



Chemical Fractionation of Heavy Metals in the Soil of Auto-Mechanic Workshops in Akure, Ondo State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AS, AMP and OOA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AS, AMP and EOA managed the analyses of the study. Authors AS, AMP and MTO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Total metal concentrations and sequential extraction scheme were employed to investigate the potential environmental risk of seven important metals in the soil of selected auto-mechanic workshops in Akure metropolis, Ondo State, Nigeria. Soil physicochemical parameters were also determined with the following results: pH ranged from 5.50-6.32, total organic carbon from 0.96-1.56%, particle size indicates the soil to be mainly sandy, Cation Exchange Capacity (CEC) ranged from 7.00-9.00 Cmol/Kg. The concentrations (mg/kg) for the seven metals in Ilesha-Garage soil samples were 4.25±1.06 (Cd), 17.00±0.00 (Cr), 20.75±0.35 (Cu), 4750.00±0.00 (Fe), 4.00±0.70 (Ni), 40.50±0.70 (Pb), 40.75±0.35 (Zn) while the mean concentrations of metals (mg/kg) in Oyemekun soil samples were 7.50±0.00 (Cd), 22.00±0.70 (Cr), 33.25±0.35 (Cu), 6475.00±0.35 (Fe), 5.00±0.01 (Ni), 60.00±0.00 (Pb) and 48.50±0.70 (Zn) respectively. Cadmium content in the soil

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samples exceeded the target values of the Department for Petroleum Resources (DPR) regulatory Standards for soil. Sequential extraction by fractionation reveals that the average percentage concentration of Cd, Cr, Ni, Pb and Fe were more prevalent in residual fractions, while Zn and Cu were found more in Iron-Manganese Oxides, carbonate in addition to residual fractions. The heavy metals speciation of the soil samples indicates that the heavy metals were predominately found in both the residual and non-residual fractions suggestive of control by geogenic and anthropogenic sources respectively. Eco-toxicological assessment of the soil samples using the mobility factor indices revealed the following sequence: Lead (31.11%) > zinc (21.11%) > Nickel (20.75%) > Copper (12.24%) > Chromium (10.73%) > Cadmium (0.80%) > Iron (0.09%). The pollution index assessment indicates that most of the metals fall within the "slight contamination" and "moderate contamination" range in the soil.

Keywords: Heavy metals; auto-mechanic; sequential extraction; pollution index; eco-toxicology.

1. INTRODUCTION

The use of metals in human history has yielded great benefit as well as unexpected harmful consequences from those classified as heavy metals. Heavy metals refer to metal elements with a specific gravity that is at least five times the specific gravity of water [1]. Although metals constitute the majority of elements, in general, they represent a small atomic and mass fractional abundance of the element comprising the earth's surface and atmosphere relative to the non-metals [2]. The impact of pollution from automobile wastes has reportedly reached a disturbing level. Environmental contaminants are widely distributed in soils, thereby having an effect on the trophic chain, plants, animals and humans [1]. Trace metals are naturally present in the biological world in acceptable quantities, but an increase of these through anthropogenic contributions has since the last century been known to affect the ecosystem [3]. Wastes from automobile workshop activities include a solvent, paints, spent heat, transfer fluids, hydraulic fluids, spent lubricants and stripped oil sludge, these accumulations negatively affect nearby farms and cause non-point source metal pollution [4]. These metals are released during different auto-mechanic operations such as fluid leakage component wear, engine oils and corrosion of metals contribute immensely to soil contamination [4]. Lead, cadmium, copper and zinc are the major metal pollutants of the auto-mechanical workshop and are released from burning of worn out tyres, leakage of oils and corrosion of batteries and metallic parts such as radiators [5-8]. This study is aimed at assessing the association and bioavailability of Cd, Cr, Cu, Fe, Ni, Pb, Zn and their environmental contamination risk between the different geochemical phases based on chemical speciation.

2. MATERIALS AND METHODS

2.1 The Study Area

Akure is a city in south-western Nigeria and it lies about 7.0°15'N of the equator and 5.0°15'E of the Meridian. The city is situated in the tropic rainforest zone in Nigeria. General information about sampling sites is given in table 1, while the map of the study sites is depicted in Figs. 1 and 2.

2.2 Preparation of Sample Containers

Polythene bags were used for the collection of soil samples. These bags were previously soaked in 14% HNO₃ for 24 hours to remove all entrained metals, washed with detergents and rinsed with deionized water.

2.3 Collection of Soil Samples

Soil samples were collected from two different strategically located auto-mechanic workshops within Akure metropolis namely: Ileasha Garage (N 07° 16.339 E 005°09.59.0), Oyemekun (N 07° 15.615 E 005° 10. 37.46') and control site from FUTA residential staff quarters (N 07° 17.809' E 005° 08.52.9'). About 500 g of the soil samples were collected within a distance of 0-5 meters from each location and at a distance of 6 poles apart (about 30 meters). All soils collected were sampled at the surface (0 to 10 cm in depth) using a plastic scoop. The soil samples were kept in labeled polythene bags and taken to the laboratory for analysis. All soil samples were air dried ground and sieved through a 2 mm sieve mesh before chemical analysis was carried out.

2.4 Determination of Soil pH

5 g of the soil sample was weighed into 250 ml beaker and 20 ml of deionized water was added.

It was manually agitated for about 20 minutes and allowed to equilibrate. Finally, a standardized pH meter was used to read the pH by dipping the electrode into the 250 ml beaker containing the solution.

2.5 Determination of Soil Organic Matter

Organic matter was determined by the Walkley–Black procedure (Nelson and Sommers, 1982). This procedure is based on the principle of oxidation of organic matter with dichromate in a strong sulphuric acid medium.

