

## **Original Research Article**

# **HEAVY METAL FRACTIONATION IN SOIL OBTAINED FROM SOME MECHANIC SHOPS AND DUMP SITES IN OBIO AKPOR LOCAL GOVERNMENT AREA, RIVERS STATE NIGERIA**

Comment [DR1]: SELECTED

### **ABSTRACT**

The improper dumping, management and siting of refuse and mechanic sites have largely contributed to the contamination of soil by heavy metals. This study evaluates heavy metal fractionation in soil obtained from some mechanic shops and dump sites in Obio Akpor Local Government Area, Rivers State Nigeria. Two mechanical shops and two dumpsites in Obio/Akpor local government area in Rivers State were selected for metal speciation analysis. The total heavy metal contents of Cu, Pb, Zn and Cd were determined; thereafter, the sequential extraction of these heavy metals were carried out using the BCR scheme to determine the bioavailability of these heavy metals in the selected sites. The four metal fractions obtained were fraction 1 (exchangeable + acid soluble, fraction), fraction 2 (reducible fraction), fraction 3 (oxidizable fraction) and fraction 4 (residual fraction). The metal concentration of in the soil samples were as follows: Copper: 72.3 mg/kg (Site B) – 78.5 mg/kg (Site D), Lead: 3.0 mg/kg (Site A) – 19.4 mg/kg (Site D), Cadmium: 4.50 mg/kg (Site D) – 6.56 mg/kg (Site B), Zinc: 7.2 mg/kg (Site D) – 63.0 mg/kg (Site D). In the dumpsites Cd, Cu, and Zn were not available for uptake by plants and animals, while Pb was bioavailable; in the mechanic shops Cu, Pb, and Zn were not bioavailable, while Cd showed bioavailability. The Contamination Factor (CF) of the heavy metals in this study revealed gave the trend: Cd > Cu > Pb > Zn, whereas the Geoaccumulation index (Igeo) showed that all samples' sites were minimally contaminated with copper, lead and zinc (Igeo < 0), except cadmium which showed high contamination in all sites. In conclusion, the pollution load index (PLI) assessment of the study sites showed that the sites are undergoing a progressive deterioration of their soil quality.

*Keywords: Heavy metals, speciation, sequential extraction, fractionation, bioavailability*

### **1. INTRODUCTION**

Heavy metals have harmful effects on human health, and exposure to these metals has been increased by industrial and anthropogenic activities and modern industrialization. Contamination of water and air by toxic metal is an environmental concern and hundreds of millions of people are being affected around the world. Concentration of heavy metals in water resources, air, and food is assessed with this regard [1][2]. The presence of heavy metals in an environment alters the structure and functions of the ecosystem due to the fact that their presence has effect on the nature of the physical and chemical properties of the soil [3]. Heavy metals are among the most serious environmental pollutants due to their high toxicity, abundance and ease of accumulation by various plant and animal organisms.

Comment [DR2]: since

According to [4], these metals finally **end up** in the soil, leading to food chain contamination, since crops absorb them from the soil. High concentrations of heavy metals in living organisms can result in morphological abnormalities, neurophysiological disturbances, genetic alteration of cells (mutation), teratogenesis and carcinogenesis. Moreover, heavy metals can affect enzymatic and hormonal activities, as well as growth rate and an increase in mortality rate [5]. Several acute and chronic toxic effects of heavy metals affect **different** body organs. Gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, etc. are **examples** of the complications of heavy metal toxic effects. Simultaneous exposure to two or more metals may have accumulative effects [6].

Comment [DR3]: accumulated

Comment [DR4]: on various

Comment [DR5]:

Heavy metal speciation study is vital because the toxicity of metals in environmental compartment is more dependent on the species of heavy metals than the total amount of metals found in the environment [7]. Speciation is defined as the identification and quantification of the different, defined species, forms, or phase in which an element occurs and is essentially a function of the mineralogy and chemistry of the soil sample examined [8]. Metals speciation in the environment is determined by a number of reactions, including complexation, precipitation and sorption. These reactions affect the partitioning of metals across solid and liquid phases, hence their mobility as well as their bioavailability. Adsorption, desorption and ion exchange processes take place with the reactive components present in soils, sediments and to lower extent in water.

