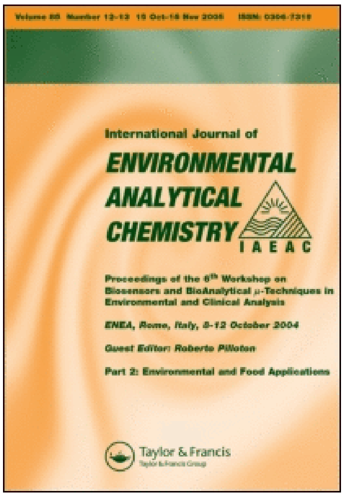

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DETERMINATION OF TRACE METALS (Cu, Pb, Zn and Ni) IN SOIL EXTRACTS BY FLOW ANALYSIS WITH VOLTAMMETRIC DETECTION

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It is shown here that flow analysis with voltammetric detection can be used to determine Cu, Pb, Zn and Ni in soil extracts. Cu, Pb and Zn were detected by square-wave anodic stripping voltammetry (SWASV), and Ni by square-wave cathodic stripping voltammetry (SWCSV). Advantages of the method are good sensitivity and the possibility to take the instrumentation into the field for on-site measurement. The reagents were: 0.2 M acetate buffer at pH 5.0 for Cu, Pb and Zn, and 0.04 M pH 9.0 ammonia buffer containing 20 μM DMG (dimethylglyoxime) for Ni. The reactive metal fraction was determined in 0.5 M HCl extracts (25 min extraction time) of soil samples from six different sites characterised by varying degrees of heavy metal pollution. The reactive metal fractions amounted to 23–73% of the metals in 5 of the 6 sites, whereas it was much lower (9–30%) at the other site. Organic matter did not interfere with the measurements as it was not extracted significantly by the 0.5 M HCl and as the extracts were diluted prior to analysis. The formation of intermetallic compounds at high levels of Cu and Zn was minimised by determining these metals in separate sample aliquots with calibration using separate standard additions, and by using different plating potentials and short plating times. Good accuracy was verified by analysis of reference materials.

Keywords: Metals in soil; anodic stripping voltammetry; cathodic stripping voltammetry; copper; lead; nickel; zinc

INTRODUCTION

Contamination of land is a problem of increasing concern to scientists and politicians. Legislation on waste disposal and soil protection has appeared to prevent further pollution [1, 2]. A substantial increase in demand for industrial and residential development has put pressure on the redevelopment of derelict lands [3, 4]. Land contaminated by industrial or waste disposal activities has the potential

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to pollute run-off as well as ground water, so convenient methods to detect contamination are essential especially to allow on-site testing.

Low levels of metals in soil are required as micronutrients for plants and microorganisms, but they can become toxic at high levels. Elements of most concern are Cd, Cr, Cu, Pb, Ni and Zn because they are present in large amount in wastes, and are potentially toxic to plants and/or animals [5]. The potential toxicity of heavy metals in the environment depends on their concentration in the soil [6] and on their remobilisation and bioavailability. Methods to assess the ecological risks of heavy metals in soils include measuring the total metal contents and the metal content in soil solution extracts. Various sequential extraction procedures have been developed to obtain a degree of fractionation of metal species [7]. An estimate of metal bioavailability and of anthropogenic contamination is comparatively readily obtained from extraction with dilute acid providing reactive metal concentrations [8–12].

Several analytical techniques have been applied to determine the metal content in soil extracts [13] including inductively coupled plasma atomic emission (ICP-AES) and atomic absorption spectroscopy (AAS) [5, 14–16]. Anodic (ASV) and cathodic stripping voltammetry (CSV) are used regularly for natural water analysis [17–20] but their application to soil analysis is rare. The metal content in soil extracts is determined by ASV with precision comparable to that of AAS [21], but is somewhat hampered by possible formation of intermetallic compounds at high metal concentrations [22, 23]. Recent development of voltammetric flow systems [24, 25] provides a possibility to adapt these systems to the analysis of soil with the aim to measure soil contamination in the field.

This paper reports the use of an experimental flow system with voltammetric detection [26] as a prototype for field analysis of reactive trace metals in soils. Our experiments show that most of the reactive metal fraction is released within an equilibration time of 25 min. The reactive metal concentration is therefore defined here as that which can be extracted within 25 min with dilute acid (0.5 M HCl). A small (50–100 µl) aliquot of this extract is diluted with buffer solutions and analysed by flow analysis with voltammetric detection. The reactive metal content is compared to the total concentration obtained after digestion with aqua regia.

