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Mobility and speciation of heavy metals in soils impacted by hazardous waste

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ABSTRACT

This study describes the mobility and chemical fractionation of heavy metals (HMs) from a site impacted by auto battery slag that was generated from secondary lead smelting operations. Samples were collected from the waste pile and from the immediate surrounding soil at four depths to assess the migration and potential bioavailability of Pb, Cd, Cr, Ni and Zn. Total levels of the HMs and their fractionation were determined. The results indicate that highest levels of HMs are present in the uppermost layer with significant migration down the depth, thereby posing a threat to groundwater quality. In the fractions, the concentrations of the metals follow this sequence: $Pb > Zn > Cd > Cr > Ni$. The chemical fractions of Pb, Cd, Cr, Ni and Zn in the samples, expressed as mean concentrations of the sum of the individual chemical fractions, demonstrate that the HMs exist mainly in the non-residual fractions. For instance, the percentage of non-residual fractions of lead in the waste pile and the surrounding soil ranged from 48.9 to 95.6% and 69.4 to 98.3% respectively. The mobility factors of the heavy metals are significantly high indicating high potential mobility and bioavailable forms [IS1]of these HMs. The high concentrations of the HMs particularly Pb in the non-residual fractions, as observed in this study, shows the impact of anthropogenic activities on enrichment of natural soil with bioavailable HMs. Consequently, there is a need to be cautious in the way waste that is generated from heavy metals projects is added to natural soil.

Keywords: mobility factor, fractionation, bioavailability, heavy metals, contamination

INTRODUCTION

Human activities, through technological advancements, have led to the introduction of high levels of heavy metals (HMs) into the soil. Heavy metals are attracting local, national and international concern due to their non-biodegradable nature in the environment as well as their ability to interfere with normal metabolic activities of living organisms. Soil is the main sink for HMs. On reaching the soil, the environmental, or health effects they produce depend on the forms in which they are added to soil and the prevailing environmental conditions. Heavy metals reaching the soil go through numerous reactions with different soil components, which affect their solubility, mobility and availability in the environment (Scokart *et al*., 1983).

Heavy metals can occur in soil environment in both solid and solution phases. When they are present in the solid phase they are immobile, inert and harmless, while HMs in aqueous phase are mobile and toxic. In the solid phase, HMs are immobilised through adsorption on organic and inorganic components of the soil or may be precipitated as pure solids. However, HM ions in the solid phase may become available if there is change in soil cation, pH or oxidation–reduction potential.

Metals can exist in soil solution phase as free metal ions (M^{n+}), as soluble complexes with inorganic (OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^-, and Cl^-) or organic ligands (McLean and Bledsoe, 1992). Migration of HMs from soil to other media such as water and air and consequently biological systems depends on these different forms in which they are

present in soil. If found mainly in the soluble form, they may be leached down the soil profile reaching the groundwater or taken up and accumulated by plants, invertebrates, animals and man (Chopin *et al*., 2003; van Straalen *et al*., 2005; Marcel *et al*., 1999; Maramba *et al*., 2006).

The environmental and human adverse effects that the HMs produce are connected with their solubility and bioavailability in soil. Excessive amounts of available heavy metals in soil have been reported to produce negative effects on the ecosystem (Ghosh *et al*., 2004; Shanker *et al*., 2005; ATSDR, 1999). In humans, following exposure to high levels, heavy metal toxicity has been associated with various physiological disturbances. For example, Pb toxicity is been linked to various reproductive effects, developmental delay and mental retardation in children (WHO, 2006; Kakkar and Jaffery, 2005).

Heavy metals exist mainly in six different geochemical forms in soil (Tessier *et al*., 1979; Abollino *et al*., 2006; Ramos *et al*., 1994; Hickey and Kittrick, 1984; Kuo *et al*., 1983). These are water soluble, exchangeable, carbonate bound, Fe−Mn oxide bound, organic matter bound and residual. The sum of the fractions with the exception of residual is termed non-residual fraction (Hickey and Kittrick, 1984). Metals in the non-residual fractions are assumed to be more available than metals associated with residual fractions. The association between the HMs and soil components increases from water soluble to residual, thus making the water soluble and the exchangeable fractions the most soluble and mobile forms. Fractionation of HMs to residual and non-residual fractions in soil and smelting waste materials has been broadly documented (Sanghoon, 2006; Basta and Gradwohl, 2000; Kabala and Singh, 2001; Ma and Rao, 1997; Hickey and Kittrick, 1984). The authors consistently reported the water soluble and the exchangeable fractions as the most mobile and bioavailable forms. Some of these reports also showed that contamination of soil by smelting waste affected the way the HMs are partitioned into various fractions. The potential dangers associated with a heavy metal contaminated site depend on the form in which HMs exist in it. Sites in which metals exist mainly in the residual forms present little, or no, hazard to the environment and living organisms. For example, Pb in the form of lead phosphates (*e.g.* $Pb_3(PO_4)_2$ and $PbHPO_4$), mixed lead chloride phosphate ($Pb_5(PO_4)_3Cl$), PbS and $PbSO_4$ exist mainly in the residual form where it presents little or no risks to the

environment. On the other hand lead nitrate [$Pb(NO_3)_2$], lead acetate ($PbCOOCH_3$) and, to some extent, lead chloride ($PbCl_2$) are soluble in soil and have a high potential for mobility. Lead in these forms may be taken up and accumulated by living organisms or leached down the soil profile reaching the groundwater (Chopin *et al*., 2003).

