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Sequential Extraction of Lead, Copper, Cadmium and Zinc in Soils near Ojota Waste Site

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Abstract: Heavy metals are potentially toxic to human life and the environment. Hence, determining the chemical form of a metal in soils is important to evaluate its mobility and bio availability. Sequential extraction was used to fractionate four heavy metals (Cd, Cu, Zn and Pb) from six contaminated soils into six operationally defined groups: water-soluble, exchangeable, carbonate, Fe-Mn oxide, organic and residual. Analysis of the extracts was carried out by atomic absorption spectrometry (AAS). Cu was predominantly associated with Fe-Mn oxide and residual, the carbonate fraction of Cd represents more than 70% of the total Cd found in the soils, and this percentage is much greater than that of other elements examined. A major portion (>60%) of Zn was associated with the Fe-Mn oxide and carbonate fractions, whereas Pb was largely associated with organic matter and Fe-Mn oxide fractions with significant amounts in the carbonate and residual fractions. The results were interpreted in terms of the environmental mobility and bioavailability of the metals.

Key words: Soil, sequential extraction, heavy metals, waste site

INTRODUCTION

One of the major sources of heavy metal input into the aquatic environment is through landfill sites of municipal solid wastes. Contamination of soils by heavy metals from refuse dump has been a major concern because of their toxicity and threat to human life and the environment (Ma and Rao, 1997). Every major urban centre is plagued with indiscriminate dumping of municipal solid wastes. Much research has been conducted on heavy metals contamination in soils from various anthropogenic sources such as industrial wastes (Yusuf, 2006; Adeniyi and Okedeyi, 2004; Ikem *et al.*, 2003; Adeniyi and Oyediji, 2001; Kakulu and Osibanjo, 1988), automobile emissions (Arowolo *et al.*, 2000; Ma and Rao, 1997), mining activity (Kabala and Singh, 2001; Ramos *et al.*, 1994; Dudka *et al.*, 1995) and agricultural practice (Chlopecka *et al.*, 1996; Gzyl, 1990).

The total heavy metal content in soils provide a convenient means of expressing a measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of metal pollutants (Yusuf, 2006). Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways (Harrison *et al.*, 1981; Chlopecka *et al.*, 1996; Singh, 1997; Ma and Rao, 1997; Kabala and Singh, 2001). The nature of this association is referred to as speciation. Thus, the chemical form is of great significance in

determining the potential bio-availability and remobilization of the soil metals to other compartments (such as water, plants and biota) when physicochemical conditions are favourable.

There are few studies on metal speciation in soils from dump sites. The aim of the present research is to provide information on the metal speciation in soils from the waste site. These data may be used in understanding the behaviour of the heavy metals in tropical environments and their mobility and bioavailability.

MATERIALS AND METHODS

The soil samples were taken (September/October 2004) from six different sampling points (0 to 20 cm depth) located at Ojota in the northern part of Lagos (Fig. 1). The waste site is surrounded by industrial/commercial centers to the east, urban motor par/mechanic garage to the west, a highway (Lagos-Ibadan Expressway) to the south. The composition of the waste received at this site is estimated to be 65% domestic including market wastes and 35% industrial waste. The waste site was established in 1990s and faces several threats from human activities.

Reagents: Analytical reagent grade chemicals and double-distilled deionized water were used for preparing all solutions. Stock solutions containing 1000 mg L⁻¹ of the analytes were prepared from nitrate salts of Cu, Cd, Pb and Zn in 1% of HNO₃ into 1L calibrated flasks.

