The impact of oil spills on prevailing metal-soil associations

Aigberua, A.O[1*]Okere, U.V[2]

[1]Department of Chemical Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria.
[2]College of Life and Natural Sciences, University of Derby, Derby, UK.

**Corresponding author: ozedee101@gmail.com; +2348032765181*

ABSTRACT

Metal-soil associations and mobility factor indices of Cu, Cr, Fe and Ni was evaluated in soils from around a crude oil transfer line in Bdere community (Ogoniland), Nigeria. The aim was to identify the impact of spilt crude oil on the prevalent metal forms that become available in soil as some metal species tend to become more bioavailable and potentially toxic. Soil extracts were analyzed for metal analysis using atomic absorption spectrophotometer. The concentration of Fe and Cr was relatively higher in the control site, but their fractions were poorly mobile and non-bioavailable when compared to metals of the oil contaminated site. This suggests that metal concentration alone does not depict potential toxicity. The residual fractions were most important for both the oil contaminated and control sites. However, the predominant affiliation of Ni (32.27%) and Cu (23.61%) to the easily mobile and bioavailable fractions of oil contaminated soils suggests a high toxicity potential for both metals. Furthermore, hierarchical cluster analysis revealed the strongest mutual independence between the carbonate bound fraction (F3) of soil station 1 and the organic matter fraction (F8) of soil station 2, hence, the concentrations of toxic metal species were reportedly within Department of Petroleum Resources (DPR) recommendation for a standard soil. Overall, soil residual metals posed no immediate threat to the affected environment.

Keywords: Bdere community, bioavailability, Ogoniland, metal fraction, mobility, residual fractions, Department of Petroleum Resources

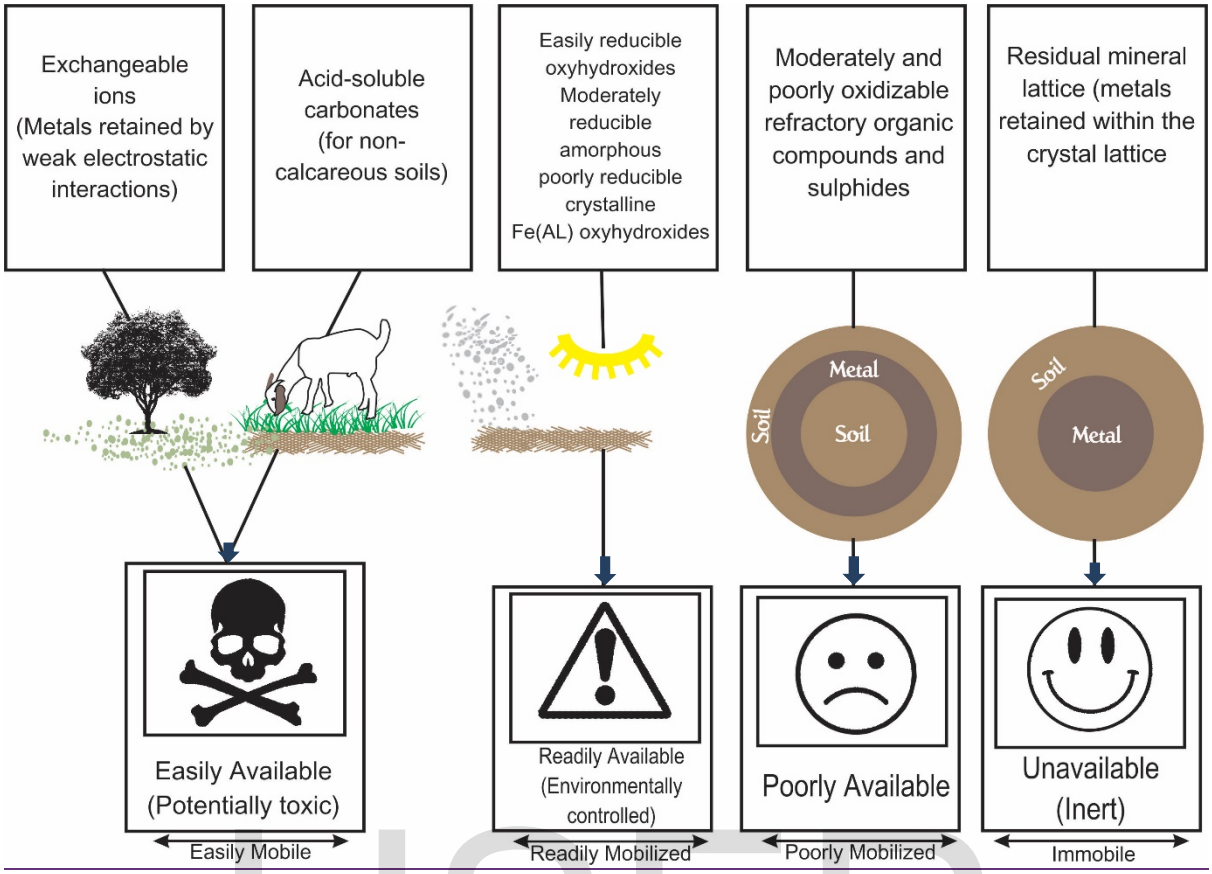

Fig 1: Schematic description of heavy metal speciation and bioavailability processes in the soil environment

1.0 INTRODUCTION

Oil contamination of soils in the Niger Delta area of Nigeria, as a result of historical and ongoing oil exploration and exploitation activities is common (Oyem and Oyem, 2013; Aigberua *et al*., 2016). Although many heavy metals are natural constituents of soil, rock, ground, surface waters and sediments at different concentrations (Tamunobereton-ari *et al*., 2011; Izah *et al*., 2016; Asimiea and Lawal, 2017; Aigberua *et al*., 2018) and fisheries (Izah and Angaye, 2016), many, including lead, cadmium, copper, zinc, nickel, vanadium and chromium are associated with crude oil production (Fatoba *et al*., 2015; Aigberua *et al*., 2016), and piping systems (Inengite *et al*., 2010; Aigberua *et al*., 2017).

The potential toxicity of some metal ions to humans, animals and plants have been reported by (Odukoya and Abimbola, 2010; Mahurpawar, 2015) and while soils are an important sink for heavy metals, they can also serve as a significant source for heavy metals into the environment (Asimiea and Lawal, 2017) making it important to understand the levels of heavy metals in soil,the chemical forms in which they are present and their fate and transport mechanisms (Adewale *et al*., 2011; Aigberua 2018a, b).

