*Received: 13th December 2024, Accepted: 14th December 2024, Published: 22nd December 2024*

ANACHEM JOURNAL
ISSN: 2006-5221 (Online)

# ASSESSMENT OF HEAVY METALS IN THE SOILS OF SOME SELECTED SECONDARY SCHOOL PREMISES IN IKOT EKPENE LOCAL GOVERNMENT AREA, AKWA IBOM STATE, NIGERIA

**M. N. Mgbemena*[1], M. I. Udo[1], M. O. kalunta[1] and K. O. Amadi[1]**
[1]Department of Chemistry, Michael Okpara University of Agriculture Umudike, Abia State, Nigeria.
Corresponding author's e-mail: nkolimgbemena@gmail.com

***DOI: https://doi.org/10.5281/zenodo.14567449***

## ABSTRACT

*Soils contain some heavy metals which are hazardous to the environment. Chemical fractionation of some heavy metals (Zn, Cr, Hg, Cd, Pb, Cu and Mn) in soils of five selected secondary school premises in Ikot Ekpene Local Government Area, Akwa Ibom State, Nigeria, was determined in this study. Five sampling sites were chosen from each secondary school, and subsets were collected from each site to form a composite sample for each school. Each sample was analyzed using a sequential extraction procedure using an atomic absorption spectrophotometer (Bulk scientific VGP 210). The results showed that the metals partitioned themselves in geochemical phases in the following order: Oxidizable > residual > Reducible > Exchangeable > Carbonate. The low levels of metals (Zn, Cr, Hg, Cd, Pb, Cu and Mn) in sites 2 and 5, retrieved from the exchangeable and carbonate fraction, emphasize their readily bioavailability for a geochemical phase in the biota. The analyzed heavy metals obtained from the studied sites from 1-5 showed the following percentage bioavailability Zn (30.72%, 27.93%, 23.11%, 25.27%, 18.18%), Cr (11.44%, 14.29%, 13.62%, 30.41%, 12.64%), Hg (16.84%, 43.63%, 15.89%, 22.03%, 22.72%), Cd (18.44%, 27.21%, 28.43%, 41.94%, 31.73%), Pb (32.25%, 21.92%, 36.40%, 43.82%, 15.52%), Cu (14.59%, 42.19%, 32.20%, 22.77%, 26.53%) and Mn (41.29%, 19.83%, 12.50%, 24.48%, 7.72%). The fractionation analysis revealed low bioavailable fractions, indicating that the heavy metals under analysis were in geochemical forms and not quickly released into soil solution to increase bioavailability.*

***Keywords:*** Bioavailability, Geochemical phases, Soil, Heavy metals.

## INTRODUCTION

As a multifaceted entity, soil has different constituents that determine its properties (Hakanson, 1992). Soil constituents significantly impact the availability and distribution of metal fractions in soils (Ahumada, 1999). Heavy metals are majorly released into the environment through anthropogenic activities in the soil, unlike organic contaminants, oxidized to carbon dioxide by microbial action. Due to their non-biodegradability, some metals do not react during microbial or chemical degradation. Instead, they accumulate and persist long in the soil (Kirprichtchikova *et al.*, 2006; Karlen *et al.*, 2017). Soils, including heavy metals, are among the most absorptive sinks for solid waste. The high

concentration of heavy metals in the soil creates the need to assess their environmental risk to the health of living organisms. However, some heavy metals like zinc, iron, manganese, etc., are available as micronutrients, and some, like mercury, lead, cadmium, etc., are not needed in the body (Khan *et al.,* 2015). Heavy metals have atomic weight, density and specific gravity more significant than 5.0 $gkm^3$ (Adiran *et al.*, 2015; Ogoke, 2015; Duffus, 2002). The sources of heavy metals in soil are the lattice structure of primary and secondary soil minerals, soil solution, exchange soil sites, soil containing iron and manganese oxides, and organic plant litter. Heavy metals are present in soil minerals and bound to different phases of soil particles through several processes, like absorption, ion exchange, complexation and co-precipitation, redox reaction, biological mobilisation, and immobilisation (Akcay *et al*., 2003), and the mobility of heavy metals is influenced by various soil properties, including profile development, soil structure, oxides, carbonates, and organic matter (Kabata-Pendias and Singh, 2007). These different phases of existence or chemical forms affect their mobility within the soil; that is, metals have varying abilities to leave the binding site and enter the soil solution, where plants then take them up.

For numerous geochemical applications, the total metal content of soils is valuable; however, for agricultural purposes, the bioavailability of these metals is more significant than their biological extraction potential (Cottenie *et al., 2*000). Sequential extraction is one of the techniques available for identifying and estimating the chemical forms of these heavy metals in contaminated soil. It x-rays the origin, mode of occurrence, biological and phytochemical availability, mobility, and transport of trace metals (Okonkwo and Eboatu, 2006). Utilizing a five-step sequential extraction process based on the capacity to fractionate heavy metal bioavailability and binding to soil main fractions is ascertained in this research by Tessier *et al.*, (1979).

Understanding heavy metal pathways, mobility, and bioavailability requires understanding their physiochemical forms, which is widely acknowledged. Identifying and quantifying heavy metal phases are crucial for assessing their environmental bioavailability and monitoring soil physiochemical properties. Most studies focus on trace metal contamination and pollution levels. Many studies have been

conducted on the availability of metals in plants and soils close to the roads. Still, information on heavy metal availability and mobility is scarce, particularly in soils in secondary schools. This study, therefore, investigates the availability of metals (Pb, Zn, Cu, Cd, Hg, Cr, and Mn) in secondary school soils. The proximity and effectiveness of metals that will leach out and bind to the soil's less mobile phase are considered in this study.

## MATERIALS AND METHODS

***Study Area:*** The study was conducted in five secondary school premises in Ikot Ekpene town, in Ikot Ekpene Local Government Area, Akwa Ibom State, Nigeria. Ikot Ekpene, known as Raffia City, is a historic town in Akwa Ibom situated between 5010'55' 0N, 70 42' 48" 0E coordinates with an elevation of 76 meters (249 feet) with a current population of 432,00 (Nair, 2001). There are some records of average commercial activities in the area. It has a tropical humid climate with little temperature variations. The area's average temperature is $30^0$C at day and $22^0$C at night (Nair, 2001).

**Soil Sample Collection and Preparation:** Five sites were mapped out in each secondary school premises, and five samples were collected from each site, comprising twenty subsamples from each secondary school. Samples were extracted from 0 -20cm depth using an automatic core driller (Ashraf *et al.*, 2011; Shamshuddin *et al.*, 2012). The soil samples were air-dried and homogenized to obtain a representative sample, then sieved through a 2mm stainless sieve and stored in a polythene bag at 40°C. The same treatment was carried out in all five secondary schools.