EXPERIMENTAL

Equipment

The instrumentation used for the metal determinations is described in detail elsewhere [26] and only adaptations necessary to the soil sample analysis are outlined here. The system consists of a flow cell attached to a hanging mercury drop electrode (HMDE), a de-oxygenation chamber, a pump for the transport of the solution and a mercury recovery vial. The reference electrode is a silver wire and the chloride in the buffer solutions (NaAc/HCl and NH_4Cl) was used as counter ion. The counter electrode is a platinum wire. Since samples and reagents were premixed a T-junction for mixing and a three way valve for standard additions were not necessary. The de-oxygenation chamber was used for the determination of Ni. A gradual decomposition of the gas permeable silicone tubing in contact with the pH 4–5 sodium acetate buffer caused the release of organic surface active compounds which interfered with the determination of Cu, Pb and Zn. These solutions were therefore purged for 5 min with nitrogen (using a gas flow of 140 ml/minute) prior to transport to the flow cell bypassing the in-line degassing unit.

Whatman 540 filter paper used for soil sample filtration was pre-washed with 20 ml 0.5 M HCl and 50–100 ml Milli-Q. Filters were rinsed with 20 ml aqua regia when this was used to obtain total metal extracts. A Gallenkamp flask shaker was used for extraction time experiments.

Reagents

Reagents were purchased from BDH (AnalaR quality) unless indicated differently. Aqueous reagent solutions (ligands and buffers) were stored in 30 ml polystyrene vials, whereas strong acid and ammonia solutions were stored in polyethylene bottles and vials. Water was purified by reverse osmosis (Milli-RO, Millipore) followed by ion-exchange (Milli-Q). Ammonia, HNO_3 and HCl were purified by sub-boiling quartz-distillation. A stock aqueous solution of 0.1 M DMG (dimethylglyoxime) was prepared in 0.2 M sodium hydroxide. A sodium acetate buffer stock solution was prepared containing 2 M sodium acetate and 1 M HCl, and electrolytically purified using a mercury pool electrode and an ESA potentiostat (model 2014PM) with the potential set to −1.3 V. Ammonium chloride (NH_4Cl) buffer (4.0 M) was prepared using quartz-distilled ammonia and HCl. Aqua regia was prepared using sub-boiling quartz-distilled HNO_3 and HCl (3:1). Metal stock solutions of 10^{-4}, 10^{-5} and 10^{-6} M Cu, Pb, Ni and Zn were prepared by dilution of BDH atomic-absorption (Spectrosol) standard solutions, and acidified to pH 2 with quartz-distilled HCl.

Analytical procedures

Square-wave ASV was used to determine Cu, Pb and Zn in 0.1 M NaAc/0.05 M HCl buffered solutions adapted from a previously published batch procedure [21]. Square-wave CSV was used to determine Ni in the presence of 20 μM DMG and ammonia buffer (0.06 M for the total and 0.04 M for the labile metal determinations). A minimum of 8 scans were recorded and peak heights reported were averaged from a minimum of 5 scans. Different scans may be seen as different measurements in the in-line determination because the solution in the small (0.4 μL) flow cell is continuously changed: therefore scans are not a repetition of the same solution but of new aliquots of the same sample. The voltammetric parameters are in Tables I and II. Short deposition times for Zn and a more positive deposition potential for Cu and Pb (Table II) were used in the determination of extracts of real samples to minimise possible interference due to the formation of intermetallic compounds between zinc and copper.

Preparation of soil extracts

Homogenised "British Gas in-house reference soil materials" (here called reference materials), and soil samples from 6 different locations (A-F) were obtained from the British Gas Research and Technology Centre. Metal concentrations in the reference materials had been determined by ICP-MS after total digestion with aqua regia. Different weights of samples (0.5–1 g) were used depending on the expected levels.

Total metal concentrations in the reference materials

1.0 g of soil (reference material I and II) was wetted with a few drops of distilled water in a Teflon beaker. Then aqua regia (20 ml) was added, and the samples were heated to 60–80 °C to allow evolution of CO_2 from organic matter for about 1 h. Then the beakers were closed with a cap and the temperature was increased to ~ 120 °C for three hours to allow full digestion. The digests were allowed to cool and then filtered through Whatman 540 filter paper, and made up to 100 ml in a glass flask. Metal concentrations were then determined by voltammetry using the voltammetric parameters in Table I.