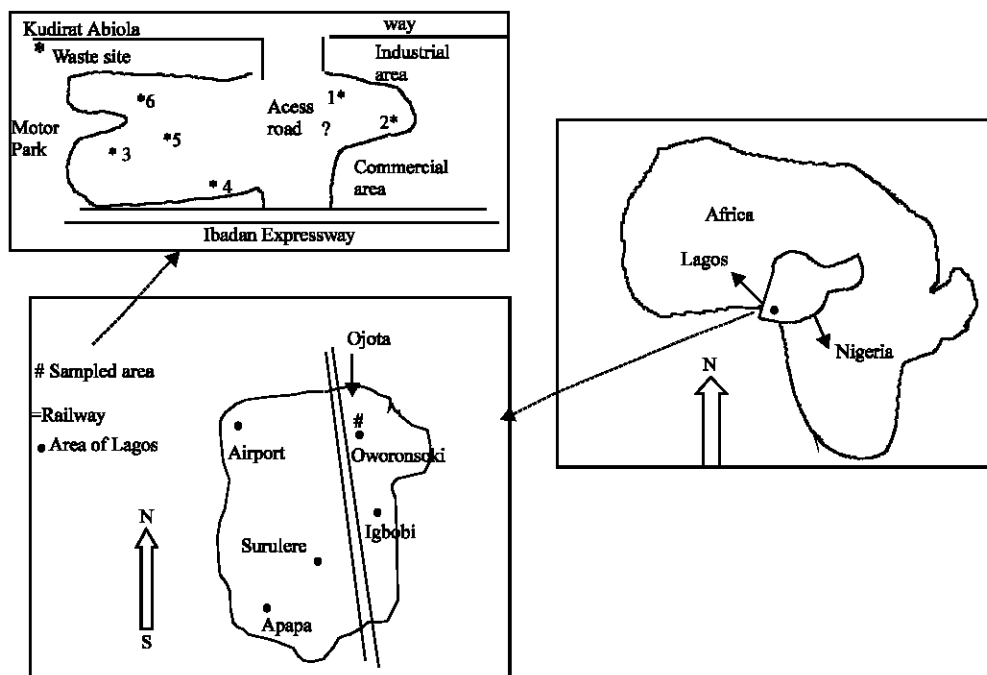


Fig. 1: Map of Ojota waste site (*Represent the study area)

Working standard solutions were prepared in $1 \text{ mol L}^{-1} \text{ HNO}_3$ by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents in equal quantities as described in the analysis procedure throughout the experiments. Solutions of $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$ were prepared in distilled water $0.04 \text{ mol NH}_2\text{OH.HCl}$ in $25\% \text{ HOAc}$. The concentrated $30\% \text{ H}_2\text{O}_2$ solution (pH 2, adjusted with HNO_3) in acidic medium and 3.2 mol L^{-1} in $20\% \text{ HNO}_3$ is often preferred for oxidizing the organic substances in analyses of soils. The digestion was performed with $7 \text{ mol L}^{-1} \text{ HNO}_3$.

Quality assurance: All chemicals used were of reagent grade and ultra pure deionized water was used throughout the experimentation. All plasticware was pre-cleaned by soaking in $10\% \text{ HNO}_3$. Procedural blanks, preparation of standard solutions under clean laboratory environment, calibration of the Buck 200A Atomic Absorption Spectrophotometer (AAS) using certified standards and the analyses of calibrated standards after 10 samples to ensure that the instrument remained calibrated were some of the measures taken during the experimentation. Recovery studies for the metal analysed using the AAS ranged between 88 and 97%.

Soil analyses: Soil samples near the waste site were collected from six different locations (Fig. 1) into polythene bags with a plastic scoop at a depth of 0-5 cm. In the laboratory, extraneous materials were removed; the samples were air-dried, crushed to a fine powder in a mortar and passed through a 2.0 mm sieve. The soil samples were homogenized and stored in clean polyethylene bags in a desiccator till the analysis. Precautions were taken to avoid contamination during sampling, grinding, sieving and storage. Subsamples of soil were taken to determine the pH and electrical conductivity in water with a 1:2.5 soil/solution ratio after equilibration for 30 min (McLean, 1982). Total organic carbon was determined by wet chemical oxidation with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (Loring and Rantala, 1992).

