Bull. Chem. Soc. Ethiop. **2008**, 22(3), 339-348. Printed in Ethiopia

ISSN 1011-3924 © 2008 Chemical Society of Ethiopia

HEAVY METALS CONTAMINATION OF TOPSOIL AND DISPERSION IN THE VICINITIES OF RECLAIMED AUTO-REPAIR WORKSHOPS IN IWO, NIGERIA

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(Received September 20, 2007; revised July 26, 2008)

ABSTRACT. Growing concern about reclamation of auto-repair workshop areas for residential and agricultural purposes makes risk assessment of heavy metal contamination of the study area imperative. In addition, the study is aimed at ascertaining the dispersion of contaminated Zn, Ni, Cr, Hg, and Pb within the soil profile. A total of 75 soil samples from auto-repair workshops and 18 soil samples from control sites were collected. Significant levels of contamination were found in view of elevated levels of these metals above background concentrations in control sites. Average topsoil metal concentrations (0-10 cm) in auto-repair workshop areas were: Zn 0.90 \pm 0.5, Ni 11.5 \pm 3.3, Cr 5.3 \pm 2.3, Hg 9.4 \pm 4.6 and Pb 133 \pm 66 mg/kg. Lead was the most significant contamination was highest for Pb followed by Hg. The detailed levels of total metal contamination for Pb and Hg exceeded international thresholds for agricultural use. Enrichment factor within the soil profile metals were Zn 3.37, Ni 3.38, Cr 6.22, Hg 14.5 and Pb 21.1. The enrichment factor reflects the ratio of average concentration at a particular sampling location to average concentration at control sites. The general trend of dispersion of metal contaminants within the soil profile studied is Pb >> Ni > Hg > Cr >>Zn.

KEY WORDS: Auto-repair, Lead, Mercury, Soil, Heavy metals, Dispersion

INTRODUCTION

Heavy metal contamination of urban topsoil has been of major concern regarding their toxicity, persistence and non-degradability in the environment [1-3]. Adverse effects of elevated concentrations of heavy metals to soil functions, soil microbial community composition and microbial growth have long been recognized under both field and laboratory conditions [4]. Heavy metal contamination of urban topsoil usually derives from anthropogenic sources such as emissions from automobile exhaust, waste incineration, land disposal of wastes, use of agricultural inputs, emissions from industrial processes, and wet and/or dry atmospheric deposits [5, 6]. A large body of literature is available concerning automobile exhaust emissions as the major non-point source of lead in roadside dusts. Other metals such as zinc, cadmium, copper, chromium, nickel, barium, aluminium and manganese are also associated with automobile-related pollution. These are often used as minor additives to gasoline and various auto-lubricants, and are released during combustion and spillage [7, 8]. In 1990, Canada banned lead and added methyl cyclopentadienyl manganese tricarbonyl (MMT) to gasoline [9]. MMT is an organic derivative of manganese, which is added to gasoline as an antiknock agent and to improve octane rating [10]. Some of these metals are components of automobile parts such as tyres and engines, from which they are released during abrasion and wears.

There has been little attention given to vicinities of automobile-workshops, which are also liable to pollution arising from gasoline combustion exhausts, lubricating oil spills, and other chemical inputs to automobile operations. In Nigeria, pollution problems associated with incidents of oils spills around automobile-repair workshops, resulting in metal contamination of topsoil, have been the subject of many reports [5, 11, 12]. Auto repair workshops are facilities where automobiles are usually operated in semi-stationary or stationary modes. This tends to aggravate the direct deposition of exhaust emissions, and scrap batteries and solder. Auto-repair workshops in Iwo town are of interest in this study because of reclamation of land upon which

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these workshops were situated for residential purposes owing to a dramatic rise in the population. The emergence of Bowen University in Iwo is enough a reason for the increasing population. Most residents exclude some portion at the backyard for vegetation. Possibility may arise to dig a well in residential houses erected on such reclaimed auto-repair workshop land. Soil, being a complex porous material, retains and transports hazardous pollutants to ground water [13, 14]. This makes residents directly vulnerable to soil contaminants. Each of these workshops usually hosts a variety of artisans such as auto-electricians, battery servicemen, vulcanisers, and panel beaters. Scrap batteries and solder, waste engine oil, brake fluid and other fluid generated by their activities in the workshop are not properly disposed off. They are usually thrown away on the soil. Since the activity of artisans in auto-repair workshops in Iwo is one of the major routes for entry of heavy metals into the environment to cause contamination of soil and drinking wells and crops, monitoring the available pools of metals in contaminated soils becomes relevant. There has not been any information in the scientific literature on soil quality, especially heavy metal distribution in auto-repair workshop soils of the study area. This investigation was carried in order to clarify the spatial distribution of heavy metals and extent of contamination in the vicinities of auto-repair workshops in Iwo town. Iwo is one of the largest town in Southwestern Nigeria. It lies on latitude $7^{\circ}36 - 7^{\circ}40$ S and longitude $4^{\circ}5 - 4^{\circ}13$ W, and is about 300 meters above the sea level. The underlying geology of the area comprise of migmatite, augen gneiss, pegmatite and quartzite.

