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Soil Profile Distribution of Heavy Metals in Automobile Workshops in Sapele, Nigeria

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Abstract

Soils samples taken at depths, 0 – 15, 15 – 30, 30 – 45, and 45 – 60 cm from ten automobile workshops in Sapele metropolis were investigated for heavy metals and physico-chemical properties using standard methods. The pH ranged observed was 5.09 - 6.39. At all locations investigated, the heavy metals (Zn, Mn, Pb, Cu, Cr, and Cd) obtained were much higher than that from the control sample. This is an indication that automobile workshops situated within the metropolis are anthropogenic sources of heavy metals in the soils that requires attention. The concentrations of Zn, Cu and Cd at most locations and depths were also higher than the recommended critical limits. The concentrations of the metals generally decrease with increase in depths. The extent of contamination level based on the average metal contents obtained from soil samples at the different depths was 57.69 - 129.58 folds for Zn, Manganese was 27.74 - 69.20 fold, while Pb, Cu, and Cr, were respectively 17.95 - 55.97, 8.39 - 14.82, and 113 - 504 fold compared with the control soil. Cadmium was not detected in control soil but values ranging from 1.70 to 8.89 mg/kg were recorded for the automobile workshops soils. The degree of metal pollution was in order: Oleh Road > Reclamation/Green-Egbede Road > Awolowo/Okpe Road > Okerigwre Road > Akintola Road > Shell Road > Gana New Road > Ajogodo Road > Ogodo Road > McPherson Road.

Keywords:
automobile workshops,
contamination,
heavy metals,
pollution,
soil profile

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Introduction

Heavy metals are group of metals and metalloids with an atomic density greater than 5 gdm^{-3} .They are widely distributed in the environment and are not biodegradable but can be transformed into different forms (species) with time as the organic molecules binding them decompose or soil conditions change (Alloway and Aryes, 1997).

Heavy metals occur naturally in rock-formation and ore minerals and so there is a range of normal background concentrations of these elements in soils, sediments, water and living organisms. The very low general level of their background concentration in the soils, and plants as well as their biological role, makes them micro or trace elements (Alloway and Aryes, 1997; Lacatusu, 1998). Some heavy metals such as Zn, Cu, Mg, and Cr are essential to maintain growth and normal functioning of living organism including Man. However, many may be toxic at higher concentrations as they tend to bioaccumulate in human bodies making them dangerous and therefore poses great health and environment risks (Igwe and Abia, 2006). Other elements such as Pb, Hg and Cd are not essential for metabolic activities and exhibit toxic properties even at very low concentrations (Klaassen, 2001; White *et al.*, 2007).

The anthropogenic sources of heavy metals include, waste from mining, metallurgical, chemical industries, battery manufacturing, dye and tannery, pigment manufacturing industries as well as Leachates from contaminated dump sites and petroleum activities (Biney *et al.*, 1994). Heavy metals are also emitted from the burning of fossil fuel, incineration of wastes, resource recovery plants in relative high levels fly ash particles (Neal *et al.*, 1990). One other source of heavy metal pollution in soil is that due to automobile workshops activities. Spent (waste) automobile 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 etc., 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 objectives of this study are to investigate the profile of heavy metals in soils within automobile workshops in Sapele metropolis, and to ascertain the extent of metal pollution in these soils.

Materials and methods

Study area

The study area is within Sapele, located on the Fresh Water Forest of Delta State, Nigeria. Automobile workshops in the metropolis were chosen with ages of establishment over seven years, obtained by personal communication with artisans working on these sites. No waste management practice has been conducted in these workshops.

Samples collection and preparation

Composite soil samples were collected from ten (10) different mechanic workshops; at each workshop four different points were chosen using cluster random sampling technique to collect the sample. Four soil samples per point were collected at depths 0-15, 15-30, 30-45 and 45-60 cm using standard soil (hand) auger. Sample of uncontaminated soil were obtained in similar manner from nearby virgin land in the metropolis to serve as control. The geographical position coordinates of the sampled locations were identified and mapped using global position system (GPS) (Figure 1 and Table 1). The collected samples were transferred into a black polythene bag, properly labelled and transported to laboratory (Aller, 1989). The samples were air-dried for a period of two weeks in a well ventilated space (Boulding, 1994). A good representative was obtained using quartering method. The dried representative soil samples were crushed in porcelain mortal and sieved through 2 mm (10 mesh size) stainless sieve. The air-dried < 2mm soil samples were stored in airtight polythene bags and labelled prior to analysis. The aggregate sample from each location used for physico-chemical analysis was prepared by

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mixing together equal amount of each of the samples from the four different depths.