Instrumentation: Metal determinations in the soil extracts and digests were carried out by means of a Bulk Scientific 200A atomic absorption spectrometer. Hollow cathode lamps have been used as excitation source. Lamp intensity and bandpass were used according to the manufacturer's recommendations. Acetylene and air flow rates for all elements were 2 to 4 L min^{-1} , respectively. The instrumental parameters used for each element are shown in Table 1.

Table 1: Instrumental and experimental parameters for the metals

Elements	Cu	Pb	Zn	Cd
Wavelength (nm)	324.8	283.3	213.9	228.8
Slit width (nm)	0.7	0.7	0.7	0.7
Analytical working range ($\mu\text{g mL}^{-1}$)	0.5-5	1-12	0.05-1	0.1-2
Range of DLs for all extraction steps of the SEP	0.02-0.13	0.09-1.39	0.04-0.22	0.1-0.66

A centrifuge was used for complete separation of the extracts from the residues; a shaker, a pH meter and an electrical heater were used throughout all the experiments. Borosilicate tubes having a volume of 50 mL were used for dissolving the soil samples.

Trace metal fractionation: The total content of Pb, Cu, Zn, Cd in the soil samples were determined on filtered extracts obtained from 1 g samples that were digested overnight by 20 mL of 7M HNO₃ (100°C) and dissolved in 1 mL of 2M HNO₃. Analyses were duplicated and recoveries of the four metals, calculated by the addition standard method, ranged from 87 to 99%.

Determination of metal speciation or distribution in soil was made by the Salbu *et al.* (1998) sequential chemical extraction scheme which is a modified version of Tessier *et al.* (1979). It is designed to separate heavy metals into six operationally defined fractions.

One gram of soil were weighed and placed in a 50 mL polypropylene centrifuge tube. The following extractions were made sequentially (Salbu *et al.*, 1998).

- (F1) Sample extracted with 20 mL of deionized water for 1 h (20°C).
- (F2) The residue from (F1) extracted with 20 mL of 1M NH₄OAc, pH 7 for 2 h.
- (F3) The residue from (F2) extracted with 20 mL of 1 M NH₄OAc, pH 5 for 2 h.
- (F4) The residue from (F3) extracted with 20 mL of 0.04 M H₂OH.HCl in 25% HOAc for 6h (water bath, 60°C).
- (F5) The residue from (F4) extracted with 15 mL of 30% H₂O₂ at pH 2 (adjusted with HNO₃) for 5.5 h (water bath, 80°C). After cooling, 5 mL of 3.2M NH₄OAc in 20% HNO₃ was added; sample was shaken for 30 min and finally diluted to 20 mL with water.
- (F6) The residue from (F5), after drying, was digested in a conical flask with 10 mL of 7M HNO₃ on a hot plate for 6 h. After evaporation, 1 mL of 2 M HNO₃ was added, and the residue after dissolution was diluted to 10 mL. The residue was washed with 10 mL of deionized water before the extraction step, followed by 30 min of centrifugation, and the wash solution discarded before the next extraction.

After each successive extraction, the mixture was centrifuged at 3000 rpm for 30 min and the supernatant decanted into polythene bottles, acidified to pH<2 and stored at 4°C before analysis. Metal content of the six fractions and total metal contents in filtered solution was determined by Atomic Absorption Spectrometry (AAS), using Buck 200A. The amount of extracted trace metals in each fraction, as a percent of total metal content, was calculated.

