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Bioavailability of potentially toxic elements (PTES) in soil from a former industrial site using EDTA/acetic acid

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Abstract

Pseudo total Potentially Toxic Elements concentration is a useful guide in evaluating the pollution level in the environment. Samples of soils from a former industrial site have been analysed for potentially toxic elements (Arsenic, Cadmium, Chromium, Copper, Nickel, Lead and Zinc) using EDTA and HOAc. The accuracy of the microwave digestion and ICP-MS analysis was assessed by determination of the elements in a certified reference material (BCR 700). Excellent agreement was obtained in all cases between certified and measured values for the elements investigated. The plant availability estimated using EDTA/AcOH varies across the sampled points. Correlation analysis has been carried out between the pseudo total PTE content and the single extraction using EDTA/HOAc and the results shows significant strong positive correlation between the EDTA/HOAc and the pseudo total concentration for all the PTEs measured. The correlation coefficients between EDTA and HOAc are as follows: - As (0.911), Cd (0.985), Cr (0.844), Cu (0.905), Ni (0.589), Pb (0.891) and Zn (0.816). This implies that both EDTA and HOAc are good for extraction of PTEs in soil.

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Introduction

Potentially Toxic Elements are well-known for their toxic effects and therefore information on their concentrations and distribution in the environment is important. Pollution of the environment by these elements can pose a serious threat to plants, animals and even human beings because of bioaccumulation, non-biodegradable properties and toxicity of the contaminants even at low concentrations. Since these elements are non-biodegradable, their pollution is long lasting.

Different approaches are used for soil and sediment analysis, many of them focussed on pollutant desorption from the solid phase; others on the pollutant adsorption from a solution by the solid phase (Weihua *et al.,* 2009). Among the approaches based on desorption, leaching procedures are the most widely accepted and used (*Rauret, 1997*). Leaching involves two processes: - (a) Mobilization of the target metal from the solid particle and (b) Dissolution of metal-containing solid phases (e.g. Al, Fe, Mn oxides or hydroxides, organic matter and silicate minerals). The dissolution process is a three step mechanism involving (1) fast ligand adsorption onto surface functional groups of solid particles (2) slow mineral metal detachment and fast protonation restoring the original surface functional groups (Lim *et al.,* 2004; Polettini *et al.,* 2007).

Changes in environmental conditions, whether natural or anthropological, can strongly influence the behaviour of both essential and potentially toxic elements by altering the forms in which they occur. The transfers of metals from soil to plants pose potential health risks because they can enter the food chain and the environment (Ghanedi *et al.,* 2008). Plant uptake is one of the major pathways by which heavy metals enter the food chain (Chaney, 1990; Muhammad *et al.,* 2009).The uptake of PTEs by plants from soils is of interest because excess dietary intakes are detrimental to human health.

Of the leaching extraction processes, single and sequential extraction has been the most widely accepted and used. Sequential extraction provides more detailed information about the different availabilities of PTEs partitioning among different geochemical phases, enabling differentiation between several physical forms of speciation: exchangeable, carbonates, oxide, organic-bound and residual forms. The most widely used method for determining sequential extraction are those proposed by Tessier *et al. (*1979) and modified by Rauret *et al.* (1999). The former method has four steps, where four fractions of extractable PTEs are released from the sample: exchangeable (ion exchange PTEs), associated with carbonates (acid soluble PTEs), associated with Fe-Mn oxides (reducible PTEs) and associated with organic matter (oxidizable PTEs) (Perez *et al.,* 2002). The modified method constitutes three steps, with the major difference to Tessier *et al.* (1979) method being the replacement of the first two steps with a single step, use of large sample size and an increase in the volume of extractant *(Bacon and Davidson, 2008*). In both cases, the residual fraction is always digested using aqua regia and summed up with those of other fractions and compared with the result of a separate aqua regia digest of the whole soil (pseudo total). This is an additional step. The conventional protocol of the *Tessier et al. 1979* method, or its modification, is a time consuming procedure owing to the lengthy operating time required in the successive extraction steps and consequently, could be considered tedious for routine analysis especially when considering the bioavailable fraction, hence the use of single extraction (Perez *et al.,* 2002).