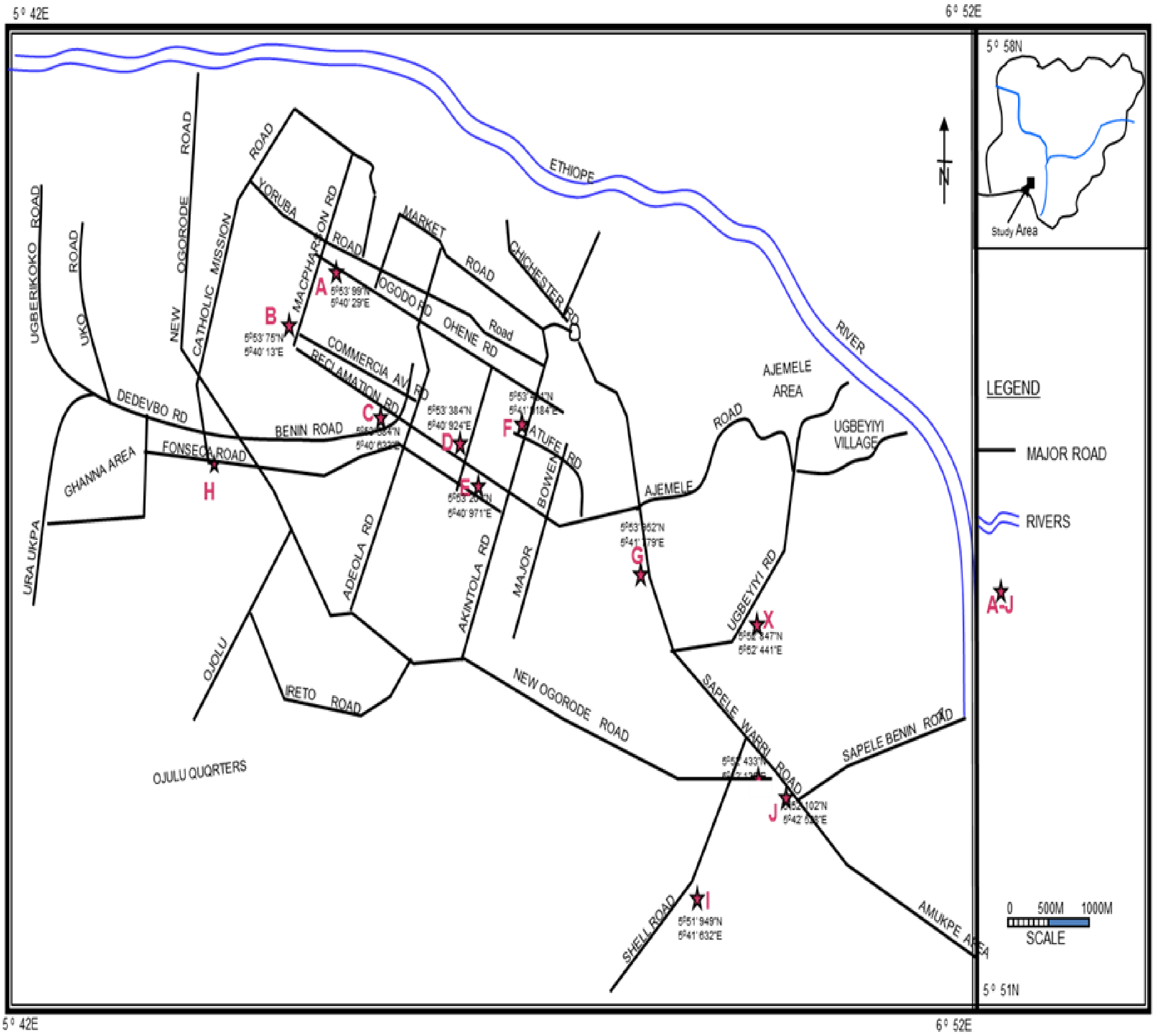

Figure 1: Map of Sapele showing the sampled locations

Table 1: Locations description and coordinates

Locations	Description	Co-ordinates
A	Ogodo Road before Zik Secondary School	N05°53.996´ E005°40.290´
B	McPherson Road by Ikomi Junction	N05°53.746´ E005°40.129´
C	Reclamation Road by Green-Egbedi	N05°53.384´ E005°40.633´
D	Okpe Road by Awolowo	N05°53.384´ E005°40.924´
E	Oleh Road close to Christ the King College	N05°53.204´ E005°40.971´
F	Akintola Road by Atufe Junction	N05°53.421´ E005°41.184´
G	Ajogodo Road opposite Christ Apostolic Church	N05°53.952´ E005°41.779´
H	Along Gana-New Road	N05°54.701´ E005°45.025´
I	Mechanic village at Shell Road	N05°52.102´ E005°41.632´
J	Okirigwre by Granite depot	N05°52.102´ E005°42.528´
X	Control-Virgin land at Ubeyiyi	N05°52.847´ E005°42.528´

Analysis of Sample

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

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Bouyoucos (1962). The total heavy metals in soils were determined with Atomic adsorption spectrophotometer (Model 210 VGP) after digestion with a mixture of Nitric and Perchloric acids (Tessier *et al.*, 1979). The analysis was carried out in triplicates and the results are expressed as mean and standard deviation from the mean (±).