RESULTS AND DISCUSSION

Total metals: The results of Table 2 ranged ($\mu\text{g g}^{-1}$) from 0.14 to 1.9 for cadmium with a mean of 0.47, 8.18 to 9.78 for copper with a mean of 8.84, 6.25 to 25.4 for lead with a mean of 13.2 and 18.4 to 50.1 for zinc with a mean of 26.98. Soil sample obtained from site 5 had the highest enrichment of Pb and Cu compared to all other sites. With the exception of Cd, the average values of Pb, Zn and Cu in this study were lower than the corresponding values reported respectively by Kabata-Pendias *et al.* (1992) for world soils. The average levels of Pb, Zn, Cd and Cu in Oworonsoki dump site in Lagos (Ikem *et al.*, 2002) were higher than the corresponding values obtained for these metals in this study. In another report, the mean Cu, Pb, and Cd of soils taken from Orita Aperin dump site in Ibadan (Ikem *et al.*, 2002) were consistently higher than the corresponding mean values obtained for these elements in this study (Table 2). Comparisons with Spanish soils (Ramos *et al.*, 1994) also revealed that Pb (3.15-126 g kg⁻¹), Zn (1.62-1340 g kg⁻¹), Cd (0.23-13.4 g kg⁻¹), Cu (1.62-1340 g kg⁻¹) in soils from Donana National Park were higher than the corresponding value for Ojota waste site soils. Similarly, the average values reported for contaminated soils from Southwest Poland (Chlopecka *et al.*, 1996) with respect to Zn (27-10,000 mg kg⁻¹), Pb (14-71,000 mg kg⁻¹) and Cd (0.2-102 mg kg⁻¹) for all twenty four sampled locations were higher than the corresponding values in this study. The extent of contamination of Cu, Pb and Zn in soil profiles in the vicinity of a copper smelter (Kabala and Singh, 2001) was 28-fold for Cu, 8-fold for Pb and 2-fold for Zn as compared with the corresponding values obtained for these metals in this study. Finally, the soil results in this study for Pb, Zn, Cd and Cu were lower than the typical soil metal contents (Grimshaw *et al.*, 1989) found in uncontaminated soils (Table 2). It can therefore be suggested that the relatively lower values obtained for Ojota waste site soils compared to most contaminated soils already discussed may due to the lesser impact of anthropogenic sources of pollution in the Ojota area.

Table 2: The total metal contents (average values in parenthesis) based on the sum of all the fractions including the residual obtained from Ojota waste site soil samples using Tessier sequential extraction scheme ($\mu\text{g/g}$ dry wt), abundances of the elements in the earth's crust, and typical soil metal contents

Metal	Ojota waste site, soils ^a	Oworonsoki waste site,	Orita-Aperin soils ^b waste site, soils	World soils ^c	Typical soil contents ^d	Abundances metals in of earth's cmst ^e
Cd	0.14-1.9 (0.47)	1.04±1.0	2.28±0.69	0.370	0.03-0.3	0.2
Cu	8.18-9.78 (8.84)	206.90±82.2	165.30±24.9	13	5-80	55
Pb	6.25-25.4 (13.2)	224.80±167.1	160.00±57.2	22	2-20	12.5
Zn	18.4-50.1 (26.98)	2008.00±773	NA	45	20-300	70
pH	6.87-7.93	8.49±0.34	9.07±0.40	-	-	-
%O.M	4.4-10.8	3.13±0.66 ^e	2.99±0.43 ^e	-	-	-
E.C.	47.2-110.6	NA	NA	-	-	-

^aPresent study; ^bIkem *et al.* (2002); Kabata-pendias *et al.* (1992); Grimshaw *et al.* (1989); Huheey, (1983); ^c%organic carbon; O.M.= organic matter E.C. = electrical conductivity

Metal speciation: Irrespective of sampling point, the distribution of metals in waste site soil samples generally followed the order below for the various metals studied.

- Cd: carbonate > Fe-Mn oxide > residual > exchangeable ≈ water-soluble > organic
- Zn: Fe-Mn oxide > carbonate > residual > organic > exchangeable > water-soluble
- Pb: organic > Fe-Mn oxide > carbonate > residual > exchangeable > water-soluble
- Cu: Fe-Mn oxide > residual > organic > carbonate ≈ exchangeable > water-soluble

