the results obtained for the samples by AAS / ICP-AES, and with certified values of a single reference material. In this respect, analysis with the P-XRF instrument may be useful for initial screening of samples from a site as part of an overall strategy to the assess contamination of industrial land. Samples with an apparently high metal contaminant concentration can then be digested and analysed using laboratory based techniques (e.g. AAS or ICP-AES) for more accurate determinations. Such an approach in this study revealed that spectral interferences can cause over-estimation of Cd and V concentrations obtained with the P-XRF instrument and so care is required in interpreting screening results obtained by P-XRFS for these elements.

It is apparent that many of the metals exhibited higher concentrations at depth than in the surface layer of the trial pits, which highlights the need for vertical as well as surface sampling when assessing contamination. There is also a general need to determine likely mobility of metal contaminants in contaminated soil. Further steps, which will endeavour to address this, include the application of column leaching experiments to material from the pit layers to simulate the effects of acidified rainfall, and the application of sequential extraction [27]. Also, moist, untreated material could be analysed by the P-XRF instrument to ascertain if direct on-site analysis produces useful semi-quantitative estimates of analyte concentrations.

The lack of appropriate reference materials of industrial land of the type considered in this study limited the validation of the methods of analysis . The development of certified reference materials of contaminated industrial land would benefit future similar investigations.

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