

The Speciation and Potential Bioavailability of Zinc, Manganese, and Lead in Soils of Automobile Workshops in Sapele, Nigeria

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Abstract

This paper presents the result of speciation of three heavy metals (Zn, Mn, & Pb) in soils from ten automobile workshops in Sapele, Nigeria. Soil samples were taken from depth 0 – 60cm and heavy metal concentration were determined. Higher concentrations of these metals were found in soils in the vicinity of the automobile mechanics workshops compared to that of the control. On speciating, 20 to 28% Zn, 23 to 39% Mn, and 15 to 23% Pb, were potentially mobile and bio-available.

Keywords: soils, heavy metals, automobile workshops, speciation, bio-available.

1. Introduction

Total amount of heavy metal provide a useful index of the degree and the extent of contaminations but furnish little or no information on bioavailability and mobility of heavy metals (Chukuma, 1993; Lo and Yang, 1998). The bioavailability and mobility of heavy metal in a contaminated soil is governed by the chemical forms in which the metals exist and are distributed in the soil fractions (Tessier *et al.*, 1979; Lo and Yang, 1998). Metal fractionation (speciation) in soils has been carried out with sequential extraction procedure to determine the metal binding forms (Tessier *et al.*, 1979; Van-Valin and Morse, 1982; Lake *et al.*, 1984; Shuman, 1985, 1991; Berti and Jacobs, 1996). It is indeed a process of separating soils, sediments and soil component into operationally defined fractions in the assessment of contamination (Asagba *et al.*; 2007). Such separation has been widely used in various environmental studies (Kennedy *et al.*, 1997; Ahumada *et al.*, 1999; Christensen and Huang, 1999; Narwal *et al.*, 1999; Kabala and Singh, 2001; Oviasogie and Ndiokwere, 2008). The study of the speciation of contaminants in the environment is necessary to: assess the ultimate impacts of contaminants on human health; understand the mechanism of chemical and microbial transformation; develop predictive models, effective remediation and waste management strategies and risks assessment. The soils surrounding the automobile workshops are being exposed to contamination. Automobile used (waste) oil contain oxidation products, sediments water and metallic particles resulting from machinery wears organic and inorganic chemicals used in oil additives and metals that are present in fuel and transferred to the crankcase during combustion (EEA, 2007). These wastes including also wastes oils used for cleaning during servicing, metal scraps, used batteries e.t.c, indiscriminately discarded on the soil by artisans, contaminates the soil. Percolation of leachates from these materials poses threat to underground water and creates concern for the normal functioning of the ecosystem.

The investigations on the metal forms, particularly using sequential extraction mainly concern surface soil (0-15cm) (Iyengar *et al.*, 1981; He and Singh, 1995; Ma and Rao, 1997; Chlopecka *et al.*, 1998; Ahumada *et al.*, 1999), studies of contaminated areas however; require that the whole soil profile including subsurface horizon be considered. This study was therefore, undertaken to:

- investigate the distribution and chemical fractions of Zn, Mn, and Pb, in the soil profile (depths: 0 – 60cm).
- assess the mobility and bioavailability of the metals and the degree of contamination in the different soils.
- determine the physiochemical properties of the soil and investigate the relationship between soil properties and the chemical fractions of the heavy metals.