Statistical analysis

The analytical results were compiled to form a multi-element data base using excels as statistical software. Pearson's correlation coefficients and p-values were calculated for all possible variable pairs.

Results

Table 2 shows some physical chemical properties of the various automobile workshops aggregate soils samples along with the control. The mean concentrations of metals at each depth in each sampled location as well as the average metals concentrations at each depth are shown in Tables 3 and 5 respectively.

Table 2: Some physico-chemical properties of aggregate soil samples from automobile workshops in Sapele and the control (x) (dry weight)

Parameter	Result ± 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	10.4 ± 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	81.1 ± 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	28.9 ± 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

Discussion

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 9.58 cmol/kg in sample F to 12.40 cmol/kg recorded for sample J. The control value was 12.27 cmol/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 ± 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 - 101.55 mg/kg against a control value of 28.94 mg/kg.

The concentrations of heavy metals obtained from this study generally decreased vertically with soil depth. This higher level of metals on the top or surface soil is expected since the top soil is the point of contact. The surface soils therefore represent better indicators of metallic burdens since the metal levels decreased with depth in all the sites. The average top - soil value for Zn (764.55 mg/Kg) obtained in this study was higher than the critical soil total content of Zn (Table 5) for the several countries indicating pollution due to automobile artisans' activities. The value was however lower than the 1086 mg/Kg Zn recorded by Nwoko *et al* (2012) for auto - mechanic villages in Imo State, Southeast Nigeria. The range (400.01 - 1126.04 mg/Kg) for the top - soil (Table 6) is comparable to that obtained in Akure (391.57 - 782.23 mg/Kg) (Oguntimehin and Ipinmoroti, 2008). High concentration of zinc kills or stunts plant growth. In human, excessive intake of Zn may aggravate Cu deficiency (Hurley and Keen, 1987). The abundance of Zn in the soil cannot be ascribed to its relative natural occurrence in soil; anthropogenic addition from the metal junkyard found in many of the auto mechanic sites is probable. Used oils that sink into the ground as leachates also contain a lot of this metal.

Table 3: Mean concentration of metals (mg/kg) at each depth in dry sample plus control (x)

