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CONCENTRATION AND CHEMICAL SPECIATION OF HEAVY METALS IN URBAN SOILS OF WARRI, NIGERIA

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ABSTRACT

The pseudo total and chemical speciation of manganese, chromium, lead and Zinc were determined by a chemical method (1) and Tessier's method (Tessier, *et al.* 1979)respectively to ascertain if significant concentration of the metals are mobile and bioavailable in Urban Soils of Warri. Intervention values were calculated to known if the metal contamination has reached the level that the soils should be treated. Ten soil samples from five sites (Esisi, Apala, Airport Road, Ugborikoko and NPA Expressway Refuse dumps) were collected (5 top soils 0 -15 and 5 bottom soils 15 - 30 cm) using a stainless steel augur. Sample solutions prepared were analysed using the Atomic Absorption spectrophotometer technique. Results showed that mean values of total heavy metals for the top soils are 4. 00 ± 0.00 to 111.00 ± 7. 00 ppm Mn, 9. 13± 0.13 to 292. 28 ± 7.82 ppm Cr, <0.08 to 493. 00 ± 3.00ppm Pb, 35.00 ± 0.00 to 1012.00+ 2.00ppm Zn. Bottom soil samples contain as much as 7.00 ± 0,00 to 160. 00 ±0.00 ppm Mn, 35.05 ± 0.40 to 263.00 ± 0.00ppm Cr, <0.08 to 286.00 ± 6.00ppm Pb and 64.00 ± 4.00 to 1458.00 ± 8.00ppm Zn. The values reported had an abundance ratio in the order Zn >Cr > Mn > Pb. The values reported in this study are higher than Federal Environmental Protection Agency (3) values in some of the soil samples. The intervention values obtained are 190.40mg/kg Cr. 312.10 mg/kg Pb and 257.67 mg/kg Zn. Total Zn is higher than intervention values in all the soil samples, total Cr-is close to intervention value while Pb is lower than intervention value. Chemical properties such as pH total organic carbon and CEC were also analyzed. Six soil samples (3 top soils and 3 bottom soils) from three sites (Esisi, Apala and NPA Expressway dump sites)'were selected and analysed for chemical partitioning using Tessier's procedure. The results showed that the metals showed highest concentration in the Fe-Mn oxide fraction except Pb. Pb is not associated to the exchangeable phase. The metals showed significant concentration in the non-residual fraction except Pb. This shows that significant concentration of the metals are mobilo and bioavailable to plants and other ecological materials. The bioavailable values reported in this study are higher than the values reported for uncontaminated soils. (Sparks, 2001) Cr, Zn and Mn contents in the soils are also positively correlated to the pH of the soil.

INTRODUCTION

The many human activities in the last decades have contributed to increase the metal mobility in the environment. The total concentration of the metal is relevant, nevertheless the availability, reactivity and mobility are determined by metal chemical form making a-chemical speciation study necessary.

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(Morrison, 1989). Chemical speciation is defined as distribution of an individual chemical element among different species or groups. Trace metals may be distributed among many components of the soil and may be associated with them in different ways.

In the last twenty years many studies related to sequential extraction schemes have been carried out (Davison, *et al. 1999;* Dawson and Macklin, 1998; Lam, *et al*. 1971 and Izquierdo, *et al.* 1997). Tessier's method is selected since it allows suitable estimation about characteristics of metal association (Tessier, *et al*. 1979). It evaluates both the actual and potential mobility of metals in the environment. This extraction scheme allows the division of the total metal content into five fractions: Exchangeable bound, carbonate bound, Iron/ manganese oxide bound, organic matter bound and residual fraction.

The concentrations of heavy metals in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities, and waste dispose 91, 390.3 kg /capita /year volume solid waste are generated in Warri (Associates, 1982) (a beehive of commercial and industrial activities).

Individual households and commercial enterprises in the city of Warri generate a vast amount of solid wastes including paints, cosmetics, batteries, chemicals, alloys, electric switches, coins, drugs, stainless steel and solders, paper, wood, plastic, rubber, leather, food, metals, glass, clothing, rags and dirt. And these materials consist of chemical elements such as zinc, lead, manganese, nickel, mercury, Copper, chromium - etc. They deteriorate and decay into small pieces and their metallic make ups are released and deposited into the soil. Disposal of solid waste has been largely into open dumps. Open dumps burn, contributing to air pollution, breed rats, a severe health hazard, pollute water sources and are offensive eye sores (Encyclopedia Britannica, 1975)).