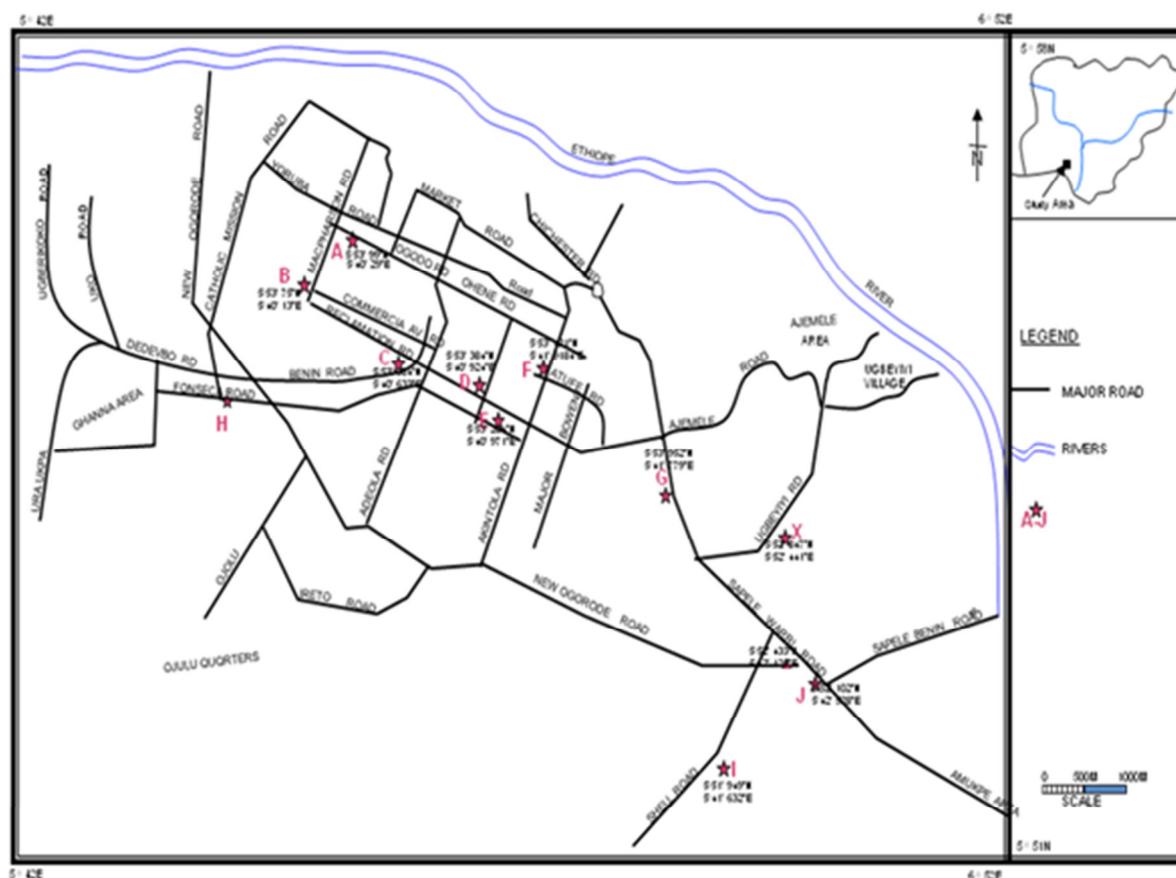


FIG.1: Map of Sapele showing the sampled locations.

2. Methodology

2.1 Study area

The study area is within Sapele, located on the Fresh Water Forest of Delta State, Nigeria. Ten Mechanic workshops (Fig. 1) in the metropolis were chosen to span a wide area of the town, with ages of establishment over seven years, obtained by personal communication with artisans working on these sites. No waste management practices are done on these workshops. Wastes are indiscriminately discarded on the soils.

2.2 Sample collection

Ten (10) composite samples were collected from ten different workshops at depths 0 – 60cm, using standard soil (Hand) Auger. A composite Sample of uncontaminated soil was obtained in similar manner from virgin land in the metropolis to serve as control.

2.3 Preparation and analysis of Samples

The collected soil samples at each boring were transferred into a black polythene bag, properly labelled before transported into laboratory (Aller, 1989). After series of quartering, samples were air-dried for a period of two weeks in a well ventilated space (Boulding, 1994) crushed in porcelain mortar and sieved through a 2mm (10mesh) stainless sieve. The air-dried <2mm samples were stored in polythene bags and properly labelled for subsequence analysis. The physicochemical properties of the samples were determined according to the standard methods. Soil pH was determined in water according to the method of Folson et al (1981), Organic Carbon (by dichromate oxidation) as described by Nelson and Sommers (1982). Available phosphorus was estimated following the procedures described by Olsen and Sommers (1982), while the ammonium acetate method was used to determine the Cation Exchange Capacity (CEC) as specified by Reeuwijk (1995). The particle size distribution (PSD) analysis of soil was carried out by the hydrometer method described by Bouyoucos (1962). The procedure of Salbu et al (1998) was used to fractionate soil samples into six operationally defined fractions: reversibly physically sorbed as(F1) water extractable (water – soluble metals); (F2) extractable with 1M NH₄OAc at pH 7 (exchangeable); (F3) extractable with 1M NH₄OAc at pH 5 (specifically sorbed and carbonate bound); (F4) extractable with hydroxylamine (metals associated (sorbed or occluded) mainly on iron and manganese oxides); (F5) extractable with H₂O₂ in 1 M HNO₃ (strongly complexed by organic matter) and (F6)

residual extracted with a mixture of HNO₃ and HClO₄ acid. The analyses were carried out in triplicates and the results are expressed as mean and standard deviation from the mean (\pm). The mobility of the metal in soil was calculated as mobility factor (MF) (Salbu et al; 1998; Narwal et al, 1999) on the basis of the following equation:

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

Since some metals forms (extracted in F3) are relatively less mobile (more strongly bound to the soil component than those extracted in F1 and F2, the above mentioned index describes the potential bioavailability/mobility (Salbu et al, 1998).