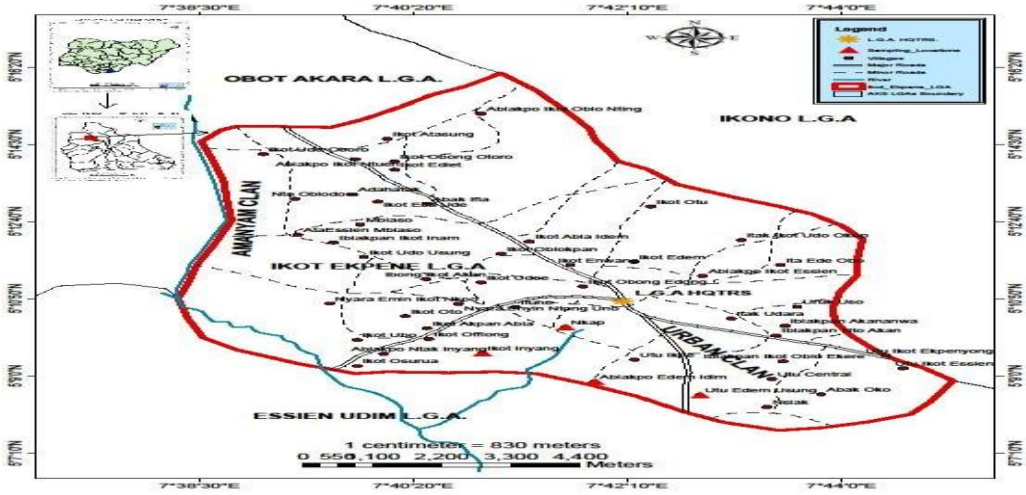

**Figure 1: Map showing the study location**

***Measurement of the overall concentration and sequential extraction procedure of heavy metals from soil samples***

Total concentrations of Zn, Cr, Hg, Cd, Pb, Cu, and Mn were determined using the USEPA method described in Ashraf *et al* (2012), Khodadoust *et al.,* (2004) and Ilori *et al.,* (2012). The geochemical forms and bioavailability of Zn, Cr, Hg, Cd, Pb, Cu, and Mn in soils were assessed using the sequential extraction schemes modified by Asagba *et al.,* (2007), and Iwegbue (2007). The heavy metals were divided into five operationally defined fractions using the techniques of Tessier *et al*.

One gram of the dried soil sample was weighed, extracted and treated for each of the fractions as follows:

Fraction I—Exchangeable fraction (F1) In a 50 ml centrifuge tube, 20 ml of 1.0 M magnesium chloride solution (pH 7.0 with NaOH) was mixed with 1 g of soil sample and shaken for 1 hour on a mechanical shaker.

Fraction II—Metals bound to carbonates (F2): 20 ml of a 1.0 M sodium acetate solution was added to the F1 residue, and the pH was adjusted to 5.0 ml with concentrated glacial acetic acid. The resulting solution and mixture were agitated in a mechanical shaker for 4 hours.

Fraction III—Metals bound to Fe-Mn oxides, also known as the reducible fraction (F3), 50 ml of 0.04 M hydroxylamine hydrochloride in 25 m% glacial acetic acid was added to the F2 residue and heated at 96 ± 3 °C with occasional agitation for 5 hours.

Fraction IV—Metals bound to organic matter or oxidisable fraction (F4), 7.5 ml of 0.02 M nitric acid, and 12.5 ml of 30 % hydrogen peroxide were added to the F3 residue and pH was adjusted to 2 with nitric acid. The mixture was heated to 85 ± 2°C in a water bath for 2 hours, with occasional agitation. After adding 7.5 ml of acidified 30 % hydrogen peroxide, the mixture was heated to 85 ± 2°C for 3 hours with intermittent agitation. The cooled mixture was then mixed with 12.5 ml of 3.2 M ammonium acetate in 20 % nitric acid, and the sample was diluted to 20 ml before being stirred continuously for 30 minutes.

Fraction V—The residual fraction (F5), the residues from step 4 were quantitatively transferred to a digestion vessel, and the metals were dissolved in aqua-regia (3:1 volume of $HNO_3$: HCl) twice sequentially.

The mixture was raised over time to reflux and held for one hour. Following each subsequent extraction procedure, the mixture was separated into liquid and solid phases by centrifuging for 15 minutes at 4000 rpm. The supernatant was then decanted into a polypropylene bottle for metal analysis. The atomic absorption spectrophotometer was used to measure the heavy metal concentrations in each supernatant. The five sample locations and the control sample underwent these processes for soil sequential fractionation analyses.

The exchangeable and carbonate fractions were determined, and % bioavailability was calculated (Kestem and Forstner, 2015).

$$\% \text{ Bioavailable } = \frac{F_1+F_2}{F_1+F_2+F_3+F_4+F_5} \times \frac{100}{1}$$

**Where, F1 = Metal content bound to exchangeable fraction. F2 = Metal content bound to carbonate fraction. F3 = Metal content bound to iron and manganese oxides. F4 = Metal content bound to organic matter, F5 = Residual fraction**

## RESULTS AND DISCUSSION

**Table 1: Site 1: Community Secondary School**

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizable | Residual | $\sum_{1-5}$ | Mean | Bioav.(%) |
|---|---|---|---|---|---|---|---|---|
| Zn | 6.9 | 6.4 | 5.6 | 14.3 | 10.1 | 43.3 | 8.66 ±1.61 | 30.72 |
| Cr | 2.6 | 0.9 | 0.61 | 12.3 | 14.2 | 30.61 | 6.12 ±2.90 | 11.44 |
| Hg | 4.7 | 1.7 | 7.0 | 13.2 | 11.4 | 38.00 | 7.60 ±2.11 | 16.84 |
| Cd | 5.5 | 2.3 | 8.0 | 11.9 | 14.6 | 42.3 | 8.46 ± 2.19 | 18.44 |
| Pb | 13.8 | 5.1 | 11.1 | 25.3 | 3.3 | 58.6 | 11.72 ±3.89 | 32.25 |
| Cu | 4.8 | 2.0 | 12.0 | 15.5 | 12.3 | 46.6 | 9.32 ±2.53 | 14.59 |
| Mn | 3.4 | 12.0 | 2.0 | 9.2 | 10.7 | 37.3 | 7.46 ± 2.01 | 41.29 |