Studies have shown that ground water can be contaminated through seepage by leachate arising from solid wastes dumped on the ground (Ademoroti, 1996).

Corn, rice (crops) in general are planted around refuse dumps. Minerals are easily assimilable and accumulate in ecological materials (Numberg, 1984) and eventually get into the bodies of inhabitants.

The aim of this study is to determine the total concentrations and the mobile and bioavailable heavy metals (Mn, Cr, Pb and Zn) which serves to evaluate the level of active heavy metal pollution of the urban soils of Warri.

EXPERIMENTAL

Study sites

Esisi, Airport road, NPA expressway, Ugborikoko and Apala street open dumps are all located in Warri metropolis (Fig. 1.)

SAMPLING

The soil samples (top soil 0 -15cm) and Bottom soil (15 -30cm) were collected using a stainless steel auger and stocked in polythene bags for further analyses.

Fig. 1 Open dumps morphology

METHODS

The soil samples were air dried, ground and sieved through a 2 - mm nylon sieve. Dried soil samples that fell below the sieve were stored in polythene bags and properly labelled for subsequent analysis. They were used for all the analyses. Chemical properties were analysed for, such as pH, total organic carbon and cation exchange capacity (CEC). Soil pH was determined using a 1: 2 (w/v) ratio of soil to water by a suntex digital pH - meter (Folson, *et al.* 1981) . Total organic carbon was determined by the Walkley -Black rapid oxidation method (Poison, *et al.* 1981). Cation Exchange capacity was estimated by summing the exchangeable cations determined by Flame photometric method -with the exchangeable acidity determined by titration method (Jackson, 1960). Hydrometer method(Ibitoye, 2006) was used to determined particle size.

The total heavy metal concentrations were determined by a chemical method. Some selected soil samples were analysed for chemical partitioning. Tessier sequential extraction procedures were used. All the analyses were performed in triplicate. Extractions were carried out on 1. 0g soil and involved the following Tessier's five - steps procedure.

A - Exchangeable fraction : The sediment was extracted at room temperature for 1 hour with 8. 0 mL of 1M $MgCI_2$ (pH-7) with continuous agitation.

B - Bond to carbonate : The residue from (A) was leached at room temperature with 8.0 mL of 1 M NaOAC/HOAc (pH-5) with continuous agitation.

C - Associated with Fe-Mn oxides : The residue form (B) was extracted with 20.0 mL of 0.04 M NH_2 OH. HCI in 25% acetic acid; the experiments were performed at 96 ± 2°C during 6 hours with occasional agitation.

D - Associated with organic matter : To the residue from (C) were added 2.3 mL of 0.02 M $HIMO_3$ and 3. 8 mL of 30% H_2O_2 (pH -$_2$ with $HN0_3$) and the mixture was heated to 85 ± 2°C for 2 hours and with occasional agitation; a second 2.3 mL aliquot of 30% H_2O_2 (pH-2) was then added and the sample was heated again to 85 ± 2°C for 3 hours with agitation. After cooling, 3. 8 mL of 3.2 M NH_4 OAc in 20% HNO_3 (v/v) was added and the sample was diluted to 20.0 mL and agitated continuously for 30 min.

E - Residual fraction : The residue from (D) was digested with 7.5 mL of HF& 1. 5 mL of $HCIO_4$ to near dryness (5 hours) : then a second addition of 7.5 mL of HF and 0.75 mL of $HCIO_4$ was made and again the mixture was evaporated to near dryness. Finally the residue was dissolved in HCI 30% and diluted to 25. 0 mL $HCIO_4$.

All reagents were analytical grade (BDH or sigma) deionized water, was used in preparing stock solutions. Extractions were carried out directly in polyethylene tubes. Residues were separated, from supernatant by centrifugation during 45 min.

Metal contents of the five fractions and total metal contents in solution was determined by Atomic Absorption Spectroscopy (Buck Scientific VGP 210 model).

RESULTS AND DISCUSSION

Warri soil has been subjected to metal contamination due to many open dumps present in the city.

Results of the concentrations of the heavy metals determined shown in Table 1 indicated that bottom soil samples (15 to 30 cm) had higher concentrations of heavy metals except in few cases The values obtained showed an abundance ratio in the soil sample: in the order Zn > Cr > Pb > Mn.