Auto workshops and dumpsites are known to be significant sources of heavy metals in the environment. Mechanic shop activities, such as welding, engine oil change, panel beating, spare parts change etc. lead to discharge of heavy metals which end up in the soil of these sites. Similarly, dumpsites comprises of all manner of household and industrial wastes which contains some amounts heavy metals that end up in the surrounding environment. Anegebe et al. [9] has stated that heavy metals found in soil of auto repair workshops in Oghara, Delta State were above the DPR limits. Similarly, Nyiramigisha [10] found that crops grown around dumpsites had high concentration of heavy metals, which was attributed to the contamination of the soil around the dumpsite. Accordingly, this study examines the speciation of heavy metals in soil obtained around dumpsites and auto repair shops in Obio Akpor, Port Harcourt

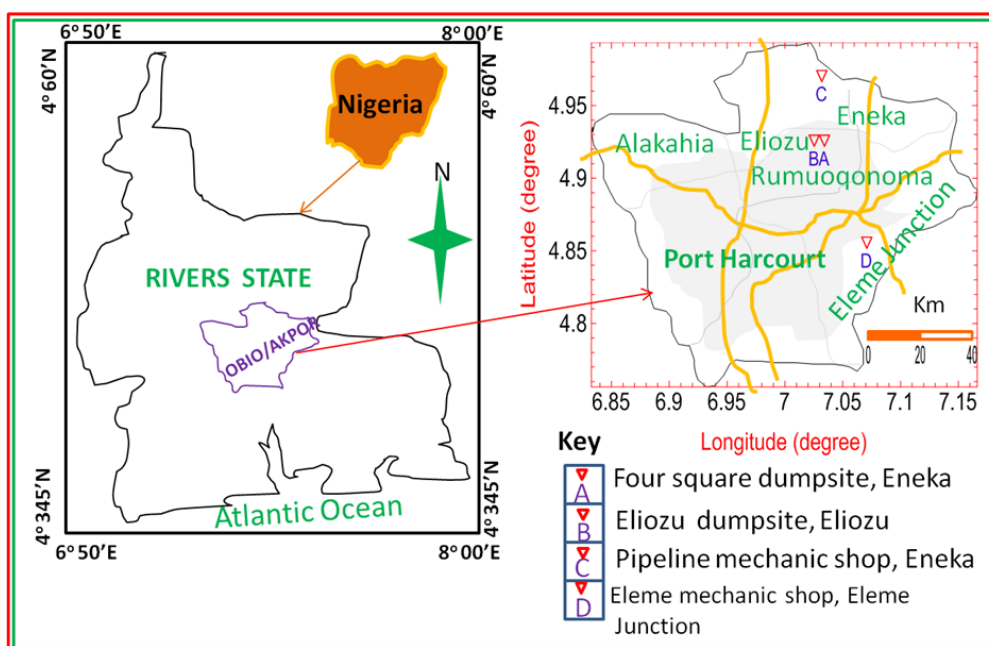
## 2. MATERIAL AND METHODS

### 2.1 The Study Area -

The study covers selected mechanic shops and dumpsites in Obio/Akpor Local Government Area, Port Harcourt, Nigeria, lying within the latitude  $4^{\circ} 45' N$  and  $4^{\circ} 60' N$  and longitudes  $6^{\circ} 50' E$  and  $8^{\circ} 00' E$  with average elevation below 30m above sea level. Samples were taken from two mechanic shops and two dumpsites; Four Square Dumpsite Eneka, Uchigbo Mechanic Shop Pipeline Eneka, Eliozu Dumpsite Eliozu and Mechanic Shop Eleme Junction adjacent to Anchor Hospital. It's situated at  $5.03^{\circ}$  North latitude,  $7.93^{\circ}$  East longitude and 196 meters elevation above the sea level.

Table 1 Geographical Locations of the sample sites

<b>Sample Area(s)</b>	<b>Latitude</b>	<b>Longitude</b>
Eneka Dumpsite(A)	4° 53' 3" N	7° 2' 31" E
Eneka Mechanic Shop(B)	4° 52' 59" N	7° 1' 31" E
Eliozu Dumpsite(C)	4° 52' 13" N	7° 1' 31" E
Eleme Junction Mechanic Shop(D)	5° 04' 60.00" N	6° 38' 59.99" E



**Fig. 1. Map of the Study Area**

## 2.2 Sample Treatment and Analysis

The soil sample was taken from range 8m depth in the soil (for the four locations). The soil sample was collected using a stainless steel grab sampler (30x30 cm). They were stored in a polythene bag prior to analysis. Once the samples reached the laboratory, the samples were air dried at room temperature in the laboratory for two weeks.

## 2.3 Methods of Research

### **2.3.1 Total Metal Analysis**

Pulverized soil sample (1.0g) was pretreated using 10 ml Aqua regia (mixture of concentrated HCl and HNO<sub>3</sub> acids in the ratio 3:1, British Drug House, BDHAnalar grade). This was then heated on a hot plate at 70°C to near dryness and then cooled. This was filtered into 50 ml volumetric flask and made up with double distilled water [ref].