2.5.1 Procedure and principle

The soil sample (1.0 g) was weighed into a 250 ml wide mouth graduated Erlenmeyer flask. Two blanks were titrated without the soil sample before titration with the soil samples in order to standardize Ferrous Sulfate solution. Potassium dichromate solution (1M 10.0 ml) was pipette into each flask containing soil samples and mixed carefully by rotating the flask to wet all of the soil after which 20 ml of concentrated sulfuric acid was added to each flask and mix gently under a fume hood. The flask was allowed to stand for 5 min under the fume hood and was made up to a

final volume of 125 ml with distilled water. The solution was allowed to cool in 30 minutes after which the volume was checked and recorded. Three drops of diphenylamine indicator was added and immediately titrated with 0.5 M ferrous ammonium sulphate solution. As the titration proceeded the solution changed from dull green to turbid blue and later changed abruptly to a brilliant green when the endpoint of the titration was reached. The volumetric reading at this point was recorded.

$$\text{Organic carbon} = \frac{(B - T) \times M \times 0.003 \times 1.33}{\text{Weight of Soil}} \times 100 \quad (1)$$

B = blank titer value

T = Titer value of the soil samples

M = Molarity of ferrous ammonium sulphate solution

Organic Matter = Organic carbon x 1.724

1.724 is the conversion factor

2.6 Determination of Soil Electrical Conductivity

5 g of the soil sample was weighed into 250 ml beaker and 20 ml of deionized water added, it

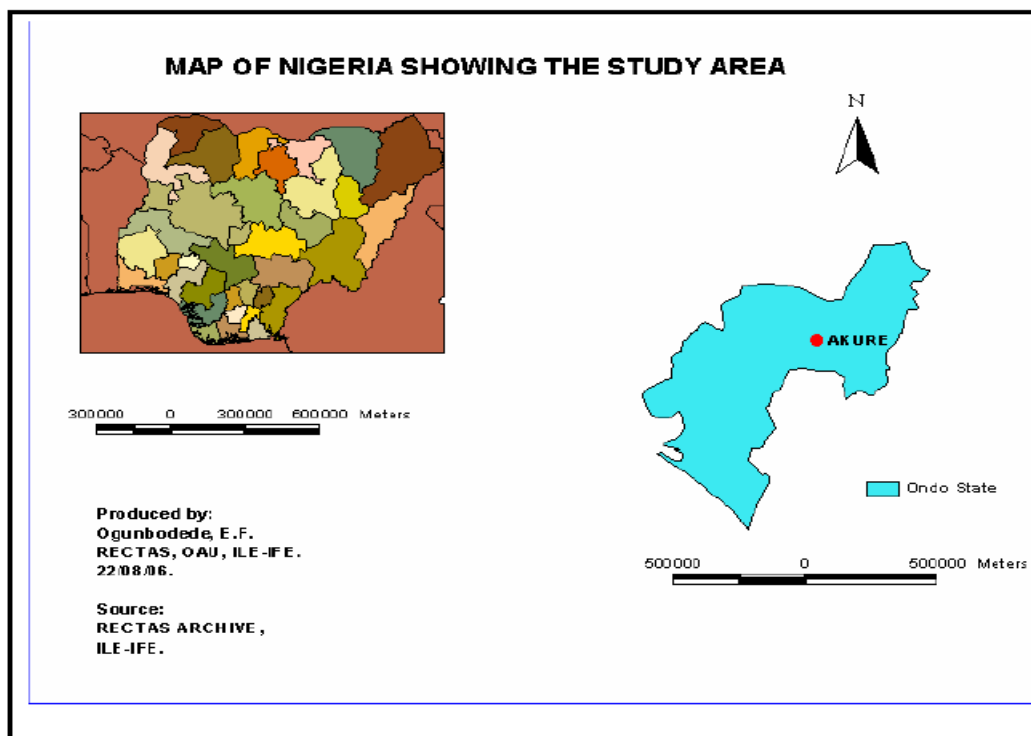


Fig. 1. Map of Nigeria showing Akure

Table 1. General information on the mechanic workshops studied

Site	Area	Location(LGA)	Year established	No. of workshops	Minimum no. of vehicles handled daily	
1	A	Ilesha garage	Akure South	1980	4	6
2	B	Oyemekun	Akure South	1992	6	20

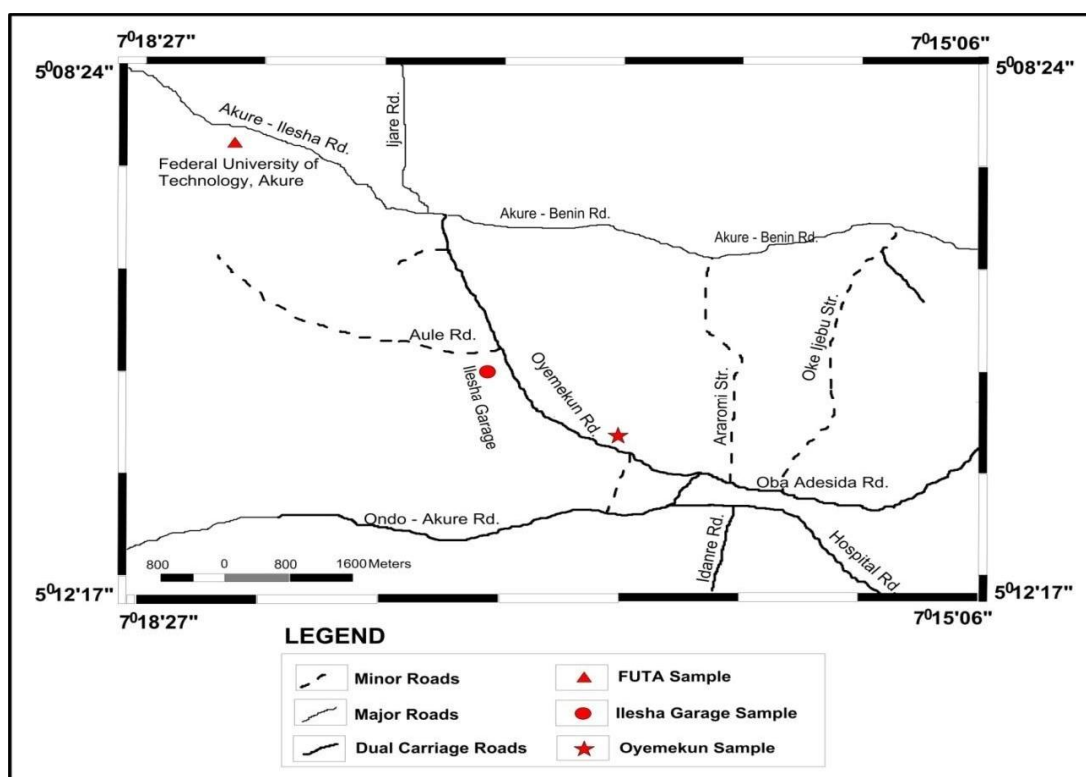


Fig. 2. Map of Akure showing the sampling sites

was gently stirred for 30 seconds and suspension was allowed to stand for 30 minutes. The water was gently stirred again before taking the electrical conductivity measurement. The electrical conductivity meter was gently inserted into the beaker and swirled gently around in the soil-water extract. Finally, after the electrical conductivity reading has stabilized, the digital display on the meter was read.