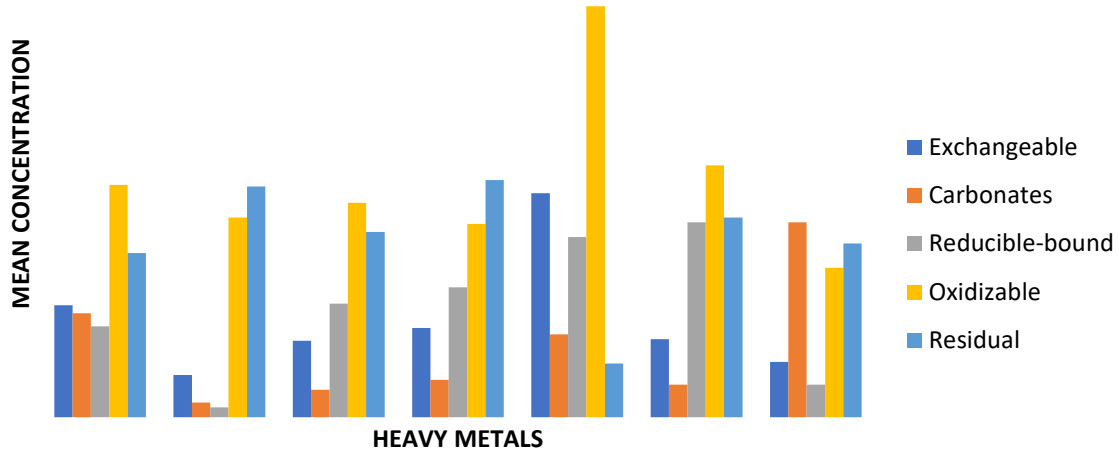


**Figure 2: The heavy metals fraction patterns of Community Secondary School**

The geochemical forms of Metals (exchangeable, carbonates, Fe-Mn oxides, organic matter, and residual) that were operationally defined were displayed in Table 1, along with the total of these forms, mean concentration levels (mg/kg), and the bioavailable fraction (%) of Zn, Cr, Hg, Cd, Pb, Cu, and Mn in the locations under study, as well as the control value. When collecting soil samples, consideration was given to factors like the gradient level (high and low) and the direction of erosion flow, which may have contributed to the variation in individual metal concentration levels across all sampling points in the studied locations. (Control Location and Figures 2–7). Most of the time, waste and metal run-off from erosion indicated high reliability in the sequential extraction procedures, as the concentration levels of each studied metal were higher in the sampling point of low gradient and then decreased in the fact of the high gradient. Most of the heavy metals examined were discovered in the organic and residual soil fractions close to the research sites. This suggested that the metals' bioavailability and mobility are low. It also implied there was little chance of any pollution from the metals under investigation. An extraction sequence in which the solubility decreased serves as an operational definition for the five geochemical forms.

Figure 2 displays the fraction patterns of heavy metals. Zinc, Lead, Mercury, and Copper are examples of heavy metals with high abundance that were phase-bound to

oxidizable fraction; chromium and cadmium were found in the residual fraction (Usero *et al.,* 2001). Most manganese was found in the reduced fraction. Others in known metals (carbonate fraction and exchangeable) are less. Figure 2: The average amount of heavy metals (mg/kg-1) in a soil sample compared to geochemical fractions: In the soils surrounding the research location, the mean concentration of heavy metals ranged from 6.12 2.90 to 11.72 3.89 mg/kg.

The geochemical form of heavy metal in soils around the studied site is presented in Table 1, and the distribution is mobile due to the low carbonate content in the soil (Smith, 2010). The heavy metals in the oxidizable fraction are relatively stable but can be mobilized under strongly oxidizing conditions due to the degradation of organic matter (Papafchppaki *et al.,* 2008; Mgbemena and Onwukeme, 2012). The percentage bioavailability in site 1 ranges as follows: 30.72%, 11.44%, 16.84%, 18.44%, 32.25%, 14.59%, 41.29%. Therefore, the accumulation of metals (Lead, Mercury, etc) in this fraction calls for concern because these metals are among the heavy metals that constitute the broadest possible health risk to humans and animals through the plant uptake dietary route (Lund, 2005).

**Table 2: Site 2: Lutheran High School**

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizable | Residual | $\sum_{1-5}$ | Mean | Bioav.(%) |
|---|---|---|---|---|---|---|---|---|
| Zn | 3.0 | 8.2 | 5.6 | 12.5 | 10.8 | 40.1 | 8.02 ± 1.72 | 27.93 |
| Cr | 1.7 | 3.3 | 13.8 | 5.0 | 11.2 | 35.0 | 7.0 ± 2.34 | 14.29 |
| Hg | 4.3 | 2.9 | 1.7 | 2.9 | 4.7 | 16.5 | 3.3 ± 0.54 | 43.63 |
| Cd | 2.4 | 5.6 | 3.8 | 4.2 | 13.4 | 29.4 | 5.88 ± 1.94 | 27.21 |
| Pb | 4.0 | 7.2 | 12.5 | 11.4 | 16.0 | 51.1 | 10.22 ± 2.09 | 21.92 |
| Cu | 5.1 | 3.0 | 1.9 | 5.3 | 3.9 | 19.2 | 3.84 ± 0.64 | 42.19 |
| Mn | 6.6 | 0.4 | 0.4 | 15.1 | 12.8 | 35.3 | 7.06 ± 3.05 | 19.83 |