The objectives of this study were as follows: (i) to establish the spatial variability in concentrations of Zn, Ni, Cr, Hg and Pb for topsoil's in some auto-repair workshops, where high levels of these metals were suspected on the basis of activities in the areas, (ii) to assess the level and extent of contamination by comparison with international soil standards and to identify any need for regular monitoring and/or remediation, and (iii) to investigate the dispersion of the metal concentrations with increasing soil depth.

EXPERIMENTAL

Description of sampling sites

Soil samples from five different auto-repair workshops and two control sites were collected in Iwo town in September 2006. A total of 75 soil samples from the auto workshops and 18 samples from control sites were collected. The sampling locations are traversed by major road. The auto-repair workshops were located around the following areas: (i) Iwo Grammar School (IWGS), (ii) Odori market (ODO), (iii) Saint Anthony Primary School (SAS), (iv) Hospital road (HPS), and (v) Fawibe street (FWS).

The common feasible features in all of these workshops include paint, engine oil, scrap batteries, refuse dumps, few scrap metals and solders, automobile exhaust and some vegetable. The control sites considered were free from auto-repair workshops and automobile exhaust.

Sampling design

Soil sampling survey was carried out between September 2006. The surrounding in each of the auto-repair workshop was divided into five radial transects to investigate the variation of heavy metal concentration at the site. The directions of those transects are as follows: North-west direction, South-west direction, North-east direction, South-east direction.

The total number of samples collected from the vicinity of each auto-workshop was fifteen. Five samples were taken from the top 0-15 cm of the soil. The topsoil represented as T was scooped with the hand towel at a location along each transect. The ground at each location along each transect was dug with a digger to a depth of 20-30 cm and 35-40 cm, respectively. Five

samples from depths 20-30 cm and 35-40 cm, respectively, were also taken at each sampling location to investigate the variation of the metal concentrations with increasing soil depth. Soil samples from two reserved locations, in Iwo town, which were free from auto-repair and related work were collected.

Soil analysis

The air-dried soil was ground and passed through a 2 mm sieve for soil analysis. Soil pH was determined with 1:1 soil/water suspension using a pH meter. The organic carbon content was determined by oxidation with potassium dichromate in the presence of concentrated sulfuric acid. The oxidation process was subsequently followed by titration with ammonium sulfate of the excess of dichromate [15]. Soil moisture content was determined by gravimetric method involving drying in an oven at 105 °C for 24 hours [16]. Particle size analysis was determined using the hydrometer method as described by Gee and Bauder [17]. The dry samples were digested with HNO₃-HCl according to US EPA method 3050B to extract the metals [18]. The digests were made up to volume with de-ionized water. The concentrations of Zn, Ni, Cr and Pb were measured by a Perkin Elmer 5000 flame atomic absorption spectrophotometer (AAS). The Hg concentration was measured using an AAS coupled to cold vapour module, UNICAM VP 90.

Data quality

For quality control, analytical blanks were prepared in the same way as the sample to check for the existence of contamination during digestion and analytical procedures. The accuracy and precision of the analytical procedure were checked by recovery study on the sample with appropriate standard solutions. Recovery ratios of heavy metals were 91.5-102 %. Attempts were also made to compare data from auto-repair workshop and control sites soils to established cause-effects relationship. Control sites soils from the same study area but free from auto-repair and related work were prepared in the same way as the samples and subjected to the same analytical procedures.

Data analysis

Means and standard deviations reported in Tables and Figures were calculated from five sampling replicates for each study site. For each parameter the significance of difference between soils from study sites and control sites was evaluated by one-way ANOVA (p < 0.01, n = 5). The enrichment factor (accumulation factor) [19, 20] was calculated to determine the degree of contamination of soil for each sampling site. Using the data obtained in the analysis, the factors of accumulation of heavy metals were calculated as ratio of average concentration at a given location to average concentration at control sites.