TABLE I Voltammetric parameters for the determination of metals by ASV and CSV in diluted soil extracts

	Cu, Pb, Zn	*Ni*
Deposition time(s)	90	30
Deposition potential (V)	-1.2	-0.8
Equilibration time(s)	10	5
Equilibration potential (V)	-1.25	-0.75
Final potential (V)	0	-1.1
Frequency (Hz)	10	10

0.1 ml aliquots for Cu, Pb and Zn, and 0.05 ml aliquots for Ni, were diluted to 20 ml with the buffer solutions prior to the analysis; separate solutions were made containing standard additions (100 nM Cu, Pb and Zn, and 50 nM Ni) for calibration.

Reactive metal concentrations in the reference materials

0.5 g of soil (reference material I) was shaken (10 min) with 20 ml of 0.5 M HCl and immediately filtered through Whatman 540 filter paper. Aliquots of 0.2 ml of the filtered extracts were diluted to 20 ml with the buffer solutions with and without added standard (300 nM Cu and Zn, 100 nM Pb and 200 nM Ni). Metal concentrations were then determined by voltammetry using the voltammetric parameters in Table I.

Extraction time experiment

Six aliquots of 0.5 g soil were extracted with 20 ml of 0.5 M HCl for 5, 10, 15, 25, 40 and 60 minutes and immediately filtered through Whatman 540 filter paper. Small volumes of the filtrates (0.04 and 0.2 ml for Zn, 0.2 ml for Ni, and 0.4 ml for Cu and Pb) were diluted to 20 ml with the buffer solutions with and without added standards (100 nM Cu, Pb, and 200 and 1000 nM Zn). The metals in the buffer solutions were determined by voltammetry. The voltammetric parameters are given in Table II.

Diluted filtrates (1:10 for Ni and Zn, and 1:5 for Cu and Pb) of some extracts were UV-digested (4h) with a 1 kW UV-lamp to destroy any co-extracted organic matter, and analysed separately.

The reactive metal fraction in soil samples

1 g of each soil was shaken (25 min) with 20 ml 0.5 M HCl and immediately filtered through Whatman 540 filter paper. Small volumes of the filtrates (0.5 ml for Cu, Pb and Zn, and 0.1 ml for Ni) were diluted to 20 ml with the buffer solutions with and without added standards (100 nM Cu, Pb, Ni and 1000 nM Zn) for calibration. The voltammetric parameters were the same as before (Table II), however, the deposition time for Zn was reduced to 10 s.

RESULTS AND DISCUSSION

Response of the system and linearity

The response of the system was tested using a diluted aliquot of 60 min soil extract. The solution contained 58 nM Cu, 68 nM Pb, 276 nM Zn and 125 nM Ni. Metal additions were made whilst recording the system response repeatedly using the voltammetric parameters in Table II. The metal concentrations added were: 50, 100, 200 and 300 nM Cu and Pb; 100, 200, 300, 500 and 1000 nM Zn; 50, 100, 150 and 200 nM Ni. Eleven repeat scans were made for Zn and Ni, and eight for Cu and Pb for solutions with and without added standard. The standard deviations of the measurements were: Zn: SD 3.1% at 276 nM and SD 3.1% at 1300 nM; Ni: 4.3% at 125 nM, and 3.8% at 325 nM; Cu: 26% at 58 nM, and 13% at 358 nM; Pb: 8% at 68 nM, and 3.8% at 370 nM. The change in response to increased metal concentrations was found to be completed within a maximum of three scans equivalent to a response time of <200 s (Figures 1a-d); the length of the response time was sufficient to flush the tubing three times suggesting that the response was delayed by longitudinal mixing in the tubing. The first three scans for new samples or standard additions were therefore always discarded. Adsorption/desorption processes on the pump tubing could be the cause of the slowly increasing Pb responses at high metal concentrations (300 nM Pb, Figure 1B), and intermetallic compound formation could be the cause for slowly decreasing Cu responses at high levels (200 and 300 nM) of Cu (Figure 1A). The relative standard deviation of measurements with the flow-cell was higher than that obtained with a batch system, which should be balanced against the much greater rate at which measurements can be achieved with the flow-cell [26].