Single step extractions are mainly applied to soil samples to identify the bioavailable fraction using a number of different reagents to extract all, or part of, the metals from soil (Jose *et al.,* 2006). A commonly used single extraction approach to characterise soil bioavailable fraction of metals is the use of the HOAc/EDTA procedure (Samani *et al.,* 1998). Using EDTA to extract metals has been proven to be effective because of its strong complexing ability (Samani *et al.,* 1998). The advantages of EDTA in heavy metal extraction are high efficiency of metal extraction, formation of metal complexes which are thermodynamically stable and soluble, low adsorption of the chelating agents and their metal complexes on soil (Abumaizar and Smith 1999; Peters, 1999; Tandy *et al.,* 2004). According to Perez *et al.* (2002), single extraction procedures provided similar amounts of extractable PTEs to those released in the first three fractions of the Tessier *et al.* (1979) method, which can be considered to be the more mobilizable fractions. Laboratory studies have shown that EDTA is effective in mobilising PTEs (Sun *et al.,* 2001).

Two major pathways in which PTEs gets to the humans is through soil-plant-humans and soil-humans (accidental ingestion). Soil-plant transfer of PTEs is the major pathway to human exposure to soil contaminants. Many researchers have assessed human risk from soil contaminants with single PTE (Cai *et al.,* 1990; Watanabe *et al.,* 2000; Jin *et al.,* 2002). However, multiple contaminants often coexist in the environment therefore health risk based on single contaminant may grossly underestimate the health risk associated with the mixed contaminants. This work is aimed at comparing the effectiveness of HOAc and EDTA in the extraction of PTEs from a contaminated land.

Material and methods

Sample collection and sample handling

Samples of soil were collected from 19 sample points on the site (Fig. 1) by digging a square hole of about 10 cm^2 from the top soil. The grass on the top of the soil was removed. The top soil collected was put inside a wax paper geochemical bag, and labelled to include the sample point, date of collection and the site where it was collected. The hole created was covered back after the collection. During sampling, sample handling and sample preparation polyethylene gloves were worn. The soil samples were dried in the sample bags in an oven at a temperature of <40^{o}C for 6 days. The dried soil samples were gently disaggregated in a porcelain pestle and mortar and passed through a plastic sieve of mesh size 2 mm and stored. A powdered sub-sample was digested using microwave digestion technique and then stored in the fridge for metal analysis using ICP-MS and FAAS.

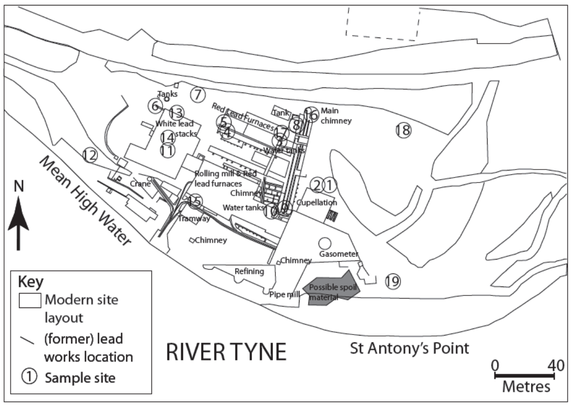

Fig. 1. Sample locations for soil samples at former St Anthonys lead site. The building are labelled to indicate previous usage.

Soil pH, LOI and CEC

Soil pH, LOI and CEC were measured by the methods described by *Strowbel et al 2005*, *Blaize 1993* and *Robertson et al 1999* respectively.

Microwave digestion protocol

A Start D Microwave Digestion System with Multiprep 42 High Throughput rotor was used for acid digestion. 0.5 g of the sample was accurately weighed into a PFA (65 ml) vessel pre-cleaned with concentrated HNO_3. Then 16 mL of aqua regia (HCl: HNO_3 3:1 v/v) was added to the sample. The vessel was sealed with the TFM cover and placed inside a rotor of the microwave digestion system and subjected to the following microwave dissolution programme: 25 mins at a power of 750 W and temperature of 160 °C. The microwave oven was operated with a nominal capacity of 4 vessels per run. A ventilation (cooling) time of 30 minutes was allowed while the vessels were still in the oven. After cooling, the digest was filtered using a Whatman filter paper into a 50 ml volumetric flask and diluted to the mark with Milli-Q water. For each batch of digestions, reagent blanks were also prepared. The filtrate obtained from the digestion was stored in the fridge (4^{o}C) prior to metal analysis.

Inductively coupled plasma mass spectrocopy potocol

An X series II ICP-MS was tuned using a 10 ppb solution of Li, Be, Bi, Ce, Co, In, Ba, Pb, Tl, U in 2% HNO_3 to verify mass resolution. The tuning was done in standard and CCT (Collision Cell Technology) mode. Elements with masses <80 were run in collision cell mode and those > 80 amu in standard mode. The conditions for standard mode and CCT mode are shown in Table 1.0. Multielement calibration standards are run in the range 0-400 ppb with eight data points and three internal standards (Sc, In and Tl); correlation coefficient data is typically >0.999.