Previous studies have identified high levels of heavy metal contamination in oil impacted soils of Niger Delta, suggesting potential risk of metal toxicity (Aigberua *et al*., 2017; Nduka

and Aigberua, 2018; Aigberua and Inengite, 2019). Co-exposure to more than one heavy metal has been reported to be potentially more dangerous to human health than individual heavy metal exposure. With the average concentrations of copper, chromium, iron and nickel in crude oil from this region between 1976 and 2014 reported to be equivalent to 0.0159, 0.1988, 0.1988 and 0.2162 g/bbl (Enegide and Chukwuma, 2018), the indigenous people of the Niger Delta region may be at risk of co-exposures to heavy metals produced by oil spills (Wang and Fowler, 2008; Tchounwou *et al*., 2012; Enegide and Chukwuma, 2018).

Other factors like metal speciation and consequent availability for transport have been shown to be important to heavy metal toxicity in contaminated soils(Aigberua and Tarawou, 2018; Aigberua *et al*., 2018; Aigberua and Inengite, 2019). However, not many studies have investigated the heavy metal speciation in oil impacted soils from the Niger Delta. Most studies have based toxicity assessment on heavy metal concentrations alone (Iwegbue *et al*., 2007; Tamunobereton-ari *et al*., 2011; Ideriah *et al*., 2013; Osakwe *et al*., 2014; Leizou *et al*., 2015).

In this study, a nine-stage sequential extraction procedure was applied to assess metal-soil associations in oil impacted soils of Bdere community in the Niger Delta region of Nigeria. The aim is to identify the effect of oil contaminated soil on the prevailing chemical forms, associations and potential toxicity of copper, chromium, iron and nickel in the soil environment.

2.0 MATERIALS AND METHODS

2.1 Study area

Oil contaminated soil samples were collected along a Shell right of way/transfer line (ROW/TL) in Bdere community, east of Kono sii-kpor road. The soil was characterized as loose sandy soil bounded by light and heavy forest vegetation covers. Nearby farmlands to the sampling location are prone to seasonal flooding (Figs 2 and 3).

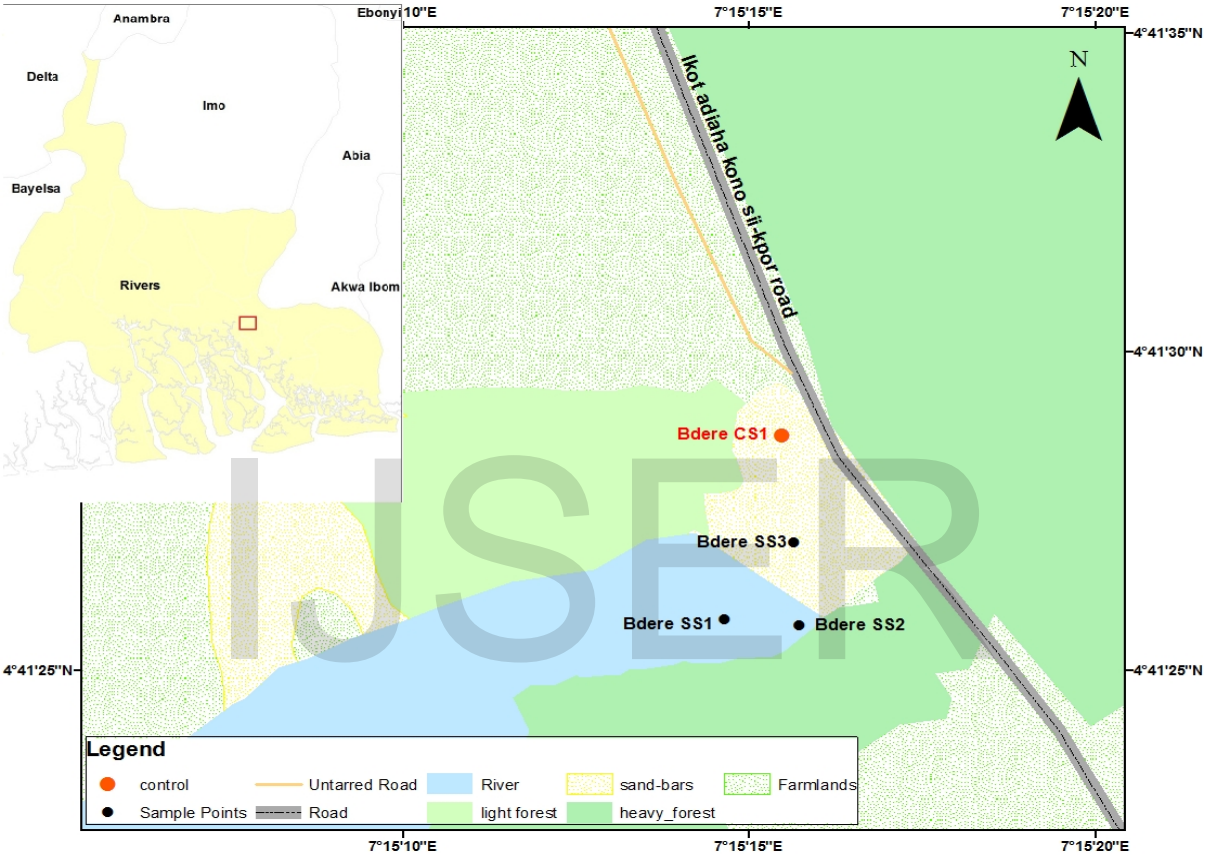

Fig2: Field location map of study area

Fig 3: Seasonal flooding of SPDC right of way and surrounding forest vegetation

2.2 Field Sampling

With a soil auger, triplicate samples of soil were randomly collected at depths of 0 - 15 cm in three (3) locations (SS1-N04.69050, E007.25407; SS2–N04.69048, E007.25437 and SS3–N04.69084, E007.25435) across the oil impacted site. Control sample was collected at about 100 m from the oil contaminated field area, showing no trace of crude oil contamination (CS1–N04.69130, E007.25430). Samples were transferred into pre-cleaned polyethylene bags, stored in an ice chest for transportation to the laboratory where they were stored in a refrigerator prior to analysis.

2.3 Statistical analysis

In order to determine the association and variation across soil metal fractions and location, statistical analysis was carried out using SPSS version 20 and the mean data was presented. One way analysis of variance (ANOVA) was used to show significant variation at $P<0.05$. Where significant variation occurred, Tukey Honestly significant test statistics was used to compare means. Hierarchical cluster analysis was carried out using Euclidean distance based on average linkage between groups.

Also, cluster analysis was carried out for two variables (sample location and heavy metals retention) across the oil contaminated soil environment. Clustering techniques are used to isolate objects associated with a specific cluster; such objects should be quite similar. Heavy metals of mutual dependence show similarity or closeness in characteristics while those of mutual independence reflect differing characteristics.