Comment [DR6]:

Comment [DR7]: reference could be given

### **2.3.2 Sequential Extraction**

Sequential extraction was performed using the BCR (Community Bureau of Reference, superseded by the Standards, Measurement and Testing Programme of the European Community) procedure [11]slightly modified in the last step (residual fraction). The complete sequence of extraction is presented below.

#### **Step 1: Fraction 1 (F1, exchangeable + acid soluble, fraction)**

An aliquot of 20 ml of acetic acid, 0.11M, was added to 0.5g of dry soil in a 100 ml volumetric flask. The tube was shaken for 10 hour at room temperature (20±2°C). The extract was separated from the solid residue by centrifugation at 3,000 rpm and the supernatant was decanted into a polyethylene container.

#### **Step 2: Fraction 2 (F2, reducible fraction)**

Twenty milliliters of 0.5M hydroxylamine hydrochloride (pH 1.5 adjusted with HNO<sub>3</sub>) was added to the residue in the centrifuge tube obtained during step 1. The tube was shaken for 10 hour at 3,000 rpm at room temperature (20±2°C). The extract was separated from the solid phase by centrifugation, as described in step 1.

#### **Step 3: Fraction 3 (F3, oxidizable fraction)**

Five milliliters of H<sub>2</sub>O<sub>2</sub> solution (8.8 M, pH of 2–3) was carefully added in small aliquots to the residue in the centrifuge tube from step 2. The tube was covered with a watch glass and digested at room temperature for 1 hour with occasional manual shaking. Then, the content was digested for 1 hour at 85±2°C in a water bath until the volume was reduced to 2–3 ml. Another aliquot of 10 ml H<sub>2</sub>O<sub>2</sub> solution was added to the residue, heated again to 85±2°C, and digested for another hour; then the volume was reduced to dryness. After cooling, 50 ml of 1.0 mol/L ammonium acetate (pH 2 adjusted with HNO<sub>3</sub>) was added to the residue, and the tube was shaken for 10 hour at room temperature. The extract was separated from the solid phase by centrifugation as described above.

#### **Step 4: Fraction 4 (F4, residual fraction)**

The final residue remaining at the end of the BCR procedure was digested in 20 ml aqua regia, although this is not part of the original procedure. The metal concentrations in the extracts obtained at each step were determined using an atomic absorption spectrophotometer Perkin Elmer AAnalyst-100; flame atomization (air/acetylene) was used for high content of heavy metals, and to determined lower concentrations, an electrothermal atomization in graphite furnace HGA-800 with auto sampler AS-72 Perkin Elmer was used. All determinations included quality control in blanks (blanks, spiked blanks) and samples (duplicate and spiked samples). The duplicates showed a difference of <10 %, while the spiked additions (blanks and samples) gave between 80-100 recovery percentage.

## **2.4 Ecological Risk Assessment**

### **2.4.1 Contamination Factor**

The CF is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background value (concentration in unpolluted soil)

$$CF = \frac{C_{heavy\ metal}}{C_{background}} \quad (1)$$

The contamination levels may be classified based on their intensities on a scale ranging from 1-6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) [12]

### **2.4.2 Potential Risk Assessment of Heavy Metals**

The risk assessment code (RAC) was used to assess the potential risk of heavy metals in soil samples. The RAC method allows for the direct evaluation of the environmental response based on the proportion of exchangeable fraction (F1) in heavy metals due to its weak binding to particulates; this results in the exchangeable fraction (F1) being more susceptible to migration and enrichment in the food chain [13] as given by

$$RAC = \frac{CF_1}{CF_1 + CF_2 + CF_3 + CF_4} \times 100 \quad (2)$$

Where  $CF_1, CF_2, CF_3, CF_4$  are the contents of the exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction, respectively. The RAC index can be categorized into five classes (Table 2) based on initial research experience and the results of numerous studies

**Table 2 RAC Index Classification**

<i>RAC INDEX %</i>	<i>RISK LEVEL</i>
<1	Low Risk
1 – 10	Low Risk
11 – 30	Medium Risk
31 – 50	High Risk
>50	Very High Risk