3. Results and Discussion

3.1 Physico-chemical properties of the soils

Table 1: shows some physical chemical properties of the various automobile workshops aggregate soils samples in Sapele along with the control.

Table 1: Some physico- chemical properties of the soil samples from automobile Workshops in Sapele and the control (x) (dry weight)

PARAMETERS	RESULTS \pm SD										
	SAMPLES										
	A	B	C	D	E	F	G	H	I	J	X
pH	5.43 ± 0.02	5.71 ± 0.00	5.09 ± 0.01	5.40 ± 0.02	6.02 ± 0.00	5.43 ± 0.01	5.60 ± 0.02	6.10 ± 0.02	6.39 ± 0.04	5.84 ± 0.00	6.20 ± 0.02
Clay(%)	9.90 ± 1.00	8.90 ± 1.30	9.90 ± 1.00	4.40 ± 0.00	3.40 ± 0.90	1.40 ± 0.30	8.40 ± 1.00	9.40 ± 0.90	4.90 ± 0.70	7.40 ± 0.00	10.40 ± 1.00
Silt(%)	10.00 ± 1.20	9.00 ± 1.80	10.00 ± 2.00	4.50 ± 1.00	4.50 ± 0.90	5.50 ± 1.00	6.50 ± 1.00	5.50 ± 1.00	9.00 ± 0.00	10.00 ± 0.00	8.50 ± 1.20
Sand(%)	80.10 ± 1.10	82.10 ± 2.00	80.10 ± 1.50	91.10 ± 1.90	92.10 ± 2.00	93.10 ± 2.20	85.10 ± 0.00	85.10 ± 1.00	86.10 ± 1.60	82.60 ± 2.00	81.10 ± 3.00
TOC(%)	0.29 ± 0.40	0.16 ± 0.00	0.58 ± 0.10	0.45 ± 0.10	0.58 ± 0.08	1.28 ± 0.00	0.16 ± 0.00	0.61 ± 0.10	0.07 ± 0.00	0.54 ± 0.10	0.06 ± 0.01
OM (%)	0.50 ± 0.40	0.28 ± 0.00	1.00 ± 0.10	0.78 ± 0.10	1.00 ± 0.08	2.21 ± 0.00	0.28 ± 0.00	1.06 ± 0.10	0.12 ± 0.00	0.93 ± 0.10	0.10 ± 0.01
P(mg/kg)	7.02 ± 1.00	67.07 ± 3.20	76.45 ± 5.90	41.29 ± 3.80	75.65 ± 6.10	64.26 ± 7.00	57.33 ± 6.40	13.75 ± 1.80	20.09 ± 8.10	101.55 ± 10.00	28.94 ± 7.40
Ca(cmol/kg)	7.20 ± 0.80	6.90 ± 1.00	5.70 ± 1.20	5.85 ± 0.90	6.20 ± 1.90	4.80 ± 1.00	6.55 ± 0.00	6.80 ± 0.00	5.90 ± 1.30	6.34 ± 2.00	6.40 ± 1.40
Mg(cmol/kg)	4.55 ± 1.00	4.83 ± 0.40	4.25 ± 1.00	4.70 ± 0.60	3.92 ± 0.00	4.34 ± 0.90	4.50 ± 1.00	3.93 ± 0.80	4.30 ± 0.80	5.52 ± 0.40	5.32 ± 0.60
Na(cmol/kg)	0.34 ± 0.50	0.33 ± 0.10	0.27 ± 0.00	0.48 ± 0.20	0.30 ± 0.10	0.27 ± 0.00	0.41 ± 0.12	0.37 ± 0.19	0.24 ± 0.00	0.34 ± 0.10	0.30 ± 0.10
K(cmol/kg)	0.18 ± 0.00	0.14 ± 0.00	0.18 ± 0.07	0.17 ± 0.09	0.20 ± 0.00	0.17 ± 0.00	0.12 ± 0.03	0.20 ± 0.09	0.16 ± 0.09	0.20 ± 0.08	0.18 ± 0.00
CEC(cmol/kg)	12.27 ± 0.52	12.20 ± 1.00	10.40 ± 1.40	11.20 ± 1.90	10.62 ± 1.50	9.58 ± 2.00	11.58 ± 3.00	11.30 ± 0.00	10.60 ± 1.70	12.40 ± 1.40	12.27 ± 0.00