RESULTS AND DISCUSSION

The composition of soil and heavy metal levels in auto-repair workshop at Iwo Grammar School (IWGS)

The soil pH varied from 6.1 to 7.4 on the average. Soil pH of the top soil (7.0 \pm 0.3) dropped with depths by 0.5 unit as soil depth increased up to 30 cm (Table 1). The average composition of total organic carbon increased from 2.0 \pm 1.5 % in the top soil to 3.42 \pm 0.83 % in deep soil D2 (25-30 cm). The total organic matter showed average values ranging from 3.5 \pm 2.5 % in the

top soil T (0-10 cm) to $5.9 \pm 1.4 \%$ in the deep soil D2 (25-30 cm) (Table 1). On the average, moisture contents of $4.0 \pm 2.1 \%$, $5.3 \pm 1.8 \%$ and $8.8 \pm 1.6 \%$ were obtained in the top soil T, deep soil D1 and D2, respectively. The mechanical analysis of soil samples indicated that sand and silt contents, on an average, ranged from $41 \pm 20 \%$ to $3 \pm 21 \%$ and $24 \pm 25 \%$ to $51 \pm 17 \%$, respectively. Table 1 revealed that lead has the highest average concentration in the topsoil followed by nickel, mercury, chromium and zinc, respectively. The average concentrations of Zn, Ni Cr, Hg and Pb decreased markedly with depths up to 30 cm (Table 1).

Table 1. Heavy metal concentrations, ranges (mg/kg) and characteristics of top (T) and deep soil samples (D) from auto-repair workshop at Iwo Grammar School (IWGS).

Depth (cm)	[*] T (0-10)	Ranges	*D1 (15-20)	Ranges	*D2 (25-30)	Ranges
pH	7.0±0.3	6.5-7.2	6.8±0.4	6.5-7.4	6.5±0.3	6.1-6.9
Moisture (%)	4.0±2.1	1.5-7.2	5.3±1.8	2.7-7.0	8.8±1.6	7.0-10.9
Sand (%)	63±21	32.4-88.4	66±25	24.4-88.4	41±20	9.6-56.4
Clay (%)	8.8±7.2	4.0-20.0	10.4±6.7	4.0-20.0	8.8±4.4	4.0-12.0
Silt (%)	29±23	7.6-64.6	24±25	7.6-63.3	51±17	39.6-78.4
TOC (%)	2.0±1.5	0.45-3.82	2.4±1.2	0.88-3.82	3.42±0.83	1.94-3.88
TOM (%)	3.5±2.5	0.78-6.58	4.1±2.1	1.52-6.70	5.9±1.4	3.35-6.70
Zn	1.74±0.27	1.35-2.05	1.03±0.41	0.85-1.55	0.69±0.28	< 0.01-1.01
Ni	13.7±3.6	8.50-17.5	9.5±2.3	6.85-12.5	6.6±2.3	4.50-12.0
Cr	6.6±4.2	1.20-13.4	9.5±2.3	2.15-9.15	6.6±2.3	1.05-6.20
Hg	7.9±4.5	3.61-14.3	4.3±3.4	1.52-9.52	3.5±2.9	< 0.01-7.72
Pb	175±77	106-298	123±80	62.4-253	91±88	28.0-237

Average value (*), total organic carbon (TOC) and total organic matter (TOM).

The composition of soil and heavy metal levels in auto-repair workshop at Odo-Ori (ODO)

Table 2 shows that soil pH ranges from 6.2 to 6.8 in the top soil T and 6.2 to 6.9 in the deep soil D2. The average total organic carbon of 0.44 ± 0.17 % in the top soil increased with depths to 2.4 ± 1.7 %. The total organic matter showed a value ranging from 0.53 % to 1.16 % in the top soil T and 1.09 % to 6.72 % in the deep soil D2. The average moisture content of the soil increased with depths, ranging from 2.9 ± 2.0 % in the top soil T (0-10 cm) to 7.8 ± 6.0 in the deep soil D2 (25-30 cm). On an average, the top soil samples consisted of 10.5 ± 1.0 % of clay, 54 ± 35 % of sand and 35 ± 34 % of clay. The corresponding compositions in the deep soil D2 (25-30 cm) are 7.5 ± 4.1 %, 59 ± 31 % and 33 ± 31 %, respectively. Average metal concentrations of Zn, Ni Cr, Hg and Pb were 0.55 ± 0.15 mg/kg, 9.44 ± 0.88 mg/kg, 5.4 ± 2.1 mg/kg and 157 ± 56 mg/kg, respectively. Relative abundance patterns of the metals in the topsoil and deep soil D1 (15-20 cm) were in the order Pb >> Ni > Hg > Cr >> Zn.

