

# Chemical Speciation, Bioavailability and Risk Assessment of Potentially Toxic Metals in Soils Around Petroleum Product Marketing Company as Environmental Degradation Indicators

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## Research Article

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# **Chemical speciation, bioavailability and risk assessment of potentially toxic metals in soils around petroleum product marketing company as environmental degradation indicators**

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## **Abstract**

The study aims at investigating chemical speciation, bioavailability and risk assessment of some selected metals in soils around refined petroleum depot using the concentrations of the metals as variables to ascertain the impacts of the activities within the petroleum depot. Surface-soils were got from within the premises of Pipelines and Product Marketing Company, Ibadan, Nigeria, while control samples were got at 200 m away from the study location. Electrical conductivity and pH were measured using a calibrated dual purpose meter, while elemental analysis was done using Atomic absorption spectroscopy analytical technique. The results showed that the soils exhibited low ecological risk; minor enrichment for Mn, moderately severe enrichment for Ni and Co, severe enrichment for Cr and extremely severe enrichment for Pb, Zn and Cd; low contamination factor by Pb, Ni, Mn, Cr, Co, and Fe and moderate contamination by Zn and Cd. Geo - accumulation index results indicated unpolluted with Ni, Mn, Cr, Co, and Fe, unpolluted to moderately polluted with Pb and Zn and moderately to strongly polluted with Cd. Inter-element clustering results indicated chemical affinity and/or similar genetic origin among the elements. Speciation analysis suggested that Fe, Co, Cr, Cd, and Ni occurred in the residual fraction; Pb, and Zn in the carbonate fraction, while Mn have its highest percentage in the Fe-Mn oxides fraction. Percentage mobility and bioavailability showed that most of the metals are immobile and non-bioavailable. Study concluded that the oil-impacted soils were contaminated with most of the metals, but with low ecological risk.

**Key words:** AAS, chemical speciation, metals, refined petroleum products, risk assessment, soil

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## **1. Introduction**

The studied petroleum product marketing company (oil depot) which is a subsidiary of Nigeria National Petroleum Corporation (NNPC), supplies various refined petroleum products to retailing outlets for end users in Southwestern part of the country, as well as some Northern states. The depot situated in Ibadan, Nigeria has the largest loading facilities in Southwestern Nigeria. It was established in a remote area suitable for depot activities, however, as a result of population explosion, expanse of land close to the perimeter fence of the storage facilities are currently being exploited for residential purposes and the occupants engage in farming activities even within and around the perimeter fence of the oil depot. Shallow stream which is used in farming and other activities transverse the depot premises and extends to the residential areas. There will be great health and environmental hazards to humans, aquatic life and other forms of life in the locality, as a result of infiltration, plant uptake, bioaccumulation and biomagnifications in the food chain when contaminated with oil products. The existence of petroleum products has significant environmental effects due to diverse petroleum development processes. It was stated by Tissot and Welte, (1980) that crude oil commonly amasses trace metals via its treatment and refining processes; source rocks, sea salt intrusion, and during migration of crude oil. These contaminants can enter the environmental matrices, affect flora, fauna and finally go into the food chain. Thus, it is necessary to evaluate the concentrations of these selected contaminants (Pb, Ni, Zn, Cd, Mn, Cr, Co and Fe.) in the premises of the study area as indicators of environmental degradation, hence this study.

In this study, the elemental analysis was carried out using Atomic absorption spectrometry (AAS) analytical technique. Its principle is founded on the absorption of electromagnetic rays at a particular wavelength by unexcited ground state gaseous atom to generate a signal that can be

assessed. The absorbed radiation is directly proportional to the concentrations of elements present in the path length of the optical device. The technique is regularly used in analytical chemistry for the determination of the concentration of a particular element that of concern (analyte) in the sample matrix for analysis. The AAS technique is capable of determining levels of more than 70 different elements in solution employed in several arenas of science (Harvey 2000).

## **2.0 Experimental**

### **2.1 Study area**

The area of study is in Ibadan, South-Western Nigeria with coordinates on latitude 7°15' 2" N and longitude 5 ° 12' 36" E in the tropic rainforest of Nigeria. Figure 1 presents the map showing the sampling points in the study area.

### **2.2 Sampling and sample treatment**

Surface soil samples from divers points in the study area were collected by dropping the soils into pre-labeled air tight vessels using hand trowel and conveyed to laboratory for analysis. Control samples were got outside the premises of the oil depot where there were little or no anthropogenic influences, about 200 m away (Table 1). Rocks, pebbles, and stones were discarded from soil samples before air-dried at room temperature for two weeks, but well protected with plain white sheets to avoid fugitive dusts from sullyng the samples. The samples were then powdered with a thoroughly cleaned agate mortar and pestle and ground samples were then mixed for homogeneity of the soil particle size. The prepared samples were then divided into two sets for pH/conductivity determination and elemental analysis respectively.

### **2.3 pH and Electrical conductivity determination**

Standard analytical methods described by Bailey (1986), and Adebisi and Adeyemi (2010) was used for pH and electrical conductivity determinations using a calibrated dual purpose digital

pH/electrical conductivity meter (Jenway 4510) at 25°C. The values of the pH were also established using hand-set glass electrode meter HI 2209 (Hanna instrument).

## **2.4 Elemental analysis**

### **2.4.1 Quality assurance**

The technique of Laxen and Harrison (1981) was implemented for the cleaning of the sample bottles and glassware, while blank and triplicates analyzes were done on the samples as reported by Adebisi and Ayeni (2010).

### **2.4.2 Recovery analysis/Quality control**

The accuracy of the AAS analytical procedure was established through spiking of 0.5g of some soil samples with 5.0 µg/g of the standard mixture of the heavy metal solution of the selected metals (Cd, Cr, Cu, and Ni), while another set 0.5g of soil samples were weighed accurately but without spiked standard solution. Both the spiked and the unspiked soil samples were taken through the same digestion process and taken for AAS analysis. The percentage of the heavy metal recovered (%R) was evaluated using the following equilibrium expression:

$$\% R = [(C' - C) / B] \times 100 \quad (1)$$

Where C' = concentration of heavy metal in the spiked soil sample, C = concentration of the heavy metal in the unspiked sample. B = amount of heavy metal used for spiking (Oyewole and Adebisi, 2017).

### **2.4.3 Total metal analysis**

Based on the description by Adebisi and Ayeni (2010), powdered soil samples (0.5 g) were weighed precisely and pretreated using 20 mL Aqua regia (HCl and HNO<sub>3</sub> acids in the ratio 3:1). The mixture of soil and aqua regia was heated on a thermostatic hot plate set at 70°C, and to near dryness and then permitted to cool. A 5 mL of HF was added to the mixture in a Teflon beaker and

again heated. The digestates were filtered into 50 mL volumetric flask and made up to mark with double distilled water, and subjected to heavy metals (Pb, Ni, Zn, Cd, Mn, Cr, Co and Fe) analysis by Atomic Absorption Spectrophotometer, Perkin Elmer (model - A Analyst 200) at the Multidisciplinary Central Research Laboratory (MCRL) University of Ibadan, Ibadan, Nigeria.

#### **2.4.4 Chemical speciation analysis**

The process was designed and engaged to extract and partition the soil composition of the target metals viz., Pb, Ni, Zn, Cd, Mn, Cr, Co and Fe into exchangeable fraction, carbonate bound fraction, Fe-Mn oxides bound fraction, organic bound fraction, and residual fractions and water-soluble fraction. Each soil sample (0.5 g) of dried and homogenized soil samples sized 2.0 were put through successive extraction to get the six operationally defined fractions for each of the soil samples. The supernatant aqueous layers that were obtained from each fraction were cautiously filtered into 75 mL analytical vial and analysed using AAS to evaluate the concentrations of Pb, Ni, Zn, Cd, Mn, Cr, Co and Fe. The summary of the adapted technique as reported by Abu-Kukati (2001) and Oyewole & Adebisi (2017) is found below.

##### **2.4.4.1 Water soluble fraction (F1)**

A 0.5 g of the homogenized soil sample each was thoroughly mixed with 10 mL distilled water and the mixture treated to constant shaking by mechanical shaker for 1 hour. It was then permitted to remain still for 30 minutes and the supernatants transferred into in a volumetric flask and made up to 25 mL with doubly distilled water. The filtrate solution is poured and stored in cleaned plastic containers for elemental analysis.

##### **2.4.4.2 Exchangeable fraction (F2)**

The residue from F1 was mixed and stirred with 20 mL 1 M  $MgCl_2$  solution at pH 7 for 1 hour at room temperature. The mixture was shaken carefully for 1 hour and then permitted to stand for 30

minutes. The supernatant was decanted and made up to mark in a 25mL standard volumetric flask with distilled water.

#### **2.4.4.3 Fraction bound to carbonates (F3)**

The residue from F2 was subjected to the treatment of 20 mL of 1 M  $C_2H_3NaO_2/CH_3COOH$  acid buffered at pH 5 for 5 hours at room temperature. The ensuing blend was permitted to stand for 30 minutes, while the supernatant transferred from the residual mixture from F2.

#### **2.5.4.4 Fraction bound to iron and manganese oxides (F4)**

The residue from F3 was also extracted through gentle reducing environments viz., 250 mL of water was used to dissolve 0.69 g of hydroxylamine hydrochloride ( $NH_2OH.HCl$ ) in a standard volumetric flask to prepare 0.04 M  $NH_2OH.HCl$ . The residue was extracted with 20 mL of the 0.04 M  $NH_2OH.HCl$  in 25% acetic acid (v/v) with shaking at  $96\text{ }^\circ\text{C} \pm 1^\circ\text{C}$  in a water bath for 6 hours. The extract was then poured from the residual soil sample into a 25 mL standard volumetric flask and made up to mark with doubly distilled water.