2.7 Determination of Particle size Distribution and Cation Exchange Capacity (CEC) of Soil

The particle size distribution and cation exchange capacity was determine using a standard analytical method taken from Rowell, 1994 [10].

2.8 Heavy Metals Determination in Soil

2 g of the air-dried soil samples wereplaced in a 100 ml Kjedadhl digestion flask, which has been previously washed with nitric acid and distilled water. The samples were subjected to digestion with 20 ml of concentrated nitric acid (HNO₃) and concentrated Hydrochloric acid in the ratio 3:1 (Aqua Ragia). The mixture was filtered through Whatman filter paper into a 100 cm³ volumetric flask, diluted to mark using distilled water [2].

2.9 Sequential Extraction of Heavy Metals from Soil

Sequential Extraction was carried out using the method proposed by Tessier et al. [11]. The

sequential extraction procedure is summarized in Fig. 3.

Fraction 1(Exchangeable): Samples (1 g) of soil samples were extracted at room temperature for 1hour with 16 ml of $MgCl_2$ solution (1M $MgCl_2$) at pH 7. Soil and extraction solution were thoroughly agitated throughout the extraction. This is mainly an adsorption – desorption process. Metals extracted in the exchangeable fraction include weakly adsorbed metals and can be released by ion-exchange process. Changes in the ionic composition of the water would strongly influence the ionic exchange process of metal ions with the major constituents of the samples like clays, hydrated oxides of iron and manganese (Abu-Kukati, 2001). The extracted metals were then decanted from the residual soil.

Fraction 2(Bound to Carbonate): The metals bound to carbonate phase are affected by ion exchange and changes of pH. The residue of Fraction 1 was extracted with 16 ml of 1M sodium acetate/acetic acid buffer at pH 5 for 5 hours at room temperature. Significant amount of trace metals can be co-precipitated with

carbonates at the appropriate pH. The extracted metal solution was decanted from the residual soil. The residual sediment was used for the next extraction.

Fraction 3(Bound to Iron and Manganese): The residue from fraction 2 was extracted under mild reducing conditions. 13.9 g of hydroxyl amine hydrochloride ($NH_2OH.HCl$) was dissolved in 500 ml of distilled water to prepare 0.4M $NH_2OH.HCl$. The residue was extracted with 20 ml of 0.4M $NH_2OH.HCl$ in 25% (v/v) acetic acid with agitation at $96^\circ C$ in a water bath for 6 hours. Iron and manganese oxides which can be present between particles or coatings on particles are excellent substrates with large surface areas for absorbing trace metals. Under reducing conditions, Fe (III) and Mn (IV) could release adsorbed trace metals. The extracted metal solution was decanted from the residual sediment which was used for the next extraction.

Fraction 4(Bound to Organic Matter):The residue from fraction 3 was oxidized as follows: 3 ml of 0.02 M HNO_3 and 5 ml of 30% (v/v) hydrogen peroxide, which has been adjusted to pH 2, was

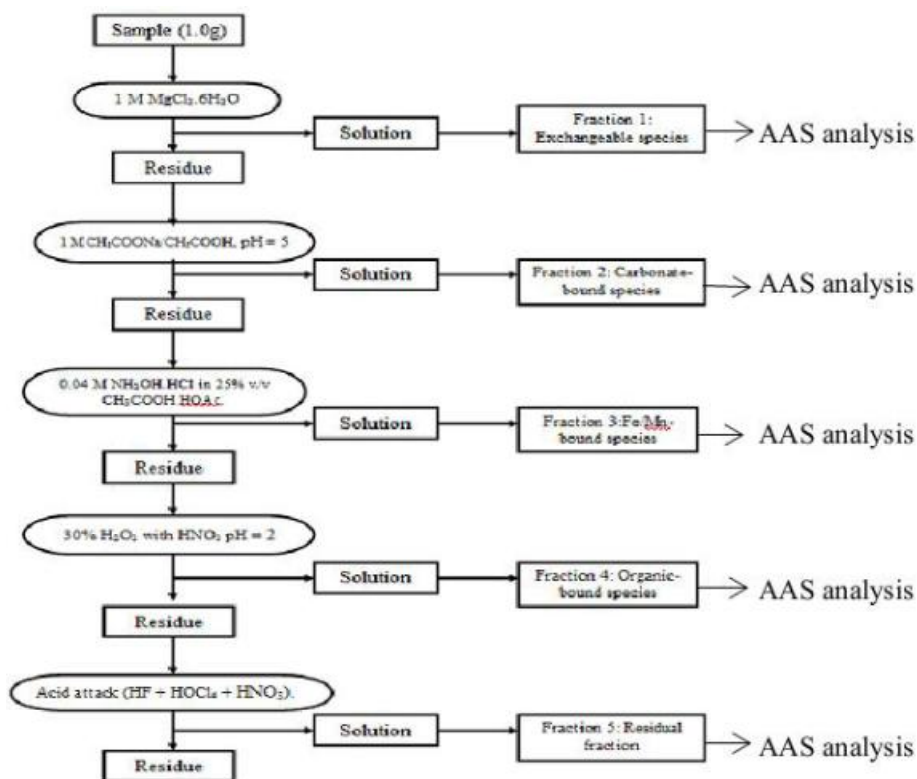


Fig. 3. Schematic diagram of sequential extraction procedure

Source: [12]