Table 1. Calibration Data As, Cd, Cr, Cu and Ni on ICP-MS and Pb, Zn on FAAS.

Element	Isotope	Calibration Equation $y = mx + c$		Correlation Coefficient r^2	
		CCT mode	Standard mode	CCT Mode	Standard Mode
As	^{75}As	$y = 562.15x + 0.02$	$y = 2952.40x - 0.04$	0.9992	0.99
Cd	^{111}Cd	N/A	$y = 435.64x + 11.15$	N/A	0.99
Cr	^{52}Cr	$y = 587.68x + 10.97$	$y = 1461.92x + 12.14$	0.9997	0.99
Cu	^{63}Cu	$y = 681.63x + 5.83$	$y = 1020.88x + 11.99$	0.9993	0.99
Ni	^{60}Ni	$y = 235.42x + 3.44$	$y = 378.93x + 35.58$	0.9996	0.99
***Pb**	^{208}Pb	*N/A*	$y = 0.0136x - 0.003$	N/A	0.99
***Zn**	^{66}Zn	*N/A*	$y = -0.0065x^2 + 0.136x +$	N/A	0.99

*Elements measured using FAAS

Flame atomic absorption spectroscopy protocol

The AAnalyst instrument was operated with an air-acetylene flame. Calibration was achieved using a 5 point graph with standard solutions in the range 0-10 ppm. Two elements were determined using FAAS, namely, Pb and Zn at wavelengths of 217.0 and 213.9 nm, respectively.

Single extraction using EDTA

0.05 M EDTA was prepared as ammonium salt solution by adding in a beaker 14.61 g EDTA to 80 mL deionised water. The dissolution was achieved by gradually adding 13 mL of ammonia solution (25%). The solution was then transferred to a 1.0 L Polyethylene container and approximately 900 mL of deionised water was added. The pH of the solution was adjusted to 7.0 by adding a few drops of NH_3 or HCl as appropriate and the solution was made up to 1.0 L with deionised water. 2 g of soil CRM (BCR 700) was weighed into a 50 mL centrifuge tube and 20 mL of 0.05 M EDTA (pH 7.0) was added. The mixture obtained was shaken in an end-over-end shaker at 30 rpm for 1 hr at room temperature. The mixture was centrifuged for 10 minutes at 3000 g and the supernatant was decanted, filtered through a Whatman No 41 filter paper and stored in a polyethylene bottle at 4°C. The extract was analysed using ICP-MS. The same procedure was adopted on the samples.

Single extraction using HOAc

0.43 M HOAc was prepared by adding 25 mL glacial HOAc to about 500mL of deionised water in a 1.0 L polyethylene container. The solution was then made up to 1.0 L with deionised water. 20 mL of 0.43 M HOAc was added to 0.5 g of soil CRM (BCR 700) in a 50 mL centrifuge tube and the mixture extracted by shaking with an end-over-end shaker at 30 rpm for 16 hrs at ambient temperature (overnight) making sure that there was no delay between the addition of the extractant solution and the beginning of the shaking. The mixture was centrifuged for 10 minutes at 3000 g and the supernatant was decanted and filtered through a Whatman no 41 filter paper and stored in a polyethylene bottle at 4°C until analysis with ICP-MS. This procedure was applied to the samples.

Results and discussion

Soil properties (pH, % LOI, CEC)

The behaviour of heavy metals varies for different types of soil and so characterising the soil sample is important. Table 3 shows the properties of the soil collected from former St Anthony's lead works. The soil characteristics such as pH, % LOI and CEC have a direct influence on the mobility and availability of PTEs (Narwal and Salbu, 1999). Soil pH is one of the most important factors in the control of the absorption, mobility and bioavailability of PTEs in the soil solution (Walid *et al.,* 2009). A high pH contributes to a decrease of PTE mobility by the formation of precipitates, which increases the number of adsorption sites and decreases the competition of H^+ for adsorption, thereby increasing the PTE stability with humic substance. The pH was carried out in water. The average pH measurement in the sampled points from the site is 7.3. There is only limited variability in the % LOI except with that of SAL 18 where the % LOI is much higher. The average % LOI is 11.47%. The % LOI contributes to the soil CEC and a high value of % LOI results in a high value of CEC, which will have direct impact on the availability of metals.