2.4 Sample Preparation, Analytical Validation and Quality Control Procedure

Soil samples were air-dried at room temperature, homogenized by grinding, sieved through a 2 mm mesh sieve and transferred into plastic vials. Glassware was acid-washed, rinsed under tap water and, further rinsed 3 to 4 times with distilled water. Thereafter, they were air-dried at room temperature and kept in a designated storage area. Reagent blanks were prepared for each fraction of the sequential extraction. Working standard solutions of 100 mg/l were prepared from an AccuStandard-USA stock standard solution (1,000 mg/l) of each test metal. Immediately after instrument calibration, method blanks were analyzed as quality control at the start, midpoint and end of run of each fractional species. The following wavelengths were applicable for the analysis of study metals: Cu (324.7 nm), Cr (357.9 nm), Fe (372.0 nm) and Ni (232.0 nm).

2.5 Reagents and Chemicals

The following analytical grade reagents and chemicals were used: ammonium nitrate (Analytical Reagent, Yueqiao chemicals, China), ammonium nitrate (Analytical Reagent, Yueqiao chemicals, China), 96% glacial acetic acid (Riedel-De Haen, Germany), hydroxylamine hydrochloride (Analytical Reagent, Guangdong Guanghua Sci-Tech Co., Ltd Shantou, China), EDTA Disodium salt (Analytical Reagent, Interchem Europe (UK) Ltd), ammonium oxalate (LabTech Chemicals, India), ascorbic acid (BDH Chemicals Ltd, Poole England), hydrofluoric acid (BDH Chemicals Ltd, Poole England), Hydrofluoric acid (BDH Chemicals Ltd, Poole England), 65% nitric acid (Riedel-De Haen, Germany), 37% hydrochloric acid (Sigma-Aldrich Chemicals, USA), sodium hexametaphosphate (Analytical Reagents – Cartivalues Scientific Enterprises, (Singapore) PTE. Ltd), potassium dichromate (Analytical Reagent, Kermel - Colmar, France), sulphuric acid (BDH Chemicals Ltd, Poole England), 1,10-phenanthroline hydrate (Hopkins & Williams, Chadwell Health Essex, UK) and ferrous sulphate (Analytical Reagent, Kermel – Colmar, France). All standard solutions were prepared in distilled water, the working standards of the four (4) study metals were prepared by diluting different known volumes of heavy metal stock solutions (1,000 mg/l).

2.6 Sequential Extraction of Heavy Metals

Metal extraction was conducted following the nine (9) stage sequential extraction procedures by Olutona *et al*., (2012); Aigberua *et al*.(2018). Heavy metals were separated into the following nine operationally defined fractions: water soluble (F1), exchangeable (F2), bound to carbonate (F3), plant available (F4), bound to Mn (F5), bound to amorphous Fe oxide (F6), bound to crystalline oxide (F7), bound to organic matter (F8), and residual fraction (F9). This fractionation scheme included; water soluble and plant available fractions not captured in the commonly used five (5) step sequential extraction procedure (Osakwe, 2010; Adewale *et al*., 2011; Ideriah *et al*., 2013; Osakwe *et al*., 2014; Leizou *et al*., 2015; Aigberua and Tarawou, 2018).

One gram of each sediment sample was weighed and sequentially extracted using different selective extraction solutions as applicable for each speciation protocol. Distilled water was used to wash the residues after each extraction to ensure selective dissolution and avoid

cross-contamination between extraction fluids. All samples were run in triplicate; the analytical protocol used is detailed below:

Fraction 1: Water soluble metals

To extract water soluble metals, 50 ml distilled water (pH 7.0; at 28°C) was added to 1.0 gram of soil in a beaker and shaken on a Stuart SSL2 type mechanical shaker at 250 rpm for 2 h. The solution was decanted.

Fraction 2: Exchangeable metals

The residue from water soluble metals was extracted with 25 ml of 1.0 M NH_4COOCH_3 (pH = 7.0). The suspension was agitated for 30 min at 28°C on a mechanical shaker.

Fraction 3: Metals bound to carbonate

The residue from exchangeable metals was extracted with 3 M sodium acetate solution (CH_3COONa) adjusted to pH 5.0 with acetic acid (CH_3COOH). The suspension was agitated for 5 h on a mechanical shaker.

Fraction 4: Plant available metals

The residue from metals bound to carbonate was extracted by shaking with a solution mixture consisting 50 ml of 0.025 M HCI + 0.05 M H_2SO_4 for 30 min in a centrifuge at 28°C.

Fraction 5: Metals bound to Mn-oxide

The residue from plant available metals was shaken for 30 min in a centrifuge at 28°C with a solution of 25 ml 0.1 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% acetic acid (CH_3COOH) (pH 2 to 3).

Fraction 6: Metals bound to amorphous Fe-oxide

The residue from Mn-oxide bound metals was extracted with 25 ml of 0.2 M Ammonium oxalate [$(NH_4)_2C_2O_4$] (pH 3.0) for 30 min in a centrifuge at 50°C using a water bath with occasional stirring.

Fraction 7: Metals bound to crystalline Fe-oxide

The residue from amorphous Fe-oxide bound metals was extracted using a mixture of 0.2 M Ammonium oxalate [$(NH_4)_2C_2O_4$] and 0.1 M ascorbic acid (pH 3.25) and it was heated in a water bath with occasional stirring at 100°C for 30 min in a centrifuge.

Fraction 8: Metals bound to organic matter

The residue from crystalline Fe-oxide bound metals was extracted with 10 ml of 0.02 M HNO_3 and 15 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was then heated to 85°C on a hot plate for 5 h with occasional agitation by hand swirling). A second 15 ml of 30% H_2O_2 (pH 2 with HNO_3) was added and the mixture was heated again to 85°C on a hot plate for 3 h with intermittent agitation on a mechanical shaker. After cooling, 5 ml of 3.2 M NH_4COOCH_3 in 20% (v/v) HNO_3 was added and the samples diluted to 20 ml and agitated continuously for 30 min on a mechanical shaker.

Fraction 9: Residual metals

The residue from organic matter bound metals was digested with a mixture of concentrated HF, HNO_3 and $HClO_4$ for 8 h. Sample digestion was done on a hot plate (Olutona *et al.*, 2012;Aigberua 2018a, 2018b).