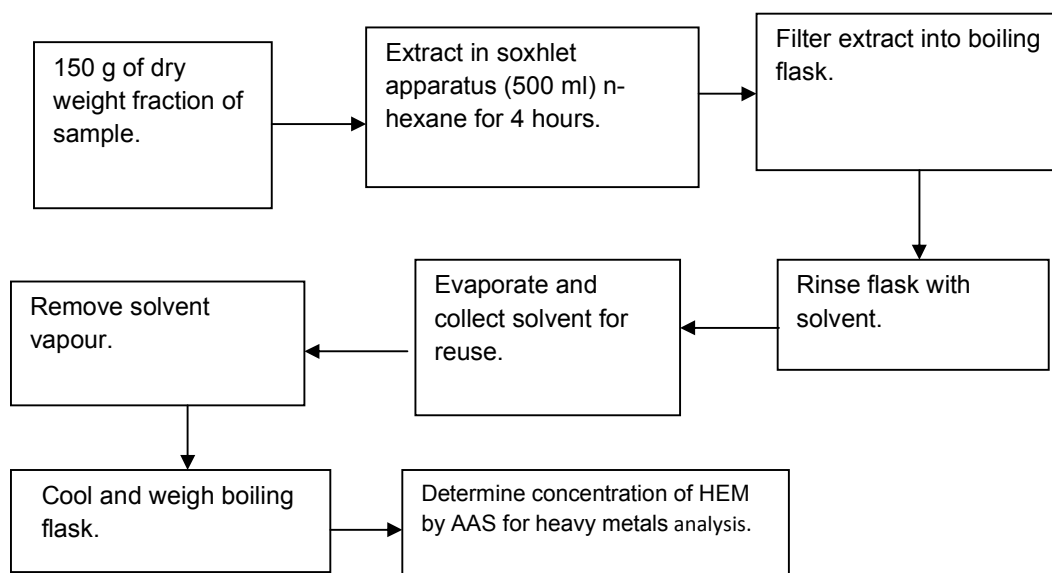


Fig. 4. Schematic diagram of EPA n-hexane extraction of oil

Source: [13]

added to the residue from fraction 3. The mixture was heated to 85°C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3 ml of 30% hydrogen peroxide, adjusted to pH 2 with HNO₃, was then added. The mixture was heated again at 85°C for 3 hours with occasional agitation and allowed to cool down. Then 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO₃ was added, followed by dilution to a final volume of 20 ml with de-ionized water. Trace metals may be bound by various forms of organic matter, living organisms and coating on mineral particles through complexation or bioaccumulation. These substances may be degraded by oxidation leading to a release of soluble metals. The extracted metal solution was decanted from the residual sediment which was used for the next extraction.

Fraction 5(Residual): Residue from fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5 ml conc. HNO₃ (HNO₃, 70% w/w), 10 ml of hydrofluoric acid or hydrochloric acid (HF/HCl, 40% w/w) and 10ml of perchloric acid (HClO₄, 60%w/w) in Teflon beakers. Fraction 5 largely consists of mineral compounds where metals are firmly bonded within crystal structure of the minerals comprising the soil. The digest was diluted with distilled water and filtered, made up to 100 ml and analyzed by Atomic Absorption Spectrometer Buck Scientific 210VGP.

2.10 Extraction Procedure of Oil from Soil Samples

150 grams of the soil samples were blended with 10 grams of anhydrous sodium Sulfate and transferred homogenized paste to an extraction thimble covered with glass wool or glass beads. The extraction thimble drained freely for the duration of the extraction period. Soxhlet apparatus containing the extraction thimble and sample was set up and attached to a 125 ml boiling flask containing 90 ml of n-hexane. Boiling chips were added by adjusting the heating control on the heating mantle so that a cycling rate of 20 cycles/h is obtained and followed by Extraction for a period of 4 hours. Taring a clean 250 ml or appropriate sized boiling flask was carried out as follows: The flask was dried in an oven at 105-115°C for a minimum of 2 hours removed from the oven and immediately transferred to a desiccators to cool at room temperature. When cooled, it was removed from the desiccators with tongs and weighed immediately on a calibrated balance. At the end of the 4 hours extraction period, filter. The extract was filtered through grease-free cotton, into the pre-weighed boiling flask with the aid gloves to avoid adding fingerprints to the flask. The boiling flask was connected to the distilling head apparatus and distilled the solvent by immersing the lower half of the flask in a water bath or a steam bath. A heating mantle may also be used. Temperature of the heating

device was adjusted to complete the distillation in less than 30 minutes and the solvent collected for reuse or appropriate disposal. When the distillation was complete, the boiling flask was cooled in a desiccator for 30 mins and weigh. Fig. 4 shows the schematic diagram of EPA n-hexane extraction of oil from soil samples.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Soil

Table 2 shows the results of the physicochemical parameters of the surface soil of Akure in the study and control areas. The pH values ranged from 5.52- 6.32 for the study and control sites. Only Oyemekun is acidic. Ilesha is near to the neutral while control is neutral. These values were within those obtained by some researcher in other areas of environmental concern [14-19]. These results however differ from those suggested by other research work [19-21]. Several studies have shown that availability of heavy metals is pH dependent [22], most of the pH values of the study areas indicate high metal uptake by plants since heavy metals are generally more mobile at pH <7 [23].

The percentage organic matter content of these soils ranged from 1.68-3.78% and organic carbon ranged from 0.96 - 2.19%, which are low but comparable with those obtained other researchers [19,24-25]. This value is also lower than the critical levels required by soils for agricultural use as suggested by [20]. Organic matter of soils immobilizes heavy metals at strongly acidic conditions and mobilizes metals at weakly acidic to alkaline reactions by forming insoluble or soluble organic metal complexes, respectively [26].

Electrical Conductivity (EC) values ranged from 57 -161 μScm^{-1} for study and control sites, the

variation observed in electrical conductivity between sites could be due to the content of available soluble salts. The electrical conductivity values were higher than those obtained in other mechanic workshop [22]. The cation exchange capacity ranged between 5.90 - 9.00 Cmol/Kg , a direct consequence of low soil CEC is that cations added will be loosely held and therefore easily lost by leaching. CEC can regulate the mobility of metals in soils and increase as pH increases. It is reported by previous research work that sandy soils have lower CEC than loamy soils, and below a pH of 6 concentrations of Zn and Cd were measured for sandy samples and lower concentration for loamy, probably due to higher CEC of loam [26]. The soil investigated is sandy with an average pH range of 5.50 – 6.32 and could increase the solution concentration of Zn, Cd and other metals [26]. The CEC is lower compared to the classification criteria of soil property [27]. This reduction in CEC and Sum of Organic Matter (SOM) could be accounted for as a reflection of nutrient depletion by waste from the activities of the mechanic workshops, the particle size distribution puts the soils in the sandy or loamy and textural classification. These properties are typical of soils in the area [28].