Table 1. Total content (ppm) and standard deviation of Mn, Cr, Pb and Zn In Soils of five opend dumps in Warri

	Manganese (ppm)	Chromium (ppm)	Lead (ppm)	Zinc (ppm)
~~Esisi (Topsoil)~~	~~58.00±2.00~~	~~201.85±1.85~~	~~40.00±2.00~~	~~482.00±2.00~~
Esisi (Bottom soil)	160.00±0.00	117.82±0.00	<0.08	1458.00±8.00
Airport Road (Topsoil)	9.00±1.00	90.42±0.78	493.00±3.00	43.00±2.00
Airport Road (Bottom soil)	14.00±5.00	115.08±5.02	130.00±0.00	64.00±4.00
NPA Expressway (Topsoil)	111.00±7.00	292.28±7.82	<0.08	456.00±5.00
NPA Expressway (Bottom soil)	138.00±3.06	263.00±0.00	10.00±2.00	500.00±0.00
Ugborikoko (Topsoil)	4.00±0.00	9.13±0.13	10.00±0.00	35.00±0.00
Ugborikoko (Bottom soil)	7.00±0.00	31.05±0.40	286.00±6.00	150.00±2.00
Apala Street (Topsoil)	41.00±1.00	167.15±0.20	<0.08	1012.00±2.00
Apala Street(Bottom soil)	9.00±3.00	46.58±1.70	20.00±2.00	241.00±1.00

Table 2. Shows the mean pH, total organic carbon and cation exchange capacity for the selected soil samples

Sample	pH	TOC (%)	CEC (meq /100g)
Esisi (Topsoil)	6. 99	4.06	12.31
ESISI (Bottom Soil)	6.74	4. 99	11.58
Apala (Topsoil)	6.84	1.09	12.27
Apala (Bottom Soil	6.92	3.90	10.69
NPA Expressway (Top soil)	6.92	9.83	15.56
NPA Expressway (Bottom soil)	6.55	0.55	14.93

Table 3. Correlation coefficients between total heavy metal contents and chemical properties of the selected soil samples

	Mn	Cr	Pb	Zn
pH	0.77	0.55	-0.30	0.75
TOC	-0.13	-0.02	0.12	0.41
CEC	-0.54	-0.43	-0.33	0.18

Table 4. Shows total heavy metal content (ppm) and Intervention values of Cr, Pb, and Zn For urban soils of Warri

Metals	Total content	Intervention values
Cr	181.45	190. 41
Pb	11.67	312.09
Zn	691.50	257.66

Zinc levels reported in this study are higher than the other heav> metals, this could be because zinc is used for various purposes such as making of alloys, paints, cosmetics, pesticides, fertilizers and it is a component of sewage effluents and these are disposed into open dumps which eventually decay and break into small pieces and are released into the soil. The values obtained in this study are higher than Federal Environmental Protection Agency (FEPA) values in some of the soil samples Correlation studies Table 3), of heavy metal concentrations and soil chemical properties show that total Cr, Zn and Mn are positively correlated to pH, total Zn is also positively correlated to CEC. Pb and Zn are positively correlated to organic carbon. Pb is negatively correlated to the pH of the soil. Results of the chemical speciation determined shown in Table 4 indicated that the non -residual fractions of Mn , Cr, Pb and Zn in Esisi site average 82. 88%, 79.13%,39. 87% and 94.68°/c respectively which suggests that the mobility and bioavailability of the four metals are in the order Zn > Mn> Cr > Pb. This shows that less than 30% of the metals except Pb are in the residual phase showing that over 70% are mobile and bioavailable.

The non -residual fractions of Mn, Cr, Pb and Zn in Apala soils shown in Table 5 average, 82. 02%, 67.20%, 44.20% 81.67% respectively which suggests that the mobility and bioavailability of the four metals are in the order Mn > Zn > Cr > Pb. This also shows that less than 30% of the metals except Pb are in the residual Phase, over 70% of them except Pb are mobile and bioavaliable. Comparing this with the soils of NPA Expressway, the non -residual fractions of Mn, Cr, Pb and Zn average 68. 27%, 70.97%, 37.69% and 89.62% respectively which suggests that the mobility and bioavailability of the metals are in the order Zn > Cr > Mn >, Pb showing that less than 30% of the metals except Mn and Pb are in the residual phase, over 70% of Cr and Zn are mobile and bioavaliable .

All the metals except Pb showed highest concentration in the Fe- Mn oxide fraction. The percentage of lead in the fractions follows the order: Organic matter > Fe-Mn oxide>Residual > Carbonate > Exchangeable in Esisi soils.