#### **2.4.4.5 Fraction bound to organic matter and sulphide (F5)**

The residue from F4 was oxidized using the following steps viz., 3 mL of 0.02 M  $HNO_3$  and 5 mL of 30% (v/v) hydrogen peroxide at pH 2, was added to the residue from F4, while the mixture heated to  $85\text{ }^\circ\text{C}$  in a water bath for 2 hours with intermittent shaking and then permitted to cool down. This was followed by the addition of 3 mL of 30% hydrogen peroxide which has been adjusted to pH 2 with  $HNO_3$ . The mixture was then heated at  $85^\circ\text{C}$  for 3 hours with intermittent shaking and permitted to cool down followed by the addition of 5 mL of 3.2 M ammonium acetate in 20% (v/v)  $HNO_3$ , followed by dilution to a final volume of 20 mL with doubly distilled water. The extracted metal solution was then poured from the residual sediment and was then used for the next but the last extraction.

#### **2.4.4.6 Residual or inert fraction (F6)**

The final fraction which is the residue from F5 was oven dried at 105°C, digested with a mixture of 5 mL conc. HNO<sub>3</sub> (HNO<sub>3</sub>, 70% w/w), 10 mL hydrofluoric acid (HF, 40% w/w) and 10 mL perchloric acid (HClO<sub>4</sub>, 60% w/w) in Teflon beakers. The supernatant was poured into 25 mL volumetric flask and made to the mark with doubly distilled water and was then taken for elemental analysis using AAS technique.

### **2.5 Data management**

The geochemical data gathered analysis in this study involved the application of statistical techniques which includes; Descriptive statistics (range, mean, standard deviation) as well as enrichment factor, geo-accumulation index, contamination factor, modified degree of contamination, pollution load index, T-test, Cluster analysis, principal component analysis/ANOVA, Geoaccumulation index ( $I_{geo}$ ), and Potential ecological risk assessment were all deployed to interpret/explain the data obtained in this research. The distribution pattern of the analysed metal temporally and spatially was evaluated using coefficient of variation. Information about the available metals to be transferred in the ecosystem studied was done through mobility factor (Oyewole and Adebisi, 2017).

#### **2.5.1 Mobility factor (MF)**

The mobility of metals in the studied soils is appraised on the ground of absolute and relative contents of fraction weakly bound to the soil components. The relative index of metal mobility was determined as a mobility factor (MF) subject to equation below (Salbu *et al.*, 1998).

$$MF = \frac{F1+F2+F3}{F1+F2+F3+F4+F5+F6} \times 100 \quad (2)$$

### 2.5.2 Contamination factor (CF)

The level of contamination of the studied soils by the elements is expressed in terms of a contamination factor ( $CF$ ) using the following equilibrium expression:

$$CF = \frac{CM_{(sample)}}{CM_{(background)}} \quad (3)$$

Where the contamination factor  $CF < 1$  indicating low contamination;  $1 \leq CF < 3$  implies moderate;  $3 \leq CF \leq 6$  denotes considerable, and  $CF > 6$  indicating contamination level is very high (Hakanson, 1980).

### 2.5.3 Geoaccumulation index ( $I_{geo}$ )

Geo-accumulation index ( $I_{geo}$ ) is employed to quantify the extent of heavy metal contamination associated with the soils. It was calculated using the equilibrium equation below.

$$I_{geo} = \log_2 (C_n / 1.5 B_n) \quad (4)$$

$C_n$  is the heavy metal 'n' concentration determined in the sample and  $B_n$  is background geochemical value of the element n, and 1.5 is the correction factor for the background matrix due to lithogenic effects. Geo-accumulation index ( $I_{geo}$ ) has been classified into seven as: class 0  $I_{geo} \leq 0$ , unpolluted; class 1,  $0 < I_{geo} \leq 1$ , unpolluted to moderately; class 2,  $1 < I_{geo} \leq 2$ , moderately; class 3,  $2 < I_{geo} \leq 3$ , from moderately to strongly; class 4,  $3 < I_{geo} \leq 4$ , strongly; class 5,  $4 < I_{geo} \leq 5$ , from strongly to extremely; and class 6,  $I_{geo} > 5$ , extremely polluted (Buccolieri *et al.*, 2006).

### 2.5.4 Enrichment factor (E.F)

Enrichment factor (EF) was used in the study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soil (Barbieri, 2016). It has also been used to indicate the degree of pollution or contamination or both. It is calculated using the expression:

$$EF = \frac{(C_d / C_{ref})_{sample}}{(B_d / B_{ref})_{crust}} \quad (5)$$

$B_d$  is the concentration of the reference element in the environment under examination,  $C_d(\text{sample})$  is the concentration of the element of interest in the soil analyzed,  $C_{ref}(\text{sample})$  is the concentration of the element in the environment of reference (Earth crust), and  $B_{ref}$  is the concentration of the reference element in the environment (Earth Crust). There are five different contamination types that have been identified (Sucharova *et al.*, 2012).

E.F < 1 means there is no enrichment; E.F < 3, minor enrichment; E.F = 3 – 5, moderate enrichment; E.F = 5 – 10, moderately severe enrichment; E.F = 10 – 25, severe enrichment; E.F = 25 – 50, very severe enrichment, and E.F > 50, extremely severe enrichment.

For the case of this study, Iron (Fe) was the referred element as a result of its abundance value of 4700 mg/kg.

### **2.5.5 Modified degree of contamination (mCd)**

Degree of contamination by metals of interest in soil in this study was determined by the equation below:

$$mCd = \frac{\sum CF}{N} \quad (6)$$

Where N is the number of analyzed metals where C.F is the contamination factor. Modified degree of contamination is broken into seven categories:  $mCd < 1.5$ , nil to very low degree of contamination;  $1.5 \leq mCd < 2$ , low degree of contamination;  $2 \leq mCd < 4$ , moderate degree of contamination;  $4 \leq mCd < 8$ , high degree of contamination;  $8 \leq mCd < 16$ , very high degree of contamination;  $16 \leq mCd < 32$ , extremely high degree of contamination; and  $mCd \geq 32$ , ultra-high degree of contamination (Abraham and Parker, 2008).

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

The pollution load index, proposed by Tomlinson *et al.* (1980) was determined by the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_N)^{1/N} \quad (7)$$

Where N is the number of metals under study where C.F is contamination factor. The PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. There are three indicators for pollution load index of a particular site. They are  $PLI < 1$  indicates perfection;  $PLI = 1$  means that only baseline levels of pollutants are present; and  $PLI > 1$  depicts the quality of the site has been deteriorated (Tomlinson *et al.*, 1980).

### 2.5.7 Potential ecological risk assessment

The potential ecological risk index (RI) determines the sensitivity of biological communities in the large contaminated areas (Hakanson, 1980). This method comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals (Singh *et al.*, 2010; Douay *et al.*, 2013). It takes into account the CF of metals, their potential ecological risk factor (Er) and the toxicological response factor (Tr) taken from Duodu *et al.* (2016). It is determined by the following equation

$$RI = \sum Er = \sum Tr \times CF \quad (8)$$

where Er indicates the potential ecological risk factor of individual metal, Tr indicates the toxicological response factor of each metal (Duodu *et al.*, 2016). CF is the contamination factor of each metal. The MRI takes into account the EF, toxicological response factor (Tr) of individual metal. It is calculated by the following equation:

$$MRI = \sum MEr = \sum Tr \times EF \quad (9)$$

where MEr is the modified potential ecological risk factor of individual metal and EF represents the enrichment factor of each metal.

The considered pollutants for the potential ecological risk index in these Pb, Ni, Zn, Cd, Mn, Cr and Co. Table 2 shows the ecological risk index group approved by Hakanson (1980).

### **3. Results and discussion**

#### **3.1 Result of recovery analysis**

The recovery, precision, accuracy and sensitivity of the analytical procedures used in this research work for the elemental analysis of the soil samples were tested and confirmed reliable. The value of the result of percentage recovery for selected heavy metals is as shown in Table 3. The percentage of the recovered metals ranged between 85 - 96%. However, the acceptable range limits for the percentage recovery analysis for elements is 70 – 110%, hence, the result of this study is reliable as it falls within the acceptable limit.

#### **3.2 pH and Electrical conductivity results**

The mean values of the analyzed parameters (pH and electrical conductivity (E.C) for the oil-impacted and control soil samples are presented in Figure 2. The pH values of the oil-impacted soils range from 7.07 to 7.33 with a mean value of 7.24. This suggests that the oil-impacted soils are slightly alkaline. The pH as well as some other properties of the soil is essential for the explanation of the factors that contribute/determine the transportation and solubility of heavy metals in the soil (Matthews–Amune and Kakulu, 2013). Phosphates and carbonate mineral forms of metals are formed at higher pHs in the soil. These minerals are not soluble in water, thus unavailable. At low pHs, however, metals are more bioavailable as they are present in the soil matrix as soluble species such as soluble organo-metals and free ions. (Egbenda *et al.*, 2015). The electrical conductivity (E.C) values of the oil-impacted soils range from 78.8 to 201  $\mu\text{Scm}^{-1}$  with a mean value of 109.22  $\mu\text{Scm}^{-1}$ . The relatively high values of E.C observed for the oil-impacted soils indicate significant presence of ionizable materials in the soils (Egbenda *et al.*, 2015), which can be due to soluble salts of metals introduced into the soil via discarded petroleum products.

#### **3.3 Elemental analysis results**

The comparison of the elemental concentrations of the oil-impacted and control soils is presented in Figure 3 using the mean values. It shows the relativity between the concentrations of elements in the oil-impacted and control soil samples. From the results, Fe has the highest mean concentration occurred in both the control and oil-impacted soils, while, Cd has the lowest mean concentrations. It is observed that highest mean concentration of 1187.08 mg/kg is recorded for Fe, while lowest mean concentration of 1.81 mg/kg is recorded for Cd in the oil – impacted soil. The control samples have a mean concentration of 725.24 mg/kg for Fe, and a mean concentration of 1.53 mg/kg for Cd. However, the relatively high mean concentration recorded for Fe in the soil studied is in agreement with the earlier observation that Nigeria soil has very high Fe content. It is observed that the elemental composition of the oil-impacted soils is higher than that of control soils. This implies that the oil-impacted soils accumulated the metals from the anthropogenic sources such as refined petroleum. Generally, the concentration of heavy metals in the oil-impacted soils is of the order: Fe > Zn > Pb > Cr > Ni > Mn > Co > Cd, while it follows the order: Fe > Zn > Cr > Pb > Mn > Ni > Co > Cd in the control soils.