CEC indicates the number of cation exchange sites and the value gives an idea of the number of cation adsorption sites in the soil (Robertson *et al.,* 1999). PTEs in soils of low CEC are more susceptible to leaching. Table 2 shows the typical CEC values for different soils. From Table 2.0, it can be seen that the CEC values at former St Anthony's lead works (SAL) (Table 3) falls within the normal range, except for SAL 18, which has a high value of 161 cmol/kg. The cation adsorption potential of PTEs in this case will be high because of the high CEC. According to *Cameron, 1992* CEC values are considered low if below 12 cmol/kg.

Quality control

The soil certified reference material (BCR 700) was analysed in two different modes (Standard and CCT) using inductively coupled plasma mass spectrometer (ICP-MS) for both HOAc and EDTA extraction. The results obtained are shown in Table 4.0. As noted previously, the CRM was run to check the accuracy and precision of the instrument. The CRM was run three times for each extractant (for a precision estimate) and the mean taken. The result of the CRM showed good agreement.

Mobility of PTEs in Soil from the industrial site

Pseudo total PTE concentration gives the overall pollution level but does not correspond to the amount of contaminants (PTE) taken up by plants or absorbed by humans. Part of the pseudo total is taken up by plants or humans and part of it remain in the soil. Therefore using pseudo total concentration to measure the bioavailable fraction will lead to overestimation. The single extraction using EDTA and HOAc has been used to demonstrate the fraction of the pseudo total content that is extracted from the soil by plant in the site. Details of the extraction using EDTA and HOAc for individual elements are discussed below.

Table 2. Typical CEC values for different soils.

Rating	CEC (cmol/Kg)	Comment
Very low	0 – 10	Very low nutrient holding capacity indicating sandy soils with little or no clay or organic matter. Nutrients will easily be leached.
Slightly low	10 -15	Slightly low nutrient holding capacity indicating a more loamy mineral soil. Nutrients will still be leached.
Normal range	15 – 40	Adequate to high nutrient holding capacity indicating soils with increasing clay content.
High	+ 40	Very high level normally found in very heavy soil with a high clay content or soils with a high organic matter level. Nutrients can be bound very tightly to the soil particles and therefore

Arsenic (As)

The total concentration of Arsenic (As) in all the sample points is greater than the SGV for residential and allotment except for SAL 1 and SAL 11 whose concentration values are 21 and 15.2 mg/kg respectively. The SGV for residential is 32 mg/kg allotment is 43 mg/kg and commercial is 640 mg/kg. The concentration values for SALs 3, 6, 13, 15, 17 and 19 are well above the SGV for commercial. The percentage of As extracted (Fig. 2) using EDTA is typically greater than those of HOAc in all the sample points except for SAL 3 and 6. The concentration of As extracted using EDTA ranges from 1.6 to 1235 mg/kg while that of HOAc and EDTA. This might be associated with the low value of CEC for this sample point (Table 2.0) thereby leading to increased mobility. Similarly the lowest mobility is obtained in site 18 which can be as a result of a high pH (pH 8.10 Table 3)which contributes to the formation of precipitates, by increasing the number of adsorption sites and decreasing the competition of H^+ for adsorption, thereby increasing the PTE stability with humic substance. Also with a high value of CEC there is higher binding force and hence low mobility.

Table 4. Single Extraction for BCR 700.

	HOAc Extraction			EDTA Extraction		
Element	**Certificate Value (mg/kg)**	**Standard Mode (mg/kg)**	**CCT Mode (mg/kg)**	**Certificate Value (mg/kg)**	**Standard Mode (mg/kg)**	**CCT Mode (mg/kg)**
Cd	67.5 ±2.8	67.5 ± 0.5 (100)	N/A	65.2 ± 3.5	63.5 ± 0.3 (97.4)	N/A
Cr	19.0 ± 1.1	16.7 ± 2.7 (87.9)	19.8 ± 0.8 (104)	10.1 ± 0.9	7.9 ± 4.2 (78.2)	10.0 ± 0.3 (100)
Cu	36.3 ±1.6	35.5 ± 1.9 (97.8)	36.4 ± 1.1 (100)	89.4 ± 2.8	78.5 ± 3.0 (87.8)	87.9 ± 0.9 (98.3)
Ni	99.0 ±5.1	87.9 ± 2.4 (88.8)	97.7 ± 0.8 (98.7)	53.2 ± 2.8	43.4 ± 0.8 (81.6)	61.0 ± 0.6 (115)
Pb	4.8±0.38	4.6 ± 1.8 (94.8)	N/A	103 ± 5	108 ± 0.7 (105)	N/A
Zn	719 ± 24	648 ± 3.3 (90)	696 ± 1.1 (96.8)	510 ± 17	471 ± 0.7 (92.4)	498 ± 0.7 (105)
Pb~	4.85±0.8	5.01 ± 0.5 (103)		103 ± 5	105 ± 3.2 (102)	
Zn~	719 ± 24	701 ± 4.5 (97.5)		510 ± 17	503 ± 24 (98.6)	

~ Measured by FAAS; N/A = Not applicable; Numbers in bracket represents % recovery.