A = Ogodo, B = Mcpherson, C = Reclamation, D = Okpe Rd, E = Oleh, F = Akintola, G = Ajogodo, H = Gana-New Rd, I = Shell Rd, J = Okirigwre, X = Control (Ubeyiyi)

The soils were moderately acidic, with pH range of 5.09 - 6.39. The moderately acidic characteristic is typical of the Niger Delta soils (Odu *et al.*, 1985; Isirimah, 1987). The soils were sandy loam, with sand fractions ranged between 80.10 - 93.10%, silt fraction; 4.50 - 10.00% and clay fractions range were from 1.40 - 9.90%. The cation exchange capacities (CEC) ranged from 9.58cmol/kg in sample F to 12.40cmol/kg recorded for sample J. The control value was 12.27cmol/kg. The values obtained for CEC were largely due to Ca and Mg. The values for Ca accounted for more than half, while Mg accounted for over one third of the total CEC for each site including the control. The total organic carbon contents ranged between 0.07% (Sample I) and 1.28% (Sample F). The values recorded for the controls was 0.06 \pm 0.1%. The slight differences in CEC values in the soil may be explain in terms of slight differences in organic matter and clay content. Many authors (Sposito, 1989; Sparks, 2003; Rodriguez-Rubio *et al.*, 2003; Yin *et al.*, 2012) have correlated organic matter content to soil CEC. The low clay content and organic matter tend to make the soils permeable. The phosphorus content of the soils ranged between 7.02 - 101.55mg/kg against a control value of 28.94mg/kg.

3.2 Geochemical forms of heavy metals in soil samples.

The geochemical forms, average total concentration of Zn, Mn, and Pb (mg/kg), percentage (%) recovery, as well as the % distribution of each forms and % bio-availabilities are presented in Tables 2 –7. The overall recovery rates which is the sum of six fractions divided by the independent total concentration from the sequential extraction procedure, ranged from 91 to 99%. This signifies a high reliability in the sequential extraction procedures.

The result of total Zn determination in the soils samples (Table 2) shows that the values of 336.50 to 796.10mg/kg were far above the 5.40mg/kg obtained for the control. Zinc was highly concentrated in the residual (F6) and organically bound (F5) fractions. The Mn-Fe-Oxides (F4) fractions also contain relatively high amount of Zn. The distribution of Zn in the last three fractions (F4+F5+F6) accounted for more than 72% of the total fraction (Table 3). The % distribution of Zn (Table 3) in the water soluble fraction, range from 2 to 5%, while that of exchangeable fraction was 3 to 7%. The percent bioavailability of Zn in all the samples ranges from 20% in sample J to 28% recorded for sample D and E. In all samples, the order of fractions tends to be:

Residual > organically complexed > Fe-Mn-Oxides > Carbonate bound > Exchangeable > Water soluble. Other authors (Ma and Rao, 1997; Narwal *et al.*, 1999) have also reported Zn to be strongly bound in the residual fraction. The control sample has 18% Zn bio-availability with the dominant fraction in the residual.

Table 2: Geochemical forms of Zn (mg/kg) in soil samples from the automobile workshops and control (x)