A preliminary investigation into the horizontal contamination status of the site under study was carried out (Ogundiran, 2007). The results revealed that the abandoned lead-acid battery waste and the surrounding soils were contaminated with Pb, Cd, Cr, Ni and Zn, where Pb is the predominant contaminant. However, the different forms in which these metals exist on the site are unknown. Therefore, the migration of the HMs down the depth and an estimation of the forms in which they occur in the waste and the waste impacted soil become imperative. This is necessary in order to predict the extent to which these heavy metals can become mobile, leach into groundwater, be bioavailable in the environment and become hazardous to the community near the site. The objectives of this work therefore included: (i) evaluating the vertical extent of contamination of the HMs down the soil profile; and (ii) determination of heavy metals distribution in the surface soils to predict the potential hazards to community near the abandoned site.

Description of the study site

The study site was an abandoned auto battery waste dumpsite situated on a hectare of land owned by a defunct lead−acid battery manufacturing company located in Lalupon, Ibadan, Nigeria. The waste was generated from the secondary lead smelting operations of the company. The abandoned waste is in an open space which is very close to residential buildings.

Sampling and sample pretreatment

Samples were collected at 10 selected points designated as WP1, WP2, WP3, WP4, WP5, SS1, SS2, SS3, SS4, and SS5 on the waste pile (WP) and the surrounding soil (SS) respectively. The waste pile is the abandoned waste while the surrounding soil is the immediate vicinity of the waste. Sampled were collected at 0−15 cm, 15−30 cm, 30−45 cm, 45−60 cm depths from a circular area of approximately 15-cm diameter using manual corer marked with the different depths. They were then transported in plastic bags to the laboratory.

The samples were air-dried at room temperature for two weeks. Large debris, stones and plant remains were removed by hand picking while soil lumps were ground using porcelain mortal and pestle to achieve homogeneity. The ground soils were sieved through a <2 mm nylon sieve and stored in Ziploc bags till analysis.

Soil analysis for environmentally available heavy metals

One gramme each of the soil samples was digested in a 50 mL centrifuge tube with 10 mL 2 M HNO_3 for 2 hours in a water bath at $90–100°C$. It was then cooled and filtered using Whatman filter paper. The resulting solution was diluted to a predetermined volume depending on the collection point and stored in clean polyethylene bottles in a refrigerator at $-4°C$ until analysis. Pb, Cd, Cr, Ni and Zn concentrations in each sample digest were determined using atomic absorption spectrophotometer (AAS) with air–acetylene flame.

Sequential extraction of the top 15 cm waste and soil samples

The sequential extraction procedures used was modified from the method developed by Tessier *et al*. (1979). Water soluble fraction was included and the determination of heavy metals in the residual fraction was carried out using 4 M nitric acid (Basta and Gradwohl, 2000) in place of nitric, hydrofluoric and perchloric acid.

Fraction 1 (F1): Water soluble

1.0 g of air-dried soil sample was placed in a 50 mL polycarbonate centrifuge tube. The soil sample was extracted with 20.0 mL deionized water for 2 hours at room temperature with continuous agitation.

Fraction 2 (F2): Exchangeable

The residue from water-soluble was extracted at room temperature with 8.0 mL of 1.0 M $MgCl_2$ at pH 7.0 for 1 hour with continuous agitation.

Fraction 3 (F3): Bound to carbonate

The residue from exchangeable fraction was leached with 8.0 mL of 1 M CH_3COONa adjusted to pH 5.0, with acetic acid, at room temperature for 5 hours with continuous agitation.

Fraction 4 (F4): Bound to Fe–Mn oxides

The residue from carbonate-bound fraction was extracted with 20.0 mL of 0.04 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% (v/v) acetic acid at $96°C$ with occasional agitation for 6 hours.

Fraction 5 (F5): Bound to organic carbon

The residue from Fe–Mn oxides bound was extracted with 3.0 mL of 0.02 M HNO_3 and 5.0 mL of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3). The mixture was heated to $85°C$ for 2 hours with occasional agitation. A second 3.0 mL aliquot of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3) and the mixture was heated again to $85°C$ for 3 hours with intermittent agitation. The mixture was cooled and 5.0 mL of 3.2 M ammonium acetate (CH_3COONH_4) in 20% (v/v) HNO_3 was then added. The sample was diluted to 20.0 mL with deionized water and agitated continuously for 30 minutes. The addition of ammonium acetate was designed to prevent adsorption of extracted metals onto the oxidized soil sample.