3.2 Total Metal Concentration

The concentrations (mg/kg) for the seven metals in Ilesha-Garage soil samples were 4.25 ± 1.06 (Cd), 17.00 ± 0.00 (Cr), 20.75 ± 0.35 (Cu), 4750.00 ± 0.00 (Fe), 4.00 ± 0.70 (Ni), 40.50 ± 0.70 (Pb), 40.75 ± 0.35 (Zn) while the metal concentrations (mg/kg) in Oyemekun soil samples were 135.75 ± 0.00 (Cd), 22.00 ± 0.70 (Cr), 33.25 ± 0.35 (Cu), 6475.00 ± 0.35 (Fe), 5.00 ± 0.01 (Ni), 60.00 ± 0.00 (Pb) and 48.50 ± 0.70 (Zn) respectively. Cd content in the soil samples exceeded the target values of the Department for Petroleum Resources (DPR) regulatory Standards for soil [29]. This could be attributed to the battery smelting area.

Table 2. Physicochemical parameters of the soil in the study areas

Site	pH	TOC (%)	SOM (%)	EC (μScm^{-1})	CEC (cmolkg^{-1})	Clay (%)	Silt (%)	Sand (%)
Ilesha Garage	6.32	1.56	2.68	119	9.00	12.21	7.35	80.44
Oyemekun	5.50	0.96	1.65	161	7.00	8.06	5.21	86.73
Control	7.12	2.19	3.78	57	5.90	13.42	13.36	73.02

TOM: Total Organic Carbon, SOM: Sum of Organic Matter

Table 3. The results of total metal concentration in soil (mg/kg)

Site	Cd	Cr	Cu	Fe	Ni	Pb	Zn
ILG	4.25 ^{ab} ±1.06	17.00 ^{ab} ±0.00	20.75 ^{ab} ±0.35	4750.00±0.00	4.00 ^{ab} ±0.70	40.50±0.70	40.75±0.35
OYM	7.50 ^b ±0.00	22.00±0.70	33.25±0.35	6475.00±0.35	5.00 ^{ab} ±0.01	60.00±0.00	48.50±0.70
FRA	0.10 ^{ab} ±0.00	0.40 ^{ab} ±0.01	18.36 ^{ab} ±0.00	3546.00 ^{ab} ±0.01	0.19 ^{ab} ±0.01	22.90 ^{ab} ±0.00	22.42 ^{ab} ±0.02
DPRTV	0.80	100.00	36.00	-	35.00	85.00	140.00
DPR IV	17.00	380.00	190.00	-	210.00	530.00	720.00

Table 4. Heavy metal pollution appraisal in the study areas

Location	v.s.l	s.l	m.l	s.t.l	v.s.t.l	s.p	m.p	s.t.p	v.s.t.p	e.p
Ilesha-Garage		Cr/0.17 Ni/0.11	Zn/0.29 Pb/0.48	Cu/0.58				Cd/5.31		
Oyemekun		Cr/0.22 Ni/0.14	Zn/0.35	Pb/0.71	Cu/0.92				Cd/9.38	
FUTA (control)	Cr/0.004 Ni/0.005	Cd/0.13 Zn/0.16 Cu/0.51	Pb/0.27							

v.s.l: very slight contamination, s.l: slight contamination, m.l: Moderate contamination, s.t.l: Severe contamination, v.s.t.l: Very severe contamination, s.p: Slight pollution, m.p: Moderate pollution, s.t.p: Severe pollution, v.s.t.p: Very severe pollution, e.p: Excessive pollution

Superscripts with the different letters across the row show significant variation, while those with the same letter do not at $p < 0.05$. ILG: Ilesha-garage, OYM: Oyemekun, FRA: Futa Residential Area, DPR TV: Department of Petroleum Resources Target Values, DPR IV: Department of Petroleum Resources Intervention [29].

3.3 Contamination/Pollution Index

The pollution index was derived by employing the pollution index as defined by Lacatusu [30].

$$\frac{C}{PI} = \frac{\text{Concentration of metal in soil}}{\text{Target value from reference point}} \quad (2)$$

A distinction between soil contamination and pollution range was established by means of the contamination/pollution index C/PI (Table 4). This represents a metal content effectively.

C/P index values greater than unities (1) defines the pollution range and when lower than unity the contamination range. The standard employed for interpreting soil heavy metals contamination/pollution index varies from country to country based on the chosen factors [31]. The pollution index assessment indicates that most of the metals fall within the "slight contamination" and "moderate contamination" range in the soil. In all samples, the soil is found to be mostly polluted by cadmium, being found in the "severe pollution" range in Ilesha-garage and very severe pollution in Oyemekun.

Table 5. Significance of intervals of contamination/pollution index (C/pi)

C/p	Significance	Symbol
<0.1	Very slight contamination	v.s.l
0.10 – 0.25	Slight contamination	s.l
0.26 – 0.50	Moderate contamination	m.l
0.51 – 0.75	Severe contamination	s.t.l
0.76 – 1.00	Very severe contamination	v.s.t.l
1.1 – 2.0	Slight pollution	s.p
2.1-4.0	Moderate pollution	m.p
4.1-8.0	Severe pollution	s.t.p
8.1-16.0	Very severe pollution	v.s.t.p
>16.0	Excessive pollution	e.p

Source: Lacatusu [30]

3.4 Fractionation of Metals

3.4.1 Cadmium

Cadmium was found mostly in the mineralogical matrix with 59.17% in Ilesha Garage and 86.44% in Oyemekun. This situation is however different from Tessier et al. [11], where insignificant amounts of Cd are associated with Fe-MnO fraction, whereas in the other fractions, Cd concentrations were below the limit of detection in both the exchangeable and parts of the carbonate fractions. Association of Cd to the residual fraction does not generally constitute an environmental risk. This is due to the stable nature of the compound and the fact that the metals are bonded firmly within a mineral lattice that restricts the bioavailability of this metal. Also, significant proportion was associated to the Fe-MnO fraction in site 1 with concentration 21.25 mg/kg. This could pose serious environmental risk under extreme conditions because much concern has been shown on the levels of Cd in soils for a long period of time because of their high toxicity. The cadmium associated with non-residual may be easily taken up by plants growing in the soil. These features, plus the hazards of Cd to human health, suggest that more frequent examination of the levels of this element in these soil samples may be necessary to determine potential health hazards to residents living near contaminated areas.