SAMPLES	RESULTS \pm SD						SUM ^a	TOTAL ^b	%RECOVERY ^R
	F1	F2	F3	F4	F5	F6			
A	16.80 \pm 0.50	28.20 \pm 0.60	67.70 \pm 2.10	94.60 \pm 1.00	107.80 \pm 5.00	165.50 \pm 4.40	480.60 \pm 14.80	491.25 \pm 8.30	97.83
B	12.10 \pm 1.00	23.60 \pm 1.90	47.30 \pm 2.70	62.92 \pm 1.00	81.20 \pm 3.30	101.68 \pm 6.40	328.80 \pm 7.30	336.50 \pm 7.80	97.71
C	24.70 \pm 1.30	36.10 \pm 2.30	79.30 \pm 4.00	88.50 \pm 4.00	127.55 \pm 10.00	190.20 \pm 11.70	546.35 \pm 9.30	553.50 \pm 9.10	98.71
D	37.30 \pm 4.90	54.80 \pm 5.00	121.10 \pm 6.70	144.40 \pm 10.00	182.80 \pm 12.30	238.80 \pm 10.00	779.20 \pm 11.90	794.55 \pm 15.00	98.07
E	35.80 \pm 3.60	57.40 \pm 5.00	124.00 \pm 10.25	148.70 \pm 16.90	184.90 \pm 14.00	229.80 \pm 17.45	780.60 \pm 13.70	796.10 \pm 11.70	98.05
F	16.10 \pm 1.60	20.00 \pm 2.60	108.80 \pm 9.90	126.70 \pm 12.30	170.80 \pm 15.00	212.00 \pm 15.00	654.40 \pm 11.80	673.60 \pm 17.90	97.15
G	12.80 \pm 1.30	15.90 \pm 1.05	84.60 \pm 5.90	108.00 \pm 17.00	136.30 \pm 19.00	150.70 \pm 10.45	508.30 \pm 13.20	520.70 \pm 11.30	97.62
H	11.40 \pm 1.00	17.30 \pm 1.40	76.80 \pm 5.00	102.60 \pm 15.00	128.50 \pm 13.90	152.00 \pm 10.00	488.60 \pm 14.60	506.40 \pm 21.90	96.48
I	16.70 \pm 1.70	18.40 \pm 1.90	84.40 \pm 4.50	112.30 \pm 8.90	160.90 \pm 15.50	186.10 \pm 21.00	574.80 \pm 15.10	592.40 \pm 13.90	97.03
J	15.80 \pm 1.50	18.80 \pm 1.55	93.70 \pm 2.70	116.20 \pm 4.90	148.80 \pm 5.90	193.50 \pm 10.00	576.80 \pm 9.30	597.30 \pm 12.70	96.57
X	0.10 \pm 0.00	0.30 \pm 0.05	0.50 \pm 0.05	0.90 \pm 0.05	1.40 \pm 0.40	1.90 \pm 0.00	5.20 \pm 0.05	5.40 \pm 0.90	96.30

The values are mean \pm S.D

a = The sum of metal concentration in the six fractions

b = The independent total concentration of metals

R = (a/b) x 100

F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction;

F4 = Fe-Mn Oxide fraction; F5 = Organic fraction; F6 = Residual fraction

Table 3: Distribution of Zn (%) in soil samples from the automobile workshops and control (x).

Samples	F1	F2	F3	F4	F5	F6	% Bioavailability
A	4	6	14	20	22	34	24
B	4	7	14	19	25	31	25
C	5	7	14	16	23	35	26
D	5	7	16	18	23	31	28
E	5	7	16	19	24	29	28
F	3	3	17	19	26	32	23
G	2	3	17	21	27	30	22
H	2	4	16	21	26	31	22
I	3	3	15	19	28	32	21
J	3	3	14	20	26	34	20
X	2	6	10	18	27	37	18

The total average concentration of Mn (mg/kg) in soil samples (Table 4) ranged from 85.40 to 202.90mg/kg. The highest value was recorded in sample A (Ogodo Rd). This was followed by sample H with value of 166.40mg/kg. The lowest value was from sample D with value of 85.40mg/kg. These values are high compared to the 2.10mg/kg observed for the control sample. Manganese in the automobile workshops soils were found mostly in the residual fractions. This was followed by Mn-Fe-Oxides fraction in samples A, B, C, and D. The other soils samples had more of Mn in organically complexed fraction than in Mn- Fe- Oxides fraction. 10 to 17% carbonate bound fraction was observed for the soils samples (Table 5). Carbonates have been implicated as immobilizing most heavy metals by providing an adsorbing or nucleating surface and buffering the soil pH (Chlopecka *et al.*, 1998). The least amount of Mn was in the Exchangeable and water soluble fractions. The percentage sum of the weakly bound fractions (F1+F2+F3) was highest in samples G and J (both 37%) followed by that in samples H and I (both 36%). The lowest value of the weakly bound fractions was 28% recorded for sample A. The weakly bound fraction of the control amount to 19%, the dominant fraction was residual (36%)

followed by the organically complexed (25%).