The study of the distribution of metals showed that Zn and Cu in Ojota waste site soils were largely associated with the Fe/Mn oxides, carbonate and residual forms in the soils. Fe/Mn oxides exist as nodules, concretions, cement between particles or as a coating on particles and are excellent trace element scavengers (Ikem *et al.*, 2003). The residual phase represents metals largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh conditions. The carbonate fraction is influenced by pH and the observed pH of the soils at sites 1-6 ranged from 6.9-7.9. The greatest percentage of Cu for this study (ca. 42.01%) was present in the Fe-Mn oxide fraction (Table 3). Fe-Mn oxides are excellent scavengers of trace metals and sorption by these oxides tend to control Cu, Mn and Zn solubility in soils (Pickering, 1986). Chlopecka *et al.* (1996) found Zn to be strongly bound in the Fe-Mn oxide fraction. Zinc oxide has stability constants high enough to be concentrated in this fraction. In agreement with these results, several other workers have also reported the dominance of the Fe-Mn oxides bound in Zn (Ahumada *et al.*, 1999; Narwal *et al.*, 1999; Karczewska *et al.*, 1996; Ramos *et al.*, 1994). Cd is

distributed more as carbonate, Fe/Mn oxides and as residual. Cd seemed to be the most mobile element. Approximately 77.5% of its total concentrations were measured in 1 M NH₄OAc (F2 and F3), these fractions include Cd held by electrostatic adsorption (exchangeable) and that specifically adsorbed (Christensen and Huang, 1999). The fraction extracted at pH 5.0 (F3) was fifteen fold higher than that extracted at pH 7.0 (F2). This high amount of Cd associated with the non-residual phases shows that it may be easily transferred into the food chain through uptake by plants growing in the soils. These characteristic plus hazards of Cd to human health, suggest that frequent examination of the levels of this element in soil samples may determine potential health hazards to residents living near the contaminated area. Such high percentage of specifically adsorbed Cd in soil samples agrees with the findings of Harrison *et al.* (1981) and Baron *et al.* (1990). Since Cd is a cumulative poison for mammals, its main ways of entering the environment as a waste product are especially from metal refining and electroplating and also from the chemical and paint industries. The minor role for the organic fraction in the speciation of Cd noted in the present study is consistent with the low adsorption constant of Cd to organic matter (Baron *et al.*, 1990; Chlopecka *et al.*, 1996) and with evidence that Cd does not appear to form strong organic complexes (Sposito *et al.*, 1982; Keefer *et al.*, 1984). Pb was largely associated with the oxidizable, Fe/Mn oxides (reducible forms) and carbonate species in the soil. Under oxidizing conditions, metals present in both natural organic matter (due to complexation and peptization) and living organisms (as a result of bioaccumulation of metals) may be remobilized into the environment.

The predominance of the Fe-Mn oxide and organic fractions is in broad agreement with the result reported by Kabata-Pendias and Pendias (1992) for the affinity of Pb to soil organic matter and Ramos *et al.* (1994) that found