### **3.4 Data analysis results**

#### **3.4.1 Analysis of variance results**

The single factor analysis of variance was carried out on the oil-impacted soils using Microsoft excel software package. If  $F > F_{critical}$ , the null hypothesis is rejected. However, this is not the case as  $0.12 < 2.01$  as shown in Table 4. Therefore, we accept the null hypothesis. By implication, the means of the ten populations are not all equal.

#### **3.4.2 Hierarchical cluster analysis results**

The hierarchical cluster analysis was used in this study to unveil the correlation among the selected heavy metals using Euclidean distance as a basis for similarity measurement. Statistical Package

for Social Scientist (SPSS) was used for this analysis. The inter – element clustering as a result of the analysis of the selected heavy metals in the oil impacted soil samples is as shown in Figure 4. The x-axis has the Euclidean distance to produce the similarity matrix, and the y –axis has the analyzed metals. The result showed two major groups; the first group being Fe and the second group being cluster of Cd, Co, Ni, Mn, Cr, Pb and Zn. In the second group, there is inter - element clustering between Zn and Cr; and another between Cd, Co, Ni, Mn, and Pb. The latter group members show closest inter-element clustering, indicating they have the same chemical affinity and/or from similar origin.

### **3.4.3 T-test analysis results**

A comparison of the concentrations of the analyzed metals in the oil-impacted and control soils using T-test values at 95% confidence interval is presented in Table 5 show the T – test results comparing the concentration of the selected metals in oil – impacted and control soils. The test was carried out at 95% confidence interval. A significant difference is confirmed when the value of T – experiment is greater than 2.13 at this limit and otherwise if less. For the sake of this study, there is a significant difference between the concentration of each of the analyzed metal in the oil – impacted and control soils.

### **3.4.4 Comparison of the elemental values with their standard permissible limits**

The comparison of the elemental values and their standard permissible limits is presented in Table 6. The mean concentrations of the metals are less than the minimum allowable limits set by the Nigeria Department of Petroleum Resources (D.P.R) aside from Zn and Cd with corresponding mean concentration values of 254.20 and 1.81 mg/kg which are greater than the standard limits set by DPR. The comparatively low mean values obtained for the other metals (Pb, Ni, Mn, Cr, Co

and Fe) in this study is an indication that the anthropogenic influences of oil spills might not have significant contribution on the general level of metals in the oil depot.

### **3.4.5 Comparison of the total elemental concentrations with similar studies**

Table 7 shows the comparison between the mean concentrations of the analysed metals in this study and that of other similar studies. The mean concentrations of the metals obtained in this study are comparatively higher than those reported by Fu *et al.* (2014), Aigberua and Inengite (2019), except for Ni and Cr. However, the mean concentration values obtained from this study is less than the one reported by Adebisi and Ayeni (2010). This difference is probably due to the variations in the soil composition of the study area compared to the other studies.

### **3.4.6 Indices of pollution**

Various indices of pollution were employed in this study in estimating the determination of contamination level as well as degree of pollution of the oil – impacted soils involved calculations using different pollution indices such as; contamination factor, geo-accumulation index, enrichment factor, modified degree of contamination and pollution load index. The results of the estimations are presented in Table 8. A Turekian and Wedepohl (1961) background geochemical value was adopted in this study as a standard reference. There is variation in the contamination factor of the analyzed metals in the oil-impacted soils as deduced from table. The oil-impacted soils exhibited low contamination by Pb, Ni, Mn, Cr, Co and Fe and moderate contamination by Zn and Cd.

With regards to the calculation of the enrichment factor for the study, Fe was chosen as the geochemical normalizer or reference element because of its conservative nature during diagenesis. The oil-impacted soils exhibited minor enrichment for Mn, moderately severe enrichment for Ni and Co, severe enrichment for Cr and extremely severe enrichment for Pb, Zn and Cd.

The geo-accumulation index is a reflection of both natural and anthropogenic metal inputs to the soils. The oil-impacted soils are unpolluted with Ni, Mn, Cr, Co and Fe, unpolluted to moderately polluted with Pb and Zn and moderately to strongly polluted with Cd.

With respect to the results of the modified degree of contamination and pollution load index, the oil-impacted soils showed a very low degree of contamination by the investigated metals. The pollution load index indicated a perfection of site (oil depot) quality.

### **3.4.7 Potential ecological risk assessment**

The potential ecological risk assessment values of the analyzed metals of the oil-impacted soils are presented in Table 9. The potential ecological risk index (RI) is a reflection of the general situation of pollution brought about by the presence of individual metals. Considering the individual modified ecological risk index/potential ecological risk factor, the oil-impacted soils exhibited a low contamination risk by Pb, Ni, Zn, Mn, Cr and Co while they exhibited a moderate contamination risk by Cd. However, results of the modified potential ecological risk factor ( $E_r$ ) showed that Cd had high adverse effects on the oil depot as a result of its significantly high  $E_r$  value. The RI value of the oil-impacted soils indicated low ecological risk by the analyzed metals.

### **3.4.8 Chemical speciation results**

The chemical speciation was used in this study to know the biological availability of the selected heavy metals in the oil-impacted soils of the area under study. The percentage mean extraction of the heavy metals for the oil-impacted soils is presented in Figure 5a while that of the control soils is presented in Figure 5b. The distribution of lead among the operationally defined fractions in the oil-impacted soils follows the trend: Carbonate fraction > Exchangeable fraction > Residual fraction > Fe-Mn oxide fraction > Organic matter fraction > Water-soluble fraction. The distribution of nickel in the oil-impacted soils follows the trend: Residual fraction > Exchangeable

fraction> Carbonate fraction>Water-soluble fraction>Organic matter fraction> Fe-Mn oxide fraction. The distribution of zinc follows the trend: Carbonate fraction>Exchangeable fraction>Fe-Mn oxide fraction>Water-soluble fraction>Residual fraction>Organic matter fraction. Cadmium fractionated in this order: Residual fraction>Organic matter fraction>Carbonate fraction>Fe-Mn oxide fraction>Water-soluble fraction>Exchangeable fraction. The partitioning of Mn in the soils is of the order: Fe-Mn oxide fraction>Residual fraction>Carbonate fraction>Organic matter fraction>Exchangeable fraction>Water-soluble fraction. Chromium was distributed among the fractions according to: Residual fraction>Organic matter fraction>Fe-Mn oxide fraction>Carbonate fraction>Exchangeable fraction>Water-soluble fraction. The distribution of cobalt among the fractions was according to: Residual fraction>Carbonate fraction>Exchangeable fraction>Fe-Mn oxide fraction>Organic matter fraction>Water-soluble fraction. The distribution of iron among the operationally defined fractions in the oil-impacted soils follows the trend: Residual fraction>Fe-Mn fraction>Carbonate fraction>Organic matter fraction>Exchangeable fraction>Water-soluble fraction.

The residual fractions constitute a significant amount of the analyzed heavy metals, most notably Nickel, Cadmium, Chromium, Cobalt and Iron. This is consistent with the reports of Ramirez *et al.*, 2005. Iron exhibited the highest percentage of extraction (43.07%) in the residual fraction. The high percentage of these metals in the residual phase is an indication that they were not available for uptake by organisms. Residual fractions usually contain abundance mineral compounds composed majorly of sand in which metals can bond strongly with its crystal structure. Hence, metals in this fraction are in non-toxic, non-mobile, non-reactive, and non-available form. A soil sample is considered pollution free with relatively higher percentage of metals. The higher the percentages of metals in this form, the more environmentally friendly the sample. Residual or inert

fraction implying low mobility and bioavailability indicates probably a low degree of pollution by the metals considered.

The Fe-Mn oxide fraction showed a relatively high extraction by the oil-impacted soils for Mn. Manganese has a percentage extraction of 33.19% in the Fe-Mn oxide fraction. This phase is also next in importance for Fe which showed a 23.90% extraction in the Fe-Mn oxide phase. The highest amount of heavy metals found in Fe-Mn oxide form may be due to the chemical composition of the parent rock of tropical soils rich in Fe-Mn minerals. The association of higher concentration of metals with these fractions is caused by adsorption of these metals by the Fe-Mn mineral surface (Zakir *et al.*, 2008). High percentage abundance of metals in the Fe-Mn oxide phase has been reported to be influenced by the high concentration of Fe-Mn minerals in the soil (Etim and Adie, 2012) and may limit the mobility and bioavailability of heavy metals attached to these minerals. Nevertheless, metals in Fe and Mn oxides fractions can be relatively more sensitive to environmental changes unlike metals in residual fraction, which are often unreactive with respect to metal dynamics scale (Akinyemi *et al.*, 2012). Precipitation and oxidation reactions control the availability of Fe and Mn in soils because they are present in appreciable quantities in tropical soils. Metals associated with oxide minerals are likely to be released in reducing conditions because; relatively small changes in pH toward reducing conditions would cause reduction of Fe and Mn oxide species leading to dissolution of associated metals (Zakir *et al.*, 2008).

The amount of Pb and Zn extracted in percentage for the carbonate fraction is 20.76% and 19.06% respectively. The implication of this is that Pb can be mobilized back at more available status with the pH and redox under reduced conditions (Iwegbue, 2011). In relative to other metals, Zn has been known to be mobile and bioavailable in the soil, all attributed to the significant percentage of

exchangeable or carbonate fraction as well as reducible fraction (Teixera et al., 2010). The significant levels of the fractions are commonly attributed to Zn adsorbed permanently on the variable charge surface sites of Fe, Mn or Al oxide (Iwegbue, 2011). However, adsorption of Zn to the carbonate fraction that is reported in this study is consistent with the report of Ideriah *et al.*, 2013.

### **3.4.9 Bioavailability of the analyzed metals**

Mobility of a metal is a measure of its bio-availability. Mobility of a metal is measured by how much of it is present in the first three geochemical fractions (the bio-available form), relative to how much of the metal is present in all the six fractions. It measures the relative amount of the metal weakly bound to the soil components (Adamma *et al.*, 2014).