### **2.4.3 Geoaccumulation Index**

The geoaccumulation index ( $I_{geo}$ ) introduced by Muller [14] and used to determine the quantitative extent of metal pollution in sediments. The  $I_{geo}$  is expressed as:

$$I_{geo} = \text{Log}_2 \left( \frac{C_n}{1.5 B_n} \right) \quad (3)$$

Where  $C_n$  is the measured concentration of a heavy metal  $n$ ,  $B_n$  is the geochemical background value in average shale of element,  $n$ : Cu – 45 ppm, Zn – 95 ppm, Cd – 0.3 ppm, Pb – 20 ppm [15] and 1.5 is the background matrix correction factor due to lithogenic effects. Result is interpreted as follows;

$I_{geo} < 0$ : practically uncontaminated (background level or low contamination)

$0 \leq I_{geo} < 1$ : Uncontaminated to moderately contaminated

$1 \leq I_{geo} < 2$ : Moderately Contaminated

$2 \leq I_{geo} < 3$ : Moderately to strong contaminated

$3 \leq I_{geo} < 4$ : Strongly contaminated

$I_{geo} \geq 4$ : Very strongly contaminated [16]

#### **2.4.4 Pollution load index (PLI)**

Quality of sediment or soil is evaluated via the pollution load index. It is defined as the  $n$ -th root of the metal multiplications of the contamination factor ( $CF$ ) [17]. The PLI was calculated by using formulae proposed by Tomlinson [18] based on the contamination factor values of individual elements.

$$PLI = [CF_1 \times CF_2 \times CF_3 \times CF_4 \dots \dots \dots \times CF_n]^{1/n} \quad (4)$$

The  $PLI$  value reflects the soil metal toxicity level. A  $PLI$  value of 0 indicates excellence,  $PLI$  value = 1 indicates baseline pollutant levels, and  $PLI$  value  $\geq 1$  indicates progressive deterioration of sediment quality [18]

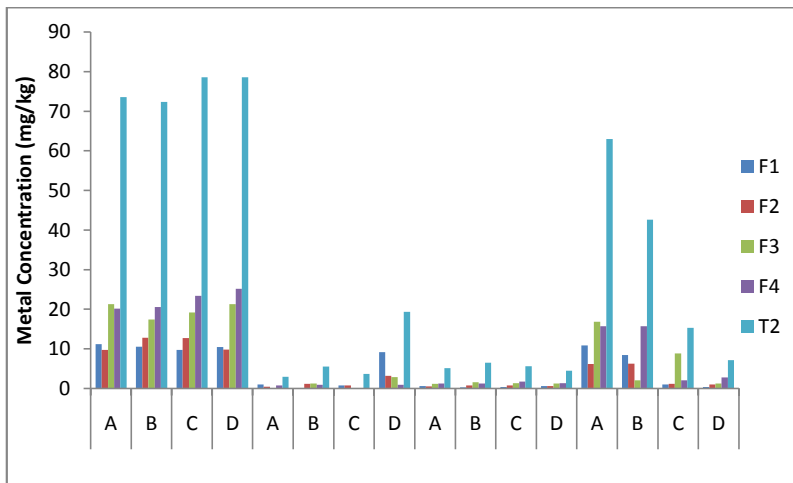
### **3. RESULTS AND DISCUSSION**

**Table 3. Heavy Metal Contents (Milligrams per kilogram, dry weight) in fractions of soil in study sites**

	Cu				Pb				Cd				Zn			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
F <sub>1</sub>	11.2	10.56	9.78	10.52	1.04	<0.02	0.8	9.2	0.64	0.36	0.44	0.64	10.88	8.5	1.08	0.44
F <sub>2</sub>	9.8	12.8	12.72	9.88	0.52	1.2	0.84	3.2	0.56	0.84	0.84	0.64	6.25	6.28	1.2	1.08
F <sub>3</sub>	21.3	17.4	19.2	21.3	<0.05	1.3	<0.5	2.9	1.2	1.6	1.4	1.3	16.9	2.1	8.9	1.3
F <sub>4</sub>	20.2	20.6	23.4	25.2	0.8	1	<0.5	1	1.3	1.3	1.8	1.4	15.7	15.7	2.1	2.8
T <sub>1</sub>	62.5	61.36	65.1	66.9	2.41	3.52	2.64	16.3	3.7	4.1	4.12	3.8	50	32.58	13.28	5.62
T <sub>2</sub>	73.5	72.3	78.5	78.5	3	5.6	3.75	19.4	5.2	6.56	5.65	4.5	63	42.65	15.35	7.2
% R	85.1	84.9	82.9	85.2	80.3	62.9	70.4	84.2	71.2	62.5	72.9	84.4	79.4	76.4	86.5	78.1