Fraction 6 (F6): Residual

The residue from organic bound was extracted with 20 mL of 4 M HNO_3 at $80°C$ for 16 hours.

1.0 g of the soil sample was extracted on an end-to-end shaker for the prescribed number of hours with the given amount of the reagent. Between each successive extraction, separation was effected by centrifuging at 5000 rpm for 30 minutes. The clear supernatant was decanted. The residue was washed with 8.0 mL of deionized water followed by vigorous hand shaking and then followed by 30 minutes centrifugation before the next extraction and the wash water was discarded. The next reagent was added. The supernatants were acidified with 0.5 mL conc. HNO_3 and stored at $4°C$ until metal analysis with AAS. Acidification of the extracts was necessary to prevent metal adsorption (Mench *et al*., 1994).

Quality control

Glass wares and plastic bottles were taken through the standard analytical processes. 10% duplicates analysis, blank determinations, laboratory controls of known concentrations and spiked samples of known concentrations were employed for quality control.

Table 1 Total environmentally available heavy metals concentrations (mean (mg kg^{-1})$\pm$ SE) in the waste pile depths

Depth (cm)	Pb	Cd	Cr	Ni	Zn
0–15	85,600 ± 29,000	11.7 ± 2.4	104.0 ± 16	51.1 ± 5.5	1,070 ± 270
15–30	86,500 ± 29,000	5.51 ± 2.2	8.9 ± 8.8	19.3 ± 12.4	988 ± 290
30–45	61,200 ± 19,000	0.24 ± 0.14	51.0 ± 34	29.1 ± 10.3	786 ± 270
45–60	46,200 ± 17,000	ND	4.3 ± 4.1	24.4 ± 10.1	668 ± 280

Table 2 Total environmentally available heavy metals concentrations (mean (mg kg^{-1})$\pm$ SE) in the soil depths

Depth (cm)	Pb	Cd	Cr	Ni	Zn
0–15	25,900 ± 1,600	3.3 ± 1.4	120 ± 34	19.0 ± 10.1	471.0 ± 180
15–30	7,370 ± 5,700	ND	ND	0.13 ± 0.06	213.0 ± 20
30–45	595 ± 320	ND	ND	1.60 ± 1.06	100.0 ± 21
45–60	1,440 ± 1,200	ND	5.3 ± 2.4	0.42 ± 0.22	53.8 ± 5.1

ND = Not detectable (below the detection limits of 0.10, 0.15, 0.36 mg kg^{-1} for Cd, Cr and Ni respectively).

STATISTICAL ANALYSIS

Pearson correlation analysis was used to determine the relationship between mean total environmentally available heavy metal concentrations with soil depth; total metal concentrations in 0–15 cm depth and HM fractions. All analysis was done using the Statistical Package for Social Science (SPSS) version 14.0 software.

RESULTS AND DISCUSSION

Migration and fractionation of heavy metals in waste and soils collected from the site under study were undertaken in order to assess the potential risks of the contaminated site to the ecosystem. Gross contamination of the ecosystem by HMs, particularly Pb, has been associated with wastes generated from lead mining and smelting operations (Liua *et al*., 2005; Ogundiran and Osibanjo, 2008). The effects that such contamination produces on the ecosystem depend on the different forms in which the HMs exist in soil. This makes it imperative to investigate the presence, the extent of migration and availability of Pb, Cd, Cr, Ni and Zn on this site that has a 2-year history of open air dumping of battery slag.

VARIATION OF HEAVY METAL CONCENTRATIONS WITH DEPTH

The extent of contamination and vertical migration in the waste and the surrounding soil was assessed using total environmentally available metal concentrations at different depths. Data presented in Tables 1 and 2 show the mean concentrations of Pb, Cd, Cr, Ni and Zn that could be environmentally available in each depth. The amount of heavy metals that can pose danger to the ecosytem is represented by the environmentally available level. Upon comparison of the environmentally available concentrations in all the depth assessed, Pb occurred in greater concentrations than does Zn, Cd, Cr or Ni. Lead concentrations ranged between 46,200 and 86,500, Cd between 0.24 and 11.7, Cr between 4.3 and 120, Ni between 19.3 and 51.4, Zn between 668 and 1,070 mg kg^{-1} in the waste. Lead ranged between 595 and 25,900, Cd between ND and 11.7, Cr between ND and 120, Ni between 0.13 and 19.3, Zn between 53.8 and 471 mg kg^{-1} in the surrounding soil. The levels of Pb are high in all the depths in the waste and in some portions of the soil, while those of Cd and Zn are relatively high when compared with the levels of these metals in uncontaminated soil. In soil the normal ranges of Pb, Cd, Cr, Ni and Zn are 2–300, 0.01–2.7, 5–1500, 2–750 and 1–900 mg kg^{-1} respectively (Kabata-Pendias and Pendias, 2001; Hague *et al*., 2008). Generally, the mean concentrations of HMs decrease with increasing depth. However, in the surrounding soil the concentration of Cd is below the limit of detection after the first depth (Table 2). The near neutral pH of the waste and the surrounding soil as revealed by the preliminary investigation (Ogundiran, 2007) might have played a significant role in restricting the movement of Cd, since Cd was reported to be less mobile as the alkalinity of soil increases (Smejkalova *et al*., 2003).