TABLE II Voltammetric parameters for the determination of easily liberatable metals by ASV and CSV in the shaking time experiment on a real soil sample. The second column for Zn indicates the parameter used in the comparative experiment on UV and not UV-digested extracts of soil samples

	Cu, Pb	*Zn*		*Ni*
Deposition time(s)	120	30	1	30
Deposition potential (V)	-1.0	-1.25	-1.25	-0.8
Equilibration time(s)	10	5	5	5
Equilibration potential (V)	-1.0	-1.25	-1.25	-0.75
Final potential (V)	0	-0.8	-0.8	-1.1
Frequency (Hz)	10	10	10	10

The ASV response for Zn, Cu and Pb, and the CSV response for Ni are shown in the inset of Figure 1A-D and linear regression results are summarised in Table II. The response was found to be linear in the tested ranges up to 1300 nM (600 nA, $r^2 = 0.997$, S = 0.46 nA/nM) Zn, 360 nM (190 nA, $r^2 = 0.990$, S = 0.60 nA/nM) Cu, 370 nM (370 nA, $r^2 = 0.9991$, S = 1.00 nA/nM) Pb, and 325 nM (660 nA, $r^2 = 0.9995$, S = 1.97 nA/nM) Ni, but the standard deviation of the response at high levels of Cu (200 and 300 nM) was high (± 7.7 and ± 12.7 %) reflecting systematic decreases possibly due to formation of intermetallic compounds. A shorter deposition time and a more positive plating potential to exclude deposition of Zn is therefore recommended when Cu is determined at such high levels. A standard addition is sufficient for calibration purposes when the peak height is inside the linear range.

Reference materials

Total metal concentrations and standard deviations (SD) obtained by flow analysis with voltammetric detection for the reference materials are compared with the confirmed values in Table III. The reproducibility of the in-line voltammetric method for Ni (4.2 % SD) was much lower than that obtained from a number of laboratories using different analytical techniques (29 % SD), and the mean value of the voltammetric results differed by only 2.5 % from the reference value confirming not only good precision but also good accuracy.

The voltammetric values for Pb were in reasonable agreement with the certified data (about 10 % lower but with overlapping standard deviations). However the voltammetric values for Cu and Zn were higher than the certified values. High levels of Cu and Zn can produce intermetallic compounds in mercury causing erroneous results by suppressing the peak height of the standard addition. In the concentration range used here it appeared that the effect could be prevented by calibration using a single metal addition instead of using a mixed standard: good agreement between the two techniques was obtained using individual calibrations (Table III). These results confirm that Cu and Zn interfered during the deposition because of formation of intermetallic compounds, which agrees with results reported in the literature [23], while no interference was apparent between Cu and Pb in contrast with other recent work [22] but in line with expectation as the lead solubility in mercury is very high and intermetallic compound between Cu and Pb are not formed.