**Table 4. Percentage (%) concentration in Metal Fractions**

	Site ID	F1 (%)	F2 (%)	F3 (%)	F4 (%)
Cu	A	17.92	15.68	34.08	32.32
	B	17.21	20.86	28.36	33.57
	C	15.02	19.54	29.49	35.94
	D	15.72	14.77	31.84	37.67
Pb	A	43.15	21.58	0.83	33.20
	B	0.28	34.09	36.93	28.41
	C	30.30	31.82	0.76	0.76
	D	56.44	19.63	17.79	6.13
Cd	A	17.30	15.14	32.43	35.14
	B	8.78	20.49	39.02	31.71
	C	10.68	20.39	33.98	43.69
	D	16.84	16.84	34.21	36.84
Zn	A	21.76	12.5	33.8	31.4
	B	26.09	19.28	6.45	48.19
	C	8.13	9.04	67.02	15.81
	D	7.83	19.22	23.13	49.82



**Fig 2 Heavy metal fractions and total concentration in soil obtained from study sites**

Generally, the order of heavy metals in all sample sites were Cu > Zn > Cd > Pb, while the following metal concentration ranges were observed; Copper: 72.3 mg/kg (Site B) – 78.5 mg/kg (Site D), Lead: 3.0 mg/kg (Site A) – 19.4 mg/kg (Site D), Cadmium: 4.50 mg/kg (Site D) – 6.56 mg/kg (Site B), Zinc: 7.2 mg/kg (Site D) – 63.0 mg/kg (Site D).

**Comment [DR8]:** Site A

### 3.1 Heavy metal fractionation in soil samples

Fractionation of these metals in the samples was investigated by the sequential extraction of the soil samples according to the BCR technique, to obtain four fractions as follows;

F<sub>1</sub> (Exchangeable + Soluble Acid), indicates the readily available and easily exchangeable forms of elements, usually the most labile fraction. The sample is first extracted using a weak acid (e.g., acetic acid) or a salt solution to dissolve substance that are loosely bound and can easily exchange with ions in the environment. This fraction represents elements available for immediate release into the aqueous phase.

F<sub>2</sub> (Reducible fraction), targets elements bound to organic matter in oxidized forms. Extraction: extraction is carried out using a mild reducing agent (eg. hydroxylamine hydrochloride in anoxic conditions) helps to release elements bound to iron and manganese oxides and those associated with organic matter in a reduced state.

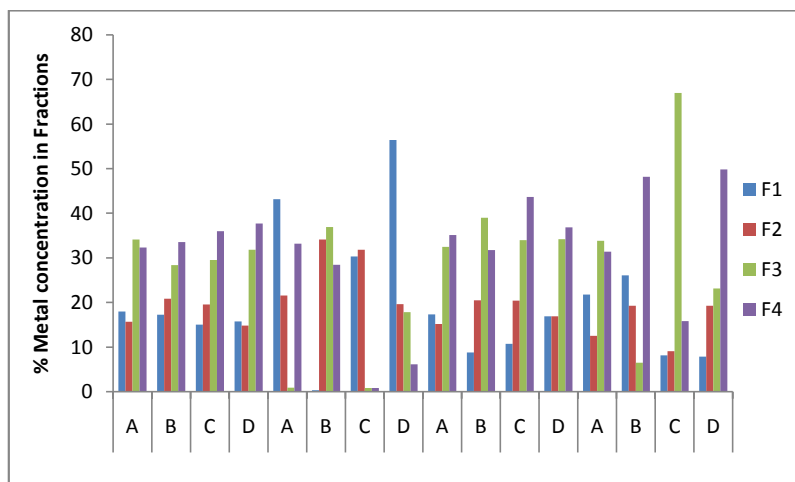
**Comment [DR9]:** Which helps

**Comment [DR10]:** That bound

F<sub>3</sub> (Oxidizable fraction) reveals elements bound to organic matter in oxidized forms. Oxidizing agents such as hydrogen peroxides are used to extract elements that are associated with organic matter in an oxidized state, providing information about potentially more stable associations.

F<sub>4</sub> (Residual Fraction): This fraction represents the fraction that is strongly bound to the mineral matrix and is resistant to extraction by common reagents. This final step involves using aggressive acids such as aqua regia to digest the remaining solid residue, extracting elements that are tightly bound or embedded within the mineral lattice.

The efficiency of the method used in the sequential extraction procedure and the precision of the results obtained were checked by comparing the sum of the four fractions ( $T_1$ , Table 3) with the values for samples extracted with aqua regia for the determination of the total metal contents ( $T_2$ , Table 3). In general, there was a good agreement between the sums of the fractions and the total metal contents, with recoveries in the range of 60 – 90%, it is considered satisfactory given the complex nature of the soil matrix.