Table 4: Geochemical forms of Mn(mg/kg) in soil samples from the automobile workshops and control (x)

SAMPLES	RESULTS \pm SD								
	F1	F2	F3	F4	F5	F6	SUM ^a	TOTAL ^b	%RECOVERY ^R
A	12.80 \pm 1.20	9.40 \pm 0.90	33.70 \pm 1.00	48.62 \pm 2.05	29.50 \pm 0.00	62.78 \pm 5.00	196.80 \pm 2.50	202.90 \pm 4.70	96.99
B	5.20 \pm 0.60	4.70 \pm 0.40	13.90 \pm 1.50	19.40 \pm 1.60	9.30 \pm 0.05	28.80 \pm 5.00	81.30 \pm 4.30	86.70 \pm 5.10	93.77
C	8.90 \pm 0.70	5.30 \pm 0.50	18.60 \pm 2.05	29.50 \pm 1.90	19.30 \pm 1.00	57.80 \pm 5.00	139.40 \pm 2.50	142.70 \pm 2.70	97.69
D	9.20 \pm 0.50	5.40 \pm 0.60	10.70 \pm 2.70	17.10 \pm 4.40	12.60 \pm 5.00	26.80 \pm 7.00	81.80 \pm 5.60	85.40 \pm 8.00	95.78
E	16.80 \pm 2.10	12.40 \pm 0.90	18.95 \pm 1.80	20.40 \pm 2.30	23.80 \pm 4.50	30.75 \pm 4.00	123.10 \pm 4.10	128.20 \pm 3.50	96.02
F	12.50 \pm 1.20	9.10 \pm 1.00	14.40 \pm 1.55	16.90 \pm 0.90	24.60 \pm 2.00	34.80 \pm 1.90	112.30 \pm 1.70	117.90 \pm 4.80	95.25
G	18.20 \pm 2.50	11.30 \pm 1.50	26.70 \pm 3.30	28.30 \pm 4.30	31.30 \pm 1.40	33.80 \pm 5.00	149.60 \pm 3.90	155.50 \pm 7.30	96.21
H	17.90 \pm 2.40	12.60 \pm 1.60	27.30 \pm 3.50	28.00 \pm 2.70	30.80 \pm 4.50	45.10 \pm 5.00	161.70 \pm 3.10	166.40 \pm 5.10	97.18
I	12.80 \pm 1.45	9.20 \pm 0.50	15.30 \pm 2.50	17.70 \pm 3.50	22.80 \pm 1.00	26.70 \pm 2.80	104.50 \pm 3.30	110.42 \pm 7.50	94.64
J	11.30 \pm 1.00	8.30 \pm 0.50	14.80 \pm 1.00	16.40 \pm 1.55	20.80 \pm 3.10	22.80 \pm 4.05	94.40 \pm 2.90	101.70 \pm 3.30	92.82
X	0.10 \pm 0.00	0.08 \pm 0.00	0.20 \pm 0.00	0.40 \pm 0.03	0.52 \pm 0.05	0.74 \pm 0.05	2.04 \pm 0.08	2.10 \pm 0.05	97.14

Table 5: Distribution of Mn (%) in soil samples from the automobile workshops and control (X).

Samples	F1	F2	F3	F4	F5	F6	% bioavailability
A	6	5	17	25	15	32	28
B	6	6	17	24	12	35	29
C	6	4	13	21	14	42	23
D	11	7	13	21	15	33	31
E	14	10	15	17	19	25	39
F	11	8	13	15	22	31	32
G	12	7	18	19	21	23	37
H	11	8	17	17	19	28	36
I	12	9	15	17	22	25	36
J	12	9	16	17	22	24	37
X	5	4	10	20	25	36	19

Table 6 shows the total concentration of Pb in the automobile workshops samples ranged from 20.54 to 31.86mg/kg against a control value of 0.71mg/kg Pb. Lead was largely present in the residual (F6) fractions of the soil accounting for over 32% of the total fractions (Table 7). A high proportion of Pb was also observed in the Fe-Mn-oxides fraction of the soils (12 to 27%). This was next followed by the organically complexed form. The dominance of oxides occluded fraction of Pd over organically complexed form has been reported by other investigators (Ramos *et al.*, 1994; Karczewska, 1996; Ahumada *et al.*, 1999). In soil polluted by lead smelting the mean percentage of lead in oxide bound fraction was estimated to be 57% while organically complexed Pb accounted for only 14% of the total Pb (Chlopecka *et al.*, 1998). The lack of correlation between Pb in the sum of the last three fractions (F4+F5+F6) and phosphorus in soils, suggest that other factors other than formation of Lead Phosphates are responsible for the immobilization of lead in the soils. The formation of Pb phosphates particularly pyromorphites in soils has been implicated for immobilizing Pb and thereby reducing its bioavailability (Ruby *et al.*, 1994; Hettiarachechi and Perzynki, 2002) The dominant fraction of Pb in the control (sample X) was in the residual. The concentration Pb in the water soluble fraction of the soils were less than 11% of the total Pb, while that of exchangeable Pb ranged from 3 to 7% of the total Pb. The carbonates fraction had a range of 4 to 7% of total Pb. The order of fractions was: residual > Fe-Mn oxide > organically complexed > water soluble > carbonate bound > exchangeable. The % bioavailability of Pb was least in Sample A (15%). Sample J had the most bioavailable Pb (23%).