The composition of soil and heavy meal levels in auto-repair workshop at Hospital road (HPS)

The pH ranged from 6.1 to 6.6 in the top soil T (0-10 cm) and 6.2 to 6.8 at 25-30 cm depth. The average moisture composition varied from 3.0 ± 1.8 % at 0-10 cm depth to 8.0 ± 1.3 % at 25-30 cm depth (Table 3). On an average, organic carbon content in the top soil was 1.27 ± 0.84 %. This level increased with depth up to 30 cm. The grain size distribution of soil at the top revealed about 42 ± 32 % of sand, 10.4 ± 3.6 % of clay and 25.2 ± 6.7 % of silt. Lead has the highest concentrations ranging from 110 mg/kg to 172 mg/kg in the top soil and 58.1 mg/kg to 120 mg/kg in the deep soil D2 (25-30 cm). The average concentrations of Pb and other metals (Zn, Ni, Cr, Hg, Pb) decreased with depth. However, a slight rize in average zinc concentration of 0.60 ± 0.42 mg/kg at 15–20 cm depth to 0.63 ± 0.36 mg/kg at 25-30 cm depth (Table 3).

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Depth (cm)	*T (0-10)	Ranges	*D1 (15-20)	Ranges	*D2 (25-30)	Ranges
pН	6.6±0.3	6.2-6.8	6.8±0.4	6.4-7.2	6.7±0.3	6.2-6.9
Moisture (%)	2.9±2.0	1.0-5.2	4.6±2.5	2.7-8.0	7.8±6.0	1.5-16.0
Sand (%)	54±35	24.4-84.4	72±23	40.4-88.4	59±31	24.4-88.4
Clay (%)	10.5±1.0	10.0-12.0	6.0±4.0	4.0-12.0	7.5±4.1	4.0-12.0
Silt (%)	35±34	5.6-65.6	22±23	7.6-55.6	33±31	5.6-55.6
TOC (%)	0.44±0.17	0.31-0.67	1.3±1.5	0.35-3.59	2.4±1.7	0.63-3.90
TOM (%)	0.76±0.30	0.53-1.16	2.3±2.6	0.60-6.19	4.1±2.9	1.09-6.72
Zn	0.55±0.15	0.40-0.75	0.31±0.06	0.25-0.40	0.20±0.13	0.05-0.35
Ni	9.44±0.88	8.50-10.5	8.31±0.24	8.00-8.50	7.14±0.49	6.50-7.55
Cr	5.4±2.1	3.40-7.50	3.6±1.4	2.35-5.25	2.59±0.69	2.05-3.50
Hg	7.4±2.1	4.65-12.1	4.6±2.1	3.55-7.50	2.42±0.93	1.34-3.61
Pb	157±56	97.6-217	112±63	30.2-184	91±34	<0.04-126

Table 2. Heavy metal concentrations, ranges (mg/kg) and characteristics of top (T) and deep soil samples (D) from auto-repair workshop at Odori (ODO).

Average value (*), total organic carbon (TOC) and total organic matter (TOM).

Table 3. Heavy metal concentrations, ranges (mg/kg) and characteristics of top (T) and deep soil samples (D) from auto-repair workshop at Hospital road (HPS).

Depth (cm)	[*] T (0-10)	Ranges	*D1 (15-20)	Ranges	*D2 (25-30)	Ranges
PH	6.4±0.2	6.1-6.6	6.7±0.4	6.2-7.1	6.6±0.2	6.2-6.8
Moisture (%)	3.0±1.8	1.5-5.6	4.7±2.2	2.0-8.1	8.0±1.3	7.0-9.8
Sand (%)	42±32	8.4-80.4	42±35	1.4-80.4	48±20	16.4-64.4
Clay (%)	10.4±3.6	4.0-12.0	8.8±4.4	4.0-12.0	5.6±3.6	4.0-12.0
Silt (%)	25.2±6.7	15.6-31.6	46±31	15.6-79.6	46±22	23.6-79.6
TOC (%)	1.27±0.84	0.08-2.08	2.5±1.4	0.20-3.57	3.1±1.5	0.36-3.87
TOM (%)	2.2±1.4	0.14-3.59	4.2±2.4	0.34-6.15	5.4±2.6	0.62-6.68
Zn	0.91±0.58	0.25-1.85	0.60±0.42	0.10-1.25	0.63±0.36	<0.05-1.10
Ni	12.1±2.4	9.25-15.5	8.4±1.9	6.50-11.5	7.0±3.1	4.50-7.05
Cr	4.99±0.74	4.05-6.05	3.46±0.64	2.35-3.95	3.18±0.79	2.05-3.65
Hg	12.6±7.2	8.74-25.5	8.86±3.6	6.24-15.0	6.5±2.0	3.28-10.2
Pb	132±24	110-172	103±30	77.0-153	80±33	54.1-120

Average value (*), total organic carbon (TOC) and total organic matter (TOM).