**Fig 3. Percentage of metal concentration in fractions**

**COPPER:** the level of copper determined from the various fractions revealed that copper was predominant in the residual fraction in sites B, C and D (Table 4) corresponding with 33.57 %, 35.94 % and 37.67 %, but was predominant in oxidizable fraction (33.57 %) in site A. This result corresponds with the findings of Ore [19] who reported the predominance nature of copper in the residual fraction, while the predominant nature of copper in the oxidizable fraction of the automobile shop was observed by Adelowotan [20]. According to Obasi [21], the predominance of copper in the residual fraction may be due to the stable bond of copper organic complexes due to the high formation constants of organic copper complexes.

**LEAD:** the level of lead determined from various fractions revealed that lead is predominant at F1 (Exchangeable + Soluble Acid) in sites A (43.15%) and D (56.44 %); F3 (Oxidizable fraction) in site B (36.93 %); F2 (Reducible fraction) in site C (31.82 %). Generally, it was observed that Pb fraction was high in fraction 1, with the exception of site B which recorded the lowest lead fraction in F1. The fractioning of lead in the dumpsite is similar to that of the work of [19] on refuse dumpsite. The comparison of the mechanic sites in this study with the work of [20] on mechanic site did not correlate as the predominant nature of lead in this study was found in the Exchangeable + Soluble Acid Fraction, while Pb in [1][20] was predominant in the residual Fraction, followed by carbonate fraction. The predominance nature of lead in the Exchangeable + Soluble Acid simple indicates its bioavailability in the soil for plants and animal uptake. This poses a threat to the exposed organisms, since lead is a hazardous chemical agent with accompanying deleterious effects.

**CADMIUM:** It was observed that cadmium was prevalent at F4 (Residual) in Sites A, C and D while site B recorded the highest Cd fraction in (Oxidizable fraction). The prevalence

nature of cadmium in the dumpsite is in agreement with the work of [19] on dumpsite and the investigation of [20] on mechanic site. In the dumpsites, cadmium was predominant in the Exchangeable + Soluble Acid Fraction indicating its bioavailability while in the mechanic sites Cadmium was predominant in the Residual fraction indicating that cadmium will not be available for uptake by plants in this environment. Cadmium may be associated with sulfides, iron oxides or organic matter which is influenced by redox conditions; hence its predominance in oxidizable fractions in site B. Cadmium may also be associated with resistant to formation of oxide, which may explain its prevalence in the residual Fraction in Sites A, C and D.

**ZINC:** the levels of zinc was predominant at F3 (Oxidizable) in all sample sites, except in site D where the highest zinc concentration was found in residual fraction (F4); however, zinc concentration in F3 was the second highest in site D. Thus, on the average F3 recorded the highest concentration of zinc in the study. This conclusion is at variance with [20] on mechanic site and [19] on dumpsite. Since zinc in this study was predominant in the oxidizable and residual fractions, they are not available for uptake by plants and animals in the study sites. The result of zinc predominance in this study may be attributed to the association of zinc with organic matter and resistant oxide phases.

### 3.2 Contamination Factor (CF) and Geoaccumulation index (Igeo)

**Table 5. Contamination Factor (CF) and Geoaccumulation Index in the study sites**

Site ID	Cu			Pb			Cd			Zn		
	Conc. (mg/kg)	C F	Ige o	Conc. (mg/kg)	C F	Ig eo	Conc. (mg/kg)	CF	Ig eo	Conc. (mg/kg)	C F	Ig eo
A	73.5	1.63	0.123	3	0.15	-3.32	5.2	17.33	3.53	63	0.66	-1.18
B	72.3	1.61	0.099	5.6	0.28	-2.42	6.56	21.87	3.87	42.65	0.45	-1.74
C	78.5	1.74	0.22	3.75	0.19	-3	5.65	18.83	3.65	15.35	0.16	-3.21
D	78.5	1.74	0.22	19.4	0.97	-0.63	4.5	15.00	3.32	7.2	0.08	-4.31

According to the Igeo classification [16], the heavy metals contamination in the study sites can be classified as; very low contamination with respect to Pb and Zn ( $I_{geo} < 0$ ), moderately contaminated with respect to Cu ( $0 \leq I_{geo} < 1$ ) and highly contaminated with respect to Cd ( $3 \leq I_{geo} < 4$ ). On the other hand, contamination factor was less than 1 for Zn and Pb, indicating very low contamination or background values of the metals in the study sites. This indicates that the anthropogenic activities at the study sites discharged minimal amounts of these heavy metals. The CF for Cu was above 1, but below 2, implying moderate contamination of the sites with copper. However, CF values for Cd were very high for all study sites, ranging from 15.00 – 21.87 (Table 5), which implies an alarming level of contamination of the study sites with cadmium. The CF values exceed those recorded by Uwem et al. [7] in dumpsites within Uyo Metropolis, Nigeria. Summarily, there was low contamination, with respect to Zn, moderate contamination, with respect to Pb and Cu; while the sites were highly contaminated with Cd in all sample sites. The CF value monitors the heavy metal enrichment in soil over a period of time

### 3.3 Comparison of the total metal content in study with Department of Petroleum Resources for Target and Intervention Values for Metals in Soils.