Generally, the Cd association with different geochemical fractions followed the order: residual>Fe-Mn oxide>organic>carbonate>exchangeable.

3.4.2 Chromium

The dominant phase was in the Fe-Mn oxides, which accounted for more than 49% (50.25±1.06 mg/kg) in ILG site in this study, while 57.14% (32.00±1.41 mg/kg) was found to be most associated to the residual fraction in OYM, which indicates that the environment (OYM) does not pose much risk for now but for the fact that the second most dominant was found in the exchangeable fraction which means increase in the anthropogenic activities could release the metal to the environment for plant uptake which will consequently affect the food chain. On the average, percent of total Cr associated with different geochemical fractions in the two soil samples was in the following order: residual > Fe-Mn oxide > exchangeable > organic > carbonate. This suggests a significant

contribution from geogenic anthropogenic sources respectively. The high concentrations of Cr and Cd found in this residual fraction are, however, not likely to be available to enter the food chain since the residual fraction is very stable, less reactive and less bio-available. Heavy metals found in this matrix are believed to be trapped and occluded within crystal lattice of layer of silicate and well crystallized oxide minerals Tessier et al. [11] had also reported that metals found in the residual fraction are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

3.4.3 Copper

Most of the Copper in these soils was present in the non-residual fraction in the average predominant percentage of this element 52.99% was found in Fe-Mn oxide fraction which was greater than that of the control site. This suggests that copper could be slightly released into the environment for plant uptake. The association of Cu with oxidizable fraction in these sites may be attributed to the high formation constant of organic-Copper complexes [32]. The highest concentration of Cu was associated with residual fraction 28.58% in Oyemekun, followed by Fe-Mn oxide fraction 11.50% and the least percentage of Cu was associated in organic 4.32%. The poor presence of Cu in exchangeable fraction may be as a result of high stability of Cu in the Copper-organic complexes; this means that Cu can be leached into the environment under oxidizing condition as reported by Venkateswaran et al. [33]. Generally, the Cu association with different geochemical fractions followed the order: residual>Fe-Mn oxide>carbonate>organic>exchangeable. The occurrence of Copper (Cu) in the soil could be attributed to both geogenic and anthropogenic, with the highest concentration recorded in the oxide fraction.

3.4.4 Iron (Fe)

The majority of iron in the soils was associated with the residual fraction, having the range from 55.74% to 60.92% with an average of 58.33%. The high percentage of iron found in residual fraction is an important repository of iron in the soil. In sandy soil that contains little clay, iron oxide could be leached through the soil and impact ground water quality. The concentrations of iron in the Fe-Mn oxide fraction in the sites have a range between 31.77% and 46.41% with

an average of 39.09%. This fraction could be considered relatively stable, slowly mobile and poorly available but could change with variations in redox conditions. The exchangeable fraction of iron ranged between 4.00% and 5.50% with an average of 4.75%, while the concentrations of iron found in the carbonate fraction varied from 4.00% to 3.00% with an average of 3.50%. This results is in agreement with the report on the low concentrations of iron in exchangeable and carbonate fractions of soil and sediment samples that has been reported by Solomon et al. [12]. The association pattern of iron in the different phases were in the order residual > Fe-Mn oxide> organic > exchangeable> carbonate. The concentrations of iron reported in the geochemical fractions in the study sites is in agreement with the results obtained on the spatial distribution and speciation of heavy metals in sediment of River Ilaje, Nigeria [12].

3.4.5 Nickel (Ni)

Residual, Fe-MnO, and carbonic bound fractions were the predominant forms of Ni in all the samples. Residual nickel varied from 50.50% to 69.54%. Nickel in Fe-Mn oxide fraction varied from 12.58% to 35.45% with an average of 24.02%. The organic and exchangeable fractions were relatively low which varied from average 2.83% to 1.00% in the studied sites. A similar concentration of nickel in carbonate fraction has been reported in previous research work [34]. The association pattern of nickel in the different phases were in the order residual > Fe-Mn oxide > carbonate> organic > exchangeable. The Ni concentrations are higher in Ilesha garage and Oyemekun compared to the control site.

3.4.6 Lead (Pb)

The dominant proportions of lead were recorded in the bound to Fe-Mn oxide in Ilesha garage as well as in the residual fraction in Oyemekun with a value of 50.89% and 54.72% respectively. Site 1 was found to contain highest concentration of Pb when compared with site 2 and the control site. The concentrations of lead reported in the geochemical fractions in the study sites is in agreement with the results obtained on the spatial distribution and speciation of heavy metals in sediment of River Ilaje, Nigeria [12].

3.4.7 Zinc (Zn)

Zinc was mostly concentrated in the non-residual fraction; a significant amount was also present in

the residual fraction. The majority of the Zn was associated with Fe-Mn Oxide fraction in Ilesha garage with percentage 39.30% (62.00 mg/kg). Percentage of metal in the mobile phase is appreciable (3.49- 39.30%). This result of

fractionation is in agreement with the report by Venkateswaran et al. [33]. The geochemical fractions of all the metals studied have shown that the metals are both of anthropogenic and geogenic sources respectively from Figs. 5-10.

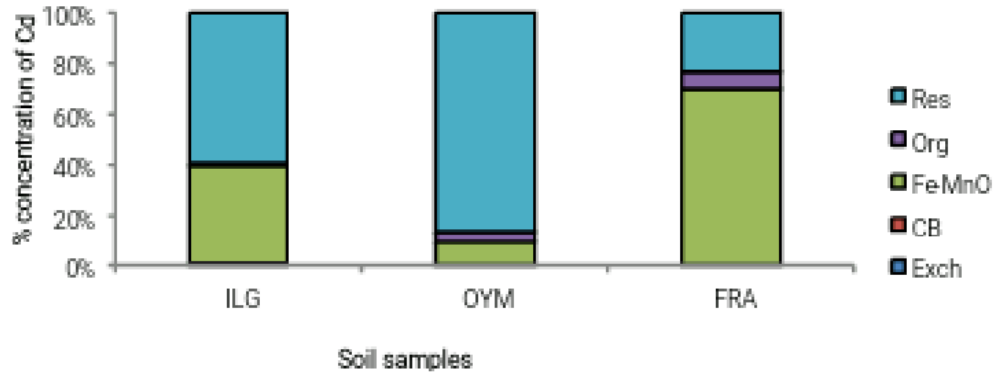


Fig. 5. Percentages of total Cd associated with each of the five sequential fractions for all samples