All the metals showed least or no concentration in the Exchangeable extracted fractions. Pb is not associated at all to the exchangeable fraction. The percentage of Pb in the fractions follows the order: organic matter > Fe -Mn oxide> Residual > carbonate in Esisi soils. In Apala soils, Pb percentage follows the order: Fe Mn oxide > organic matter > carbonate > Residual while in NPA Expressway soils, the percentage of Pb follows the order: Organic matter > Residual > Fe- Mn Oxide > carbonate.

The intervention values indicate the quality for which the functionality of soil for human, animal and plant life are threatened with being seriously impaired. Concentration levels in excess of the intervention values correspond to serious contamination. The intervention values are calculated using a formula (EGASPIN, 1991). Results of the total heavy metal content and intervention values of Cr, Pb and Zn for urban soils of Warri shown in Table 4 indicated that total Zn is higher than the intervention value, total Cr is close to the intervention value while total Pb is lower than the intervention value.

The percentage recovery ranged between 91 to 97 % as shown in Table 5. This indicates a high reliability in the Tessier's sequential extraction procedure.

Table 5. Mn, Cr, Pb and Zn concentrations and recovery percentages ofthe sum of the five fractions in the selected soil samples and in the total digestion samples

Metal	Sum of the five fractions in the selected soil samples	Total	% Recovery
Mn	81.77	86.17	94.80
Cr	176.38	181.44	97.21
Pb	10.97	11.60•	94.59
Zn	631.03	691.50	91.26

Table 6. Shows bioavailable Concentrations of Mn, Cr, Pb, Zn and uncontaminated soil values .

Sample	Bioavailable concentrations parameters			
	Mn	Cr	Pb	Zn
Esisi (Top Soil)	45. 87+0.74	147.20±2.14	31. 48±1.34	402.92+4.30
Esisi (Bottom soil)	128. 88+ 0.25	97.84±1.14	0	1,181.80+4.14
Akpala (Top Soil)	30.68+3. 32	114.24+5.00	0	800.59+4.00
Akpala (Bottom Soil	7.57+0.70	29.07±2.14	15.22+2.00	184.60+4.24
NPA Expressway (Top soil)	66. 32+1.04	228.32±1.34	0	390.32+3.71
NPA Expressway (Bottom Soil)	92.06+2.46	156.02+1.20	6.89±0.34	440.90+1.28
Uncontaminated soil	960	100	14	75