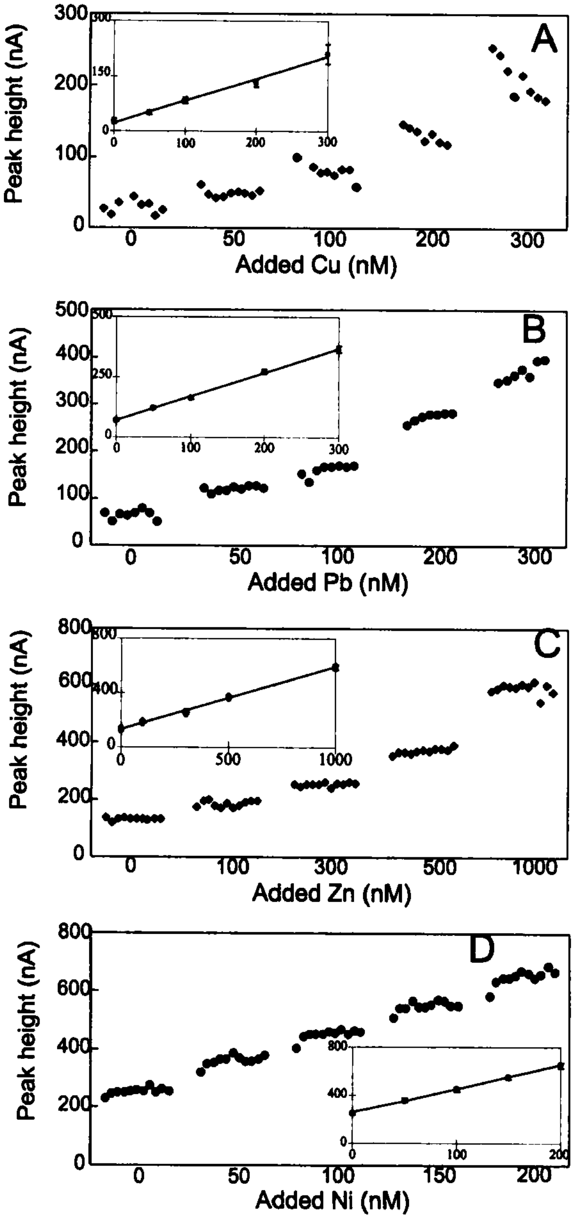

FIGURE 1 Response of the flow cell for Cu, Pb and Zn (ASV) using pH 5.0 acetate buffer and for Ni (CSV) using 0.04 M NH_4Cl and 20 μM DMG in 60 min extracted soil samples. The deposition time was 30 s for Zn and Ni, and 120 s for Cu and Pb

TABLE III Comparison of metal concentrations (mg/kg) and relative standard deviations (SD%) obtained by in-line voltammetry with values obtained by a number of laboratories using different techniques for two reference soil materials (I and II). The voltammetric response was calibrated by separate standard addition of Cu, Pb, Zn and Ni

	I						*II*			
	Voltammetry				*Confirmed values*		*Voltammetry*		*Confirmed values*	
	Concentration (mg/kg)	*n*	*SD (%)*	*Separate standards (mg/kg)*	*Concentration (mg/kg)*	*SD (%)*	*Concentration (mg/kg)*	*SD (%)*	*Concentration (mg/kg)*	*SD (%)*
Cu	138.3	3	23	117.0	93.5	18	134	-	122	8
Pb	297.3	3	8.4	296.0	342	10	32	-	39.2	27
Zn	103.0	3	10.7	62.6	62.3	10	121	-	90.3	3
Ni	130.1	3	4.2	-	133	29	68	-	63.9	15

Reactive metal concentrations in reference materials

The reactive metal concentrations in the reference material I are listed in Table IV, along with standard deviations. The reactive metal as percentage of total metal concentrations (R/T %) were calculated using the voltammetric data for the total metal levels. Clearly a large part of the metals is not released by leaching the soil with 0.5 M HCl: this fraction probably occurs chiefly in the crystal lattice and is not of environmental relevance as it is not readily available.

TABLE IV Reactive metal concentration (mg/kg), relative standard deviations (SD%) and reactive metal fractions (%) in extracts of a reference soil material (reference material I). The sensitivity was calibrated using a simultaneous standard addition of Cu, Pb and Zn

	[Reactive metal] (mg/kg)	*n*	*SD (%)*	*Reactive/total (%)*
Zn	63.7	3	6.7	60
Pb	109.0	3	10.1	40
Cu	14.5	3	20.0	10
Ni	11.9	3	8.4	10

The formation of intermetallic compounds of Cu and Zn during the measurements could be minimised by using separate calibrations to keep the combined metal concentrations low. A short deposition time (10 s) at −1.25 V during the Zn determination further minimise this type of interference, whereas deposition at a potential more positive than that of Zn (-1.0 V) reduce interference by this metal during the Cu determination. These conditions were therefore applied for subsequent experiments, and a simultaneous addition was used only for Cu with Pb.

Overall analysis times

After a flushing period of 200 s a scan was obtained every 120 s for Cu and Pb, and every 30 s for Zn and Ni; five scans were averaged for each analysis. The total analysis time for Cu and Pb was therefore 600 s, and for Zn and Ni 150 s; between samples and prior to the Ni analysis a flushing time of 200 s has to be added giving an overall analysis time of 1150 (19 min) for all the metals in a sample. The sensitivity was consistent for given conditions (at fixed deposition times) so calibration was necessary only at the onset and finish of a series of samples. The analysis time is shorter than that for batch-wise analysis (around 45 min for the metals combined) as some of the sample preparation is carried out on-line (de-oxygenation for Ni) or off-line and does not contribute to the analysis time as it can be efficiently carried out during analysis of other metals or samples (e.g. purging for Cu, Pb and Zn, and reagent additions). The analysis time is probably slower than automated AAS but work is in progress on battery a powered voltammetric flow instrumentation which can be used in the field more easily.