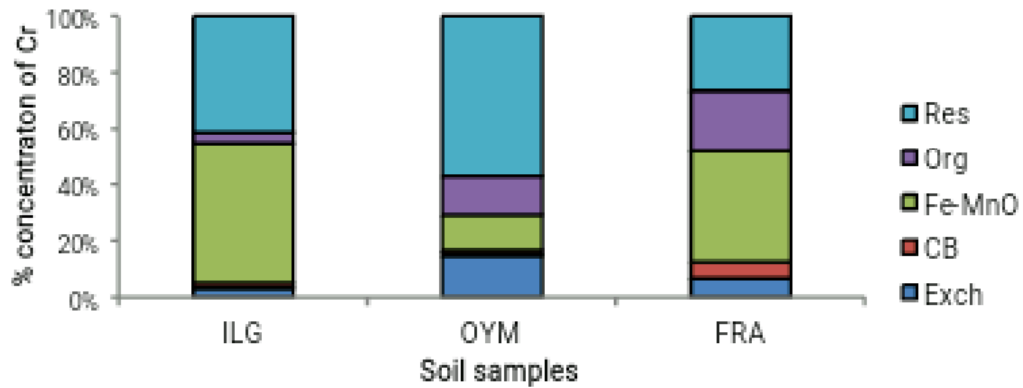


Fig. 6. Percentages of total Cr associated with each of the five sequential fractions for all samples

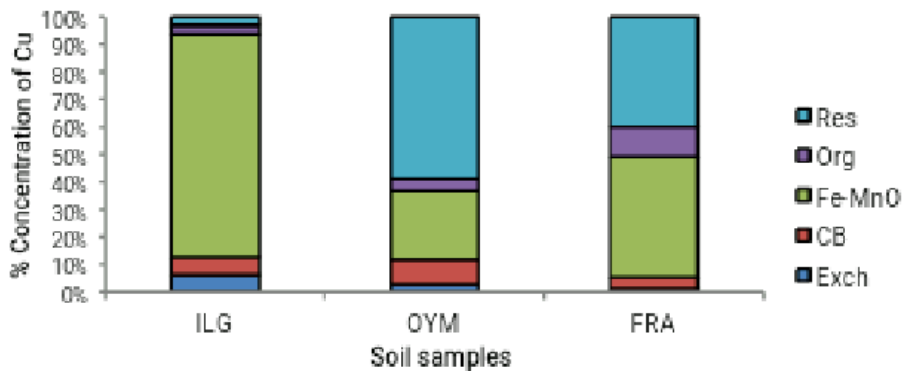


Fig. 7. Percentages of total Cu associated with each of the five sequential fractions for all soil samples

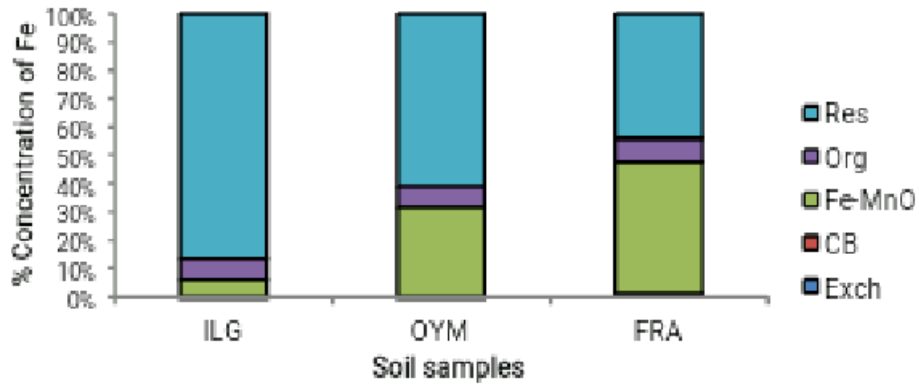


Fig. 8. Percentages of total Fe associated with each of the five sequential fractions for all soil samples

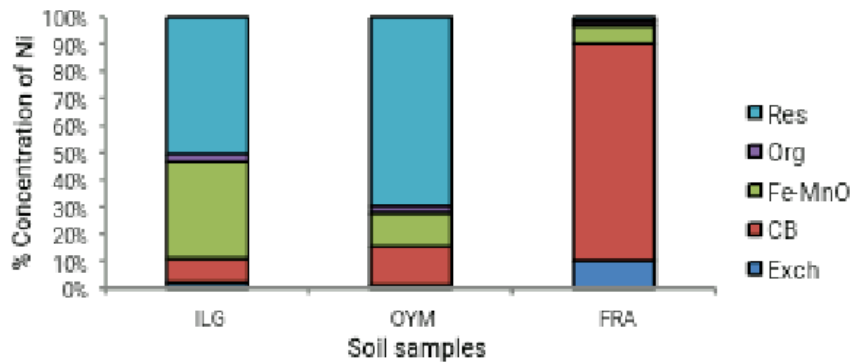


Fig. 9. Percentages of total Ni associated with each of the five sequential fractions for all soil samples

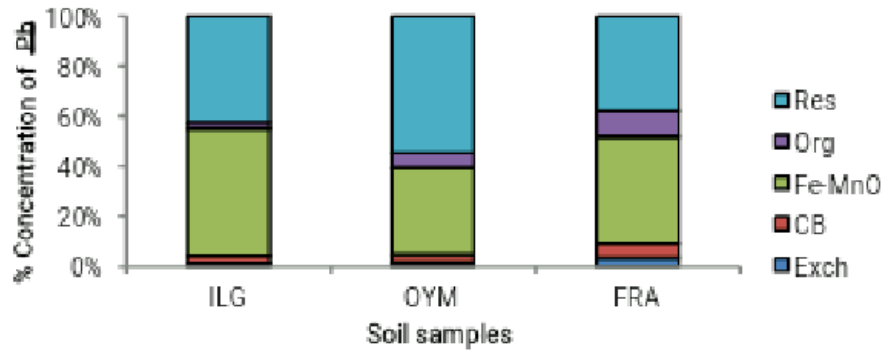


Fig. 10. Percentages of total Pb associated with each of the five sequential fractions for all soil samples

3.5 Comparison between Oil Soil Samples and Oil Extracted Soil Residues

Comparison between oil soil samples and oil extracted soil residues are shown in Fig. 11. Generally, the percentage concentration of heavy metals determined in both ILG1 (Ilesha-garage

soil with oil) and OYM1 (Oyemekun soil with oil) were higher than the ILG2 (Ilesha-garage soil after oil extraction) and OYM2 (Oyemekun soil after oil extraction) indicating that the pollution of these areas majorly came from different auto-mechanic activities.