Table 6. Comparison of Department of Petroleum Resources for Target and Intervention Values for Metals in Soils [22] with the total metal content of this study

Metals	Ranges	DPR Target Values	DPR Intervention Values
Cu	72.5 – 78.5	36	190
Pb	3 – 19.35	85	530
Cd	4.5 – 6.5	0.80	12
Zn	7.2 – 63	146	720

From the comparison it was observed that Copper was higher than the DPR targeted values but lower than the intervention values. Lead was lower for both DPR target and intervention values. Cadmium was higher than the DPR target values but lower than the intervention values and zinc was lower for both DPR target and intervention values. From this comparison it is safe to say that the content of heavy metals in this study is within the limit according to DPR intervention values; however, copper and cadmium exceeded the DPR target values.

### 3.4 RAC and Pollution Load Index

Table 7. RAC of metals in study sites

SAMPLE SITE	Cu	Pb	Cd	Zn
Dumpsite Eneka (A)	17.92	43.15	17.29	21.88
Mechanic Eneka (B)	17.21	0.57	8.78	26.11
Dumpsite Elioizu (C)	15.02	30.30	9.73	8.13
Mechanic Eleme (D)	15.72	36.08	16.08	7.83

The RAC quantifies the risk of releasing heavy metals in the environment based on the percentage of exchangeable form (F1), with respect of the total of all metal fractions. The RAC result for the top soil in this study are shown in Table 7, indicating that Pb poses a high risk in Site A (Eneka Dumpsite), Site C (Elozu Dumpsite) and Site D (Eleme Mechanic). Other metals pose medium risk, except Cd in Sites B & C and Zn in sites C and D, which showed low risk; however, Pb posed a very minimal risk in Site B. The characterization of the risk posed by these metals is their bioavailability for uptake by plants and humans in the study sites

Table 8. Pollution Load Index of study sites

Sample ID	CF <sub>Copper</sub>	CF <sub>Lead</sub>	CF <sub>Cadmium</sub>	CF <sub>Zinc</sub>	Pollution Load Index (PLI)
A	1.63	0.15	17.33	0.66	1.29
B	1.61	0.28	21.87	0.45	1.45

C	1.74	0.19	18.83	0.16	1.0
D	1.74	0.97	15.00	0.08	1.19

The *PLI* value reflects the soil metal toxicity level. A PLO level value of 0 indicates excellence, PLO value = 1 indicates baseline pollutant levels, and PLO value  $\geq 1$  indicates progressive deterioration of sediment quality[18]. The PLI of Sites A, B and D were higher than 1, corresponding with 1.29, 1.45 and 1.19, respectively. These indicate progressive deterioration of the soil quality in these sites. However, the lowest PLI value of 1 was recorded in site C, implying baseline pollutant levels, according to Tomlinson [18].

#### 4. CONCLUSION

This study aimed to identify the bioavailability of certain heavy metals such as Copper, Lead, Cadmium and Zinc in selected dumpsites and Mechanic shops in Obio/Akpor Local Government Area; the total metal content of these heavy metals was first investigated, followed by its bioavailability using the BCR sequential extraction method. Furthermore, the Contamination Factor (CF), Geoaccumulation Index (Igeo), Risk Assessment Code (RAC) and Pollution Load Index (PLI) were calculated for the study area. The study of the contamination factor of these areas revealed; low contamination with respect to Pb and Zn, moderately contaminated with respect to Cu and Highly contaminated with respect to Cd in the study sites. The geoaccumulation index revealed that all samples sites were minimally contaminated with copper, lead and zinc (Igeo < 0), except cadmium which showed high contamination in all sites. RAC revealed that Pb poses a high risk in Sites A, C and D indicating that Pb is bioavailable for uptake by plants and humans in the study area. Other metals posed medium risk to low risk in all the study sites, according to RAC. The pollution load index (PLI) assessment has shown that the sample sites are undergoing a progressive deterioration of their soil quality. Therefore, there is need to put measures in place that will mitigate the on-going environmental degradation of the study areas.