Figure 6 is a diagram showing the bioavailable and non-bioavailable fractions of the analyzed metals in the oil-impacted soils. Generally, the bio-availability of the metals follows the trend: Ni > Zn > Pb > Co > Cr > Cd > Mn > Fe. The relatively high percentage observed for some of these metals suggest that the metals are available for uptake, and when these metals are present in soils via anthropogenic inputs such as oil spills, they have a high potential to be mobile and bioavailable.

## **4. Conclusion and recommendations**

Oil-impacted soils in the premises of Pipelines and Product Marketing Company (PPMC), Ibadan, Nigeria were analyzed for potentially toxic metal levels using Atomic Absorption spectrophotometer. This was determined to evaluate the levels of potential toxic metals and ecological risk of the contaminants in the area of study. The levels of the heavy metals were assessed in terms of their total elemental concentrations and chemical speciation as well as various statistical approaches in order to assess the distribution and chemical forms of the analysed metals soils. The clustering analysis result showed the correlation between the metals, indicating chemical

affinity and/or common sources. The study indicated that the oil-impacted soils have elevated levels of metals than the control soils. The contamination factor indicated a low contamination for all the analyzed heavy metals, other than Zn and Cd which have moderate contamination. The geo accumulation index equally revealed varying levels of contamination associated with the oil depot by the heavy metals. The potential ecological risk assessment indicated a low ecological risk by the metals. The speciation of the heavy metals revealed the chemical behavior and forms of the analysed metals in the soils. The chemical fractionation gave information on the percentage of the heavy metals that are mobile and bioavailable. Variations existed in the behavior of these metals in the soil; some reside in the residual fraction while some are available for uptake. This investigation will also serve as a reference guard for studies of similar settings.

It is therefore recommended that the levels of the analysed metals should be monitored periodically for effects of anthropogenic contributions; also indiscriminate disposal of used oils should be prevented.

### **Conflict of Interest Statement**

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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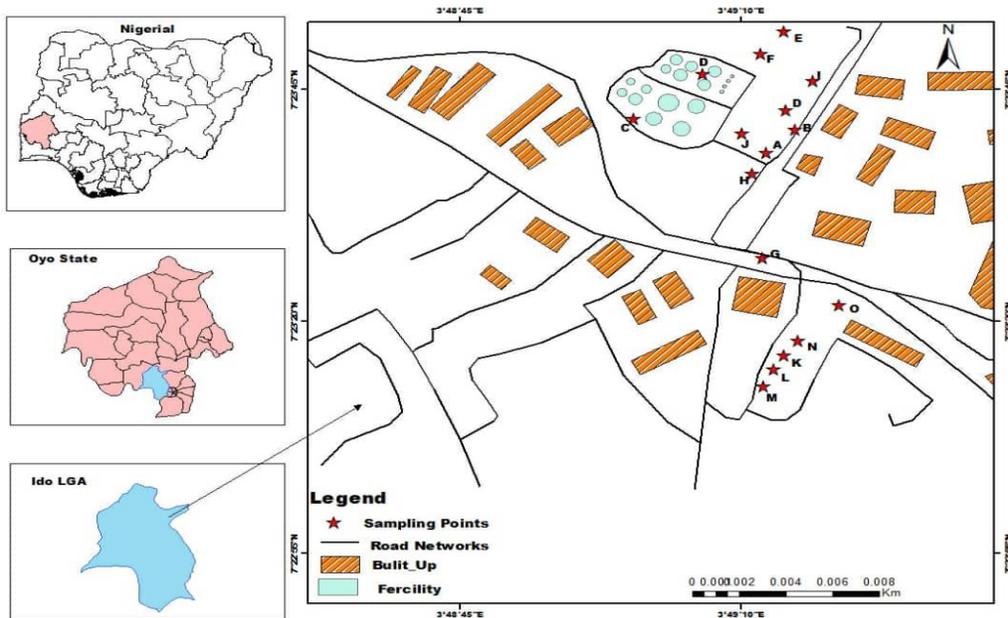


Figure 1: Map showing the Sampling Locations of the Study Area

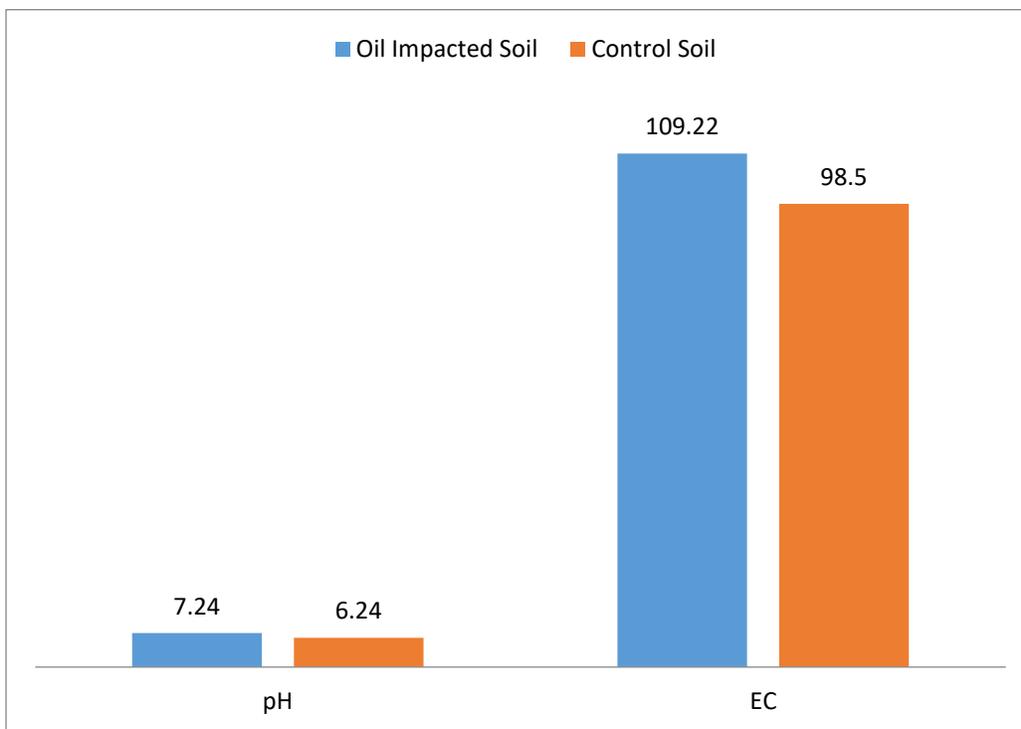


Figure 2: Graph comparing the mean values of pH and Electrical Conductivity of oil-impacted and control soils

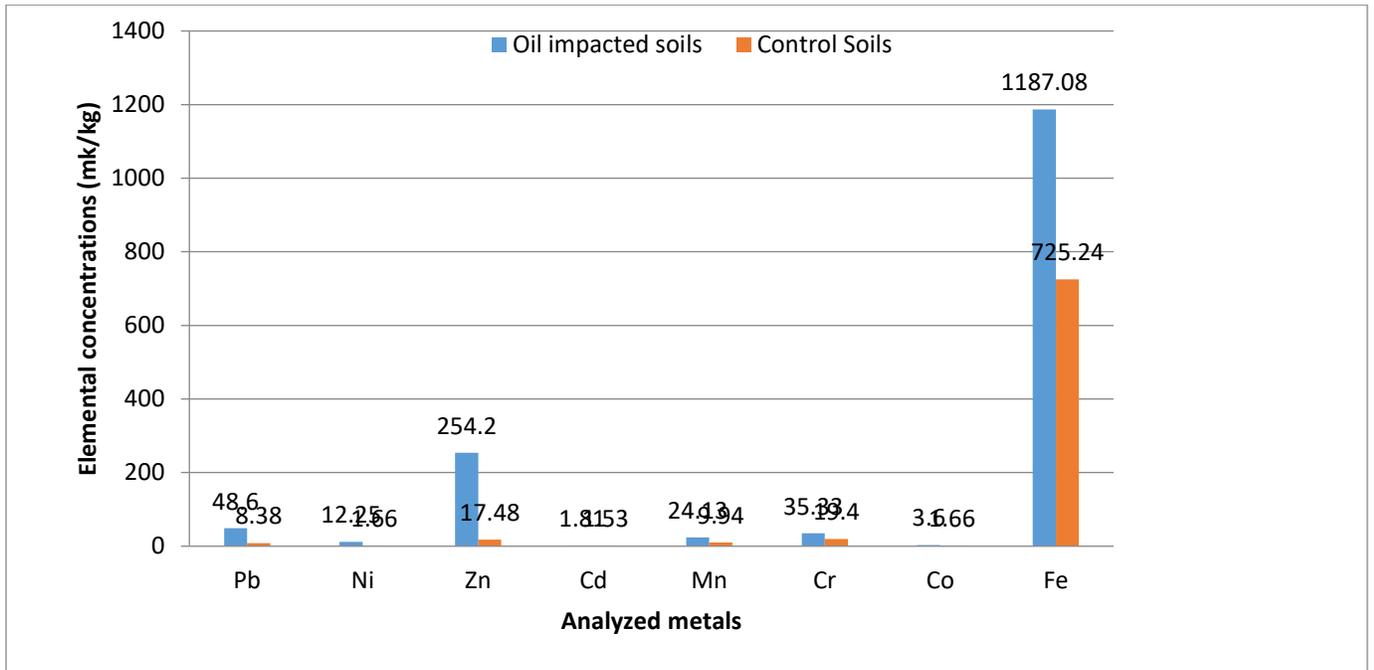


Figure 3: Graph comparing the mean elemental concentrations of the oil-impacted and control soils