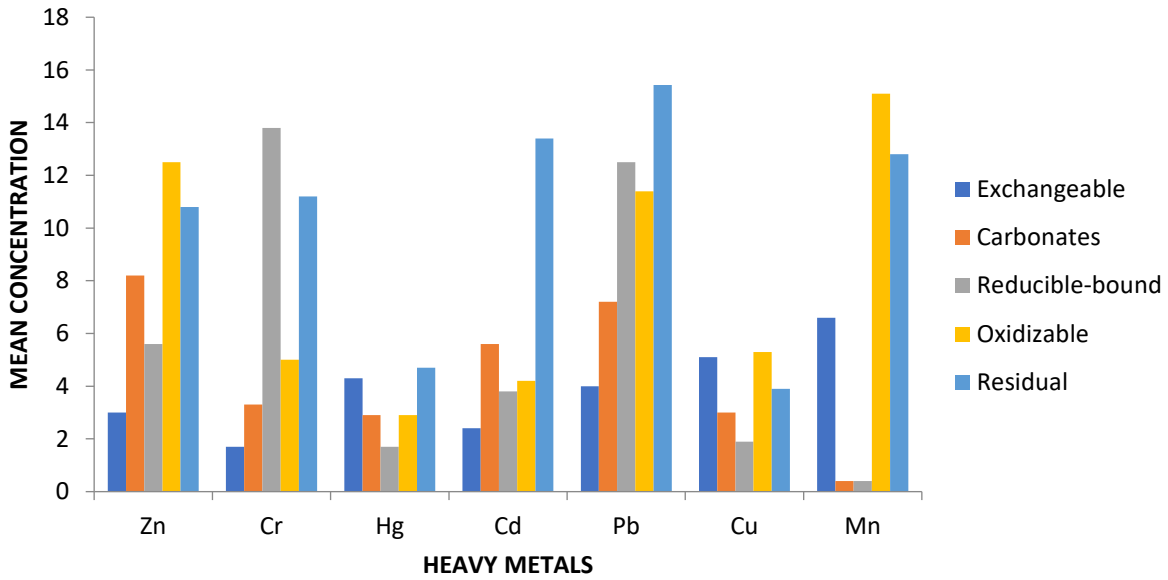


**Figure 3: Mean concentration of heavy metals in soil sample against geochemical fractions (mg/kg$^{-1}$)**

The mean concentration level of heavy metals in the soil around the studied site, as shown in Table 2 and Figure 3, ranged between 3.30±0.54 to 10.22± **2**.09. Cadmium and Lead were most retained in the residual fraction; Chromium was significant in the reducible fraction with 13.9mg/kg. Zinc and Manganese bounded most with Oxidizable fractions (12.5 and 15.1mg/kg, respectively). Mercury and Copper were associated in all the geochemical forms with minimal values of less than 6mg/kg. In Table 2 above, manganese was primarily found in the oxidizable fraction, with 15.1mg/kg, and was accumulated in carbonates and the reducible fraction. The metals retained in the residual fraction were firmly bound to the crystal lattices of minerals and were thus not released into the environment. The higher the metals present in this fraction, the lower the degree of pollution (Howari and Banat, 2001). The strong complex that manganese tends to form with humic matter is why the high manganese content is in the oxidizable fraction (NRC, 2003). Papafchppaki *et al.*, (2008) had previously reported a similar outcome. The bioavailability percentages of the metals were 14.29%, 43.63%, 27.21%, 21.92%, 42.19%, and 19.83%.

**Table 3: Site 3: Okop Eto Secondary School**

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizable | Residual | $\sum_{1-5}$ | Mean Bioav.(%) | |
|---|---|---|---|---|---|---|---|---|
| Zn | 2.5 | 3.3 | 5.0 | 9.7 | 4.6 | 25.1 | $5.02 \pm 1.25$ | 23.11 |
| Cr | 1.6 | 3.7 | 10.2 | 10.9 | 12.5 | 38.9 | $7.78 \pm 2.15$ | 13.62 |
| Hg | 1.8 | 4.3 | 9.9 | 11.7 | 10.7 | 38.4 | $7.6 \pm 1.95$ | 15.89 |
| Cd | 6.4 | 4.8 | 2.2 | 12.0 | 14.0 | 39.4 | $7.88 \pm 2.22$ | 28.43 |
| Pb | 11.5 | 6.1 | 10.8 | 13.1 | 6.2 | 47.7 | $9.54 \pm 1.43$ | 36.40 |
| Cu | 7.9 | 5.3 | 4.1 | 12.4 | 11.3 | 41.0 | $8.20 \pm 1.62$ | 32.20 |
| Mn | 3.0 | 0.5 | 4.4 | 14.5 | 5.6 | 28.0 | $5.60 \pm 2.38$ | 12.50 |

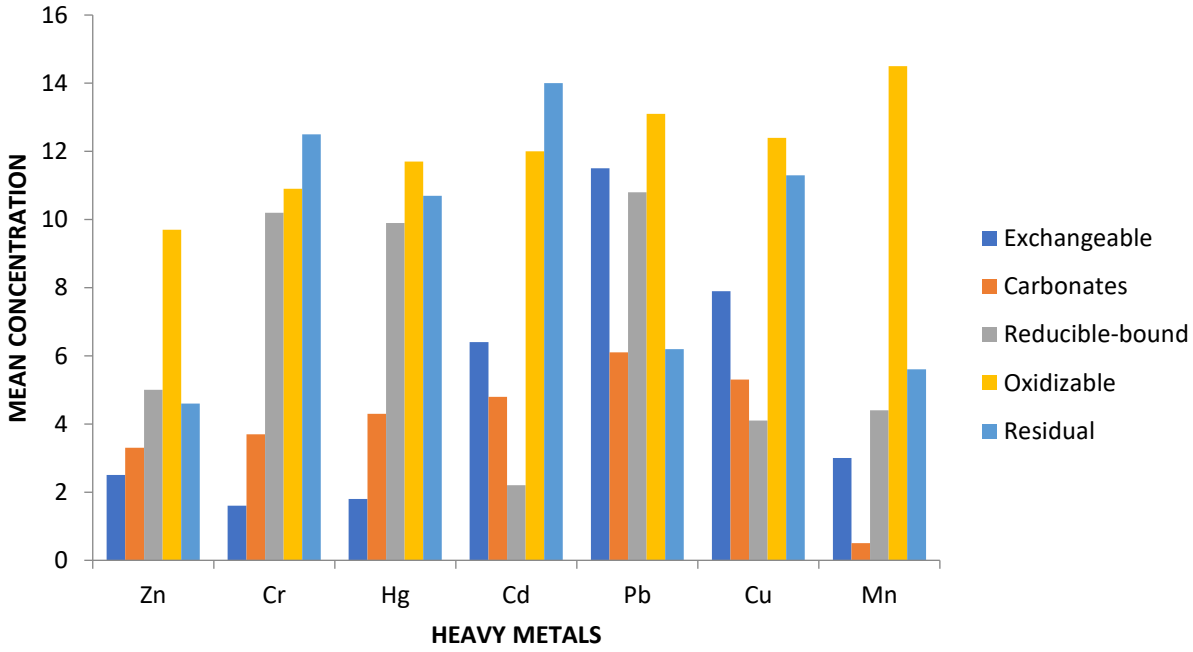


**Figure 4: Mean concentration of heavy metals in soil sample against geochemical fractions (mg/kg$^{-1}$)**

The mean concentration of heavy metals in soil around the studied site varied between 5.02 ± 1.25 to 9.54 ± 1.43mg/kg. The geochemical fraction of heavy metals in soil within the research location was presented in Table 3 (site 3), and the distribution pattern for heavy metals fraction is in Figure 4. Zinc, mercury, lead, copper, manganese, and other metals were strongly correlated with the oxidizable fraction, suggesting that humic material is where metals accumulate most frequently. Humic material forms strong complexes with a wide range of inorganic and organic ligands, making it highly soluble in oxidised aquatic systems (Akcay, 2003).