Pearson correlation analysis indicated that the mean concentrations of Pb decreased with depth although not significant ($r = -0.9$; $P > 0.05$), while that of Zn was significant ($r = -0.9$; $P < 0.05$). Nonetheless, at deeper depths in the waste pile

significant levels of Pb and Zn were observed. Accumulation of the waste over the years as well as migration of dissolved forms of these heavy metals down the profile might be accountable for this observation. The high concentrations of Pb and relatively high concentrations of Cd and Zn with depth reveal that, with time, an unconfined heavy metals mining waste has the potential to affect the quality of groundwater around it.

No clear trends were observed with Cr and Ni with respect to depth. Their highest concentrations occured at the top depth. The concentrations of Cr and Ni were within the normal background levels in uncontaminted soil, but their levels in the waste pile showed some evidence of contamination.

The concentrations of the HMs at the various sampling points especially in the waste varied as shown by the large standard error (Tables 1 and 2). Also, mean levels for all the metals were greatest at 0–15 cm depth in all the samples. These observations are in agreement with previous reports that soil contaminated by anthropogenic activities typically contains highest and varied concentrations of heavy metals in the surface horizons (Boularbah *et al*., 2006; Chopin *et al*., 2003; Horvath and Gruiz, 1996). In the 15 cm depth of the waste pile, concentrations of Pb and Cd were strongly correlated ($r = 0.97$, $P < 0.01$) suggesting that these contaminants were likely to be of similar origin. The origin of the other metals in this waste could be traced to these metals being present as impurities or as alloys in Pb used for secondary smelting. It can therefore be inferred from these findings that battery slag generated from secondary lead smelting activities has the potential to pollute the environment with heavy metals that are of environmental concern. Now, globally, there is recycling of used automobile batteries and the wastes that result from this activity have been shown in this study to pose serious threats to the ecosystem in terms of heavy metal contamination. To safeguard the environment and biological life from deleterious effects of heavy metals, there is need to exercise caution in handling the waste that results from lead recycling activities.

FRACTIONATION OF HEAVY METALS IN THE CONTAMINATED WASTE AND SOILS

Heavy metals are present in different chemical forms in soil due to interactions with soil constituents and this leads to redistribution of metals into mobile and inert forms. Low concentration of immobile forms (residual fraction) when compared with mobile forms (non-residual fraction) has been identified as a feature of soil contaminated by anthropogenic activities (Kabala and Singh, 2001). Fractionation of heavy metals is crucial in environmental studies to estimate the amount of heavy metals that can be potentially soluble, mobile and available to the ecosystem which could not be ascertained with total metal concentration alone. The sum of water soluble and exchangeable metal fractions is generally used to indicate bioavailable HMs, equally the forms that can leach into groundwater. The fractionations of heavy metals in the investigated samples are shown in Figures 1 to 3. From these, it could be observed that the percentages of the heavy metals in the non-residual fractions in the surrounding soil are much higher when compared with those in the waste pile. For instance the percentages of non-residual fractions of Pb in the waste pile and the surrounding soil ranged from 48.9–95.6% and 69.4–98.3% respectively. Furthermore, the percentage of water soluble Cd in the surrounding soils was more than that obtained in the waste pile (Figure 1). Chromium indicated more water soluble, exchangeable and carbonate bound forms in the surrounding soil (SS) with no detectable level of Fe–Mn oxide bound fraction. Also, there is reduction in the residual fraction in the SS when compared with the levels in the waste pile (WP) (Figure 2). For Ni, the carbonate bound and Fe–Mn oxide fractions predominate in the waste whereas water soluble and exchangeable fractions predominate in the surrounding soil (Figure 2).