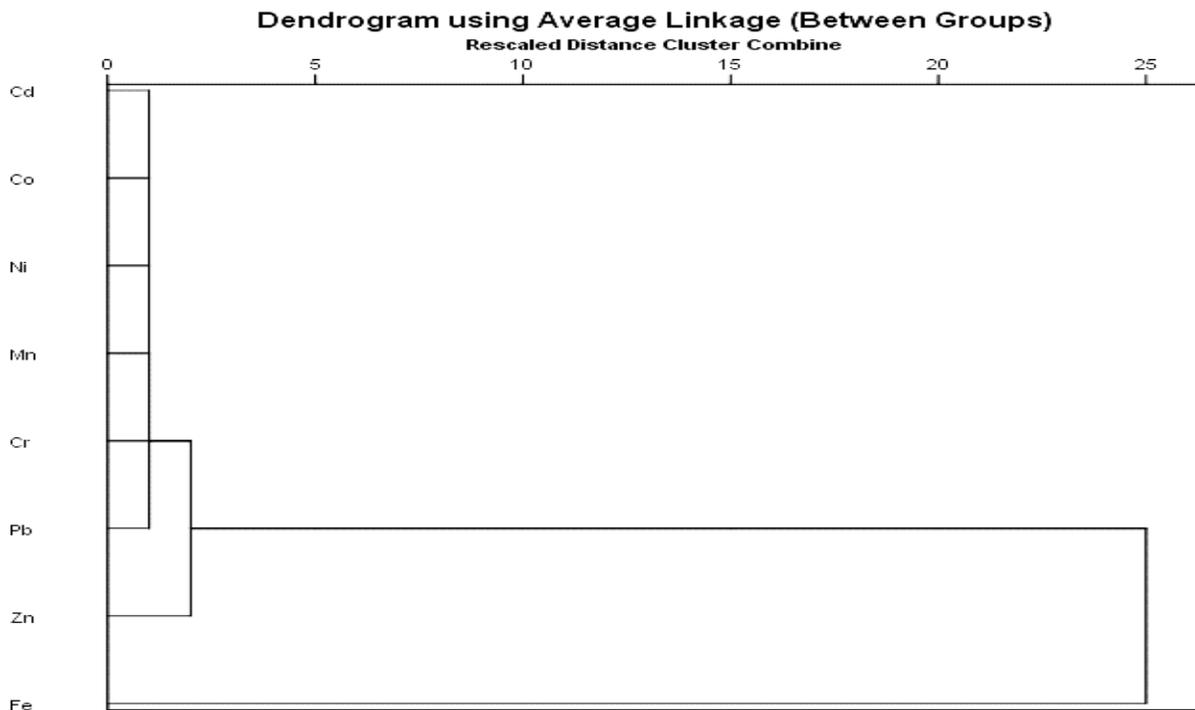


Figure 4: Dendrogram showing the hierarchical cluster analysis of the analyzed metals in the oil-impacted soils

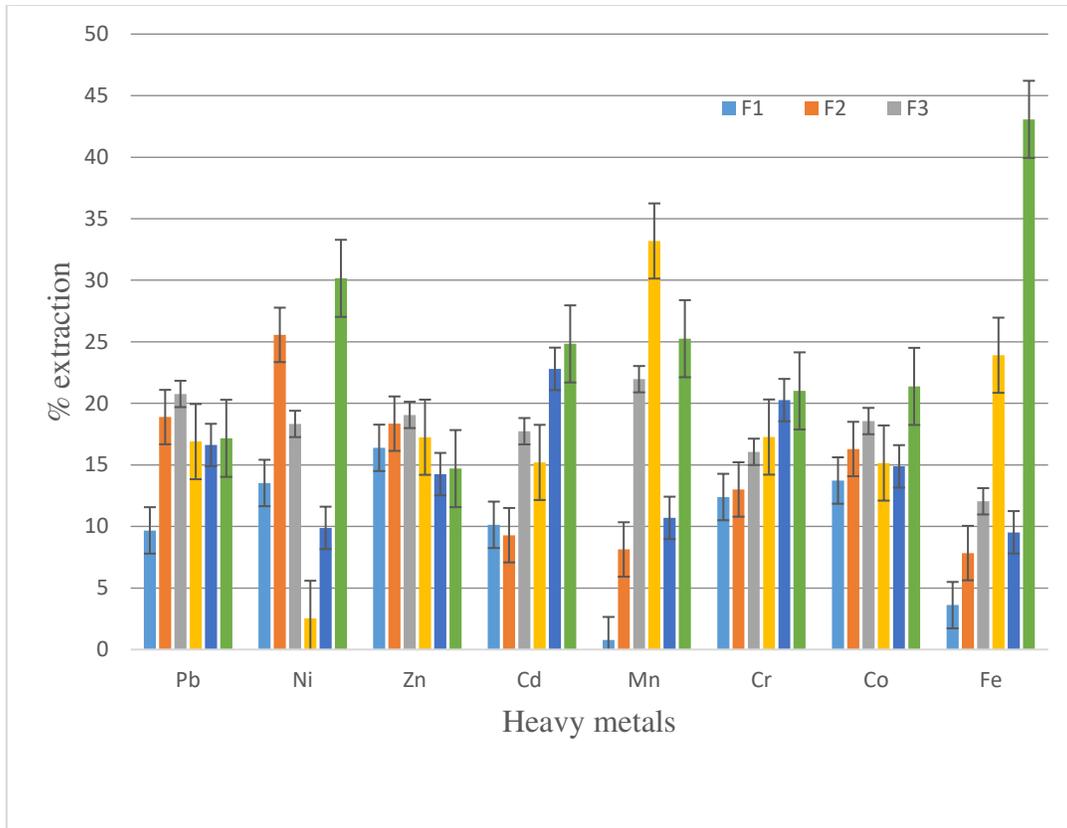


Figure 5a: Distribution of the heavy metals among the operationally defined fractions in the oil-impacted soils

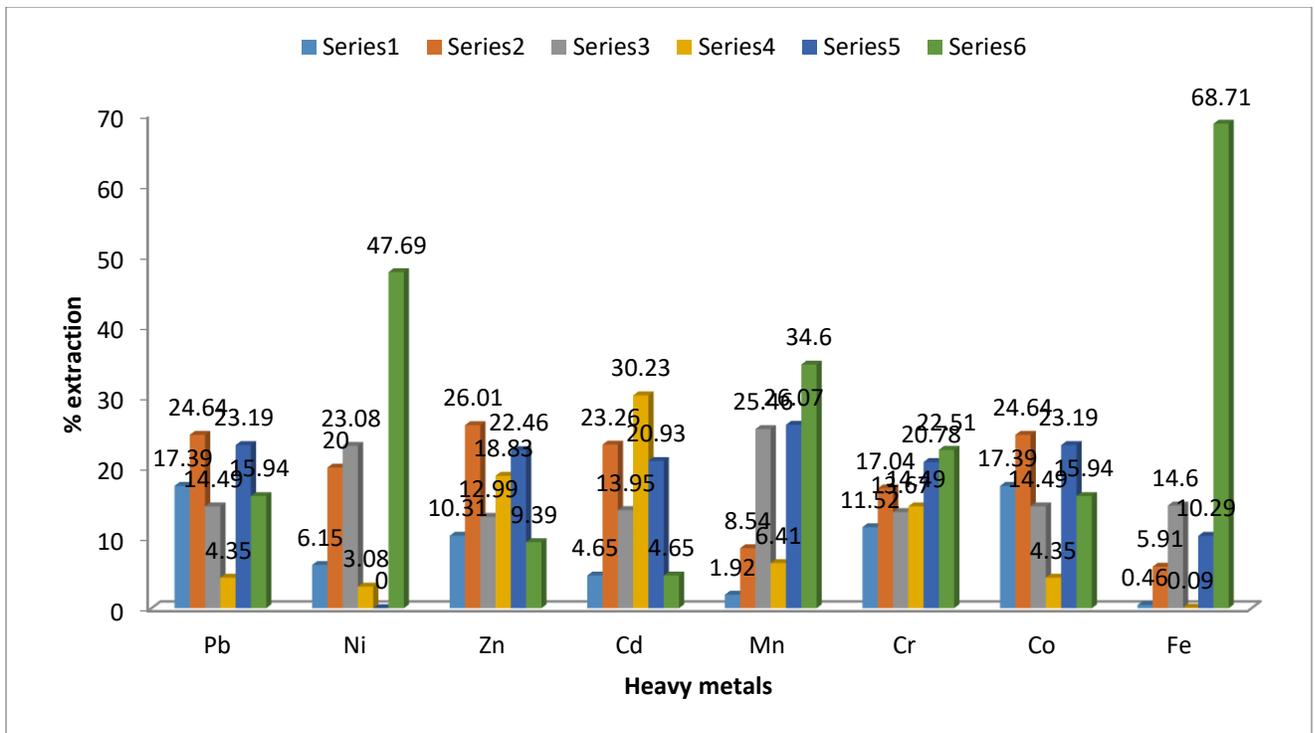


Figure 5b: Distribution of the heavy metals among the operationally defined fraction in the control soils