The study's findings regarding the dominance of different metals in the oxidisable fraction supported those of Adiran *et al.*, (2015) who found that copper was present in contaminated soil in Imo State, Nigeria, with oxidizable and residual fractions of 26.2 and 25.8 mg/kg, respectively. However, in Agbabu bitumen deposit sediments, Cottenie *et al.*, (2000) discovered that the residual fraction had the highest concentration of copper, ranging from 45.4 to 65.6 mg/kg in both wet and dry seasons, with a very low probably bioavailable fraction of 0.6%. The high concentration of metals linked to the oxidizable fraction in the soil surrounding the study location may be explained by the metals' easy complexation with the soil organic matter due to the high formation of organo-copper compounds with it (Mgbemena and Onwukeme, 2012)

Because heavy metals interact with organic matter through various mechanisms, the presence of organic matter and acid-resistant minerals may be responsible for the high levels of chromium and cadmium in the residual fraction found in the study (Adiran, 2006). Site (Location) 3 had acceptable percentages of metal bioavailability at 23.11%, 13.62%, 15.89%, 28.43%, 36.40%, 32.20%, and 12.50%.

**Table 4: Site 4: Technical College**

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizable | Residual | $\sum_{1-5}$ | Mean Bioav.(%) |
|---|---|---|---|---|---|---|---|
| Zn | 6.2 | 8.0 | 10.9 | 13.7 | 17.4 | 56.2 | 11.24 ± 2.00 25.27 |
| Cr | 9.5 | 4.7 | 11.2 | 18.8 | 2.5 | 46.7 | 9.34 ± 2.84 30.41 |
| Hg | 5.4 | 5.0 | 13.7 | 11.1 | 12.0 | 47.2 | 9.44 ± 1.78 22.03 |
| Cd | 15.2 | 6.9 | 2.5 | 17.0 | 11.1 | 52.7 | 10.54 ± 2.66 41.94 |
| Pb | 7.5 | 12.0 | 8.8 | 1.8 | 14.4 | 44.5 | 8.90 ± 1.45 43.82 |
| Cu | 4.7 | 4.0 | 5.5 | 13.3 | 10.7 | 38.2 | 7.64 ± 1.84 22.77 |
| Mn | 6.5 | 4.0 | 0.9 | 18.4 | 13.1 | 42.9 | 8.58 ± 3.17 24.48 |

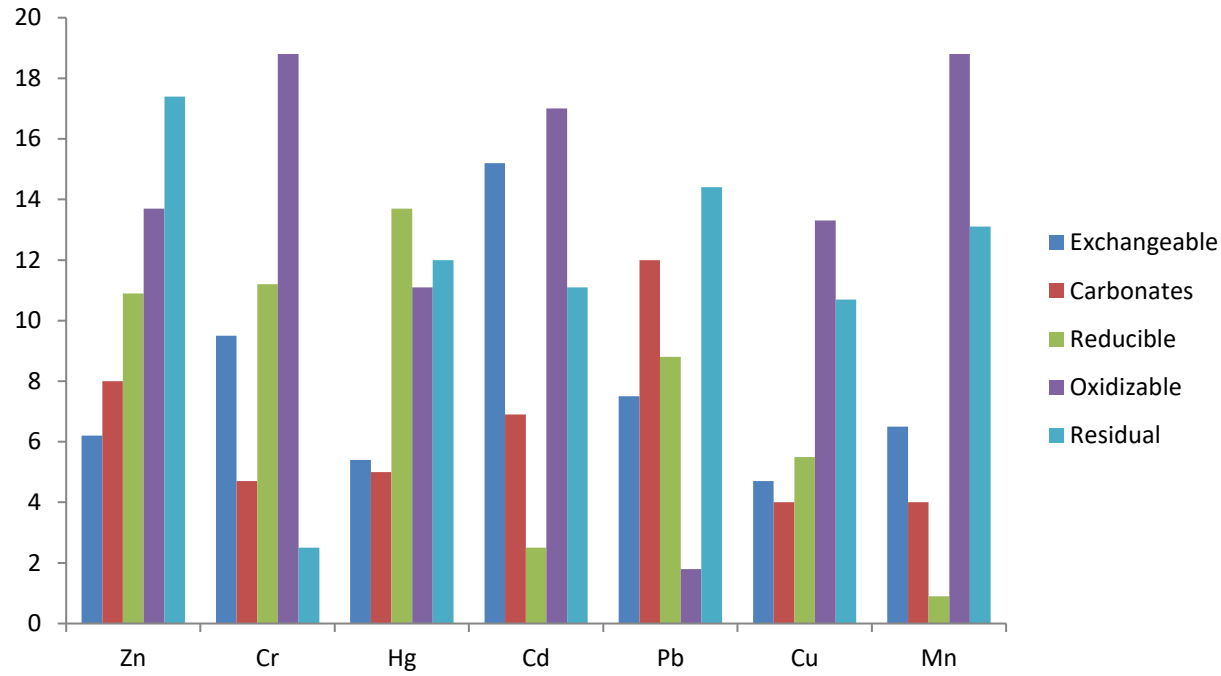


**Figure 5: Mean concentration of heavy metals in soil sample against geochemical fractions (mg/kg$^{-1}$)**

The soil surrounding the research site's mean concentration of heavy metals ranged from 7.64 ± 1.84 to 11.24 ± 2.00. Figure 5 residual fraction (17.4 and 14.4 mg/kg) was primarily lead and zinc, respectively. The high metal concentrations in the fraction indicated that trace metals were held within the crystal matrix of the residual fraction and were most likely retained under silicate minerals (Osakwe, 2012). As a result, under typical circumstances, metals in this fraction would be difficult to release into solution over an extended period (Okonkwo, 2006; Forkle, 1979; Skvaria, 1991).