Extraction time experiment on a real sample

The rate of metal dissolution from soil samples was determined by equilibrating a fresh soil sample (site F) containing 20 mg/Kg Cu, 72 mg/Kg Pb, 550 mg/Kg Zn and 76 mg/Kg Ni with 0.5 M HCl; the sensitivity was calibrated by standard additions and averaged. Dissolution of the metals increased with time, the increase levelling off after ~ 10 min (Figure 2) for Cu, Pb and Zn; most of reactive Pb was released very rapidly, within 5 min equilibration, suggesting that this metal is released most readily. After 60 min equilibration 29 % Cu, 42 % Pb, 66 % Zn and 39% Ni were released, whilst after 25 minutes ~ 24 % Cu, 50 % Pb, 71 % Zn and 31 % Ni were released. An extraction time of 25 min was selected as a trade-off between maximised metal extraction and minimised extraction time.

Effect of UV-irradiation

It is likely that some organic matter is co-extracted with the metals even though the solubility of humic acids is low at low pH. To evaluate interference by co-extracted organic matter, Zn concentrations in UV and not UV-digested extracts of soil samples (site F) were compared after various extracting times (Figure 3). The sensitivity was calibrated by a standard addition to each of six extraction aliquots (n=6) and averaged giving a mean sensitivity of 4.22 ± 0.28 nA/(nM min) for not UV-irradiated samples, and 4.05 ± 0.16 nA/(nM min) for UV-irradiated samples. The difference in the sensitivity was statistically insignif-

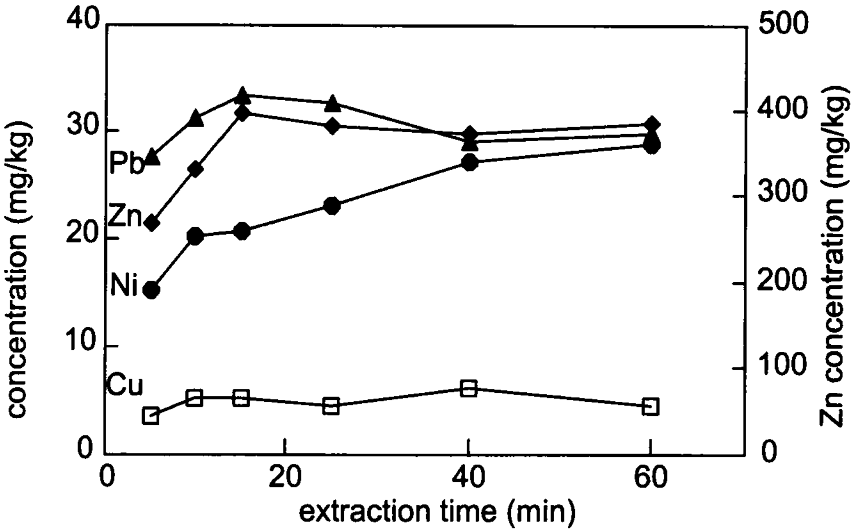

FIGURE 2 Effect of the extraction time on the concentration of reactive metal released. Sensitivities (normalised to 1 min deposition) were: Cu 0.38 ± 0.03 nA/nM; Pb 0.97 ± 0.05 nA/nM; Zn 0.91 ± 0.06 nA/nM; Ni 4.13 ± 0.13 nA/nM

icant suggesting that only little organic matter was extracted; no significant difference was found in the reactive (without UV-irradiation) and total zinc concentrations, suggesting that zinc masking by organic matter was insignificant in the procedure employed here, possibly because only a minor concentration of organic matter was extracted using 0.5 M HCl (Figure 3).

Cu, Pb and Ni concentrations obtained with and without UV-digestion (calculated from a standard addition using 5 repeated scans) in the 60 min extracts (Table V) also showed no significant difference indicating that the reactive metal concentration was not affected by organic matter in the soil. Differences in sensitivities in UV-digested and un-digested aliquots were negligible suggesting that levels of any interfering surface-active organics were negligible due to the dilution of the sample.