Samples	Depths (cm)	Zn	Mn	Pb	Cu	Cr	Cd
A	0 - 15	615.57 ± 3.50	262.22 ± 10.00	36.33 ± 2.00	59.30 ± 6.60	80.10 ± 3.00	9.30 ± 0.00
	15 - 30	519.75 ± 5.10	212.00 ± 11.00	26,22 ± 1.14	55.65 ± 3.50	61.80 ± 10.00	6.78 ± 0.00
	30 - 45	445.24 ±11.40	181.14 ± 0.00	23.71 ± 1.40	50.19 ± 7.17	31.1010 ± 4.00	3.05 ± 0.00
	45 - 60	199.09 ± 10.20	113.41 ± 8.00	18.60 ± 2.90	39.80 ± 13.70	11.60 ± 1.00	0.65 ± 0.00
B	0 - 15	400.01 ± 9.80	159.00 ± 12.00	37.40 ± 2.90	50.04 ± 10.00	87.10 ± 14.00	9.35 ± 1.00
	15 - 30	392.00 ± 12.50	73.38 ± 5.00	32.36 ± 2.00	47.30 ± 12.00	61.31 ± 3.00	5.90 ± 1.00
	30 - 45	336.00 ± 20.00	66.08 ± 9.00	20.00 ± 3.00	38.40 ± 14.00	36.10 ± 2.00	3.40 ± 0.50
	45 - 60	277.43 ± 14.00	34.09 ± 4.90	11.13 ± 00	30.10 ± 14.00	11.60 ± 1.00	1.40 ± 0.00
C	0 - 15	744.32 ± 7.17	179.45 ± 23.00	35.93 ± 0.00	89.86 ± 22.00	77.31 ± 12.00	8.95 ± 1.55
	15 - 30	599.88 ± 12.10	137.79 ± 12.10	37.21 ± 0.00	93.04 ± 20.40	60.88 ± 14.40	8.40 ± 1.00
	30 - 45	474.41 ± 13.10	107.78 ± 10.00	33.58 ± 2.00	85.88 ± 30.00	37.19 ± 0.00	5.65 ± 1.60
	45 - 60	203.48 ± 0.00	79.00 ± 2.80	16.93 ± 1.70	55.98 ± 12.00	18.60 ± 2.00	4.05 ± 0.50
D	0 - 15	1016.25 ± 24.50	131.08 ± 4.70	50.82 ± 5.00	155.03 ± 20.00	55.15 ± 5.00	6.80 ± 1.00
	15 - 30	842.68 ± 10.20	108.12 ± 5.00	35.20 ± 4.40	127.33 ± 18.10	31.57 ± 3.00	3.77 ± 0.05
	30 - 45	656.20 ± 14.50	48.12 ± 3.00	21.34 ± 1.20	130.35 ± 40.00	20.65 ± 3.00	1.55 ± 0.50
	45 - 60	522.67 ± 17.14	34.48 ± 3.80	10.51 ± 8.20	112.49 ± 20.00	10.30 ± 3.00	0.83 ± 0.00
E	0 - 15	1126.04 ± 10.00	191.79 ± 14.40	48.22 ± 10.00	120.58 ± 11.00	24.11 ± 2.10	8.60 ± 1.50
	15 - 30	783.52 ± 8.90	148.42 ± 7.50	39.15 ± 3.40	97.94 ± 12.40	19.59 ± 1.00	6.09 ± 1.50
	30 - 4	618.08 ± 9.40	103.05 ± 4.50	28.34 ± 6.00	91.20 ± 8.00	9.72 ± 0.80	4.29 ± 0.50
	45 - 60	520.00 ± 1.00	48.22 ± 2.30	11.75 ± 3.00	80.50 ± 11.00	5.19 ± 0.00	0.97 ± 0.00
F	0 - 15	796.36 ± 5.50	181.98 ± 0.00	39.32 ± 2.00	99.54 ± 20.00	20.20 ± 2.00	8.18 ± 2.25
	15 - 30	672.44 ± 10.20	138.72 ± 0.00	39.80 ± 2.00	84.68 ± 12.00	36.90 ± 4.00	5.45 ± 1.50
	30 - 45	605.56 ± 7.50	99.97 ± 10.20	27.86 ± 4.50	54.59 ± 10.00	13.69 ± 2.20	3.49 ± 0.50
	45 - 60	396.16 ± 11.00	58.29 ± 7.70	16.36 ± 2.00	46.88 ± 10.00	9.90 ± 1.10	1.95 ± 0.50
G	0 - 15	780.00 ± 11.30	176.20 ± 9.80	35.34 ± 4.30	88.10 ± 0.00	62.70 ± 5.70	8.80 ± 1.00
	15 - 30	506.81 ± 20.00	173.52 ± 10.20	24.40 ± 10.00	77.55 ± 0.00	51.55 ± 12.00	6.08 ± 1.50
	30 - 45	396.04 ± 12.80	152.40 ± 10.00	15.24 ± 8.50	55.35 ± 5.00	31.70 ± 10.00	3.81 ± 0.55
	45 - 60	218.03 ± 10.30	102.30 ± 9.80	7.20 ± 3.70	47.99 ± 4.40	20.16 ± 5.40	1.35 ± 0.00
H	0 - 15	615.04 ± 15.40	179.05 ± 14.20	30.78 ± 1.00	76.94 ± 10.00	38.95 ± 4.80	9.97 ± 1.55
	15 - 30	499.96 ± 22.00	188.24 ± 17.30	25.99 ± 3.00	64.94 ± 11.00	29.94 ± 3.80	6.22 ± 1.55
	30 - 45	432.28 ± 17.30	172.23 ± 13.10	19.87 ± 0.00	54.69 ± 14.14	18.55 ± 2.00	4.76 ± 1.05
	45 - 60	318.92 ± 10.00	138.72 ± 12.00	9.89 ± 0.00	46.97 ± 17.00	9.21 ± 1.40	2.11 ± 0.50
I	0 - 15	755.27 ± 8.90	165.76 ± 12.10	37.76 ± 0.90	94.41 ± 10.00	34.17 ± 1.20	9.41 ± 1.00
	15 - 30	575.12 ± 14.70	139.82 ± 10.00	27.56 ± 10.00	89.17 ± 13.70	21.88 ± 1.00	6.69 ± 0.75
	30 - 45	473.73 ± 18.20	86.34 ± 9.00	18.20 ± 5.00	71.41 ± 10.00	12.34 ± 2.00	4.14 ± 0.60
	45 - 60	364.64 ± 12.30	57.76 ± 8.40	12.40 ± 2.00	44.19 ± 5.00	8.12 ± 1.10	1.55 ± 0.50
J	0 - 15	796.64 ± 30.00	192.37 ± 12.80	39.85 ± 3.90	99.58 ± 0.00	23.90 ± 4.90	9.58 ± 1.50
	15 - 30	643.60 ± 32.40	121.89 ± 10.00	32.80 ± 2.80	95.23 ± 12.00	19.46 ± 3.40	7.30 ± 1.55
	30 - 45	467.96 ± 21.50	93.80 ± 10.20	19.60 ± 3.10	58.52 ± 11.00	11.60 ± 3.00	4.70 ± 1.00
	45 - 60	383.52 ± 14.00	63.34 ± 4.80	10.95 ± 2.00	23.99 ± 3.30	8.40 ± 2.10	2.13 ± 0.50
X	0 - 15	11.80 ± 1.40	4.49 ± 1.10	1.45 ± 0.00	15.58 ± 3.00	0.20 ± 0.00	0.02 ± 0.00
	15 - 30	6.60 ± 0.90	2.80 ± 0.90	0.75 ± 0.10	7.55 ± 0.00	0.14 ± 0.00	< 0.01
	30 - 45	4.20 ± 1.00	1.984 ± 0.30	0.44 ± 0.00	1.47 ± 0.00	0.06 ± 0.10	< 0.01
	45 - 60	1.00 ± 0.40	1.244 ± 0.30	0.15 ± 0.00	0.57 ± 0.00	< 0.04	< 0.01