The composition of soil and heavy metal levels in auto-repair workshops at St Anthony (SAS)

The pH of the topsoil samples ranged from 6.3 to 7.2. The average pH values in the topsoil and deep soil were about the same values (Table 4). The percentage moisture composition varied from 0.5 % to 3.9 % at 0-10 cm depth, and 1.5 % to 15.0 % at 25-30 cm depth. The moisture content increased with depth up to 30 cm depth (Table 4). The topsoil consisted of 45 ± 39 % of sand, 5.8 ± 4.0 % of clay and 49 ± 38 % of silt. The proportion of distribution of particle sizes in deep soil D2 (15-20 cm) followed similar order silt > sand >> clay as in the topsoil. T (0-10 cm). The total organic carbon levels varied from 1.41 % to 3.25 % at 0-10 cm depth and 3.05 % to 3.90 % at 25-30 cm depth. Lead was quite high in concentrations at 0-10 cm depth. The average lead concentration at this depth was 104 ± 58 mg/kg. It decreased with depth to reflect concentration of 72 ± 21 mg/kg at 25-30 cm depth. The distribution patterns of other metals (Zn, Ni, Cr and Hg) were similar to that of Pb (Table 4). The relative abundance of the metals in both topsoil and deepsoil was Pb >> Ni > Hg >> Cr >> Zn.

The composition of soil and heavy metal levels in auto-repair workshop along Fawibe Street (FWS)

The average pH values of the top soil and deep soil at 0-10 cm, 15-20 cm and 25-30 cm were 5.8 \pm 0.4, 6.2 \pm 0.3 and 5.8 \pm 0.4, respectively (Table 5). The average percentage moisture increased with depth from 4.4 \pm 2.5 % at 0-10 cm depth to 10.9 \pm 8.6 at 25-30 cm depth. The size distribution of particles in soil revealed 43.6 \pm 7.1 % of sand, 83.0 \pm 4.4 % of clay and 68 \pm 18 % of sand as the dominant minerals at 0-10 cm, 15-20 cm and 25-30 cm depths, respectively. The average total organic carbon level of the soil increased with depth from 2.58 \pm 0.99 % at 0-10 cm to 3.6 \pm 0.6 % at 25-30 cm (Table 5). Table 5 shows that lead has the highest average concentration of 105 \pm 88 mg/kg in topsoil. However this level decreased with depth such that lead concentration of 60 \pm 41 mg/kg was obtained at 25-30 cm depth. The relative abundance of the metals in both topsoil and deep soil up to 25-30 cm was Pb >> Hg > Ni > Cr > Zn (Table 5).

Table 4. Heavy metal concentrations, ranges (mg/kg) and characteristics of top (T) and deep soil samples (D) from auto-repair workshop at St. Anthony Primary School (SAS).

Depth (cm)	[*] T (0-10)	Ranges	*D1 (15-20)	Ranges	*D2 (25-30)	Ranges
рН	6.6±0.4	6.3-7.2	6.6±0.2	6.4-6.8	6.7±0.1	6.6-6.8
Moisture (%)	2.0±1.2	0.5-3.9	2.6±1.8	0.5-5.2	7.2±5.1	1.5-15.0
Sand (%)	45±39	16.4-88.4	41±33	8.4-88.4	59±26	32.4-88.4
Clay (%)	5.8±4.0	4.0-13.0	11.0±8.3	4.0-24.0	5.6±3.6	4.0-12.0
Silt (%)	49±38	7.6-79.6	47±34	7.6-79.6	35±29	7.6-63.6
TOC (%)	2.54±0.82	1.41-3.25	3.1±0.7	2.29-3.67	3.68±0.36	3.05-3.90
TOM (%)	4.4±1.4	2.43-5.60	5.3±1.3	3.65-6.33	6.35±0.61	5.27-6.70
Zn	0.67±0.12	0.55-0.85	0.45±0.09	0.35-0.60	0.26±0.15	0.15-0.50
Ni	13.4±4.1	9.00-17.5	11.4±4.1	7.00-15.5	8.0±2.6	5.25-11.5
Cr	5.8±1.9	3.55-8.10	4.54±1.8	2.95-7.20	3.0±1.5	1.50-5.50
Hg	10.3±3.4	6.85-15.2	6.70±2.5	3.93-9.52	4.6±1.7	3.05-7.20
Pb	104±58	12.0-168	75±43	5.25-121	72±21	<0.04-101

Average value (*), total organic carbon (TOC) and total organic matter (TOM).