3.0 RESULTS AND DISCUSSION

3.1 Concentration of heavy metal species in soil

Table 1a: Heavy metal fractions in oil contaminated soils

Sample Identity	Ni mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg
Soil1 F1	<0.001	0.34	<0.001	18.41
	<0.001	0.27	<0.001	22.08
	<0.001	0.41	<0.001	20.17
Soil2 F1	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
Soil3 F1	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
Soil1 F2	<0.001	0.18	1.10	<0.001
	<0.001	0.15	1.51	<0.001
	<0.001	0.23	1.34	<0.001
Soil2 F2	4.16	<0.001	0.46	<0.001
	3.87	<0.001	0.58	<0.001
	4.40	<0.001	0.52	<0.001
Soil3 F2	5.04	<0.001	<0.001	<0.001
	5.59	<0.001	<0.001	<0.001
	4.63	<0.001	<0.001	<0.001
Soil1 F3	2.83	<0.001	<0.001	<0.001
	3.39	<0.001	<0.001	<0.001
	3.10	<0.001	<0.001	<0.001
Soil2 F3	0.53	1.41	0.88	<0.001
	1.02	2.05	1.10	<0.001
	0.77	1.89	0.96	<0.001
Soil3 F3	<0.001	0.02	0.06	<0.001
	<0.001	0.05	0.11	<0.001
	<0.001	0.03	0.10	<0.001
Soil1 F4	<0.001	0.53	<0.001	2.58
	<0.001	0.64	<0.001	3.97
	<0.001	0.57	<0.001	3.16
Soil2 F4	<0.001	<0.001	<0.001	0.28
	<0.001	<0.001	<0.001	0.41
	<0.001	<0.001	<0.001	0.37
Soil3 F4	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
	<0.001	<0.001	<0.001	<0.001
Soil1 F5	<0.001	<0.001	1.54	17.84
	<0.001	<0.001	2.02	20.07
	<0.001	<0.001	1.87	21.29
Soil2 F5	<0.001	1.18	0.69	24.03
	<0.001	1.43	0.76	23.47
	<0.001	1.27	0.81	26.09

Table 1b: Heavy metal fractions in oil contaminated soils

Sample Identity	Ni mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg
Soil3 F5	<0.001	<0.001	0.35	<0.001
	<0.001	<0.001	0.43	<0.001
	<0.001	<0.001	0.39	<0.001
Soil1 F6	<0.001	0.67	0.30	38.40
	<0.001	0.58	0.45	42.17
	<0.001	0.52	0.39	39.81
Soil2 F6	<0.001	0.56	<0.001	36.40
	<0.001	0.65	<0.001	37.13
	<0.001	0.71	<0.001	35.78
Soil3 F6	<0.001	0.55	0.66	20.77
	<0.001	0.38	1.03	18.28
	<0.001	0.47	0.89	21.15
Soil1 F7	<0.001	0.73	1.41	142.67
	<0.001	1.04	1.55	167.20
	<0.001	0.92	1.36	140.94
Soil2 F7	<0.001	0.20	<0.001	141.69
	<0.001	0.30	<0.001	146.83
	<0.001	0.19	<0.001	144.05
Soil3 F7	<0.001	0.54	0.63	3.36
	<0.001	0.44	0.84	4.15
	<0.001	0.59	0.75	3.70
Soil1 F8	<0.001	1.09	<0.001	37.81
	<0.001	0.85	<0.001	41.26
	<0.001	0.94	<0.001	35.69
Soil2 F8	<0.001	2.86	0.11	57.87
	<0.001	3.41	0.20	63.14
	<0.001	3.10	0.15	60.24
Soil3 F8	<0.001	2.92	0.45	19.04
	<0.001	2.56	0.63	17.18
	<0.001	2.78	0.52	20.13
Soil1 F9	10.34	9.39	1.13	177.90
	9.92	10.10	1.28	210.59
	9.87	9.61	1.19	195.67
Soil2 F9	5.22	9.31	0.21	152.94
	5.95	8.59	0.32	188.13
	5.20	9.04	0.26	159.32
Soil3 F9	10.80	9.33	0.61	132.84
	11.59	9.14	0.82	160.21
	11.07	9.02	0.67	154.40
Mean concentration of mobile metals (F1 + F2 + F3)	1.46	0.26	0.32	2.25
DPRtarget values (2018)	**35**	**100**	**36**	**-**

Table 2: Heavy metal fractions in uncontaminated (control) soils

Sample Identity	Ni mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg
Soil Control F1	<0.001	<0.001	0.58	<0.001
	<0.001	<0.001	0.77	<0.001
	<0.001	<0.001	0.49	<0.001
Soil Control F2	<0.001	<0.001	0.03	<0.001
	<0.001	<0.001	0.06	<0.001
	<0.001	<0.001	0.05	<0.001
Soil Control F3	0.06	0.60	0.41	2.68
	0.11	0.45	0.33	3.21
	0.08	0.63	0.43	2.95
Soil Control F4	<0.001	0.59	0.42	19.30
	<0.001	0.67	0.36	25.10
	<0.001	0.55	0.49	21.93
Soil Control F5	2.85	1.14	0.41	57.37
	3.48	1.29	0.50	51.02
	3.11	1.05	0.44	55.14
Soil Control F6	<0.001	1.48	0.72	180.16
	<0.001	2.05	1.00	201.45
	<0.001	1.87	0.91	197.22
Soil Control F7	<0.001	0.98	1.18	614.17
	<0.001	1.15	0.97	598.70
	<0.001	1.21	1.10	623.41
Soil Control F8	<0.001	2.42	1.24	562.48
	<0.001	2.98	1.40	605.39
	<0.001	2.66	1.29	587.80
Soil Control F9	8.77	11.14	0.81	498.18
	9.65	10.65	1.04	550.11
	9.87	11.34	0.94	487.46
Mean concentration of mobile metals (F1 + F2 + F3)	<0.001	<0.001	0.35	<0.001
DPRtarget values (2018)	**35**	**100**	**36**	**-**

Tables 1a and b shows a higher concentration of mobile and potentially bioavailable heavy metals in oil contaminated soil, values were relatively higher than levels recorded in samples of control location (Table 2). In this study, the levels of heavy metals in the oil contaminated soil were similar to findings from previous studies. Ideriah *et al*. (2013) reported significantly higher heavy metal concentrations for samples from oil contaminated soils surrounding abandoned oil wells in Abara and Ozuzu communities in the Niger Delta region. Findings from this present study also follow patterns from a previous study by Aigberua *et al*. (2017) where nickel reportedly depicted higher mean concentration in the oil contaminated site. The heavy metals studied pose no immediate threat to both the contaminated and uncontaminated soil environment because they are predominantly associated with the residual fractions, thereby rendering them immobile and environmentally inert (Tables 1a,b and 2).