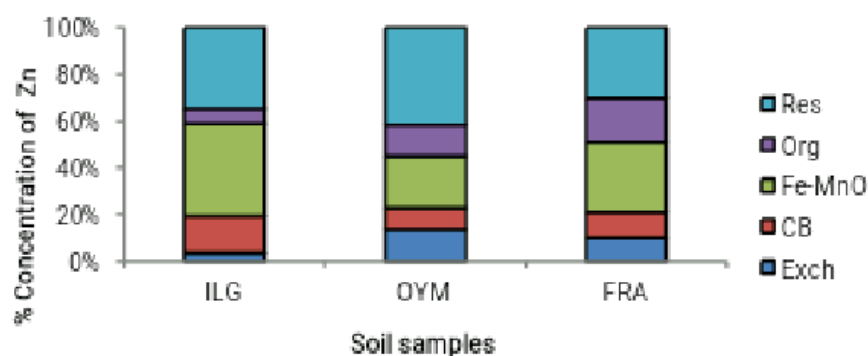


Fig. 11. Percentages of total Zn associated with each of the five sequential fractions for all soil samples

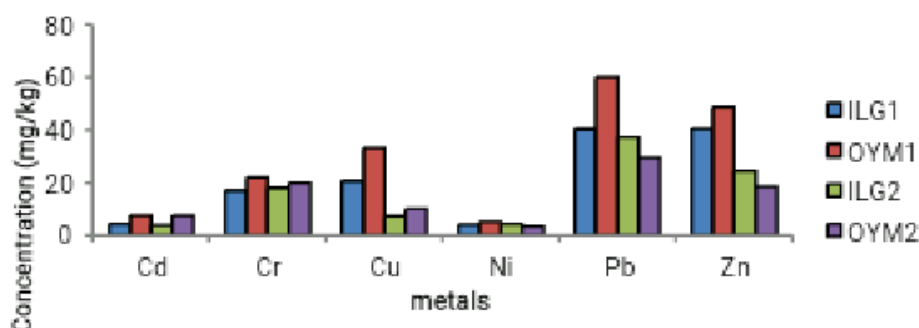


Fig. 12. Comparison between total metal concentration of oil soil samples and oil extracted soil residues; ILG1: Ilesha-garage soil with oil. ILG2: Ilesha-garage soil after oil extraction. OYM1: Oyemekun soil with oil. OYM2: Oyemekun soil after oil extraction

3.6 Mobility and Bioavailability Factors of the Metals in the Soil Profile

The operationally defined sequential extraction fractionates the heavy metals in the soil in order of decreasing solubility. As a result, the exchangeable and carbonate ($F_1 + F_2$) fractions which are the early fractions, capture the most reactive and presumably the most mobile and bioavailable fractions [31]. The relative index of metal mobility was calculated as a mobility factor (MF) on the basis of the following equation [35,36].

$$MF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100$$

$$BF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5}$$

F_1 = Fraction 1, F_2 = Fraction 2, F_3 = Fraction 3, F_4 = Fraction 4, F_5 =Fraction 5

F_1 = Fraction 1, F_2 = Fraction 2, F_3 = Fraction 3, F_4 = Fraction 4, F_5 =Fraction 5

The MF gives values less than 50% for all metals as shown in Table 6, which is an indication of moderate stability of the above metals in the soil samples. This could be linked to the organic matter content in the soil which can result to the formation of insoluble complex compounds which may be limiting the mobility of heavy metals. The mobility factor of the metals are; Cu: 12.24% Zn: 21.12%, Pb: 31.11%, Ni: 20.75% and Cr: 10.73%. This indicates a moderately high availability of the metals. Studies have shown that heavy metal is potentially available for plant uptake, if the mobility factor is above 10% [35]. It was observed from our study that all the metals have their mobility factor higher than 10% except for Cd and Fe.

The high mobility factor values have been interpreted as an indication of relatively high liability and biological availability of heavy metals in soils [36,37]. Many soil factors such as pH, organic matter content, amounts and forms of oxides and carbonates, charge characteristics, as well as mineral composition influence the bioavailability and transport of heavy metals in

the soil [38]. The bioavailability factor values were found to be moderate; this could be linked to the high organic matter content, which may lead to the formation of insoluble complex compounds limiting the bioavailability of heavy metals. These findings are in agreement with the report that heavy metals are capable of forming insoluble complex compound with soil organic matter [39]. The sequence of bioavailability factor was; Pb>Zn>Ni>Cu>Cr>Cd>Fe. Water soluble and exchangeable fractions are considered to be bio-available, oxide, carbonate and organic matter bound fraction may be potentially bioavailable, to either plants or microorganisms [40].

Table 6. Mobility, bioavailability factors and percentage recovery of heavy metals in auto 216 mechanic workshop samples

Heavy metals	Mobility factor (%)	Bioavailability
Cadmium (Cd)	0.80	0.0080
Chromium (Cr)	10.73	0.1073
Copper (Cu)	12.24	0.1224
Iron (Fe)	0.09	0.0009
Nickel	20.75	0.2075
Lead (Pb)	31.11	0.3100
Zinc (Zn)	21.12	0.2112

4. CONCLUSION

An assessment of the soil metals (Cd, Zn, Cu, Ni, Cr, Pb and Fe) from the two selected locations in Akure in comparison with the control soil sample and the environmental soil guidelines. The results revealed that the areas are considerably polluted with heavy metals but still have large metal concentrations below the intervention/alert level provided by the Department for Petroleum Resources except that of cadmium. The mobility factor indicates that the heavy metals have values above 10% and are available for plant uptake. The pollution index assessment suggests that most of the metals fall within the "slight contamination" and "moderate contamination" range in the soil, with the exception cadmium, been found in the "severe pollution" range in Ilesha-garage and very severe pollution in Oyemekun.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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