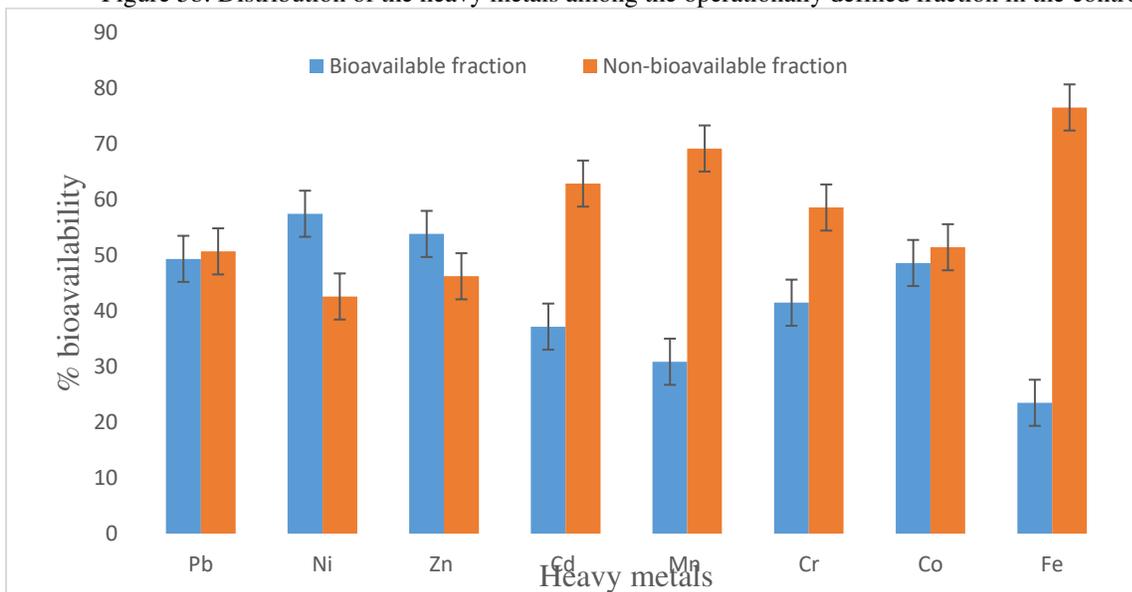


Figure 6: Bioavailability of the Analyzed Metals in the Oil-impacted Soils

Table 1: A Table showing the Sampling Sites and their Coordinates

S/N	Site	Coordinate
1.	A	07° 23.592' N 003° 49.187' E
2.	B	07° 23.640' N 003° 49.233' E
3.	C	07° 33.009' N 003° 24.519' E
4.	D	07° 23.677' N 003° 49.221' E
5.	E	07° 23.658' N 003° 49.080' E
6.	F	07° 23.742' N 003° 49.115' E
7.	G	07° 23.406' N 003° 49.176' E
8.	H	07° 23.564' N 003° 49.170' E
9.	I	07° 23.743' N 003° 49.264' E
10.	J	07° 23.633' N 003° 49.161' E
11.	CTR 1	07° 23.260' N 003° 49.195' E
12.	CTR 2	07° 23.250' N 003° 49.182' E
13.	CTR 3	07° 23.231' N 003° 49.173' E
14.	CTR 4	07° 23.280' N 003° 49.206' E
15.	CTR 5	07° 23.337' N 003° 49.265' E

Table 2: Indices for corresponding degrees of potential ecological risk (Hakanson, 1980)

Er value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environment
$Er < 40$	Low risk	$RI < 150$	Low risk
$40 \leq Er < 80$	Moderate risk	$150 \leq RI < 300$	Moderate risk
$80 \leq Er < 160$	Considerable risk	$300 \leq RI < 600$	Considerable risk
$160 \leq Er < 320$	High risk	$RI > 600$	Very high risk
$Er > 320$	Very high risk		

Table 3: Analytical Results for Calibration Curve and Percentage Recovery (%R) for Heavy Metals

Heavy metals	Amount spiked( $\mu\text{g/g}$ )	Amount recovered ( $\mu\text{g/g}$ )	% Recovery
Pb	5.00	4.30	86.00
Cu	5.00	4.75	95.00
Cd	5.00	4.45	89.00
Zn	5.00	4.80	96.00
Fe	5.00	4.25	85.00

Table 4: Single Factor Analysis of Variance

Groups	Count	Sum	Average	Variance			
A	8	1759.2	219.9	189827.1			
B	8	1607.78	200.9725	158700			
C	8	969.99	121.2488	82638.91			
D	8	2168.35	271.0438	291821.2			
E	8	921.14	115.1425	47871.05			
F	8	2217.31	277.1638	437640			
G	8	1502.95	187.8688	213914.7			
H	8	1245.6	155.7	125324.7			
I	8	1658.64	207.33	159844.9			
J	8	1619.11	202.3888	137145.5			
Source of Variation		SS	Df	MS	F	P-value	F <sub>critical</sub>
Between Groups		214399.8	9	23822.2	0.12	0.99	2.01
Within Groups		12913097	70	184472.8			
Total		13127497	79				

Table 5: T-test Comparison of the Total Elemental Concentrations of the Oil-impacted and Control soils at 95 % Confidence Interval

Element (mg/kg)	$t_{\text{calculated}}$	Remark
Pb	3656.36	SD
Ni	441.25	SD
Zn	78906.66	SD
Cd	7.38	SD
Mn	492.70	SD
Cr	612.69	SD
Co	102.10	SD
Fe	38486.66	SD

❖ SD = Significant difference,  $t_{\text{critical}} = 2.13$

Table 6: Comparison of the Elemental Concentrations and their Standard Permissible Limits

Element (mg/kg)	Oil-impacted soils	Background value (DPR, 2002)
Pb	10.22 – 163.81 (48.60)	85
Ni	5.9 – 26.60 (12.25)	35
Zn	75.80– 492.00 (254.20)	140
Cd	ND – 4.00 (1.81)	0.80
Mn	13.80– 31.40 (241.30)	850
Cr	11.27 – 72.81 (35.33)	100
Co	0.20 – 7.50 (3.60)	20
Fe	645.40 – 1908.90 (1187.08)	47000

ND = Not Detected

Table 7: Comparison of the Total Elemental Concentrations with Similar Studies

Element (mg/kg)	Metal concentration				
	This study (Mean ± SD)	Adebiyi & Ayeni, 2009 (Shagamu, Nigeria)	Fu <i>et al.</i> , 2014 (Shandong, China)	Ogoko, 2018 (Aba, Nigeria)	Aigberua and Inengite, 2019 (Bdere, Nigeria)
Pb	48.60	512.40	16.22	32.30	0.55
Ni	12.25	329.10	33.80	NDT	NDT
Zn	254.20	910.80	67.12	202.10	1.66
Cd	1.81	NDT	0.18	11.78	0.02
Mn	241.30	2458	NDT	NDT	0.45
Cr	35.33	451.30	61.66	NDT	NDT
Co	3.60	NDT	NDT	NDT	NDT
Fe	1187.08	2777	NDT	NDT	NDT

❖ NDT = Not determined; STD = Standard Deviation

Table 8: Contamination factor (CF), Geo-accumulation index ( $I_{geo}$ ), Enrichment factor (EF), Modified degree of contamination (mCd) and Pollution load index (PLI) of the oil-impacted soils ( $\pm$  SD)

Element (mg/kg)	Oil-impacted soils	Background value (DPR, 2002)	Geochemical baseline (Turekian and Wedepohl, 1961)	CF	$I_{geo}$	EF
Pb	10.22 – 163.81 (48.60 ± 0.026)	85	20	0.57	0.69	96.21
Ni	5.9 – 26.60 (12.25 ± 0.032)	35	68	0.35	-3.05	7.13
Zn	75.80 – 492.00 (254.20 ± 0.004)	140	95	1.81	0.83	105.94
Cd	ND – 40 (1.81 ± 0.105)	0.80	0.3	2.26	2.00	238.87
Mn	13.80 – 31.40 (241.30 ± 0.040)	850	850	0.02	-5.72	1.12
Cr	11.27 – 72.81 (35.33 ± 0.037)	100	90	0.35	-1.93	15.54
Co	0.20 – 7.50 (3.60 ± 0.024)	20	19	0.18	-2.98	7.50
Fe	645.40 – 1908.90 (1187.08 ± 0.026)	47000	47000	0.02	-5.89	-
mCd				0.69		
PLI				0.27		

ND = Not Detected; STD = Standard Deviation

Table 9: Potential ecological risk assessment of the analyzed metals in the oil-impacted soils

Heavy metal	Tr	E <sub>r</sub>	ME <sub>r</sub>
Pb	5	2.85	481.09
Ni	5	1.75	35.66
Zn	1	1.81	105.94
Cd	30	67.87	7166.32
Mn	1	0.02	1.12
Cr	2	0.70	31.08
Co	5	0.90	37.50
RI		75.93	
MRI			7858.74

❖ Tr = Toxicological response factor, E<sub>r</sub> = Potential ecological risk factor, ME<sub>r</sub> = Modified ecological risk factor, RI = Potential ecological risk index and MRI = Modified potential ecological risk index