Table 3: Amount of Cu, Pb, Cd and Zn in soil fractions from Ojota waste site

Fraction	Conc ^a µg g ⁻¹ dry wt						Fraction % mean
	S1	S2	S3	S4	S5	S6	
Lead							
Water-soluble	0.05	0.07	0.3	0.2	0.3	0.06	1.2
Exchangeable	0.1	0.14	0.5	0.4	0.1	0.14	1.7
Carbonate	0.5	1.0	5.3	2.0	5.4	0.7	18.8
Fe-Mn oxide	1.5	1.8	6.8	2.8	7.4	1.9	28.0
Organic	2.3	2.8	6.2	3.5	8.5	2.5	32.6
Residual	1.8	2.3	2.3	1.9	3.7	2.0	17.6
Sum total	6.25	8.1	21.4	10.8	25.4	7.3	
Total digestion	3.2	7.1	15.3	14.0	33.0	9.9	
Zinc							
Water-soluble	0.0	0.0	0.0	0.0	0.0	0.02	0.01
Exchangeable	0.3	0.3	1.3	0.8	2.1	4.4	5.69
Carbonate	4.1	3.9	5.7	5.4	6.0	12.5	23.3
Fe-Mn oxide	31.3	8.6	11.3	6.1	2.5	5.2	40.2
Organic	5.1	2.5	2.7	2.5	6.1	2.6	13.3
Residual	9.3	4.6	3.6	3.5	4.5	2.9	17.6
Sum total	50.1	19.9	24.6	18.3	21.2	27.6	
Total digestion	50.6	22.96	34.7	21.6	20.4	31.8	
Cadmium							
Water-soluble	0.008	0.047	0.026	0.02	0.033	0.003	4.9
Exchangeable	0.022	0.032	0.020	0.012	0.035	0.018	4.9
Carbonate	0.014	0.039	0.020	1.74	0.17	0.057	72.6
Fe-Mn oxide	0.054	0.045	0.0	0.042	0.057	0.043	8.58
Organic	0.013	0.015	0.03	0.011	0.022	0.018	3.85
Residual	0.026	0.027	0.022	0.021	0.025	0.024	5.13
Sum total	0.14	0.21	0.11	1.85	0.34	0.16	
Total digestion	0.09	0.21	0.07	3.25	0.31	0.17	
Copper							
Water-soluble	0.15	0.10	0.13	0.13	0.20	0.18	1.67
Exchangeable	0.20	0.20	0.18	0.20	0.25	0.23	2.38
Carbonate	0.20	0.20	0.25	0.35	0.28	0.35	3.05
Fe-Mn oxide	4.33	3.38	3.38	3.37	4.36	3.41	42.01
Organic	1.40	1.28	0.55	1.35	0.80	0.75	11.5
Residual	4.53	3.13	3.30	3.58	3.32	3.30	39.9
sum total	9.78	8.69	8.18	9.28	8.31	8.80	
Total digestion	7.58	6.74	4.28	7.73	8.48	8.38	

^a Mean of duplicate analyses

most Pb associated with the oxide fraction in their study of polluted Spanish soils, with only very low amounts in the exchangeable fraction. Similar findings were reported by Ahumada *et al.* (1999), Karczewska (1996), Chlopecka (1993), Dudka *et al.* (1995) and Sposito *et al.* (1982). In general, it seems that the oxide fraction is able to scavenge Pb in natural and polluted soils (Xian, 1989; Kuo *et al.*, 1983).

Mobility of cadmium, lead, copper and zinc: The mobility of metals in soil samples may be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a “mobility factor” (MF; Kabala and Singh, 2001; Narwal *et al.*, 1999; Salbu *et al.*, 1998) on the basis of the following equation:

$$MF = \frac{(F1 + F2 + F3) \times 100}{(F1 + F2 + F3 + F4 + F5 + F6)}$$

Since some metal forms (extracted in F3) are relatively less mobile (more strongly bound to the soil components than those extracted in F1 and F2), the above mentioned index describes the potential mobility (Kabala and Singh, 2001). The MF gave values not higher than 10% for Cu, which is a symptom of high stability of Cu in the soil samples. The indices of mobility were considerably higher (particularly for Cd). The MF_{Pb} increased from 10 to 48%, the indexes for Zn ranged between 9 and 61% and for Cd 31 and 96%. The high MF values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils (Kabala and Singh, 2001; Narwal *et al.*, 1999; Ahumada *et al.*, 1999; Ma and Rao, 1997; Karczewska, 1996). In overall terms the results of the present study suggest that the mobility and bioavailability of the four metals probably declines in the following order:

Cd >> Zn > Pb > Cu

CONCLUSIONS

The total content of polluted elements in the soil can be a useful parameter for characterization of contamination intensity. However, the speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behaviour of the metals in soils. Anthropogenic input of Cd was primarily in the carbonate. Inputs of Zn and Cu appear mainly in the oxides form in addition to the residual form in Cu and carbonate form in Zn. Inputs of Pb was found in organic, oxide and carbonate fractions. The distribution of the four studied metals in the various fractions confirms their differences in mobility.

Of the elements studied Cd appeared to be the most readily solubilized, thus making this element the most potentially bioavailable. This may present a real threat as Cd is transferred into the food chain from soil contaminated by this metal.

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