Comment [DR11]: of

#### REFERENCES

1. Hirner A. Trace element speciation in soils and sediments using sequential chemical extraction methods. *International Journal of Environmental Analytical Chemistry*. 1992;46(1-3):77-85.
2. Morillo J, Usero J, Gracia I. Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*. 2004;55(3):431-442
3. Ubong U, Ikpe E, Ekanem A, Jacob J, Archibong U. Heavy Metals, Profile of the Proposed Dump-Site at Ntak-Inyang Itam, Akwa Ibom State, Nigeria. *Journal of Geography, Environment and Earth Science International*. 2023;27(2):17-28.
4. Ubong U, Nsi E, Ite A, Ikpe E. Health risk assessment of trace metals contamination in vegetables (*Telferia occidentalis*) irrigated with polluted effluent water from mechanic village, Uyo. *International Journal of Scientific & Engineering Research*. 2020;11(10):381-398
5. Bubb I, Lester J. Factors controlling the accumulation of metals within fluvial systems. *Environmental Monitoring and Assessment*. 1996;41:87-105.
6. Coetzee P. Determination and speciation of heavy metals in sediments of the Hartbeespoort Dam by sequential chemical extraction. *Water Sa*. 1993;19(4):291-300

Comment [DR12]: Italics

Comment [DR13]: italics

Comment [DR14]: Italics

7. Ubong U, Ekwere I, Obadimu C, Uwanta E. Pollution Status of Dumpsites within Uyo Metropolis, Akwa Ibom State, Nigeria. *Journal of Geography, Environment and Earth Science International*. 2023;27(1):1-10.

8. TackFMG, Verloo MG. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry*. 1995;59:225–238

9. Anegebe B, Okuo J, Atenaga M, Ighodaro A, Emina A, Oladejo N. Distribution and speciation of heavy metals in soils around some selected auto repair workshops in Oghara, Delta State, Nigeria. *International Journal of Environment, Agriculture and Biotechnology*. 2018;3(2):574-584

10. Nyiramigisha, P. Harmful impacts of heavy metal contamination in the soil and crops grown around dumpsites. *Reviews in Agricultural Science*. 2021;9:271-282

11. Ure A, Quevauviller P, Muntau H, Griepink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International journal of environmental analytical chemistry*. 1993;51(1-4):135-151

12. Håkanson L. Metal monitoring in coastal environments, In *Metals in coastal environments of Latin America*. Springer, 239-257; 1988

13. Sundaray SK, Nayak BB, Lin S, Bhatta D. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—a case study: Mahanadi basin, India. *Journal of Hazardous Materials*. 2011;186(2-3):1837-1846

**Comment [DR15]:** Italics

14. Müller U, Steinhoff U, Reis LF, Hemmi S, Pavlovic J, Zinkernagel RM, Aguet M. Functional role of type I and type II interferons in antiviral defense. *Science*, 1994;264(5167):1918-1921

**Comment [DR16]:** Italics

15. Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*, 1961;72(2):175-192

**Comment [DR17]:** Italics

16. Barbieri M. The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. *Journal of Geology & Geophysics*. 2016;5(1): 1-4

**Comment [DR18]:** Italics

17. Islam S, Ahmed K, Masunaga S. Potential ecological risk of hazardous elements in different land-use urban soils of Bangladesh. *Science of the total environment*, 2015;512:94-102

18. Tomlinson D, Wilson J, Harris C, Jeffrey D. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländermeeresuntersuchungen*, 1980;33:566-575

19. Ore OT, Akhigbe GE, Adegunwa AO, OlalekanEO, Ayeni DA, Omirin OM, Adebisi PE. Total and chemical speciation analyses of potential toxic metals in refuse dumpsite soils. *World J. Appl. Chem*. 2019;4:25-35

20. Adelowotan O, Olabanji IO, Makinde OW, Oluyemi EA. Heavy Metals Speciation of Soil from Automobile Mechanic Workshops in Oshogbo Metropolis, South Western Nigeria. Open Science Journal of Analytical Chemistry. 2018;~~3~~(1):1-10

**Comment [DR19]:** Italics

21. Obasi N, Akubugwo E, Kalu K, Ugbogu O. Speciation of heavy metals and phyto-accumulation potentials of selected plants on major dumpsites in Umuahia, Abia State, Nigeria. International Journal of Current Biochemistry Research.2013;~~1~~(4):16-28

**Comment [DR20]:** Italics

22. Nigerian Department of Petroleum Resources (DPR). Target and Intervention Values for Metals in Soils; 2002.

UNDER PEER REVIEW