Blanks and limits of detection

Reagent and handling blanks were determined from the metal concentrations in acid which was taken through the same procedure as the samples except that no soil was added. Longer deposition times were used in the analysis (90 s for Ni, and 180 s for Cu, Pb and Zn, to detect the low metal concentrations using the

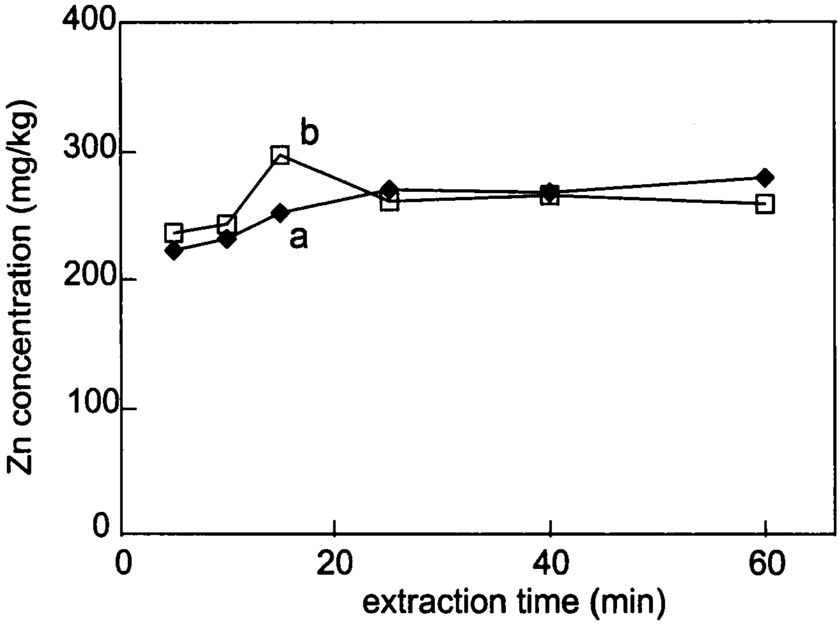

FIGURE 3 Effect of UV-digestion : comparison of Zn concentrations in UV (a) and not UV-digested (b) extracts of a soil sample as a function of the extraction time

flow analysis method. The sensitivity was calibrated by standard metal additions for each metal separately. The blank levels were 6.8 nM Cu, 0.18 nM Pb, 24 nM Zn and 0.9 nM Ni. Limits of detection in aqueous solution were calculated from 3x the standard deviation (n=10): 7 nM Cu, 0.2 nM Pb, 3 nM Zn, and 0.4 nM Ni. Using the deposition times used for the soil analyses the limits of detection of the metals in mg kg^{-1} soil amount to: 1.8 (Cu), 0.14 (Pb), 0.7 (Zn), and 0.09 (Ni). These limits of detection would be increased by interference by organic matter unless this is removed by UV-irradiation of the extracts. However, the limits of detection could be lowered by using a larger soil sample in the extraction step.

Cd was not detected in the soil samples even though the Cd concentration in the reference materials was 1.4 – 1.6 mg kg^{-1}. It is possible that the Cd detection suffered from interference by organic matter as Cd is more subject to this kind of interference than lead. Furthermore a rather large dilution was used to eliminate the formation of intermetallic compounds between zinc and copper, and to minimise interference by organic matter; the resulting cadmium concentrations in the diluted extracts were therefore <0.5 nM, apparently too low for the voltammetric settings used.

TABLE V Cu, Pb and Ni concentrations in UV-digested and un-digested extracts of soil samples (extraction time 60 min)

	not UV	*UV*
Cu (mg / kg)	4.45	4.96
Pb (mg / kg)	28.08	29.42
Ni (mg / kg)	29.37	29.96

Application to soil samples

Reactive and total metal concentrations of 6 soil samples (sites A-F) are compared in Table VI along with R/T (%) mean values, while Table VII reports typical metals content in soils, continental crust and "limit" values in soils reported in an EEC Directive [27] on the protection of the environment and in the ICRCL guidance notes [2].

Comparison of the total metal concentrations shows that those from sites D and E sites were always inside the ranges reported for soil and upper crust and lower than the limit values reported in the EEC Directive and in the ICRCL guidance notes, apart from the Ni value in site E which was higher than that normal for upper crust material. Concentrations in samples from the other sites were higher than typical upper crust values for all the metals. Compared with normal soil levels only the concentration of Ni in sites A and F, Cu in B and F, and Pb in C were inside the reported ranges. Total metal concentration were inside the limit values for all sites except F: at this site the total concentrations of Zn and Ni were higher than the limit reported in the EEC Directive and in the ICRCL guidance notes.