Considering the percentages of the heavy metals fractionation in WP and SS, a redistribution of heavy metals from less available forms (in the waste) to more available forms (in the surrounding soil) was apparent. This could suggest that the heavy metals in the waste pile have undergone some transformations into the mobile forms probably due to changes in environmental conditions and the activities of metal tolerant microbes in the environment. Many studies have also observed high mobile and bioavailable fractions of HMs in wastes generated from heavy metal mining and smelting activities (Ramos *et al*., 1994; Hickey and Kittrick, 1984; Kuo *et al*., 1983). These findings show that hazardous wastes that are not well managed can contaminate the environment with high concentrations of mobile heavy metals.
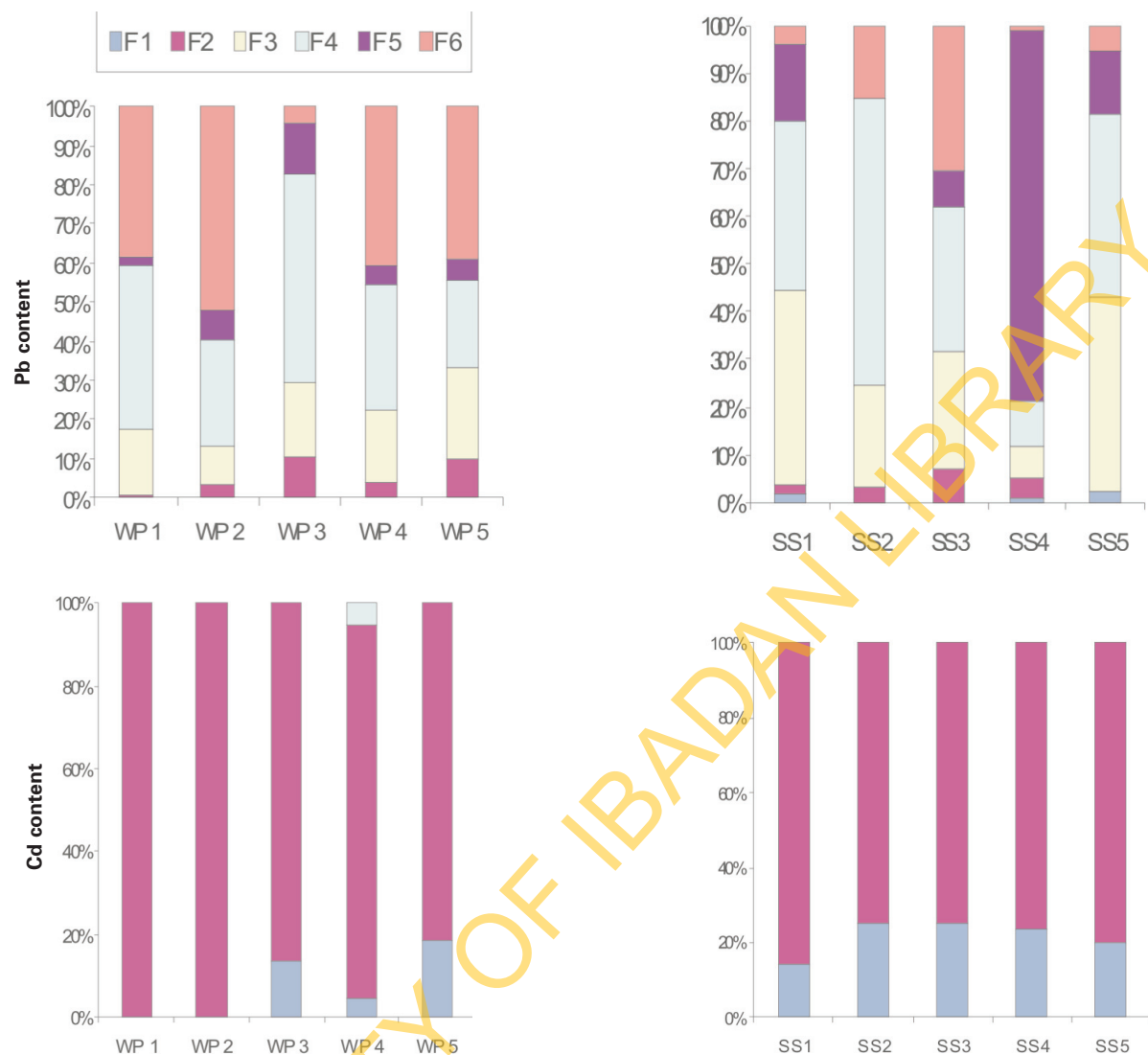
Figure 1   Distribution of Pb and Cd in the 15 cm depth waste pile (WP) and surrounding soil (SS). F1, Water soluble; F2, exchangeable; F3, carbonate bound; F4, Fe–Mn oxide bound; F5, organic matter bound; F6, residual.

Lead

Figure 1 shows that Pb is substantially associated with residual fraction in waste pile with a mean of 73,200 mg kg^{-1}, followed by Fe–Mn oxide (68,300 mg kg^{-1}), carbonate bound (33,700 mg kg^{-1}), organic matter bound (10,700 mg kg^{-1}), exchangeable (8,870 mg kg^{-1}) and water soluble (133 mg kg^{-1}) fractions (data not shown). Pearson correlation analysis also indicated that there was positive correlations of total environmentally available Pb concentrations in 0–15 cm depth with water soluble Pb ($r = 0.90*$) and Fe–Mn oxide bound Pb ($r = 0.99$).