The higher level of nickel detected in the oil contaminated site may have resulted from the presence of crude oil in the soil (Osuji and Adesiyan, 2005; Mustafa *et al*., 2015; Aigberua *et al*., 2017; Asimiea and Lawal, 2017). On the other hand, the lower levels of the other metals may have resulted from losses due to leaching during seasonal floods in the area (Aigberua *et al*., 2017). Also, the soil color (whitish-brown) which is typical of the sampling field under observation may be responsible for the relatively low concentration of heavy metals (especially, iron) in the oil contaminated site. Sandy type sediments have been classified as organically poor sediments because they depict low retention capacity for heavy metals, unlike clay and silt which are organically rich with high cationic exchangeable capacities (Liao *et al*., 2009; Asimiea and Lawal, 2017).

3.2 Identification of metal species in oil contaminated and control site of Bdere

All metals assessed in this study were found to be prevalent in the poorly mobile and immobile fractions (Figs 4 to 7) of the soils. In the oil contaminated soil, the most prevalent metal-soil associations were: Cu (24.36%) Mn-oxide fraction, while the other metals; Cr (67.04%), Fe (45.24%) and Ni (67.73%) were prevalently associated to the residual fractions. On the other hand, predominant metal-soil associations in the control soil were: Cu (21.38%) organic-matter bound fraction, Fe (31.75%) crystalline Fe-oxide fraction, while Cr (60.71%) and Ni (75.23%) were both predominantly affiliated to the residual fractions (Figs 4 to 7). Aigberua (2018a) had reported metals to be strongly bound to the matrix of bottom sediments in the Middleton river system, an estuary of the Nun River within the Niger Delta region of Nigeria. Also, Leizou *et al*. (2015) adopted the 5-step sequential extraction procedure and found that heavy metals (As, Co, Cu, Fe, Pb and Zn) were mostly affiliated to the inert fractions of the sediment environment and therefore do not pose significant environmental threat to sediment dwelling fauna and to humans through the consumption of aquatic animals from the Pennington river system in Bayelsa state for food.

Despite the relative prevalence of metals to the immobile fractions, significant concentrations of metals were affiliated to the easily transportable and bioavailable fractions of the soil especially in the oil contaminated soil. Easily mobile fractions (made of the water-soluble, exchangeable and carbonate bound fractions) for contaminated and control soil samples, added up to the following levels: Cu (23.61% and 17.59%); Cr (4.66% and 3.27%); Fe (1.80% and 0.14%) and Ni (32.27% and 0.51%) (Figs 4 to 7). Overall, nickel showed the highest potential for mobility and consequent toxicity within the soils. Ideriah *et al*. (2013) assessed the presence of Pb, Cu, Cd, Cr, Ni, Mn and Zn in soils around abandoned oil wells of Abara and Ozuzu communities in the Nigerian Niger Delta and findings from this study are similar to theirs. The dry season had depicted heavy metals in the exchangeable fractions with potential bioavailability posing adverse effect to the environment despite the metal concentrations been below permissible limits as recommended by the Rivers State Ministry of Environment. Similarly, Osakwe *et al*. (2014) showed high environmental contamination risk for Ni and Cd as a result of elevated mobility factor indices for sediments of Imo river system in Southeastern Nigeria, thereby revealing environmental threat to the river ecosystem.

Expectedly, most of the iron species in the soil are from the natural environment as reflected by the poor mobility and strong association with residual fractions of the soil matrix (Osakwe, 2010; Osakwe *et al*., 2014; Aigberua 2018a). Therefore, the presence of crude oil in soil may be responsible for the elevation in potential toxicity of heavy metals in soil (Ideriah *et al*., 2013).

Results from this study are similar to those by Ideriah *et al*. (2013) who reported exchangeable metal fractions in oil contaminated soils as follows: Cu (25.41%), Cr (22.24%) and Ni (24.84%). Also, it was consistent with the findings of Aigberua (2018a) that majority of Fe was affiliated to the poorly mobile organic matter bound (24.7%) and amorphous Fe-oxide (28.6%) fractions of sediments within the Middleton river system in the dry and wet seasons respectively. Range and mean concentrations of metals were found below limits stipulated by the Department of Petroleum Resources (DPR) in Nigeria: Cu (36 mg/kg), Cr (100 mg/kg) and Ni (35 mg/kg) (DPR, 2018).