Chromium, Cadmium, Copper and Manganese were associated with oxidizable fraction. As the mean concentration level in some geochemical fractions in these soils increased, the amount of metals in oxidizable and residual fractions increased. Hence, the potential bioavailability in these soils was reduced. The overall metal content of the soils from the research site also influenced the distribution of metals in different geochemical fractions. In the soils surrounding car waste dumpsites in Oyo State, Nigeria, Osakwe, (2010) reported high levels of metals in the residual fraction, ranging from 14.96 to 39.71 mg/kg, with a potentially bioavailable fraction varying between 28.41 and 50.83%. In a related study, Skvaria (1991) and Forkle, (1979) found that the sediments of the Diobu River in Port Harcourt,

Nigeria, had a higher residual level fraction of 54.81%. Mercury can be trapped by being soluble in water and volatile in the air (Smith, 2010), and it is also present in the oxidizable and residual fractions. Mercury exposure has been linked to kidney damage (Mergher *et al.*, 2007). The percentage bioavailability in site 4 were 25.27%, 30.41%, 22.03%, 41.94%, 43.82%, 22.77%, 24.48%.

**Table 5: Site 5: State Government College**

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizble | Residual | $\sum_{1-5}$ | Mean | Bioav. (%) |
|---|---|---|---|---|---|---|---|---|
| Zn | 2.5 | 4.1 | 6.8 | 12.3 | 10.6 | 36.3 | 7.26 ± 1.86 | 18.18 |
| Cr | 1.6 | 3.0 | 1.5 | 17.5 | 12.8 | 36.4 | 7.28 ± 3.31 | 12.64 |
| Hg | 3.7 | 3.8 | 10.1 | 10.5 | 4.9 | 33.0 | 6.60 ± 1.52 | 22.72 |
| Cd | 2.0 | 5.9 | 0.8 | 3.2 | 13.0 | 24.9 | 4.98 ± 2.18 | 31.73 |
| Pb | 4.4 | 2.6 | 11.9 | 15.4 | 10.8 | 45.1 | 9.02 ± 2.40 | 15.52 |
| Cu | 4.0 | 6.4 | 11.2 | 2.2 | 15.4 | 39.2 | 7.84 ± 2.42 | 26.53 |
| Mn | 1.7 | 0.2 | 0.3 | 11.4 | 11.0 | 24.6 | 4.92 ± 2.58 | 7.72 |

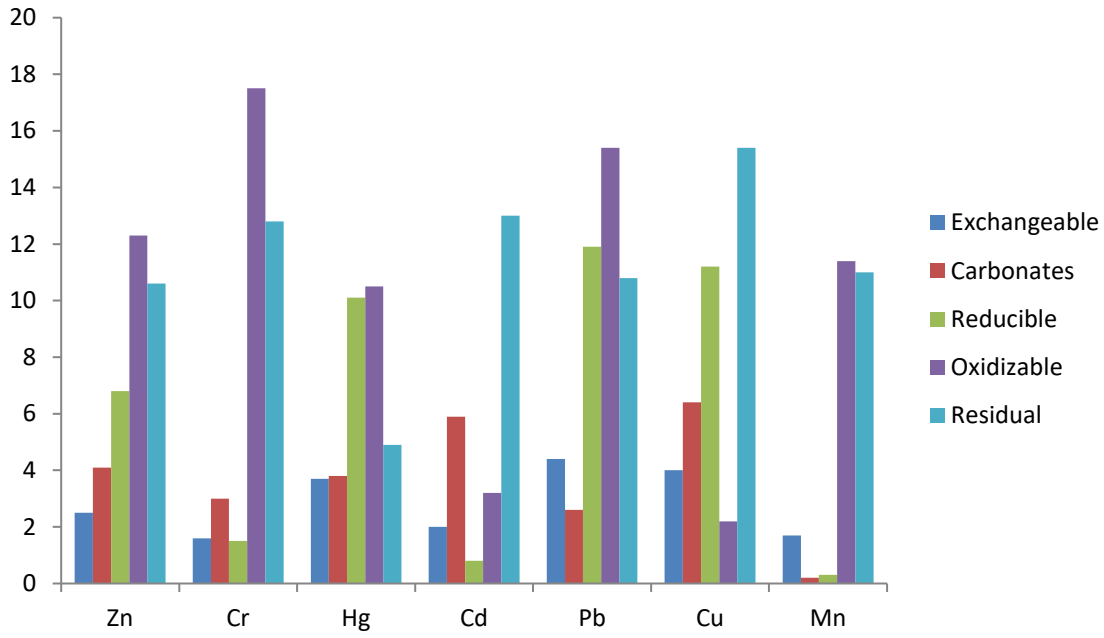


**Figure 6: Mean concentration levels of metals in soil**

In Figure 6, Zinc, Chromium, Mercury, Lead, and Manganese were the most abundant in the oxidizable fraction. In contrast, Cadmium and Copper were the most abundant in the residual fraction. The mean concentrations of metals in soil around the studied site ranged from 4.92 ± 2.58 to 9.02 ± 2.40 mg/kg. The percentage bioavailability of metals at Site 5 was 18.18%, 12.64%, 22.72%, 31.73%, 15.52%, 26.53%, and 7.72%, respectively. The high level of metals in the non-bioavailability form indicated that metals like manganese could be embedded in the crystal lattices of clay minerals and silicate, which are usually insoluble. The formation of lead phosphates, particularly Pyromorphites, in soils has been linked to immobilising lead and thus reducing its bioavailability (Hettiarachech and Perzynki, 2002; Ruby *et al*., 1994). The high concentration of non-bioavailable metals suggested that certain metals, like manganese, might be trapped in the crystal lattices of silicate and clay minerals. These metals are usually insoluble in form, like the ionic compounds $Mn^{2+}$ and $Mn^{4+}$, and are not easily released into solution, where they could form MnO2 and MnO4 (McBride, 1997). Cadmium is produced as an unavoidable byproduct of zinc metabolic processes when it irreversibly binds to an active site. This destroys normal metabolism (Osakwe, 2012).