Table 5. Heavy metal concentrations, ranges (mg/kg) and characteristics of top (T) and deep soil samples (D) from auto-repair workshop along Fawibe Street (FWS).

Depth (cm)	[*] T (0-10)	Ranges	*D1 (15-20)	Ranges	*D2 (25-30)	Ranges
pH	5.8±0.4	5.2-6.2	6.2±0.3	5.7-6.6	5.8±0.4	5.5-6.4
Moisture (%)	4.4±2.5	2.4-8.4	6.2±3.8	2.8-12.0	10.9±8.6	2.8-22.0
Sand (%)	43.6±7.1	40.4-56.4	48±21	24.4-80.4	68±18	40.4-88.4
Clay (%)	8.8±4.4	4.0-12.0	8.3±4.4	4.0-12.0	8.8±4.4	4.0-12.0
Silt (%)	47.6±9.8	31.6-55.6	43±22	7.6-63.6	24±16	7.1-47.6
TOC (%)	2.58±0.99	1.04-3.72	3.1±1.0	1.30-3.88	3.6±0.6	2.51-3.92
TOM (%)	4.4±1.7	1.79-6.41	5.4±1.8	2.25-5.97	6.1±1.0	4.33-6.75
Zn	0.54±0.51	0.05-1.42	0.46±0.43	< 0.01-1.10	0.14±0.09	< 0.01-0.15
Ni	8.4±1.4	6.50-10.5	5.4±1.2	4.01-7.25	2.7±1.2	0.95-4.05
Cr	3.71±0.12	3.50-3.80	2.3±0.55	1.80-3.20	1.43±0.35	0.85-2.50
Hg	8.5±2.3	6.41-11.8	5.9±2.8	3.41-9.74	3.8±1.9	2.26-6.26
Pb	105±88	18.7-254	84±67	14.9	60±41	9.25-115

Average value (*), total organic carbon (TOC) and total organic matter (TOM).

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Soils from the auto-repair workshops in Iwo town are coarse to moderately coarse in texture. This is deduced from high percentage sand and silt contents of the soil traceable to the geological formation of the area. The basement rocks underlying Iwo town are notably migmitite, quartizite, augen gneiss, charnockite and pegmatite. The auto-repair workshop soils, with neutral pH values, have more organic carbon. Soil organic matter within the organic surface layer is an important factor influencing metal concentration in the surface soils. Mechanisms for the release of metals from the surface layer include: (i) mineral chemical weathering via acid attack [21]; (ii) direct oxidation of the sulfides present, releasing bound metals; and (iii) reductive dissolution of iron minerals due to flooding which releases trace metals that were associated with the iron oxides possibly present.

Sampling site code									
	Bowen (Control 1)			Water works (Control 2)					
Depth (cm)	T (0-10)	D1 (15-20)	D2 (25-30)	T (0-10)	D1 (15-20)	D2 (25-30)			
pН	6.4±0.1	6.1±0.1	6.4±0.2	7.2±0.5	7.6±0.4	7.4±0.5			
Moisture (%)	6.2±1.5	7.4±1.3	13.6±2.5	8.7±1.5	11.2±5.1	12.9±4.2			
Sand (%)	54±10	42±18	60±13	42±18	59±21	54±13			
Clay (%)	6.0±2.6	8.8±3.9	5.6±1.2	7.5±2.8	5.8±1.5	5.8±1.0			
Silt (%)	40.0±17	49.2±0.8	34.4±4.7	50.5±1.2	35.2±1.5	40.2±5.6			
TOC (%)	3.87±0.45	4.52±0.36	4.31±0.40	3.28±0.27	4.28±0.51	5.62±0.32			
TOM (%)	6.67±0.52	7.79±0.30	7.43±0.31	5.65±0.56	7.38±0.31	9.69±0.50			
Zn	0.08±0.01	0.06±0.05	< 0.05	0.21±0.03	0.15±0.02	0.12±0.02			
Ni	6.24±0.25	4.11±0.14	4.90±0.25	0.17±0.11	0.13±0.08	0,10±0.04			
Cr	0.76±0.35	0.52±0.07	0.05±0.15	1.05±0.08	0.56±0.05	0.74±0.03			
Hg	1.52±0.64	0.25±0.08	0.56±0.05	0.89±0.05	0.25±0.05	0.10±0.07			
Pb	8.24±0.25	10.4±1.3	< 0.04	15.0±2.1	5.74±0.34	2.04±0.15			

Table 6. Average heavy metal concentrations (mg/kg) and characteristics of soil samples from control sites in Iwo town.