The exceptionally high concentration of Pb in the residual fraction of the waste samples might be due to the presence of PbS (galena) which is the main form of an insoluble Pb that occurs in nature. Waste rich in galena has been reported to have the potential to release bioavailable Pb into the environment through conversion of PbS to $PbSO_4$ and $PbCO_3$ (which are more soluble than galena) when environmental conditions are altered (Abdel-Saheb *et al*., 1994; ATSDR 2005; Zhang and Ryan, 1999; Chen *et al*., 2003). Transformation of PbS to $PbCO_3$ might also account for the high concentrations of carbonate bound fractions. The predominant forms of lead that have been reported in the environment around lead mining and smeltering operations included PbO, $PbSO_4$, PbS and $PbCO_3$ (Yang and Mosby, 2006; Manceau *et al*., 1996; Scokart *et al*., 1983; Melamed *et al*., 2003)
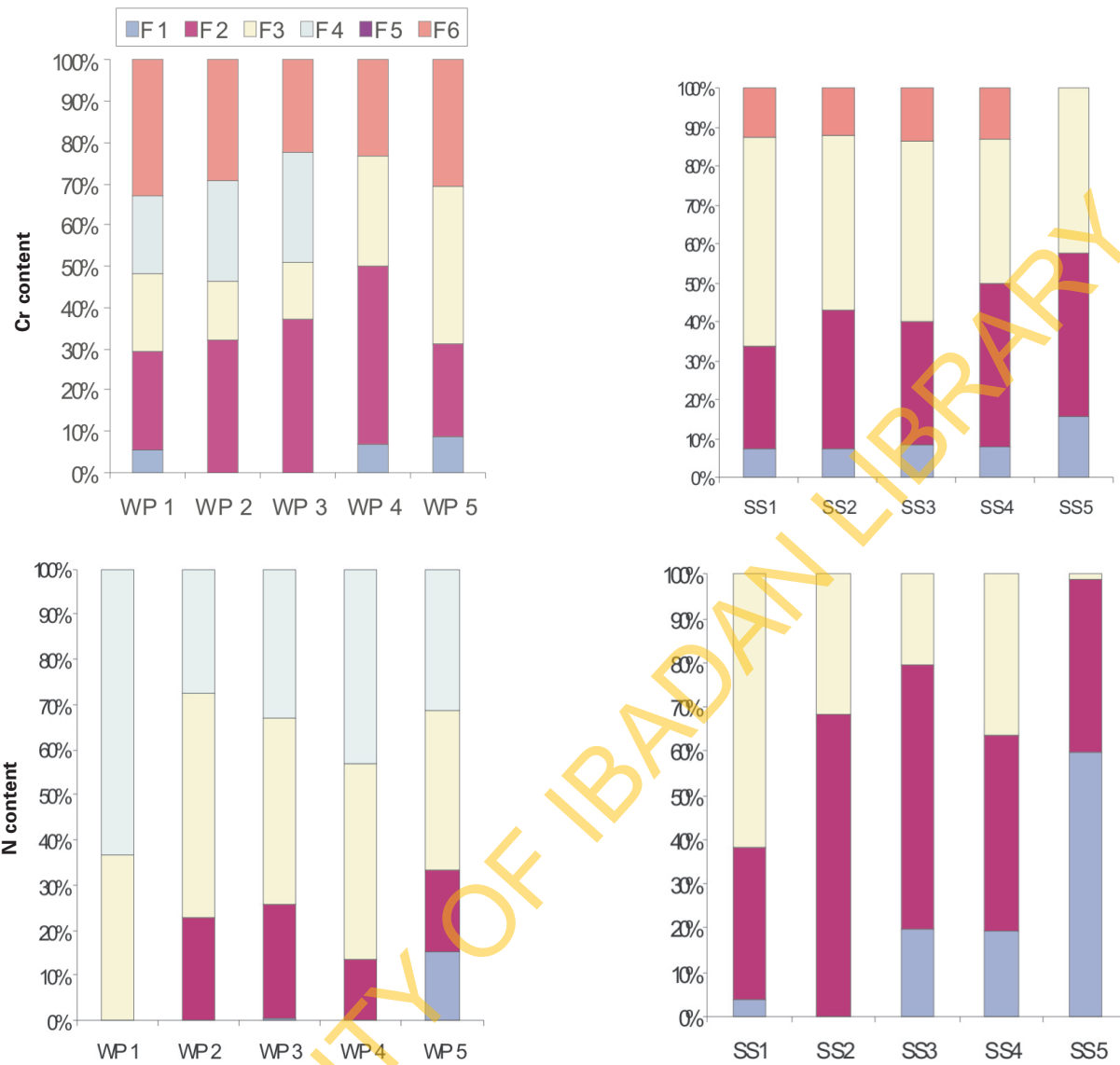
Figure 2 Distribution of Cr and Ni in the 15 cm depth waste pile (WP) and surrounding soil (SS).
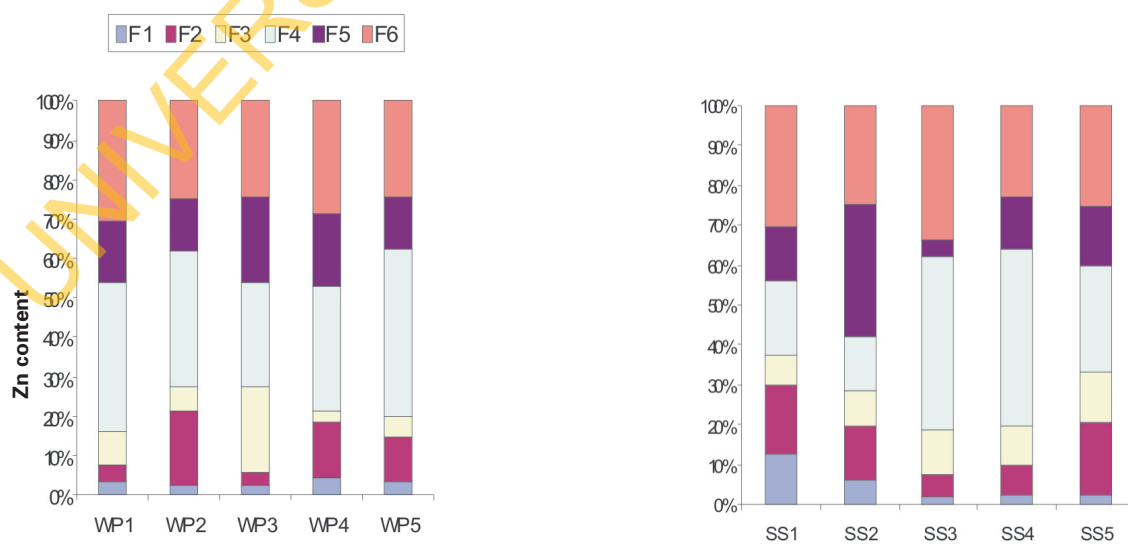