The average top - soil value of 181.89 mg/Kg Mn obtained in this study was lower than the concentration recorded in Yauri (608.11 mg/Kg) for road side soils (Yahaya *et al.*, 2009). The value compared with similar studies from other countries is lower than that recorded in the United States (2532 mg/Kg), China (1740 mg/Kg), and Poland (1122 mg/Kg) (Dudka, 1992; Bradford *et al.*, 1996; Abida *et al.*, 2009). Manganese though an essential element, may be toxic at elevated concentrations. The toxic effect in humans is associated with severe psychiatric disorder resembling schizophrenia, followed by permanently crippling neurological disorder clinically similar to Parkinson's disease (Klaassen, 2001).

Lead in the soils has an average top - soil value of 39.18 mg/Kg. This value was higher than the critical soil Pb content for Canada (25 mg/Kg), Finland (38 mg/Kg), and Eastern Europe (32 mg/Kg); but lower than those of Denmark (40 mg/Kg), Czech Republic (70 mg/Kg), Netherland (85 mg/Kg), and Switzerland and Ireland (50 mg/Kg). The value was also lower than those obtained in Kaduna (76.92 mg/Kg), Iwo (126 mg/Kg), Makurdi (123 mg/Kg), and

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Owerri (1162 mg/Kg) (Okunola *et al.*, 2007; Ayodele and Dawodu, 2008; Nwachukwu *et al.*,2011; Pam *et al.*,2013). The upper limit of the range (30.78 - 50.82 mg/Kg) obtained here are much lower those of 70.80 - 192.03 mg/Kg, 11.75 - 2882.50 mg/Kg and 99.00 - 1090.00 mg/Kg Pb ranges recorded by Oguntimehin and Ipinmoroti (2008), Adelekan and Abegunde (2011), and Nwachukwu et al (2010) for Akure, Ibadan, and Okigwe respectively. Lead has no known physiological relevant role in body and its harmful effects are wide ranging (White *et al.*, 2007). Lead impaired mental and physical development, decrease heme biosynthesis, elevate hearing threshold and decrease serum levels of vitamin D (Needleman, 1990).

Table 4: The average metal content of soil samples at the different depths in Sapele automobile workshops

	Result ± SD					
Depths (cm)	**Zn (mg/kg)**	**Mn (mg/kg)**	**Pb (mg/kg)**	**Cu (mg/kg)**	**Cr (mg/kg)**	**Cd (mg/kg)**
0 - 15	764.55 ± 12.60	181.89 ± 11.30	39.18 ± 3.20	93.34 ± 10.96	50.40 ± 5.47	8.89 ± 1.24
15 - 30	603.58 ± 14.70	144.19 ± 9.09	32.07 ± 3.87	83.28 ± 12.01	39.49 ± 5.56	6.26 ± 1.04
30 - 45	490.55 ± 16.39	111.09 ± 7.90	22.77 ± 3.47	69.06 ± 14.93	22.26 ± 2.90	3.88 ± 0.67
45 - 60	340.40 ± 10.02	72.96 ± 6.45	12.57 ± 2.55	52.89 ± 11.04	11.31 ± 1.81	1.70 ± 0.25