Table 6: Geochemical forms of Pb (mg/kg) in soil samples from the automobile workshops and control

SAMPLES	RESULTS \pm SD								
	F1	F2	F3	F4	F5	F6	SUM ^a	TOTAL ^b	%RECOVERY ^R
A	1.70 ± 0.30	0.80 ± 0.00	1.25 ± 0.10	6.47 ± 0.50	4.74 ± 0.00	9.98 ± 0.50	24.94 ± 1.00	26.23 ± 2.30	95.08
B	1.76 ± 0.20	1.70 ± 0.00	1.10 ± 0.00	4.48 ± 0.50	3.50 ± 0.55	12.45 ± 1.40	24.90 ± 2.50	25.22 ± 2.00	98.73
C	2.85 ± 0.50	1.10 ± 0.15	1.47 ± 0.25	6.55 ± 0.50	3.98 ± 0.50	12.50 ± 1.80	28.45 ± 2.40	30.91 ± 1.50	92.04
D	2.50 ± 0.40	1.67 ± 0.27	1.95 ± 0.45	5.84 ± 0.50	3.90 ± 0.55	11.95 ± 1.50	27.81 ± 3.00	29.47 ± 1.80	94.37
E	2.70 ± 0.45	1.50 ± 0.10	2.20 ± 0.10	6.50 ± 0.50	4.73 ± 0.60	12.20 ± 0.00	29.83 ± 1.00	31.86 ± 1.50	93.63
F	2.30 ± 0.15	1.45 ± 0.15	2.02 ± 0.00	8.10 ± 0.50	5.78 ± 0.55	9.25 ± 1.00	28.90 ± 2.20	30.84 ± 2.00	93.71
G	1.55 ± 0.15	0.60 ± 0.00	1.20 ± 0.05	5.30 ± 0.45	4.35 ± 0.25	6.70 ± 0.40	19.70 ± 0.90	20.54 ± 1.40	95.91
H	2.15 ± 0.45	1.00 ± 0.05	1.20 ± 0.00	3.65 ± 0.10	4.30 ± 0.50	7.50 ± 0.70	19.80 ± 1.30	21.63 ± 1.90	91.54
I	1.95 ± 0.45	1.10 ± 0.00	1.40 ± 0.00	3.30 ± 0.05	5.51 ± 0.50	8.85 ± 0.00	22.10 ± 1.00	23.98 ± 1.70	92.16
J	2.30 ± 0.45	1.45 ± 0.30	1.90 ± 0.15	3.00 ± 0.45	3.65 ± 0.50	12.00 ± 2.20	24.30 ± 4.40	25.80 ± 2.10	94.19
X	<0.08 ± 0.00	<0.08 ± 0.00	0.10 ± 0.00	0.12 ± 0.03	0.22 ± 0.02	0.26 ± 0.00	0.70 ± 0.05	0.71 ± 0.05	98.59

The values are mean \pm S.D

a = The sum of metal concentration in the six fractions

b = The independent total concentration of metals

R = (a/b) x 100

F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction;

F4 = Fe-Mn Oxide fraction; F5 = Organic fraction; F6 = Residual fraction

Table 7: Distribution of Pb (%) in soil samples from the automobile workshops and control (X).