Figure 3 Distribution of Zn in the 15 cm depth waste pile (WP) and surrounding soil (SS).

and they are reported to be susceptible to changes in the face of varied environmental conditions such as chemical and biological processes (Birkefeld, 2007). In addition, high concentrations of Pb in Fe–Mn oxide and organic matter bound fractions in smelter-contaminated soils have been associated with sorption of Pb to manganese and iron oxides as well as to humic acids (Morin *et al*., 1999; Kotoky *et al*., 2003).

In the waste samples, the concentrations of water soluble Pb ranged from 99.2 to 188 mg kg^{-1} (mean 133 mg kg^{-1}) and from 2400 to 16200 mg kg^{-1} (mean 8870 mg kg^{-1}) for exchangeable fraction. These levels of lead in the water soluble and exchangeable fractions are very high, as opposed to the low solubility of lead that is generally reported in normal soils. This may signal the occurrence of adsorption of Pb on easily soluble organic or mineral particles which can become mobile and bioavailable subsequent to changes in soil environmental conditions. The formation of soluble heavy metal complexes through reaction with organic matter was reported to result in the solubilisation of Cd, Pb and Zn. Chen *et al*. (2003) attributed high levels of Pb he obtained in the water soluble and exchangeable fractions to dissolution of PbCO$_3$ at pH < 6.

In the surrounding soils the highest level of Pb was found in Fe–Mn oxide followed by residual fraction, carbonate, organic matter bounds, exchangeable and water soluble fractions. The concentrations of water soluble Pb ranged from 19.5 to 76.5 mg kg^{-1} (mean 42.6 mg kg^{-1}) and ND-5,150 mg kg^{-1} (mean 1,720 mg kg^{-1}) in the exchangeable fraction. The stated results of lead in the water soluble and exchangeable fractions in the surrounding soil are evidence of gross contamination of the environment with mobile and bioavailable Pb resulting from the impact of industrial waste. The observed results present this site that is contaminated by an auto battery slag as a ''chemical time bomb''. The extent of absorption, distribution, storage, mechanisms of binding to proteins and eventual toxic activity of heavy metals to humans has been documented to depend on the bioavailable heavy metals (WHO, 2006). With the high concentrations of bioavailable Pb present at this site and the potential hazards to human health and the environment through soil ingestion, it is reasonable to predict plant Pb uptake, leaching into the groundwaters and environmental contamination by the auto battery slag.

Cadmium

Cd was mainly associated with the exchangeable fraction with a mean of 31.3 and 33.2 mg kg^{-1} in WP and SS respectively (Figure 1). It was below detection limits in the carbonate and organic matter bound fractions in WP and in the last four fractions in SS. From previous findings, Cd was reported to be mostly associated with the exchangeable forms in the contaminated soils (Ramos *et al*., 1994; Hickey and Kittrick, 1984; Kuo *et al*., 1983) which is consistent with the results of this work. This observation according to Ramos *et al*. (1994) was due to the low adsorption constant of the complex that Cd formed with the organic matter, the organic matter being considered labile. Cadmium in the form found on this site reveals that the site, contaminated by auto battery slag, presents a potential danger to communities around it.