Table 5. Pseudo-total PTE concentration of soil from former St Anthony's lead works.

Site	**Measured value in mg/kg (mean ± SD)**						
	As	**Cd**	**Cr**	**Cu**	**Ni**	**Pb***	**Zn***
SAL 1	19 ± 1.7	0.5 ± 3.6	70 ± 0.9	46 ± 3.7	30.7 ± 4.5	174 ± 0.4	169 ± 0.6
SAL 2	59 ± 1.4	1.1 ± 1.8	84 ± 0.6	70 ± 2.1	42.6 ± 2.3	1381 ± 1.5	332 ± 1.0
SAL 3	905 ± 3.6	36.8 ± 0.2	81 ± 5.9	501 ± 0.4	94.6 ± 0.4	29302 ± 7.9	10620 ± 5.6
SAL 4	140 ± 0.8	2.2 ± 1.8	75 ± 0.8	61.8 ± 1.9	30.5 ± 1.9	1048 ± 2.5	427 ± 3.4
SAL 5	140 ± 0.6	3.0 ± 1.5	74 ± 1.0	99 ± 1.1	32.6 ± 0.7	2452 ± 1.9	540 ± 1.9
SAL 6	1156 ± 2.3	10.2 ± 1.5	84 ± 4.7	598 ± 2.9	156.8 ±0.8	29286 ± 5.3	5464 ± 2.5
SAL 7	178 ± 3.2	2.7 ± 1.4	107 ± 7.2	214 ± 4	52.5 ± 5.1	5071 ± 1.9	959 ± 4.1
SAL 8	266 ± 0.9	3.7 ± 1.2	74 ± 1.0	147 ± 1.3	39.8 ± 1.2	4833 ± 1.6	1522 ± 4.3
SAL 9	398 ± 0.9	9.0 ± 1.8	93 ± 6.9	238 ± 4.7	38.2 ± 2.9	7214 ± 1.8	2172 ± 3.9
SAL 10	178 ± 0.9	2.8 ± 1.1	93 ± 6.9	127 ± 1.7	31 ± 4.5	2691 ± 1.3	879 ± 4.7
SAL 11	10 ± 0.7	0.4 ± 2.4	82 ± 0.9	22 ± 1.5	22.2 ± 1.8	221 ± 3.2	123 ± 1.1
SAL 12	669 ± 2.7	24.5 ± 2.2	164 ± 0.8	320 ± 1.7	142 ± 1.8	17443 ± 6	3233 ± 0.7
SAL 13	722 ± 2.8	12.0 ± 1.6	543 ± 0.7	465 ± 1.74	135 ± 0.5	15024 ± 10	4355 ± 0.8
SAL 14	148 ± 2.6	7.9 ± 4.9	117 ± 1.1	181 ± 1.1	73 ± 0.5	4266 ± 12	2189 ± 2.3
SAL 15	856 ± 2.7	13.5 ± 1.4	620 ± 0.6	682 ± 1.5	100 ± 1.2	28709 ± 28	7092 ± 2.0
SAL 16	358 ± 2.7	9.8 ± 1.7	116 ± 1.2	171 ± 1.7	59 ± 2.7	4968 ± 16	1133 ± 1.6
SAL 17	2816 ± 4.6	23.6 ± 1.0	121 ± 0.3	404 ± 1.3	96 ± 1.3	22822 ± 18	8488 ± 4.2
SAL 18	61 ± 2.6	1.8 ± 9.9	402 ± 1.1	102 ± 1.4	55 ± 1.6	1338 ± 15	537 ± 2.5
SAL 19	6502 ± 2.9	43.7 ± 0.9	93 ± 0.9	104.7 ±0.7	56 ± 1.3	33306 ± 11	3268 ± 1.2
SGVs/GAC	32**R**, 43**A**, 640**I**	10**R**, 1.8**A**, 230**I**	*4.3R, 2.1A Cr(VI) 3000A Cr (III)*	*2330R, 524A*	130**R**, 230**A** 1800**I**	450**RA**, 750**I**	*3750R, 618A 188000I*

*Concentrations measured using FAAS; R = Residential; A = Allotment; I = Industrial; SGVs = Soil Guideline values; Nos in italics represents the Generic Assessment Criteria (GAC) values.