Comparison of the reactive metal concentrations in the sites A-F (Table VI) with typical metal concentrations and limit values (Table VII) shows that the reactive concentration of Ni in sites A, B and F, and Zn in F were higher than the limit values; however, direct comparison is not possible as we used 0.1 M HCl to obtain reactive concentrations whereas the limit values are based on extraction with 0.05 M EDTA (0.1 M HCl was selected as there is no doubt about other parameters as pH, whereas the pH of EDTA extracts depends on the method of preparation). This suggests extractable metal concentrations should be used as indicating factor of soil pollution, because these extractable forms are the most readily available to plant and could enter the food chain, but could also transport heavy metals to groundwater if acid rain occurs.

TABLE VI Reactive (R) and total (T) metal concentrations (mg/kg) and the R/T ratio × 100 (%) for soil samples from various sites. The R/T mean is the average of the R/T ratios calculated from all sites, and SD mean is its standard deviation

	A			*B*			*C*			*D*			*E*			*F*			*R/T mean*	*SD mean*
	T	*R*	*%*	*T*	*R*	*%*	*T*	*R*	*%*	*T*	*R*	*%*	*T*	*R*	*%*	*T*	*E*	*%*	*%*	
Cu	28	9.4	34	16	7.2	45	24	2.2	9	<10	1.2	>12	10	3.1	31	20	4.8	24	29	13
Pb	41	20.3	49	38	21.3	56	20	6.0	30	12	6.0	50	10	5.7	57	72	36	50	49	10
Zn	60	43.8	73	100	38.8	39	82	8.8	11	35	11.9	34	38	14.4	38	550	390	71	44	24
Ni	49	23.3	47	52	28.2	54	46	6.2	13	14	3.2	23	40	10.3	40	76	27.9	31	35	15

TABLE VII Typical metal concentrations (mg/kg) in soil, in the upper (UC) and lower (LC) continental crust, and "limit values" reported in the EEC Directive and British guidance notes

	Soil[a]		*Continental crust*[b]		*Directives*		
	Frequent	*Tolerable*	*UC*	*LC*	*86/278/EEC*[c]	*ICRCL 59/83*[d]	*ICRCL 70/90*[e]
						Total	*Extractable **
Cu	1–20	100	14.3	37.4	50–140	130	50*
Pb	0.1–20	100	17	12.5	50–300	500	-
Zn	3–50	300	52	79	150–300	300	130*
Ni	2–50	50	18.6	99	30–75	70	20*

*Extracted in 0.05 M EDTA
References: a (29);b (30);c (27); d (2); e (31)

Comparison of the R/T ratios between the sites A-F shows that the R/T ratios were quite constant for most sites, but some sites differed: Zn values obtained in samples from sites A and F, and Cu and Ni values obtained from site B were above the R/T mean and outside its standard deviation values. The R/T mean is the average of the R/T ratios calculated from all sites. The standard deviation (SD) of the R/T mean calculated from the sites is used to evaluate sites with reactive metal concentrations outside these values. A higher fraction of reactive metal could suggest that a greater fraction is of anthropogenic origin, whereas the low reactive concentrations of the metals in the sample from site C suggest that their origin is not mainly anthropogenic and that they occur mainly in the crystal lattice [8, 10].

The relatively high extractability (30–60 %) of the metals from the soil samples suggests that removal of heavy metal contamination due to anthropogenic input can be achieved by extracting the soil with 0.1 M HCl. This method of extraction could be a comparatively simple remedy to clean contaminated land affected by heavy metal pollution. This method is known to remove 60 to 90% of anthropogenic derived metals after three repeated extractions [9, 28]. However, a problem is that it could cause the soil to become sterilised too.

CONCLUSIONS

The experiments show that flow-analysis with voltammetric detection can be used successfully to determine metals in acid extracts of contaminated soils: a reproducible response was obtained at low and high concentrations. Advantage of the flow-analysis procedure over conventional voltammetry is a reduced analysis time. Development of battery powered instrumentation in an automated system would enable on-site measurements, and such an instrument could play an important role for monitoring of metals in contaminated lands, avoiding sample transport.

The data showed that organic matter did not interfere with the metal analysis. Reactive metal concentrations were found to increase with extraction time but the extraction was mostly completed within 10–20 min; at that point the reactive metal concentration amounted to 30–60% of the total metal content and did not increase significantly using a longer extraction period.

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