The average top - soil value for Cu was higher than the critical soil total Cu content for the several countries. The value was also higher than the 24.60 mg/Kg Cu obtained for North Bank mechanic village in Makurdi by Pam *et al* (2013). It was however lower than the 1004 mg/KgCu recorded by Nwoko *et al* (2012) for soil in auto - mechanic village in Southeast region of Nigeria. The range (50.04 - 155.03 mg/kg Cu) obtained in this study is within the 40.72 - 151.43 mg/Kg and 1.48 - 476.00 mg/Kg obtained by Oguntimehin and Ipinmoroti (2008); Adelekan and Abegunde (2011), but was lower than the 102.00 - 1001.00 mg/Kg Cu recorded by Nwachukwu *et al* (2010). Copper, though an essential element may be harmful at high concentration. Copper effects on plants physiology are wide ranging, including interference with fatty acid and protein metabolism and inhibition of respiration and nitrogen fixation process. At the whole plant levels Cu is an effective inhibitor of vegetative growth and induces general symptom of senescence (Fernandez and Henrigues, 1991; Konstantinidis *et al.*, 2003). In mammals excessive dietary copper produces nausea, vomiting and diarrhoea as well as pathological changes in brain tissue (Pizzarro *et al.*, 1999). A spongy transformation of the white matter of the Midbrain and Cerebellum in lambs has long been reported (Doherty *et al*, 1969). Copper accumulates in livers, kidney, cornea, and brain. The accumulation in brain causes trauma, which lead to death (Davis *et al.*, 2000; Varela - Nallar *et al.*, 2006).

Chromium average top - soil value was 50.40 mg/Kg and was only higher than the critical soil total Cr content for Canada (20 mg/Kg) and Denmark (50 mg/Kg). The upper (87.10 mg/Kg) and least (20.20 mg/Kg) limits obtained in this study were both higher than the 20 mg/Kg critical soil total Cr content recommended in Canada. The range in this study was also higher than the 4.00 - 27.00 mg/Kg Cr obtained by Nwachukwu *et al* (2010) within and around mechanic villages in South - east Nigeria. Chromium though an essential element may be toxic at high levels. Chromium (VI) has been reported to exhibit mutagenic, carcinogenic and teratogenic effects (Cheng and Dixon, 1998; Asmatullah *et al*, 1998; Kaltreider *et al*, 1999; Soils - Heredia *et al.*, 2000).

The average Cd content for the top - soils was 8.89 mg/Kg. This value was higher than the critical soil total Cd for several countries (Table 5).This is an indication of pollution by cadmium in the soil. The value was much lower than the 43.00 mg/Kg Cd obtained by Nwoko *et al* (2012), but much higher than the 0.60 mg/Kg recorded by Pam *et al* (2013) for auto - mechanic villages in Makurdi. The range of value obtained (6.80 - 9.41 mg/Kg) is within the range (0.43 - 17.23 mg/kg) recorded by Adelekan and Abegunde (2011) in Ibadan. Shear off from metal plating, leachates from used oils and old tyres frequently burnt on these sites are likely source of cadmium (Kabata - Pendias, 1995; Rabie *et al.*, 1996). Cadmium has no constructive purpose in human body. Cadmium and its compounds are extremely toxic even in low concentration, and will bio - accumulate in organisms and ecosystem. Ingestion of any significant amount of Cadmium causes immediate poisoning and damage to the liver and the kidneys. Compounds containing cadmium are also carcinogenic (Kalonel, 1976; Kazantzis, 1979; Fasanya - Odewumi *et al.*, 1998; II'yasova, 2005; Sahmoun *et al.*, 2005). Ingestion of Cadmium in excess leads to a disease known as Itai - Itai, a disease resulting in soft bones, shrinking body and death (Ademoroti, 1996; Kazantzis, 2004).

Table 5: Critical soil total contents of heavy metals for several countries

Countries	**Critical limit (mg/kg)**				
	Zn	**Pb**	**Cu**	**Cr**	**Cd**
Canada	50	25	30	20	0.5
Denmark	100	40	30	50	0.3
Finland	90	38	32	80	0.3
Czech republic	150	70	70	130	0.4
Netherland	140	85	36	100	0.8
Switzerland	200	50	50	75	0.8
Ireland	150	50	50	100	1.0
Eastern Europe	100	32	55	90	0.2

(Eastern Europe include Russia, Ukraine, Moldova and Belarus)
Source: De Vries and Bakker, 1998

To explain the heavy metal profile on the locations, an appraising method by calculating the contamination/ pollution (C/P) index values for each metal in each location was calculated using the Canadian critical values for heavy metals in soil (Table 5). This index represents the metal content effectively measured in soil by chemical analysis and the critical values from a reference table (Lacatusu, 1998). Table 7 show the C/P indices distribution for different depths in all locations.

Unlike the pattern observed in Table 3, there is much difference between the concentration of metal in soil and the potential treat pose by them expressed though their c/p index value. Lacatusu (1998) established that the c/p value index is directly proportional to their level of contamination and pollution of specific metal species in each case. Higher value > 1 indicate higher risk while lower values < 1 connote minimal risk to the environment (Table 8).

Manganese (Mn) is not in the lists of standards critical soil total contents of heavy metals for several countries. Manganese, though an essential metals is toxic to a varying degree, depending upon the type of manganese ion and its oxidation state. Permanganates appear to be a highly toxic form of manganese because of their high solubility and powerful oxidizing action on the tissues (Bouchard et al., 2007).