Table 3. Soil properties at st anthony's lead works (SAL).

Sample Points	pH	(%) LOI	CEC (cmol/Kg)
SAL 1	6.6	10.1	14.4
SAL 2	7.5	10.9	21.4
SAL 3	7.2	10.7	19.0
SAL 4	6.6	13.0	18.5
SAL 5	7.4	11.5	19.1
SAL 6	6.5	9.1	9.4
SAL 7	6.6	16.1	-
SAL 8	7.7	14.6	-
SAL 9	7.7	11.6	27.5
SAL 10	7.6	9.4	19.7
SAL 11	7.4	7.5	24.6
SAL 12	7.7	8.2	21.7
SAL 13	7.0	10.6	22.4
SAL 14	7.9	9.6	25.8
SAL 15	8.0	8.4	23.5
SAL 16	6.9	10.7	18.0
SAL 17	7.1	15.1	21.8
SAL 18	8.1	24.7	161.0
SAL 19	7.8	6.4	18.8
Mean Values	**7.3**	**11.5**	**28.6**

Cadmium (Cd)

As expected, the concentration of Cd in all the sample points is low compared to other metals measured. Though the concentrations are small, there is reasonable mobility of the metal in the sampled points except in SAL1 and 2 (Fig. 3). The % of Cd extracted using EDTA is higher than those using HOAc. Cadmium is relatively mobile in surface water and ground water systems and exists mainly as hydrated ions or as complexes with humic acids and organic ligands such as EDTA (*Callahan et al., 1979*). Sorption is influenced by the CEC of clays, carbonate minerals and organic matter present in the soil *(Smith et al., 1995)*. SAL 18 has the highest CEC value and this implies low mobility of Cd as opposed to SAL 6 with high mobility. The % Cd extracted using HOAc ranges from 6.4 to 53.9 (0.14 to 16.4 mg/kg) as opposed to that of EDTA which is 10.0 to 74.5 (0.07 to 14.9 mg/kg). The % extraction using HOAc is higher in SAL 3, 5, 7, 8 and 14 and an equal value of extraction using both EDTA and HOAc in SAL 19 and SAL 4.

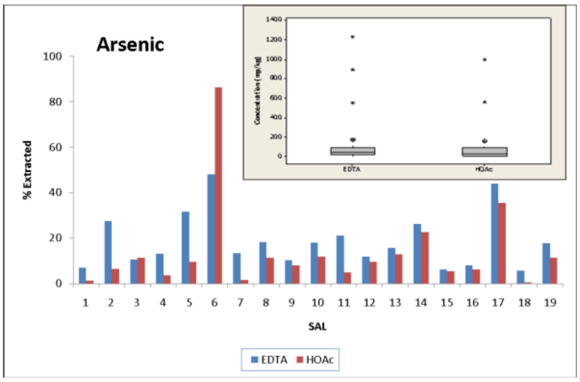

Fig. 2. Percentage/concentration (mg/kg) of As extracted in EDTA and HOAc.

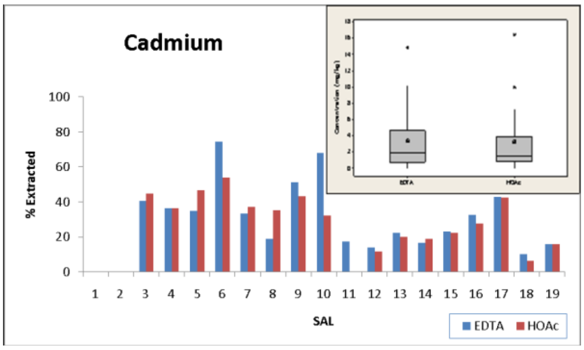

Fig. 3. Percentage/concentration (mg/kg) of Cd extracted in EDTA and HOAc.

Chromium (Cr)

All of the sampled points in this study had total soil Cr concentrations below the industrial/commercial SGV of 5000 mg/kg, although SAL 12, 13, 15 and 18 (with 173, 576, 655 and 404 mg/kg Cr respectively) exceed the SGV for residential and allotments (130 mg/kg). Using HOAc extraction, the mobility of Cr ranges from 0.2 to 21.7% total Cr (0.1 to 18.2 mg/kg) (Fig. 4.0). Similarly using EDTA, the concentration extracted ranges from 0.1 to 2.7% of the total Cr (0.12 to 2.3 mg/kg). Of all the points sampled, Cr has the least mobility compared to other metals with the highest mobility obtained using HOAc except SAL 2 and 9 which has 0.4% extraction using the acid and 0.3% using EDTA.