Table 6: Control (Uncontaminated Soil)

| Metals/Fraction | Exchangeable | Carbonates | Reducible | Oxidizble | Residual | $\sum_{1-5}$ | Mean | Biov.(%) |
|---|---|---|---|---|---|---|---|---|
| Zn | 0.5 | 0.4 | 0.5 | 1.3 | 2.0 | 4.7 | 0.94 ± 0.31 | 19.15 |
| Cr | 0.1 | 1.2 | 0.1 | 0.8 | 1.6 | 3.8 | 0.76 ± 0.29 | 34.21 |
| Hg | 1.3 | 2.0 | 0.2 | 1.1 | 1.0 | 5.6 | 1.12 ± 0.28 | 58.93 |
| Cd | 0.8 | 0.4 | 1.1 | 0.9 | 1.7 | 4.9 | 0.98 ± 0.21 | 24.49 |
| Pb | 0.6 | 1.0 | 0.0 | 2.1 | 0.9 | 4.6 | 0.92 ± 0.34 | 34.78 |
| Cu | 2.0 | 0.2 | 0.3 | 1.2 | 2.2 | 5.9 | 1.18 ± 0.42 | 37.29 |
| Mn | 0.7 | 1.1 | 0.4 | 1.3 | 1.9 | 5.4 | 1.08 ± 0.26 | 33.33 |

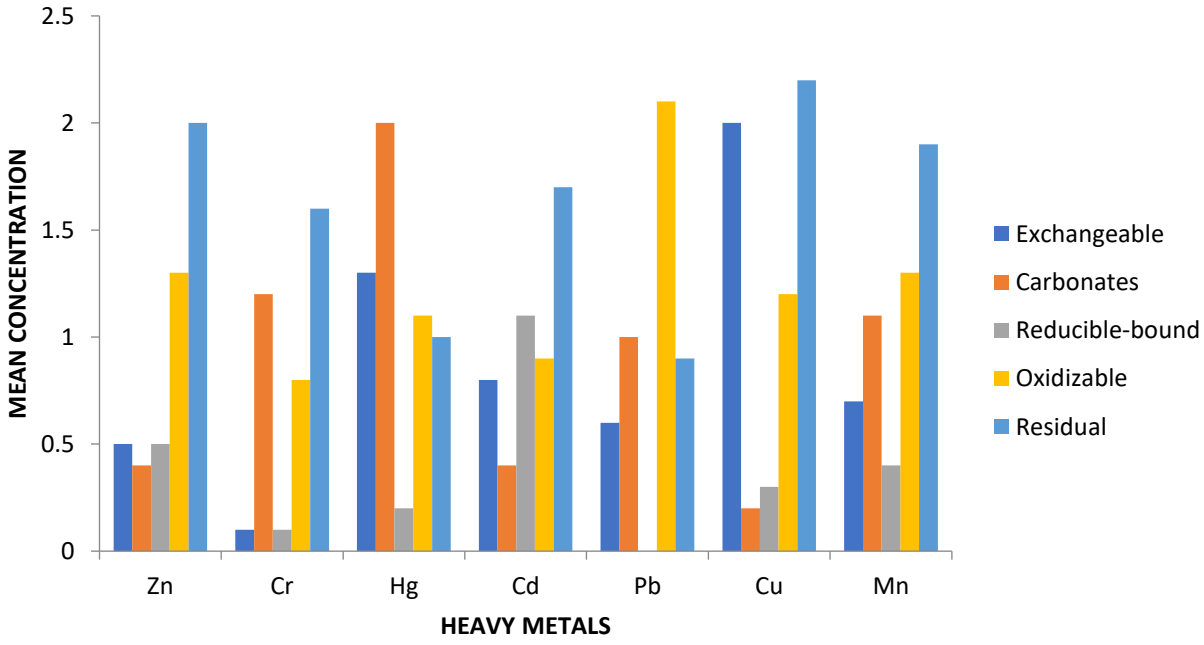


**Figure 7: Mean concentration of heavy metals in soil sample against geochemical fractions (mg/kg) Control Site (x)**

The mean concentration of metals in control soil around the site ranged from 0.92 ± 0.34 to 1.18 ± 0.42. The percentage bioavailability values were 19.15%, 34.21%, 58.93%, 24.49%, 34.78%, 37.29%, and 33.33%. Mercury had a high percentage bioavailability value of 58.93%, indicating gradual pollution by this metal,

given its toxic nature even at low concentrations (Osakwe, 2010). The residual fractions of zinc, chromium, cadmium, copper, and manganese in the control site were also more abundant among the stabile fractions. In contrast, mercury and copper were significantly more abundant in the bioavailable or weakly bound fractions, which included carbonate and exchangeable fractions. The oxidizable lead fractions were the most abundant in control soils, with a 2.1mg/kg value. Metals that are absorbed on the exchangeable and carbonate fraction, which were significant in some sites, were considered weakly bound and may equilibrate with the aqueous phase, thus becoming readily bioavailable. A system or mechanisms that affect the mineral precipitation, dissolution absorption/desorption, and aqueous complexation reactions due to variations in particular combinations of environmental parameters and soil physiochemical properties, such as pH, cation exchange capacity, and organic matter oxidation and reduction reaction potentials, may generally have an impact on the dispersion in the concentration levels of the geochemical forms of metals from one soil location to another. Though it may be thought of as relatively stable, slowly mobile, and poorly available, the reducible and oxidizable bound fraction may alter in response to changes in redox conditions, becoming more soluble in acidic conditions and less soluble in oxidising conditions (Ashraf *et al.*, 2012; Olalade, 2014). Since the residual fraction of metals is incorporated into the crystal lattices of silicates and clay minerals, it is not readily released into solution under typical conditions, making it stable, less reactive, and less bioavailable (Chwarzenbach, 1993)

## CONCLUSION AND RECOMMENDATIONS

This study assessed the distribution, retention, and release of Zn, Cr, Hg, Cd, Cu, Pb, and Mn in selected soils on secondary school grounds. According to the bioavailability study, the bulk of the metals tested had the highest abundance in the oxidizable and residual fractions, suggesting that the metals were rigid. The highest proportions of the oxidizable fraction were extracted from various sites, implying that the metals studied were in stable complexes with very low bioavailability. This demonstrated that it does not appear to pose significant environmental risks. Some geochemical fractions may pose a health risk throughout the food chain. As a result, ecological monitoring is required because the continuous accumulation of heavy metals

may occur over time, posing health risks shortly.

## REFERENCES

Adiran, T., Srecko, N., Mitar, L., Rade, B., Sonja, K. & Nusret, O. (2015). The heavy metals in Agrosystems and impact on health and quality of life, *Macedonian Journal of Medical Sciences.* 3(2), 345-355.

Ahumada, I., Mendoza, J. & Ascar, L. (1999). Sequential extraction in soils irrigated with waste water, commun soil *Sci Plant Anal.* 30, 1057-1519.

Akcay, H., Oguz, A. & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menders and Gedis River sediments. *Water Res*. 31, 813-822.

Asagba, E. U Okiemen, F. E & Osokpor, J. (2007). Screening and speciation of heavy metal contaminated soil from an automobile sparepart market. *Chem speciat Bioavailab*. 19(1), 9-15.

Ashraf, M.A., Maah, M. J. & Yusof, I. (2011). Heavy metals accumulation in plants growing in ex tin mining Catchment. *International Journal of Environmental Science and Technology.* 8(2), 401-416.