Samples	F1	F2	F3	F4	F5	F6	%Bioavailability
A	7	3	5	26	19	40	15
B	7	7	4	18	14	50	18
C	10	4	5	23	14	44	19
D	9	6	7	21	14	43	22
E	9	5	7	22	16	41	21
F	8	5	7	28	20	32	20
G	8	3	6	27	22	34	17
H	11	5	6	18	22	38	22
I	9	5	6	15	25	40	20
J	10	6	7	12	15	50	23
X	0	0	14	17	32	37	14

Table 8: Coefficient of relations between heavy metal fractions (dependent variable) and clay, silt, sand, organic matter, cation exchange capacity (independent variables) in soils samples.

		f1	f2	f3	f4	f5	f6	Mt
Zn	Clay	-0.4464	-0.3277	-0.7844**	-0.7659**	-0.8247**	-0.6958**	-0.7579**
	Silt	-0.4487	-0.4308	-0.6834**	-0.6928**	-0.6245*	-0.4446	-0.6218*
	Sand	0.4995	0.4162	0.8265**	0.8195**	0.8231**	0.6543*	0.7798**
	OM	0.1273	0.0787	0.4900	0.3856	0.4143	0.4781	0.4251
	CEC	-0.3107	-0.2007	-0.5204*	-0.4260	-0.5913*	-0.5386*	-0.5221*
Mn	Clay	-0.0903	-0.1324	0.5786*	0.6408*	0.1297	0.5631*	0.4952
	Silt	-0.4615	-0.4130	0.1416	0.3456	-0.1145	0.3219	0.1429
	Sand	0.2819	0.2847	-0.4329	-0.5714*	-0.0256	-0.5111	-0.3810
	OM	0.0873	0.1165	-0.2035	-0.2300	0.1184	0.0737	-0.0369
	CEC	-0.1577	-0.1138	0.3143	0.3315	-0.0878	-0.0117	0.1165
Pb	Clay	-0.3397	-0.5028	-0.7903**	-0.3619	-0.5987*	-0.0615	-0.5164
	Silt	-0.2453	-0.2291	-0.4632	-0.3217	-0.2324	0.2302	-0.1767
	Sand	0.3332	0.4278	0.7228**	0.3845	0.4897	-0.0736	0.4108
	OM	0.5335	0.2966	0.6044*	0.5678*	0.3533	0.0534	0.5653*
	CEC	-0.5310*	-0.1033	-0.4450	-0.5407*	-0.6714*	0.1049	-0.5219*

**significant at the %1 level, *significant at the %5 level

F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction, F4 = Fe-Mn Oxide fraction; F5 = Organic fraction; F6 = Residual fraction, Mt = Total metal content.

Table 9: Coefficient of relations between heavy metal content and mobility index in soils.

Mobility index	Zn	Mn	Pb
	0.9484**	0.8568**	0.8358**

**significant at the %1 level, *significant at the %5 level

3.3 Statistical analysis

The analytical results were compiled to form a multi-element data base using excel as statistical software. Pearson's correlation coefficients and P-values were calculated for all possible variable pairs (Tables 8 - 9). Significant positive correlations were present between Zn fractions and sand fractions, sand fraction and total Zn content, clay fraction and F3, F4, and F6 fractions of Mn, sand fraction and F3 fraction of Pb, organic matter content and F1, F3, F4 of Pb, organic matter and total Pb. Strong positive correlations of mobility index with total metals content was also found. This indicates overloading of the geochemical system in the contaminated soils where anthropogenically added metals remained weakly bound to soil constituents (Ramos *et al.*, 1994). Negative correlations were found for silt fraction and Zn fractions, clay and Zn fractions, clay and total Zn, CEC and F3, F5, & F6 fractions of Zn, CEC and total Zn, sand and F4 fraction of Mn, clay fraction and F3, F5 fractions of Pb, CEC and F1, F4, F5 fractions of Pb,

4. Conclusion

The result of sequential chemical fractionation of the heavy metal contaminated soils shows that heavy metals distributions among chemical fractions were generally dependent on the metal, its total content and soil texture. In all soils samples analysed (for Zn, Mn, & Pb) the last three fractions, (residual, organically complexed, and Fe-Mn-oxides bound) were predominant, with the residual taking the lead. The potentially mobile and bioavailable fractions for the metals in soils were generally less than 39% with Mn being the most mobile (23 - 39%) of the metals. The general order of percentage bioavailability of the metals in the soils was: Mn > Zn > Pb. The percentage potential bioavailability/mobility of Mn, and Pb in the soils taken into consideration their total concentrations does not constitute much threat to the environment. However, the high concentration of Zn coupled with its fair mobility required attention. Also, as a result of possible accumulation of metals in soils, measures such as legislation and education on waste management in automobile workshops should be put in place to forestall the effects of heavy metals' related problems on the environment.

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