# Figures

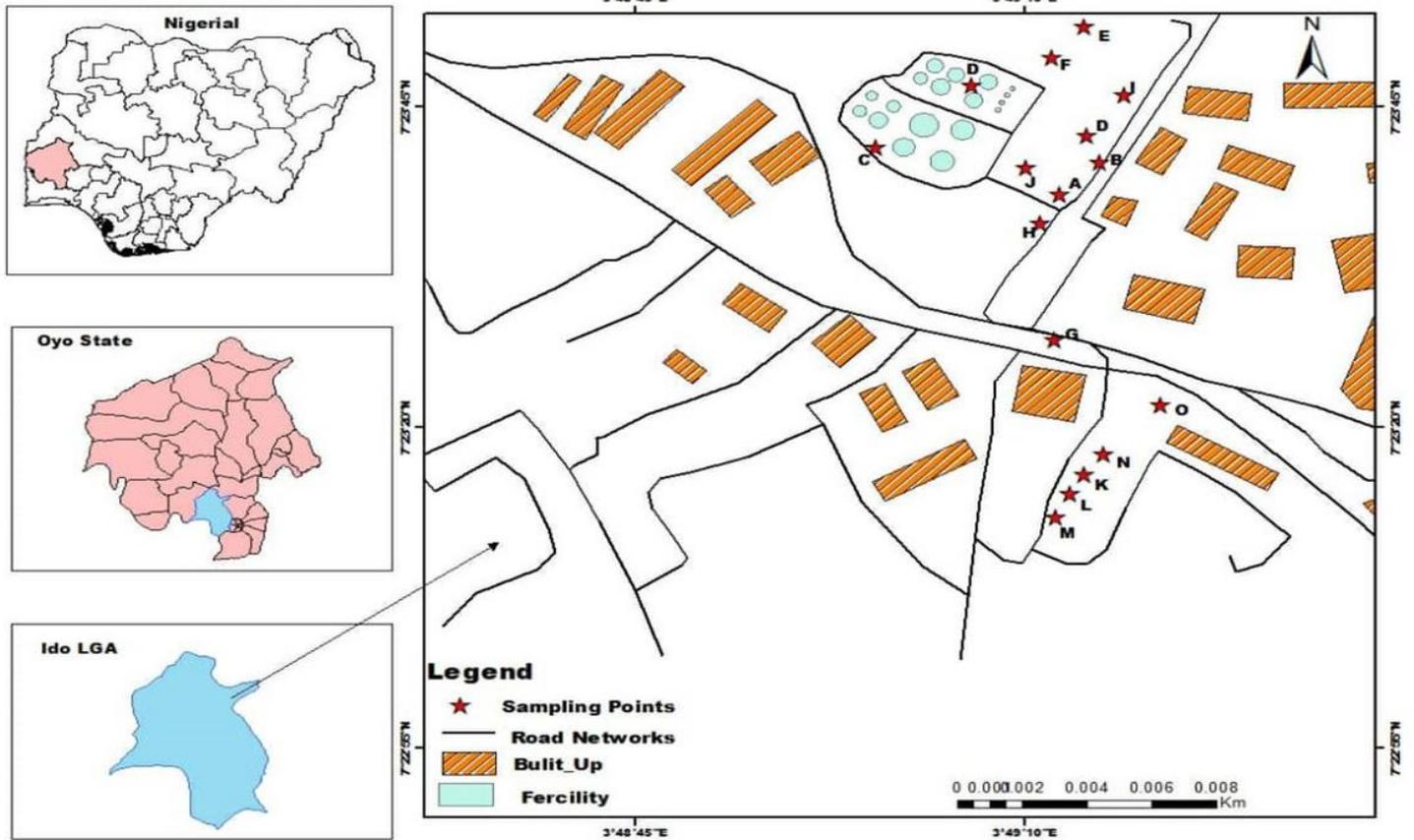
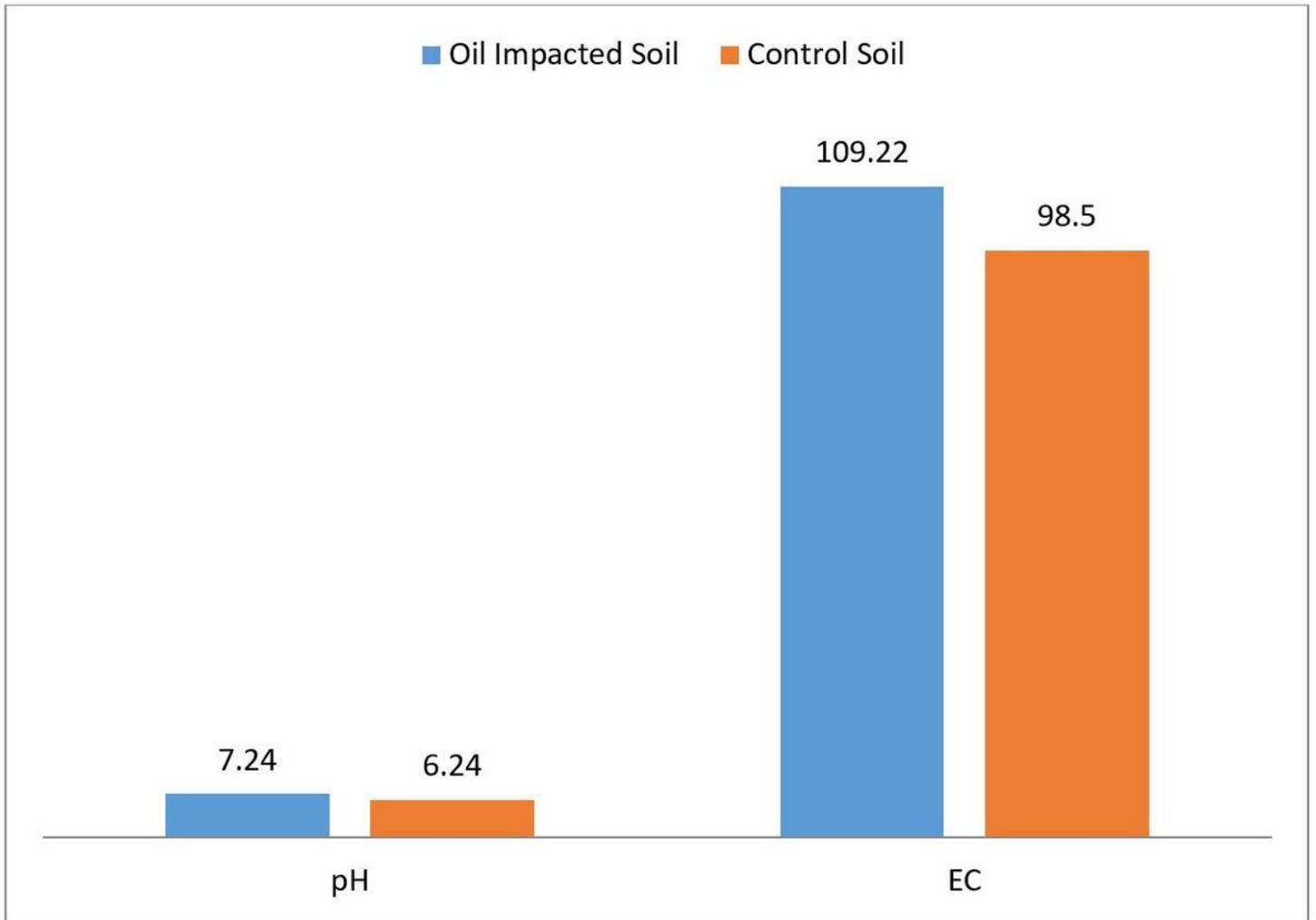


Figure 1

Map showing the Sampling Locations of the Study Area. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



**Figure 2**

Graph comparing the mean values of pH and Electrical Conductivity of oil-impacted and control soils

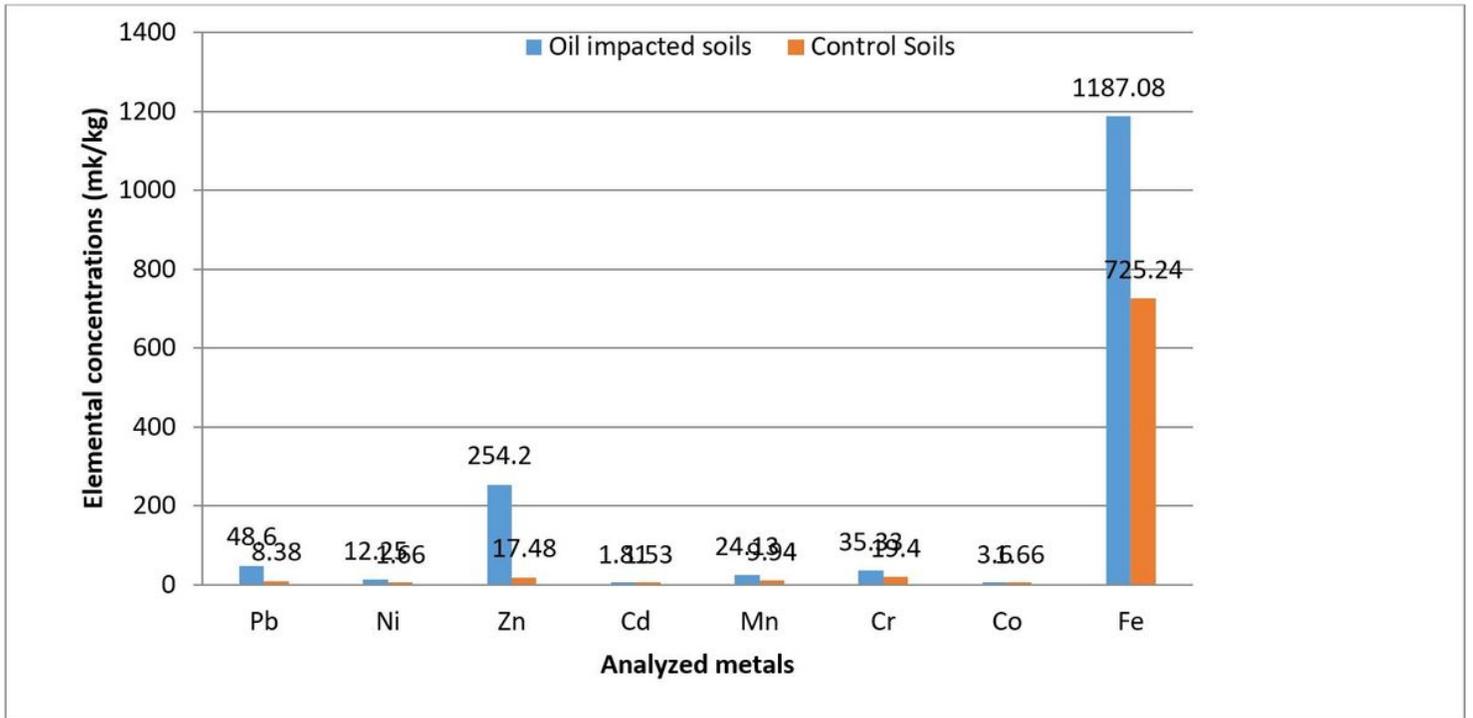


Figure 3

Graph comparing the mean elemental concentrations of the oil-impacted and control soils