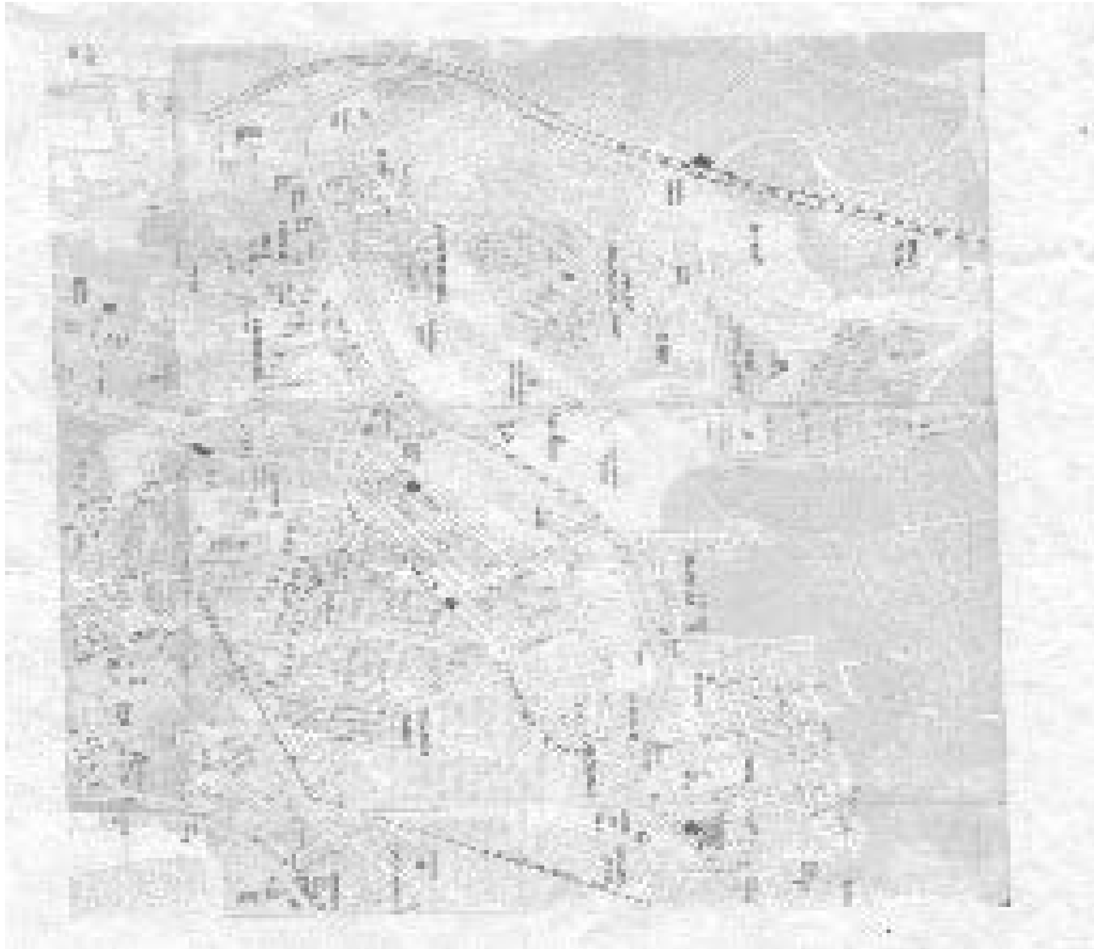

Fig. 2 Map of Warri showing locations of the open dumps.

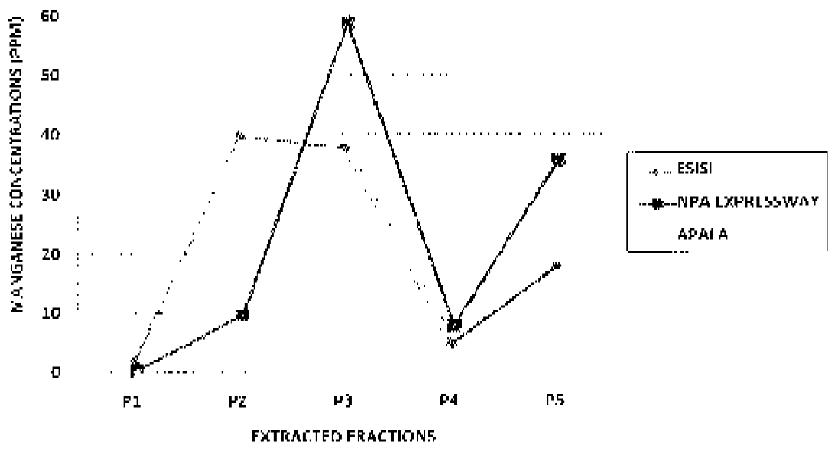

Fig. 3 Plot of manganese concentrations against extracted fractions

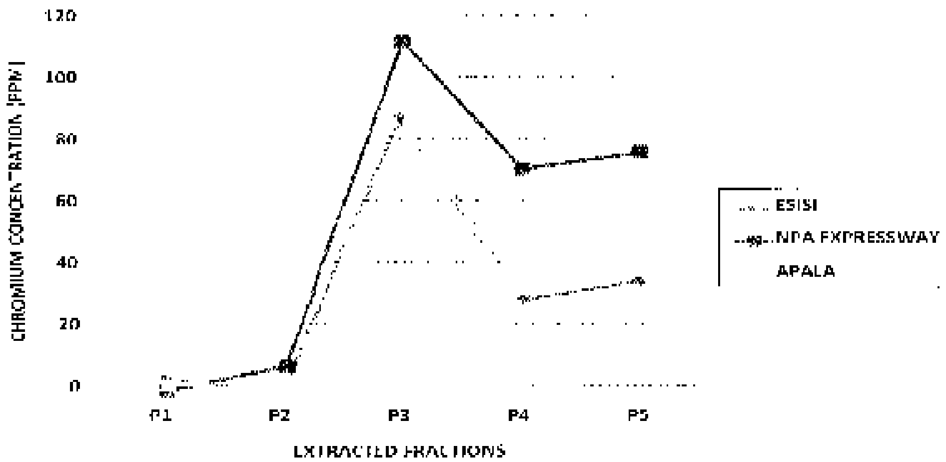

Fig. 4 Plot of chromium concentrations against extracted fractions

P_1= Exchangable phase; P_2= Carbonate phase; P_3= Fe - Mn Oxide phase; P_4= Organic matter phase ; P_5= Residual phase

Table 6 indicates that bioavailable concentrations of Mn, Cr, Pb and Zn, is higher in some of the soil samples than uncontaminated soil values (Sparks, 2001).