Table 6: Range of total metal content (mg/kg) of top-soil samples in Sapele automobile workshops relative to other areas

Metal	Values of study area (Sapele)		Akure[a]	Ibadan[b]
Zn	Min.	400.01	391.57	-----
	Max.	1126.04	782.23	-----
Mn	Min.	131.08	----	-----
	Max.	262.22	----	-----
Pb	Min.	30.78	70.80	11.75
	Max.	50.82	192.03	2882.50
Cu	Min.	50.04	40.72	1.48
	Max.	155.03	151.43	476.00
Cr	Min.	20.20	21.50	5.50
	Max.	87.10	181.80	29.75
Cd	Min	6.80	-----	0.43
	Max.	9.41	-----	17.23

Source: a = Oguntimehin and Ipinmoroti (2008), b = Adelekan and Adegunde (2011)

Table 7: Heavy metal pollution profile in Sapele, calculated from total metal C/P index

Samples	Results (Depths, cm)				
	0 – 15	**15 – 30**	**30 - 45**	**45 - 60**	**Total**
A	38.35	29.95	19.18	7.93	95.41
B	34.22	23.58	17.41	10.38	85.59
C	41.08	36.43	26.85	15.64	120.00
D	43.88	31.69	22.46	16.80	114.83
E	46.87	33.66	25.60	15.75	121.88
F	38.19	30.61	22.71	14.54	106.05
G	40.69	28.43	19.58	9.96	98.66
H	37.98	27.14	21.71	13.02	99.85
I	40.29	30.05	21.48	12.77	104.59
J	41.20	32.93	22.07	13.59	109.79
X	0.86	0.42	0.15	0.05	1.48

Table 7 shows the profile of the heavy metals in the soils. To obtain a profile the total pollution ranges defined by multiple pollution found from contribution from each metal contamination/ pollution status were used. The observed trend for all samples shows that the top - soils are heavily loaded with heavy metals than the sub - soils. Location E had the highest total pollution by heavy metals with value of 121.88. The values for the other locations are A (95.41), B (85.59), C (120.00), D (114.83), F (106.05), G (98.66), H (99.85), I (104.59), and J (109.79). These values are much higher than the control value (1.48). The degree of metal pollution in the locations was in the order: Oleh Road > Reclamation/Green - Egbede Road > Awolowo/Okpe Road > Okerigwre Road > Akintola Road > Shell Road > Gana New Road > Ajogodo Road > Ogodo Road > McPherson Road Characterization based on the significance of intervals of contamination/pollution (C/P) index in Table 8, reveals that due to multiple pollutions, all the locations are severely polluted with respect to the five heavy metals.

Figure 2 shows the graph of c/p index versus depth for each metal calculated from the average concentrations of the metals using the Canadian critical values for heavy metals in soil. The soils were polluted at all depths with zinc, cadmium and copper. Depths 0 - 15 and 15 – 30 cm too were polluted with Cr; while only the topmost soils (0 – 15 cm) were polluted with lead. Generally, the metals contents decreases with increase in depths. The relative high concentrations found for most metals even at depth 45 – 60 cm signifies that heavy metals in these locations are not restricted to top - soil (0 – 15 cm), and that there are possibilities of leaching of these heavy metals to underground water and subsequent effects on public health.

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Table 8: Significance of intervals of contamination/pollution (C/P) index

C/P	Significance
<0.1	Very slight contamination
0.10-0.25	Slight contamination
0.26-0.50	Moderate contamination
0.51-0.75	Severe contamination
0.76-1.0	Very severe contamination
1.1-2.0	Slight pollution
2.1-4.0	Moderate pollution
4.1-8.0	Severe pollution
8.1-16.0	Very severe pollution
>16	Excessive pollution