Ashraf, M. A., Maah, M. J. & Yusoff, I. (2012). Chemical speciation and potential mobility of heavy metals in the soil of former tin mining catchment. *Sci world J.* https://doi.org/10.1100/2012/125608.

Chwarzenbach, R. P. Gschwen, P. M. & Imboden, D. M. (1993). Environmental organic Chemistry. *Wiley*, New York, 259-261.

Cottenie, A., Camerlynck R., Verloo, M. & Dhaese, A. (2000). Fractionation and determination of trace elements in plants, soils and sediments, *Pure and Applied Chemistry*. 52(1), 45-53

Duffus, J.H. (2002). Heavy metals- A meaningless Term? *Pure and Applied Chemistry*. 7, 793-807.

Forkle, K. (1979). Trace element analysis of food and beverages. *Ass. Prig. and Atom Spectrums*. 185-286.

Hakanson, L. (1992). Sediment variability. In: Burton G. A. Jr (ed) sediment toxicity assessment. CRC Publishers, Boca Ration, 19-36.

Hettiarachech, G.M. & Perzynki, G. M. (2002). In-situ stabilization of soil lead using phosphorus and manganese oxide: Influence of plant growth. *J Environ Qual*, 564-572.

Howari, F.M. & Banat, K. M. (2001). Assessment of Fe, Zn, Cd, Hg, and Pb in the Jordan and Yarmouk River sediments in relation to their physiochemical properties and sequential extraction characterization. *Water, Air and Soil Pollution.* 132(1-2), 43-59.

Ilori, F.E.G., Aisuem,N. O., Sulaiman-Ilobu, B. B., Ekhafor, F., Eneje, R. C. & Efetie-Osie, A. (2012 ). Immobilization effect of cow dung on lead and chromium in soil cultivated with oil palm. *Bull Environ pharmcol life sci.* 19, 74-80.

Iwegbue , C. M. A. (2007). Metal fractionation in soil profiles at automobile mechanic waste dumpsite, Niger Delta, Nigeria. *Waste Manage Res.* 25, 1-9.

Kabata-Pendias, A. & Mukherjee, A.B. (2007). Trace Elements from soil to human. *springer-verlag, Berlin,* 23, 193-195.

Kabala, C. & Singh, B. R. (2001). Fractionation and mobility of copper, lead and zinc in soil profile in the vicinity of a

copper smelter. *J Environ Qual.* 30, 485-495.

Karlen, J., Zalifah, M. K., Yin, Y. H. & Aminah, A. (2017). The uptake of heavy metals by fruit type vegetables grown in selected agricultural area. *Pakistan Journal of Biological Sciences,* 7(8), 1422-1438.

Kestem, M. & Forstner, U. (2015). Speciation of trace elements in sediments. In: Batley G. (ed). Trace element speciation. *Analytical methods of problems.* CRC press, Boca Ration, Florida. 245.

Khan, S., Cao, Q., Zhang, Y.M., Haung, Y.Z. & Gao, B. (2010). Health risks of heavy metals in contaminated soils and foodstuffs irrigated with waste water in Beinjin, China. *Environmental Pollut*. 152 (3), 686-692.

Khodadoust, A. P., Reddy, K. R. & Maturi, K. (2004). Removal of Nickel and Phenanthrene from Kaolin soil using different extractants. *Environ. Eng. Sci.* 21(6), 691-704.

Lund, W. (2015). Speciation analysis-why and how? Fresenius *Journal of Analytical of Chemistry.* 337, 557-564.

McBride, M.B. (1997). Environmental Chemistry of Soil. *Oxford University Press,* New York, 406.

Mgbemena, N.M. & Onwukeme, V.I. (2012). Bioaccumulation of heavy metals in fishes from Aba rivers, Abia State, Nigeria as an indicator of human dietary exposure to toxic substances. *International Journal of Chemistry*. 22, 191-196.

Nair, K.K. (2014). Politics and society in South eastern Nigeria, 1841-1906: A study of power diplomacy and commerce in old calabar. Frank cass 201-214.

NRC (2003). Bioavailability of contaminants in soils and sediments: processes, tools and applications. *National Research Council. Commission on Bioavailability of contaminants in soils and sediments. National* Academy Press, Washington, D. C. US. 420.

Ogoko, E. (2015a). Accumulation of heavy metal in soil and their transfer to leafy vegetables with phytoremediation potentials. *American Journal of Applied Chemistry*. 5(5), 125. 131.

Okonwko, E.M. & Eboatu, A. N. (2006). Environmental pollution and degradation. *Abimac Publishers, Nigeria. 46.*

Ololade, I.A. (2014). An Assessment of heavy metal contamination in soils within auto-mechanic workshops using enrichment and contamination factors with geo-accumulation indexes. *J. Environ Protect.* 5, 970-982.

Osakwe, S. A. (2010). Chemical speciation and mobility of some heavy metals in soils around automobile waste dumpsites in Northern part of Niger Delta, South Central Nigeria. *J. Applied Sci. Env. Mgt.* 14(4), 123-130.

Osakwe, S. A. (2013). Chemical partitioning of iron, Cadmium, nickel and Chromium in contaminated soil of south-eastern Nigeria. *Chemical speciation and bioavailability*,25(1), 71-78

Papafchppaki, A. K., Kotti, M. E. & Stavroulakis, G. G. (2008). Seasonal variation in dissolved heavy metals in the Keritis river, Chania, Greece. *Global Nest Journal.* 10, 320-325.

Ruby, M. V., Davis, A. & Nicholson, A. (1994). In-situ formation of lead phosphates on soils as a method to immobilize lead. *Environ Sci. Technology* 28, 646-654.

Shamshuddin, S., Mokhtar, N. & Paramananthan, S. (2006). Morphology, mineralogy and chemistry of an ex-mining land in Ipoh, perak. Pertanike, 9(1), 89-97.

Skvaria, J. A. (1991). A study on the trace metal speciation in the Ruzin reserviour sediment. *Acta montanistica slovaca Rocmik* 3(2) 177-182.

Smith, R. D., Salt, D. E. & Raskin, (2010). Phyto-remediation, *Annual Reviews in Plant Physiology and Plant Molecular Biology*. 49, 643-668.

Tessier, A., P., Campbell, G. C & Blsson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 52(1), 45-53.

Usero, J, Gamero, M., Morillo, J & Gracia, I. (2001). Comparative study of three sequential extraction procedures for metals in marine sediments, *Environment International*. 24, (4), 487-496.