CONCLUSION

The total heavy metal concentrations reported in this study are higher than Federal Environmental Protection Agency (FEPA, 1991) values in some of the soil samples.

All examinated metals are present in the different fractions. Zinc is the most concentrated metal in the soil samples.

The four metals showed significant concentration in the non -residual fraction except Pb. This shows that significant concentration of the metals are active, mobile and bioavailable. The concentration values for the active, bioavailable fractions of Mn, Cr, Pb and Zn are higher in some soil samples than uncontarninated soil values (Sparks, 2001). Zinc is higher in all the soil samples analysed. Cr ishigher than uncontaminated soil values in all the soil samples analysed except Apala bottom soil and close to uncontaminated soil values in Esisi bottom soil. Pb is lower than uncontaminated soil values in all the soil samples analysed. Mn is not specified. Total zinc is higher than intervention value in all the soil

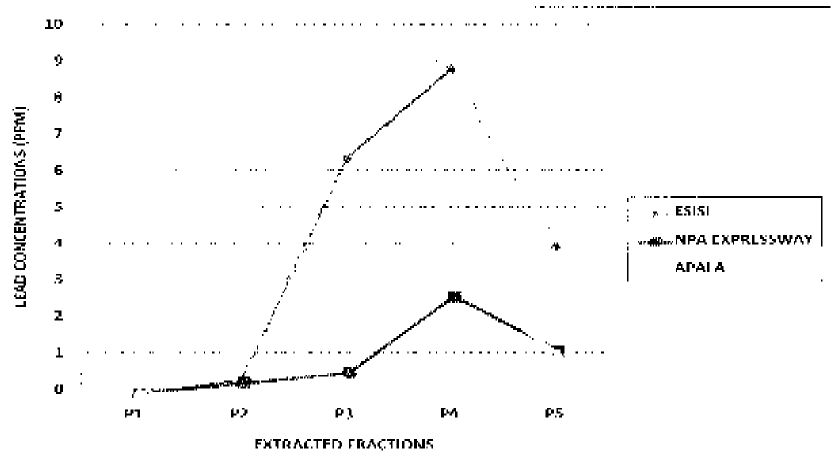

Fig. 5 Plot of lead concentrations against extracted fractions

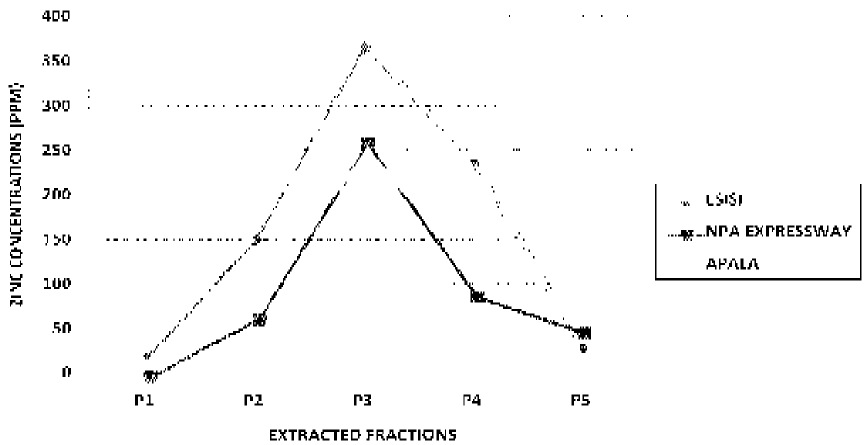

Fig. 6 Plot of zinc concentrations against extracted fractions

P_1= Exchangable phase; P_2= Carbonate phase; P_3= Fe - Mn Oxide phase; P_4= Organic matter phase ; P_5= Residual phase

samples. Cr is close to intervention value in all the samples. Pb is lower than intervention values in all the samples.

The soil samples are sandy loam, this supports leaching, as a result, there is gradual spread of these heavy metals towards the various settlements near the open dumps. Thus, workers and people living in these settlements are exposed to the possibility of metal poisoning. Significant concentrations of the metals are mobile and bioavailable to plants and other ecological materials. People who therefore eat corn, rice and crops planted close to the open dumps are contaminated by these heavy metals. This study may serve as useful information if in future the people of the area suffer from certain diseases as cancer, vomiting, mental retardation, central nervous system damage, liver, kidneys, brain and reproductive system damages. The study may also serve as yardstick for future investigation.

RECOMMENDATION

It is therefore recommended that appropriate measures should be put in place for proper waste disposal and people should be well educated about heavy metal poisoning and stop planting crops near open dumps for purposes of high yield.

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