Heavy metals in auto-repair workshop soils are not significantly derived from the natural geology of the area as are evident from the low level of metals in control samples (Table 6). One of the major components of element in soil is the aluminosilicate material. If there were no anthropogenic sources, concentrations of elements should have been explained by this source. However, composition of soil is modified from various man-made sources. The degree of the modification in the chemical composition of soil may be different at each sampling point due to different magnitude of source contribution. Hence enrichment factor, which is sometimes referred to accumulation factor, becomes relevant. The factor reflects the ratio of the elemental composition of supposed contaminated soil to the corresponding composition in reference or control soil sample. The factors of enrichment of Zn, Ni, Cr, Hg and Pb in auto-repair workshop soils were above unity (EF > 1) (Table 7). This revealed that average levels of all the metals in auto-repair workshop soils were generally higher than the prevailing background levels in control sites. Metals can be divided into three major groups with respect to their corresponding median enrichment factors. These are metals without accumulation (EF < 10), metals with medium-level accumulation (10 < EF < 100) and finally highly accumulated (EF > 100) [19, 20]. In this study, Zn, Ni and Cr have accumulation factors less than 10, thus fall in the group of metals without accumulation in the study areas. Only Hg and Pb are in the group 'median accumulation' (10 < EF < 100).

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Therefore it indicates significant level of pollution of reclaimed auto-repair workshop soils with Hg and Pb. The high concentration of Pb obtained in this study compared well to other metal concentrations from other city (Table 8), and is indicative of Pb being one of the major pollutants in the auto-workshop soils. The comparatively high Pb levels in auto-repair workshop soils may be due to fall-out of lead from batteries or lead accumulators, which are commonly used and abandoned in the workshops. The proximity of the workshop areas to a major road would have contributed to the Pb level accumulated in the soils. This is because lead is derived mostly from exhausts of vehicles, which in Nigeria is still used as minor additives to gasoline and various auto-lubricants. It is estimated that about 2800 metric tones of vehicular gaseous lead emission is deposited to urban areas in Nigeria annually.

Sampling site code	Depth (cm)	Zn	Ni	Cr	Hg	Pb
IWGS	T (0-10)	3.3	4.3	7.3	6.5	15.1
	D1 (15-20)	9.4	4.5	7.0	17.2	15.2
	D2 (25-30)	5.8	2.6	5.8	10.6	44.6
ODO	T (0-10)	1.0	2.9	5.9	6.1	13.5
	D1 (15-20)	2.8	3.9	6.7	18.4	13.9
	D2 (25-30)	1.7	2.9	6.5	1.36	45.5
HPS	T (0-10)	1.7	3.8	5.5	10.4	14.4
	D1 (15-20)	5.5	4.0	6.3	35.4	12.8
	D2 (25-30)	5.3	2.8	8.0	19.7	39.2
SAS	T (0-10)	1.3	4.2	6.4	8.5	9.0
	D1 (15-20)	4.1	5.4	8.4	26.8	9.3
	D2 (25-30)	2.2	3.2	7.5	13.9	35.3
FWS	T (0-10)	1.1	2.6	4.1	7.0	9.1
	D1 (15-20)	4.2	2.5	4.3	23.6	10.4
	D2 (25-30)	1.2	1.1	3.6	11.5	29.4
*						

Table 7. Enrichment factors (*EF) of heavy metals in top and deep soil.

^{*} Ratio of average concentration at a given location to concentration at control site.

Table 8. Comparison of metal levels (mg/kg) in this study with levels obtained from other cities and soil criteria for some countries.