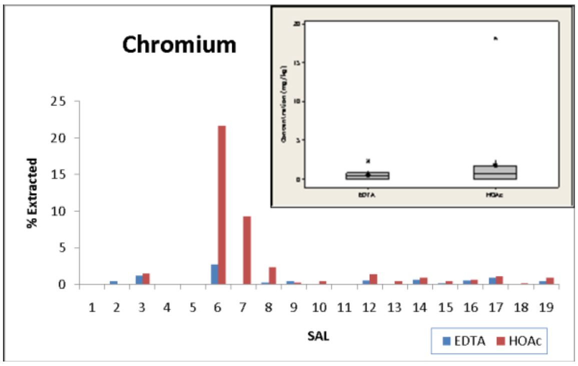

Fig. 4. Percentage/concentration (mg/kg) of Cr extracted in EDTA and HOAc

Copper (Cu)

The concentration of Cu likely to exist in uncontaminated soil ranges from 5-20 mg/kg. When these values were compared with the pseudo-total Cu concentration obtained in this work, all the sampled points showed elevated concentration.

The % of Cu extracted using EDTA ranges from13.2 to 52.6 of the total Cu while that of HOAc ranges from 4.5 to 54.5 of the total Cu (Figure 5.0). The mobility of Cu determined by EDTA ranges from 8.4 to 315 mg/kg while that of HOAc ranges from 0.7 to 326 mg/kg and EDTA mobility is higher than that of HOAc except in SAL 6 and SAL 19. The HOAc extractable contents were approximately a factor of two to twelve times lower than that of EDTA except for SAL 8, 12, 13 and 15 which were less than twice those of EDTA. The lower values of HOAc extraction may be associated with the fact that HOAc only poorly breaks down strong copper-humic acid complex, as reported by *Whalley and Grant* 1994. Also the acetate anion is a less effective complexing ligand compared to EDTA which makes re-adsorption processes more likely (*Schramel et al., 2000*). The effect of pH on copper mobility has been studied by many scholars (*Lucia and Murray 1982, Linn and Elliott 1998, Reddy et al., 1995*). In all their studies they found out that the mobility of Cu increases with a decrease in pH. This is in agreement with the result obtained in Walker Riverside Park as shown in SAL 6 and 18 (Table 3.0). SAL 6 with the lowest pH (6.53) has the highest mobility in both HOAc and EDTA while SAL 18 with the highest pH has the least mobility.

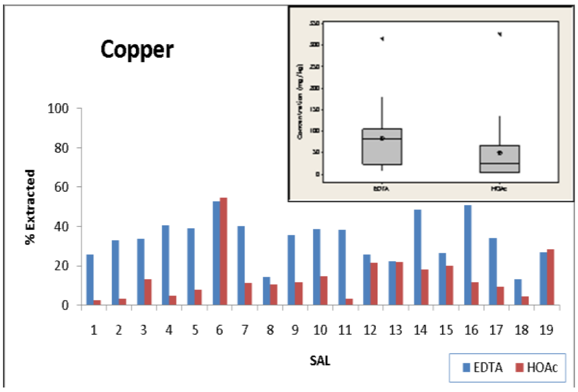

Fig. 5. Percentage/concentration (mg/kg) of Cu extracted in EDTA and HOAc

Nickel (Ni)

All of the soils analysed have Ni concentration below that of the SGV for residential (130 mg/kg), except SAL 6 and 13 whose values are 140.4 and 136 mg/kg respectively.

The SGV for allotment and commercial are 230 and 1,800 mg/kg. These values are well above the concentrations of Ni in all the sampled points. The ability of Ni to form soluble complexes with soil controls its mobility. In top soils, Ni binds to organic matter and can form soluble chelates which are more mobile in the presence of fulvic and humic acids (Kabata-Pendias and Mukherjee 2007). Soil pH is the most important factor controlling Ni solubility, sorption and mobility (Ge *et al.,* 2000; McGrath, 1995; Suave *et al.,* 2000). The solubility and mobility of Ni increases with decreasing pH (McGrath, 1995). From the results at the site, the lowest pH of 6.53 was found in SAL 6 (Table 3.0) and has the highest corresponding mobility in both EDTA and HOAc compared to other sampled points (Figure 6.0). SAL18 produces the highest pH (8.10) and has the lowest percentage mobility of 0.5 and 1.1 for HOAc and EDTA respectively. Of all the elements, Ni displays the least mobility in the soils at the site after Cr.