Source: Lacatusu, 1998

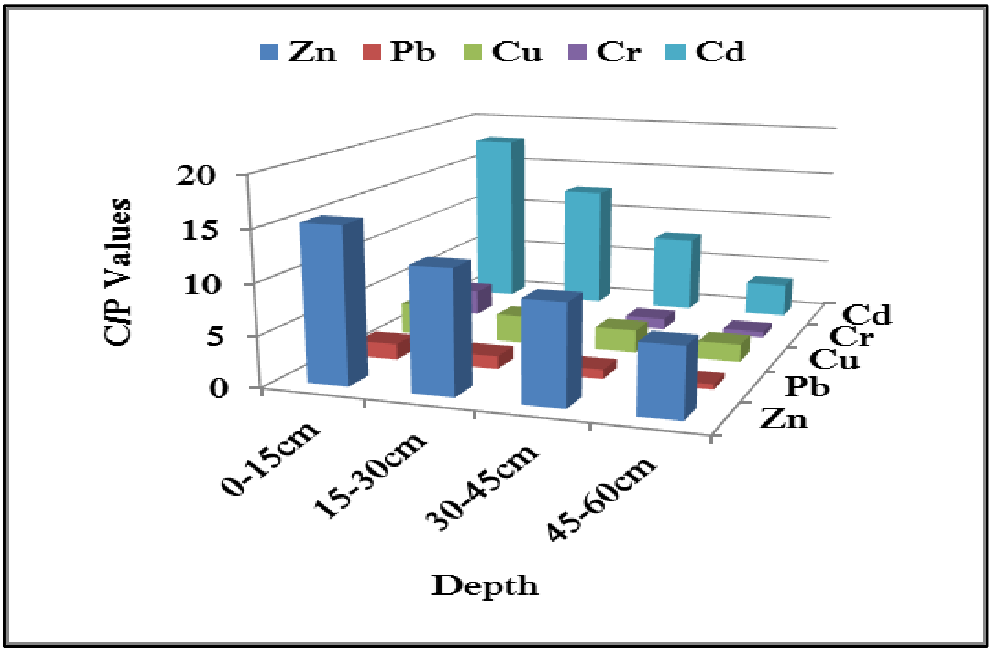

Figure 2: Plot of C/P versus depth for heavy metals

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 9 - 10). The total contents of metals were negatively correlated with soil depth. Very significant positive correlations were present between Zn/Pb, Zn/Cu, Mn/Cd, Pb/Cd, and Cr/Cd. Significant positive correlation were also observed for Zn/Cd, Mn/Pb, Mn/Cr, Pb/Cu, and Pb/Cr in soils samples. These positive correlations among metals tend to suggest same source. Insignificant positive correlations were found between Zn/Mn, Mn/Cu, Zn/Cr, Cu/Cr, and Cu/Cd. These insignificant positive correlations between metals indicate that the appearance of local high concentration for metal by possible contamination does not necessarily indicate high values for others metals. Slight correlations (except for few instances) between soil properties (clay, organic matter content, cation exchange capacity etc.) and the total concentration of metals were found.

Table 9: Correlation matrix showing the relationship between concentration levels of heavy metals in soil samples

	Zn	Mn	Pb	Cu	Cr	Cd
Zn	1.000	0.427	0.8147**	0.8374**	0.2419	0.5974*
Mn		1.000	0.5862*	0.1549	0.5674*	0.7605**
Pb			1.000	0.6264*	0.5626*	0.8144**
Cu				1.000	0.1161	0.3582
Cr					1.000	0.6729**
Cd						1.000

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

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Table 10: Coefficient of relations between heavy metal content (dependent variable) and soil depth, clay, silt, sand, organic matter and cation exchange capacity (independent variables) in soil samples.

	Zn	Mn	Pb	Cu	Cr	Cd
Soil depths (cm)	-0.7063**	-0.7249**	-0.8602**	-0.4956	-0.6803**	-0.9237**
Clay (%)	-0.7627**	0.4539	-0.5166	-0.4278	0.6996**	0.4979
Silt (%)	-0.6314*	0.1408	-0.1770	-0.4369	0.4391	0.5984
Sand (%)	0.7875**	-0.3541	0.4111	0.4820	-0.6540*	-0.6050*
pH	0.0260	0.0035	-0.4387	-0.1377	-0.6173	0.0834
Organic matter (%)	0.3969	-0.0003	0.5655	0.1523	-0.0396	0.0124
CEC	-0.4633	0.1794	-0.5522	-0.3423	0.3366	-0.0145

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

Conclusion

Type of contaminant, concentration and vertical distribution in soil are required inputs for development of predictive models, effective remediation and risk assessment. The concentration of heavy metals (Zn, Mn, Pb, Cu, Cr and Cd) found for soil in the vicinity of auto mechanic workshops were much higher than that from the control source. This is an indication that mechanic workshops situated within the metropolis are anthropogenic sources of heavy metals in soil. The concentrations of Zn, Cu, and Cd at most sites and depths were also higher than the recommended criteria values for several countries. Lead and Chromium have their top - soil (0 – 30 cm) values higher than most established criteria values but the sub - soil (30 – 60 cm) were within the stipulated values. The relative high concentrations found for most metals even at depth 45 – 60 cm, signifies that heavy metals in these sites are not restricted to top – soil (0 - 15 cm), and that there are possibilities of leaching of these heavy metals to underground water and subsequent effects on public health. Restriction should be imposed on auto - mobile workshops artisans to prevent them from dumping their waste indiscriminately and proper enlightenment carried out, to alert all stake - holders on the dangers inherent in indiscriminate dumping. Auto mobile workshops soil should be heavily cemented and proper drainage constructed to channel used oils, lubricants and spilled gasoline to a reservoirs where they can be properly treated or chemically re - processed to harness these heavy metals in them.

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