	Zn	Ni	Cr	Hg	Pb	Ref.
Iwo town, Nigeria (this study)	0.90±0.57	11.5±3.3	5.3±2.3	9.4±4.6	133±66	-
Ibadan city, Nigeria	48±37	10.5±9.7	22.1±9.6	-	81±140	[5]
Netherlands (action levels)	720	210	380	-	530	[6]
Chinese soil	< 3-790	35	< 100	0.04	13-42	[6]
CCME (Agricultural use)	200	50	64	6.6	70	[29]
CCME (Residential use)	200	50	64	6.6	140	[29]
CCME (Commercial use)	360	50	87	24	260	[29]
CCME (Industrial use)	360	50	87	50	600	[29]

Metals in soils of the auto-repair workshop are not all retained within the profile depth of 0-15 cm. Average concentrations of Zn, Ni, Cr, Hg and Pb obtained from this study generally decreased vertically with soil depth. This illustrates the mobility potential of heavy metals down the soil profile. The reduction in metal concentrations with soil depth indicates the presence of bioavailable phases of the metals (exchangeable, carbonate-bound, reducible and oxidizable). Changes in soil electrode potentials and soil redox reactions will influence the release and retention of elements in all these phases [22, 23]. These soil chemical properties may be attributed to the readily percolation, mobilization and dispersion of elements in all these phases

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down the soil profile. The general trend in the dispersion pattern of metals in the soils of autorepair workshops is Pb >> Ni > Hg > Cr >> Zn.

Pb was a major contaminant at all sampling sites with a mean accumulation factor of 21.2. Improper disposal of waste lubricants and auto-exhaust emission are likely source of high Pb contamination. There is possibility of lead, being carcinogen, leaching into the soil to contaminate water from wells not too far from the sampling site. This indicates the need for further investigation and an assessment of the suitability of the auto-workshop lands for agricultural use. Lead together with other heavy metals such as zinc, cadmium, copper, manganese and nickel, which are often contained as additives, in some of the lubricants and gasoline, are non-degradable in the soil. Chromium is classified as priority pollutants by United States Environmental Protection Agency (USEPA) with a carcinogenicity classification A (human carcinogen), while lead is classified in the same list with a carcinogenicity B (probable human carcinogen) [24]. Heavy metals of this kind are not without detrimental effects on the environment. Crops raised on the metal-contaminated soils accumulate metals in quantities excessive enough to cause clinical problems both to animals and human beings consuming those metal rich plants [25, 26]. Thus, accumulation of heavy metals in the soil has potential to restrict the soil's function, causing toxicity to plants and contaminate the food chain. In recent years, it has been investigated that heavy metals from point and non-point sources impair water system including drinking wells, causing lesions [27]. Possibility exits for lateral migration of heavy metals towards drinking wells dug in these reclaimed auto-repair workshop areas. Filtration and settling of heavy metals via soil into such well exposes residents of such areas to unsafe water for drinking and domestic use. Exposure of residents of these areas to high concentrations of metals such as Pb can lead to numerous health problems, especially in neurological, respiratory and excretory (gastrointestinal absorption) systems [28]. There were significant correlation (p < 0.01) for all pairs of Hg/Cr, Ni/Cr, Ni/Hg, Pb/Cr, Pb/Hg, Pb/Ni, Zn/Cr, Zn/Ni and Zn/Pb. This implies that these metals in the soils of auto-repair workshops are all contributes from automobile sources such as lubricants and auto-exhaust emission. Average concentrations in topsoils obtained from this study are evaluated for their risk significance by comparison with some quality guidelines specified for the protection of human health. Since no soil quality guideline is available for Nigeria, those of Canada and the Netherlands were used for assessment (Table 8). The levels of Pb and Hg in top soils from this study exceed the Canadian 7.0 mg/kg and 6.6 mg/kg guides, respectively, for agricultural use. Given that locations of the auto-repair workshops are easily accessible for plant or crop production, it is significant that a number of the sampling points have Pb and Hg levels which exceed the Canadian limits for agricultural use. The overall level of contamination of auto-workshop soils in Iwo with Pb and Hg cannot thus produce foods that are adequate for animals or human beings in terms of health and nutrition, particularly in view of increasing degree of contamination within soil profile. Therefore, close monitoring and some remedial actions such as remediation of auto-workshop soils contaminated mostly with Pb and Hg are required. Average levels of Zn, Ni and Cr in topsoils of auto-repair workshops at all locations are generally lower than the respective soil guidelines for these metals.

In conclusion, soils in the vicinities of reclaimed auto-repair workshops were noted to be significantly contaminated with Pb and Hg. The disposal of waste lubricant oil and auto-exhaust emission are suspected to be a significant source of meal contamination of topsoil in these workshops. Metals concentrations were generally found to decrease substantially with increasing soil depth, underscoring the fact that metals in contaminated soils are not all retained in topsoil of 0-15 cm. The study reported here provides data as information in the literature, since there is lack of previous findings on soil quality of this study area. The finding suggests the need for closer examination of speciation studies to quantify the proportion of the bio-available phases of the metals.

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