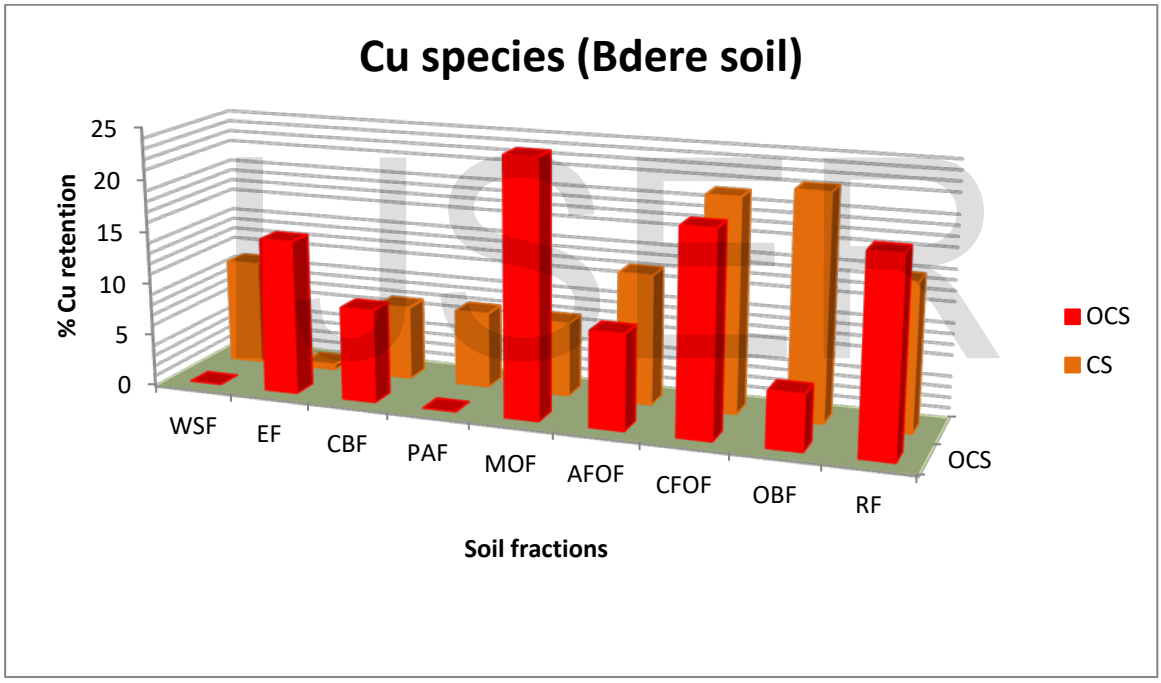

Fig4: Soil-metal associations of Cu in the oil contaminated and control site

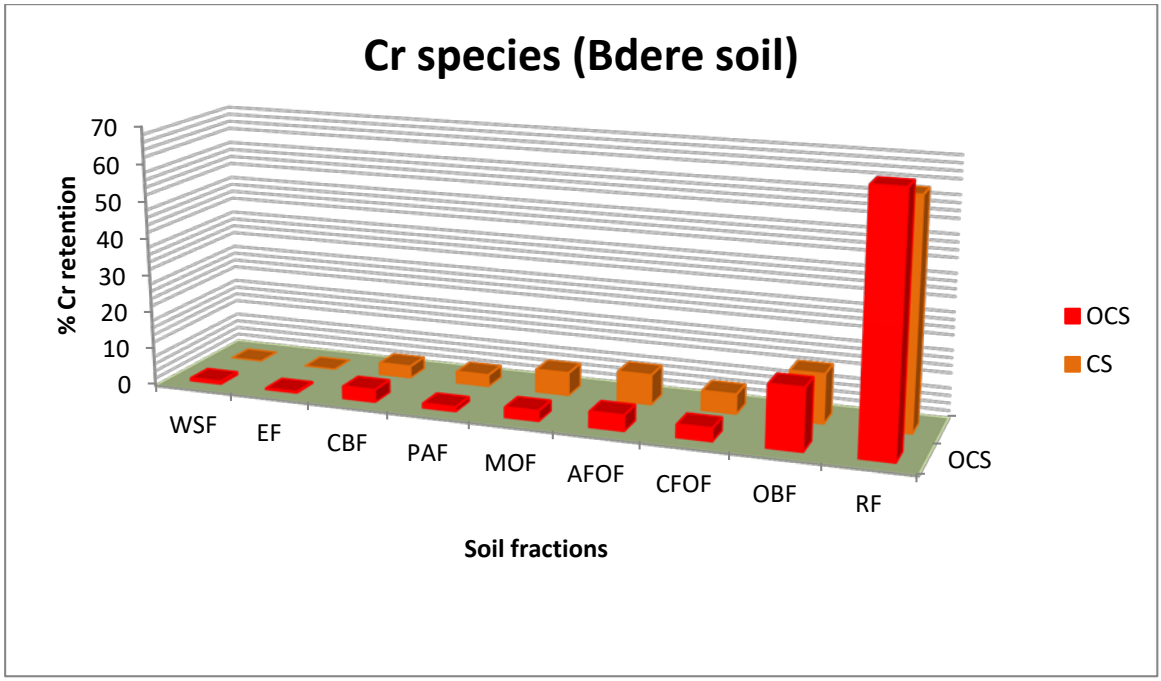

Fig 5: Soil-metal associations of Cr in the oil contaminated and control site

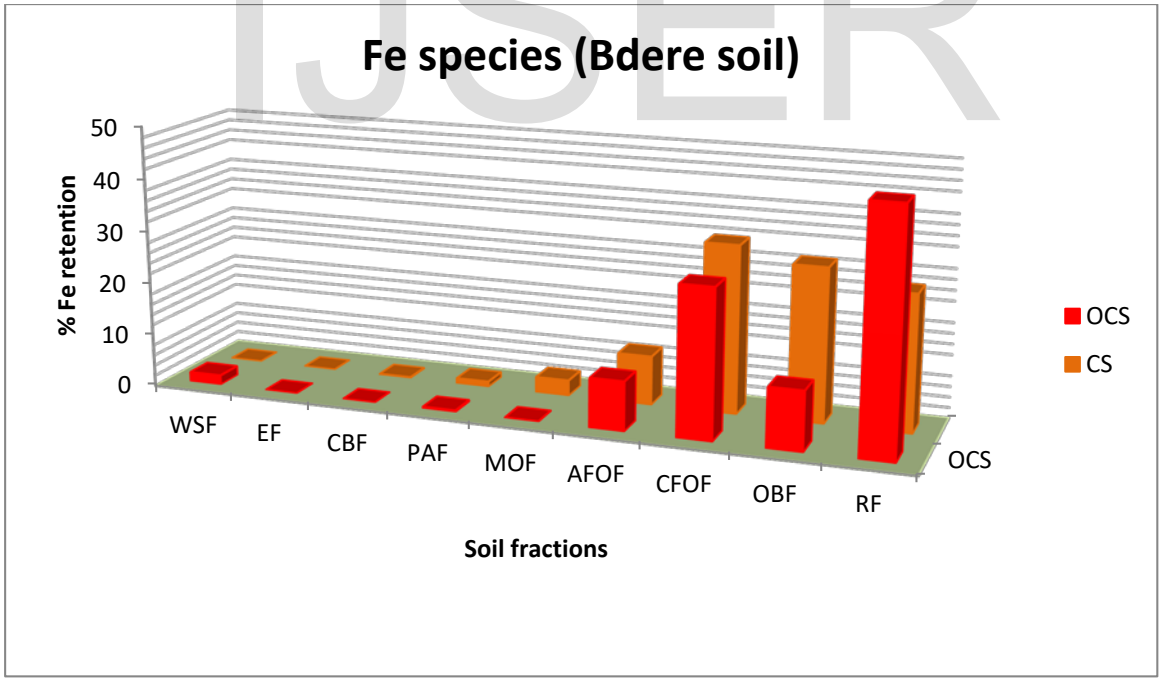

Fig 6: Soil-metal associations of Fe in the oil contaminated and control site

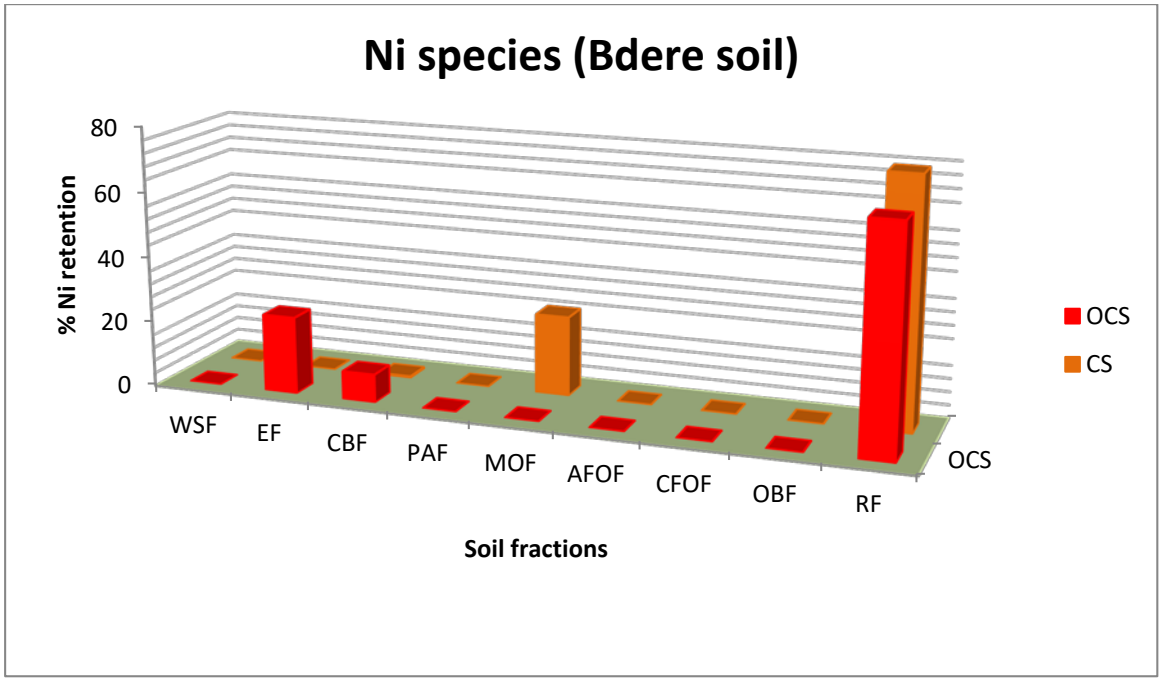

Fig 7: Soil-metal associations of Ni in the oil contaminated and control site

Definition of terms (Figs 4 to 7): OCS: oil contaminated site, CS: control site, WSF: water soluble fraction, EF: exchangeable fraction, CBF: carbonate bound fraction, PAF: plant available fraction, MOF: Mn-oxide fraction, AFOF: amorphous Fe-oxide fraction, CFOF: crystalline Fe-oxide fraction, OBF: organic bound fraction and RF: residual fraction.

3.3 Mobility factor indices of heavy metals in contaminated and control soils of Bdere

The fate of metal ions in soil is dependent on their form or species which are in turn reflected by the resulting mobility factor indices. Mobility factors (MF) of metals provide an indication of metal bioavailability or biological inactivity (Aigberua, 2018a, 2018b; Aigberua *et al*., 2018). Soil metals are fractionated in the order of decreasing solubility, therefore, the water soluble, exchangeable and carbonate-bound (F1 + F2 + F3) fractions which are the free and easily available metal ion species reflect the level of bioavailable forms (Figures 8 and 9). The relative index of metal mobility was calculated as a mobility factor (MF) (Aigberua *et al*., 2018) using the equation:

$$MF = [(F1 + F2 + F3) \div (F1 + F2 + F3 + F4 + F5 + F6 + F7 + F8 + F9)] \, x \, 100$$

Definition of variables:

F1: water soluble metal fraction

F2: exchangeable metal fraction

F3: carbonate-bound metal fraction

F4: plant available metal fraction

F5: Mn-oxide bound metal fraction

F6: amorphous Fe-oxide bound metal fraction

F7: crystalline Fe-oxide bound metal fraction

F8: organic matter bound metal fraction

F9: residual metal fraction

A high mobility factor index can be interpreted as evidence of relatively high potential for toxicity and biological availability for metals (Aigberua, 2018a, 2018b; Aigberua *et al*., 2018) (see Table 1).

Table 3: Defined fraction and extracted components (Fedotov and Miro, 2008; Aigberua *et al*., 2018)

Defined Fraction	Extracted Components	Physicochemical mobility	Potential bioavailability
Water soluble	Free ions	Mobile	Easily available
Exchangeable	Exchangeable ions (metals retained by weak electrostatic interactions)	Mobile	Easily available
Acid soluble	Carbonates (for non-calcareous soils)	Easily mobilizable	Easily available
Easily reducible	Mn oxyhydroxides	Readily mobilizable	Readily available
Easily oxidizable	Metal-organic complexes	Readily mobilizable	Readily available
Moderately reducible	Amorphous Fe (and Al) oxyhydroxides	Poorly mobilizable	Poorly available
Moderately and poorly oxidizable	Refractory organic compounds and sulfides	Poorly mobilizable	Poorly available
Poorly reducible	Crystalline Fe and Al oxyhydroxides	Poorly mobilizable	Poorly available
Residual	Mineral lattice (metals retained within the crystal structure)	Immobile	Unavailable