Chromium

In the waste samples, chromium was present in all the fractions except organic matter fraction and was not detected in the Fe–Mn oxide and organic matter bound fractions in the SS (Figure 2). Chromium is associated mainly with the non-residual fractions both in the WP and SS. Again, this suggests that Cr too is linked with human activities on this site.

Nickel

In the WP, a larger percentage of Ni is associated with Fe–Mn oxide (Figure 2) which is consistent with the previous report that adsorption by Mn oxide controls the mobility of Ni in polluted soils (Hickey and Kittrick, 1984). However, in the surrounding soils, Ni was associated mainly with the exchangeable fraction, followed by the carbonate bound and the water soluble fractions (Figure 2). This is evidence of conversion of Ni from less bioavailable forms in the waste to bioavailable forms in the impacted soil, a characteristic of metals of anthropogenic origin. Ni that is of natural origin has been reported to be associated primarily in soil with residual fraction (Ma and Rao, 1997; Hickey and Kittrick, 1984). Meanwhile, the levels of Ni, when compared with the normal levels in uncontaminated soil, does not suggest that there is any serious hazard to the environment.

Zinc

The distributions of Zn in the various fractions in both the WP and SS follow this order: Fe–Mn

Table 3 Mobility factors of Pb, Cd, Cr, Ni and Zn

Sampling location	Pb (%)	Cd (%)	Cr (%)	Ni (%)	Zn (%)
WP	21.9	98.7	55.5	58.1	23.2
SS	26.9	100.0	89.3	100.0	24.2

oxide > residual > organic matter > carbonate bound > exchangeable > water soluble. The highest concentrations of Zn both in the waste and surrounding soil are associated with the Fe–Mn oxide fraction (Figure 3). This is similar to the observation of many authors that Zn has the affinity to be sorbed to the Fe–Mn oxide in soil (Kotoky *et al.*, 2003; Hickey and Kittrick, 1984; Kuo *et al.*, 1983). It could also be observed that the levels of Zn in the first three fractions of soil were higher than the levels in the waste showing that there was mobility into the environment.

There were positive correlations of total Zn concentrations in 0–15 cm depth in the WP with water soluble Zn ($r = 0.89^*$), Fe–Mn oxide bound Zn ($r = 0.94^*$), organic matter bound Zn ($r = 0.95^*$) and residual Zn ($r = 0.98^{**}$). The positive correlations of total Zn concentration with the Zn fractions may imply that the distribution of Zn in the various forms is directly related to the total Zn level in the samples. This shows that heavy metal distributions in the various chemical forms can be influenced by the amount of the total metal content of the soils. Pb, Cd, Cr and Ni do not show these relationships.

Metal mobility factor

Mobility factor describes the potential movement of the metals out of the contaminating medium (Kabala and Singh, 2001) and it is calculated as

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

(MMF, metal mobility factor, F, concentration of metal in the different fractions).

The mobility factors of Pb, Cd, Cr, Ni and Zn are presented in Table 3. The potential of a metal to become mobile in the environment and to be bioavailable has been connected with high percentage of MF. In this work, the mobility factors of Pb, Cd, Cr, Ni and Zn were higher in the surrounding soil than in the waste. The mobility factor of Pb in the waste increased from 21.9 to 26.9%, Cd from 98.7 to 100%, Cr from 55.5 to 89.3%, Ni from 58.1 to 100% and Zn

from 23.2 to 24.2% in the soil. The mobility factors of Cd, Cr and Ni reveal that when they are present in soil as metals of anthropogenic origin, they have high potentials to be mobile and consequently bioavailable. Lead which shows significant high total metal content (Tables 1 and 2) indicates the least mobility factor corroborating the immobile nature of lead in the soil as previously established (Kotoky *et al.*, 2003; Hickey and Kittrick, 1984; Kuo *et al.*, 1983). Moreover, Zn which showed much higher concentrations than Cd, Cr and Ni has a lower mobility factor. This is due to nature's way of keeping Zn in Fe–Mn oxide. Nevertheless, the relatively high mobility factors of Pb and Zn pose potential hazards to the ecosystem.

CONCLUSION

In this study, migration of Pb, Cd, Cr, Ni and Zn down the depths was obvious with consequent potential dangers from heavy metals contamination of groundwater quality resulting from human activities. Moreover, transformation of Pb,Cd , Cr, Ni and Zn from residual to non residual fractions was observed and this indicates that auto battery wastes can supply the environment with soluble and mobile heavy metals that are of environmental concern. Mobility factors were quite high and this shows that HMs of anthropogenic origin have great potential to distribute and be bioavailable fast within the environment if not restricted. Hence, there is need for concerted efforts against introduction of wastes generated from heavy metals projects into the natural soil.

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