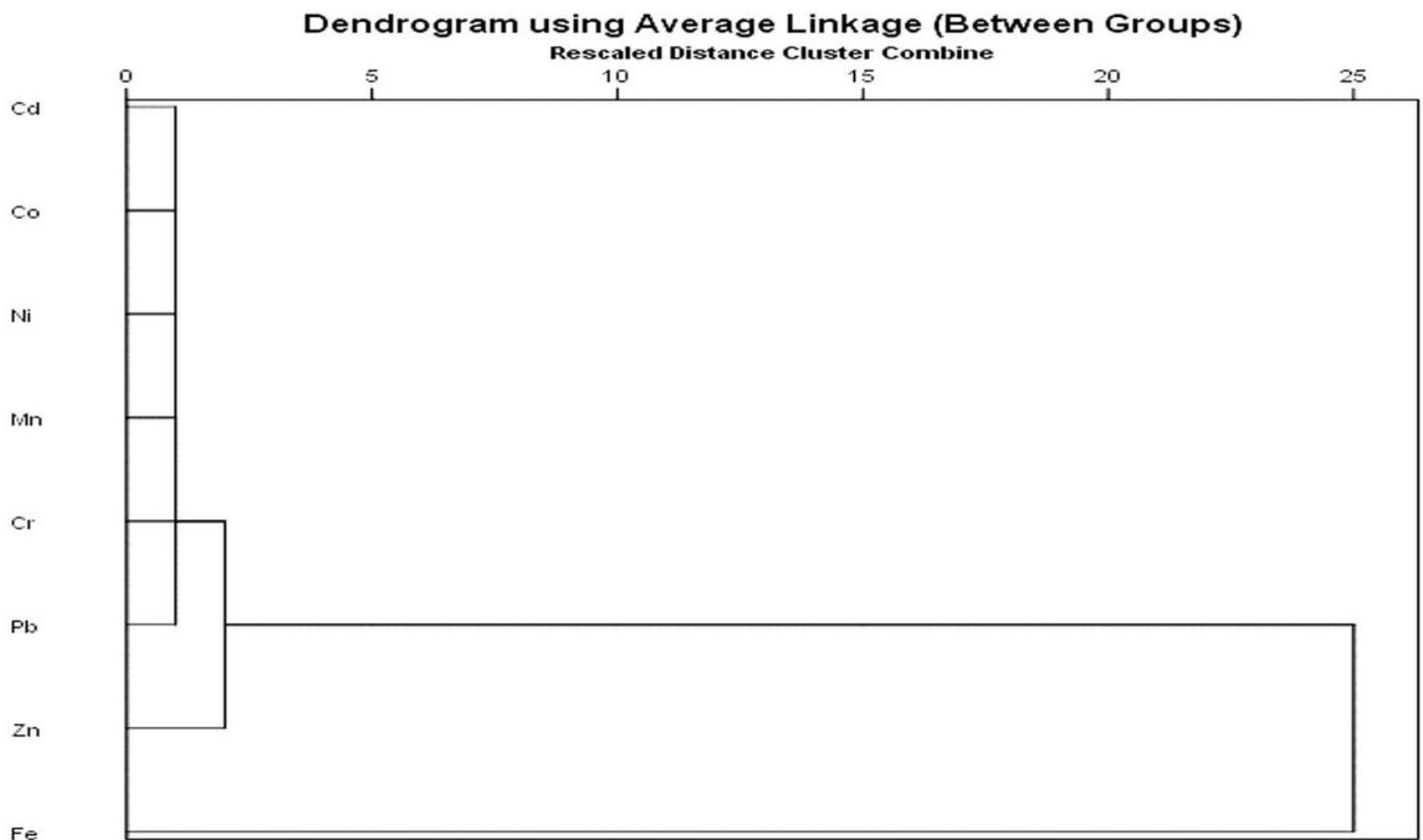
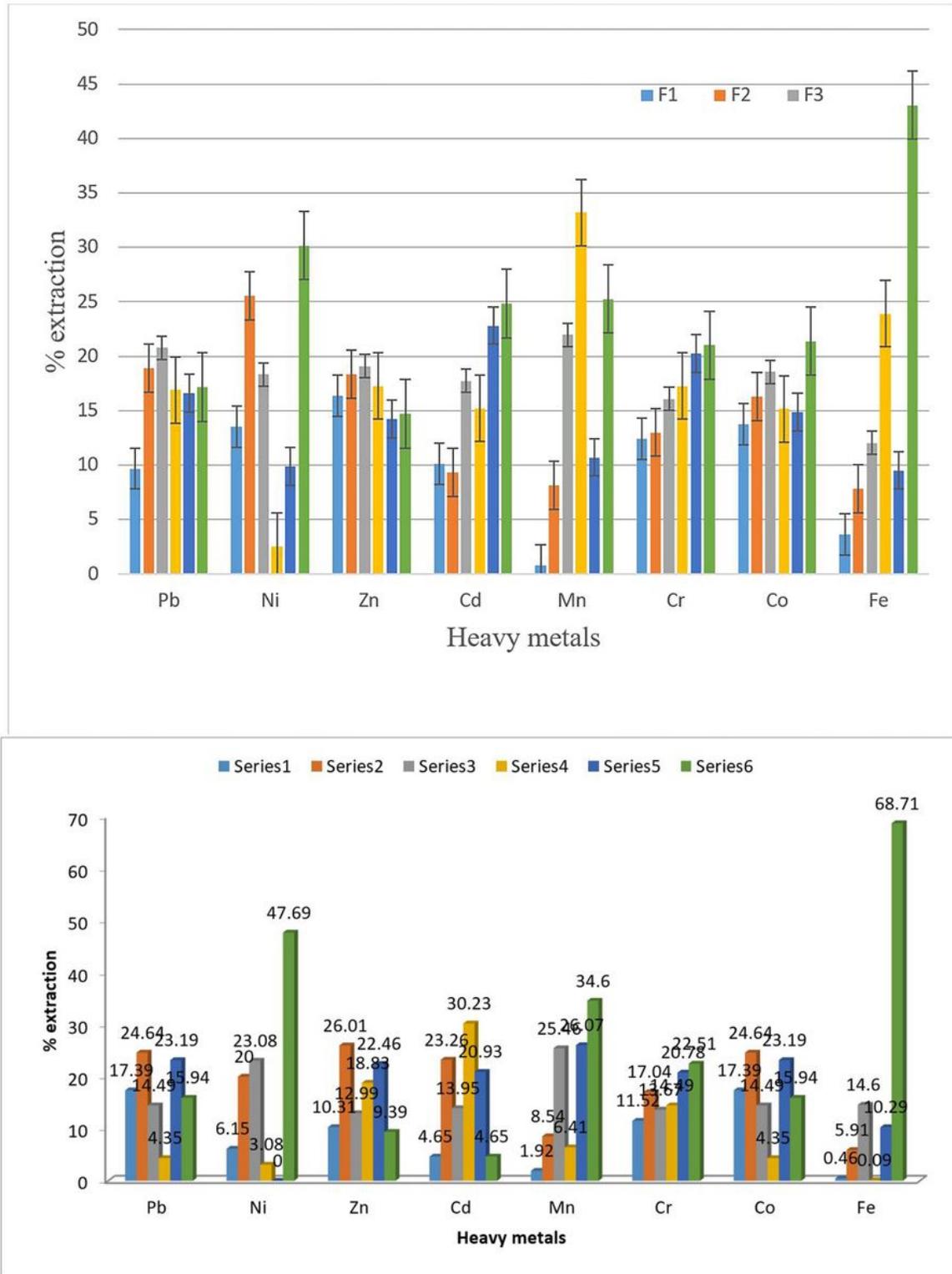


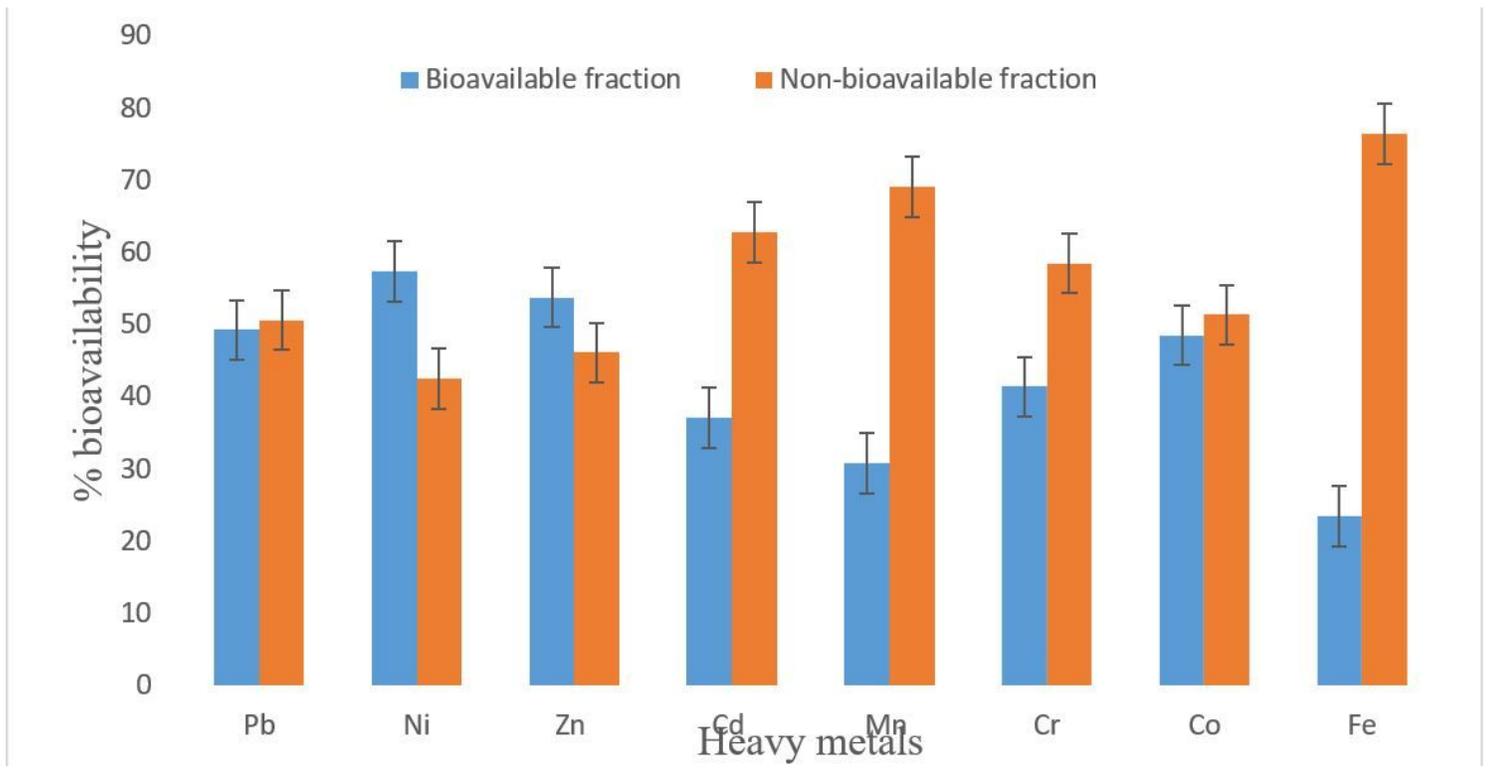
Figure 4

Dendrogram showing the hierarchical cluster analysis of the analyzed metals in the oil-impacted soils



**Figure 5**

a: Distribution of the heavy metals among the operationally defined fractions in the oil-impacted soils. b: Distribution of the heavy metals among the operationally defined fraction in the control soils.



**Figure 6**

Bioavailability of the Analyzed Metals in the Oil-impacted Soils.