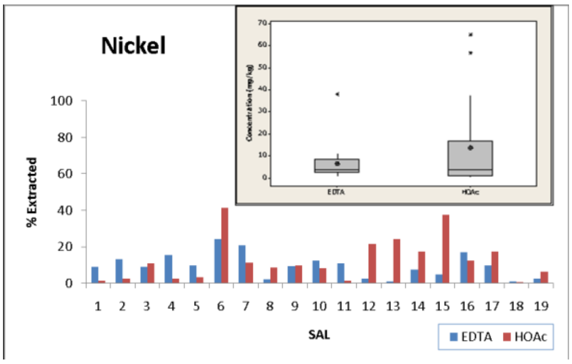

Fig. 6. Percentage/concentration (mg/kg) of Ni extracted in EDTA and HOAc.

Lead (Pb)

Figure 7.0 show the % extracted using both extractants and the box plot of the concentrations. The concentrations of Pb from all the sampled points are well above the recently withdrawn SGV except are extremely high, well above SGVs and the numbers reflect plant available rather than total concentration. From this result, additional risk assessment is required to consider the use of the site and extent of potential receptor exposure with respect to Pb.

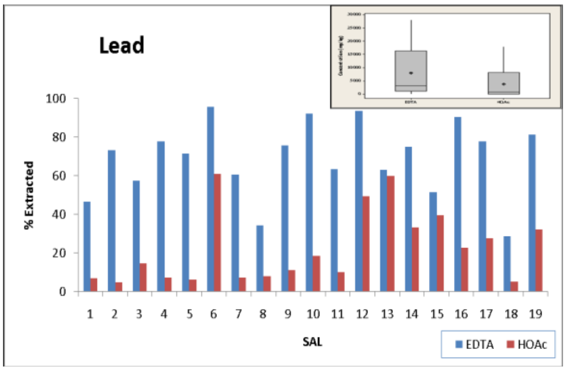

Fig. 7. Percentage/concentration (mg/kg) of Pb extracted in EDTA and HOAc.

Zinc (Zn)

All of the soils tested are well above the Zn GAC value for residential and plant uptake (320 mg/kg) except SAL 1 and 11 whose values are 169 and 144 mg/kg respectively. All of the soil tested is well below Zn GAC for commercial/industrial lands (188000 mg/kg). The mobility of Zn is higher in HOAc than in EDTA for the entire sample studied from the site (Fig. 8.0). Schafer *et al.* (1998) have classified

SAL 1 and 11 whose values are 188 and 270 mg/kg respectively. The SGV for lead is 450 mg/kg for residential and allotment and 750 mg/kg for industrial (Environment Agency, 2002). Lead has the highest overall concentration (Table 5.0) and the highest concentration in each of the sampled points. This is expected because this site was a former lead industrial site. Mobility of metals in soil depends among other things on the concentration of the metal in the soil. The mobility of Pb using EDTA ranges from 87 to 28,100 mg/kg and that of HOAc ranges from 12.5 to 17,100 mg/kg. The % of the total concentration of Pb extracted by EDTA and HOAc tends to mask the actual concentration extracted. For instance, the concentration of Pb extracted by EDTA in SAL 6 is 25,100 mg/kg and that for acetic acid is 16,100 mg/kg. These concentrations several heavy metals according to their mobility properties.

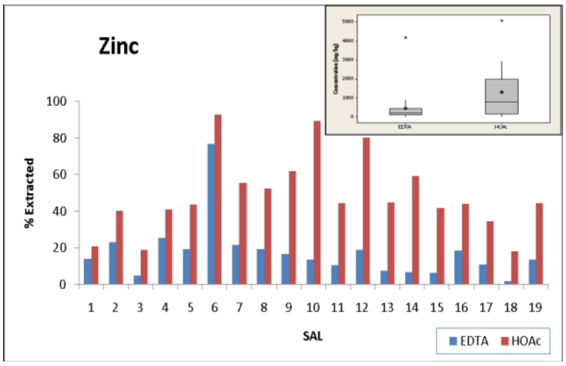

Fig. 8. Percentage/concentration (mg/kg) of Zn extracted in EDTA and HOAc.

They observed that mobility of Zn is the highest and is the easiest to be transferred from one medium to another because it is present as soluble compounds at neutral and acidic pH values. Potentially mobile Zn concentration as measured in HOAc ranges from 54.4 to 5073 mg/kg with the highest corresponding to SAL 6, forming about 92.8% of the total concentration, while SAL 18 has the lowest percentage of about 18.2% of the total. The amount of Zn extraction using EDTA ranges from 10 to 4200 mg/kg.

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