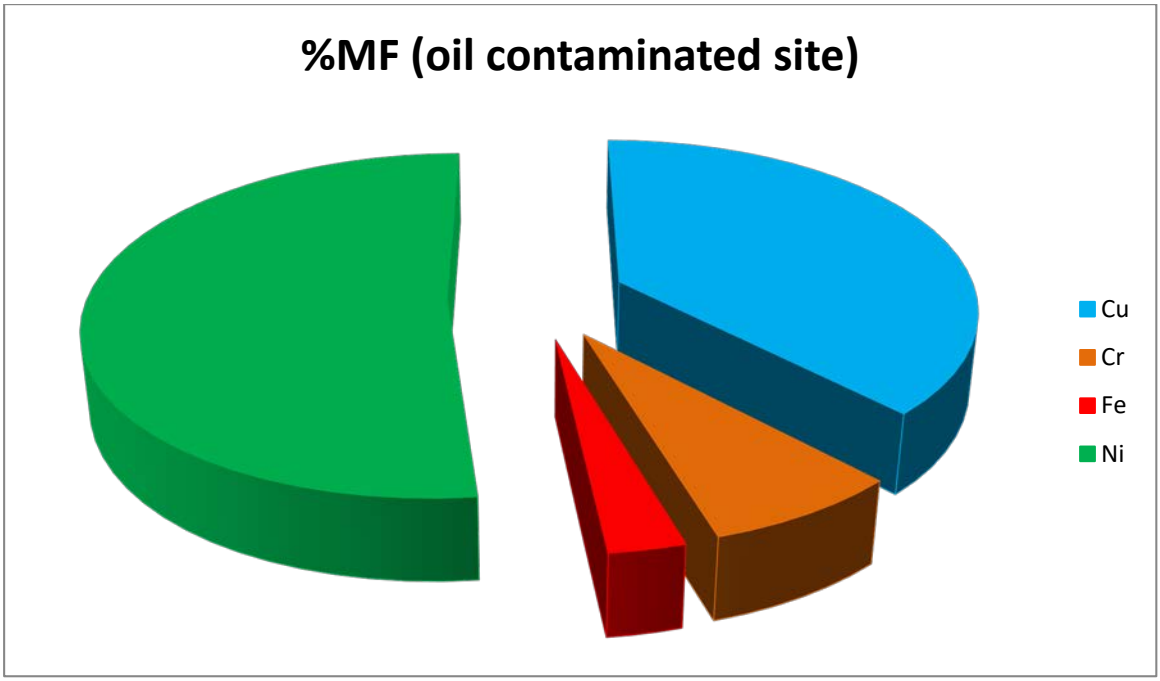

Fig 8: Percentage metal mobility factor (MF) in oil contaminated site

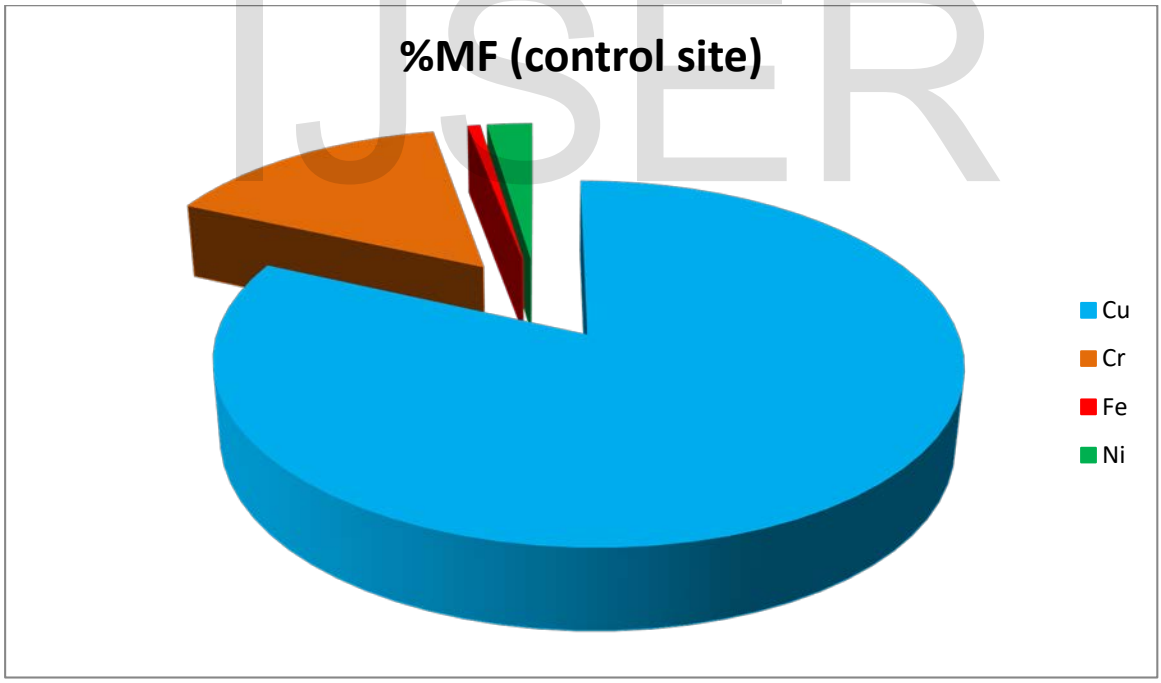

Fig 9: Percentage metal mobility factor (MF) in control site

The mobility factors of oil contaminated and control sites (Figs6 to 7) represent samples collected in the rainy season month of August 2017. The observed sequence for metal mobility factor depicted (Ni>Cu>Cr>Fe) and (Cu>Cr>Ni>Fe) for the oil contaminated and control sites respectively. Consequently, the increased level of nickel mobility in oil contaminated soil was attributed to the activities of oil industries within the oil contaminated site. Similarly, crude oil contaminated sediments from the Middleton River have also showed

an increase in heavy metal mobility factor indices when compared to samples collected from a control station (Aigberua, 2018a).The higher mobility of nickel and its vastly reported association with crude oil could give credence to its use as a diagnostic trace metal for oil spill studies (Aigberua *et al*., 2017). The trend in mobility factor indices from this study had similarities with Osakwe *et al*. (2014) where the potential for heavy metal toxicity revealed the sequence: (Ni>Cu>Cr>Fe) and (Cu>Cr>Ni>Fe) for the oil contaminated and control soils respectively. Iron species in the soil were revealed to be natural constituents of the soil matrix as they were strongly embedded in the interstitial matrices of the soil (as residual fractions). This agreed with Aigberua (2018a) where Fe was reported to be mostly associated to the residual fractions of bottom sediments of the Middleton river system in Bayelsa State, Nigeria. Crops cultivated from farmlands in Bdere and sold in local markets will most likely be enriched with copper. This study reveals that copper is the most mobile element in the uncontaminated environment and therefore, most available for plant uptake. Osakwe *et al*. (2014) also found copper to be the most mobile element in control (uncontaminated) sediments of the Imo River system in Southeastern Nigeria. On the other hand, crops which may sprout along the SPDC right of way (ROW) are likely to be enriched with nickel (human carcinogen). This study was in agreement with Osakwe (2010) that reported mobility factor indices of 15.83 to 62.07% for nickel and 16.49 to 32.13% for iron, with a mobility factor sequence revealing (Ni>Fe) for soils around automobile waste dumpsites.

Although, copper is required for good health and is important for several metabolic and biochemical activities (Prashanth *et al*., 2015),exposure to high doses from food consumption can result in nausea, vomiting, stomach cramps, or diarrhea, while excessive ingestion can become hazardous to the liver and kidney, while even leading to death (ATSDR, 2004).Also, nickel could be poisonous at high concentrations causing gastrointestinal disorder, skin dermatitis, reproductive decline, immune, cardiovascular, lung and kidney disorder (ATSDR, 2004; Izah *et al*., 2016).

Statistical analysis

3.4 Variation in soil metal fractions across oil contaminated and control sites of Bdere (using one-way ANOVA)

Table 4: Heavy metal fractions in oil contaminated soils of Bdere community, Rivers State

Location(s)	Ni (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)
Soil1 F1	0.00a	0.34ab	0.00a	20.22bcd
Soil2 F1	0.00a	0.00a	0.00a	0.00a
Soil3 F1	0.00a	0.00a	0.00a	0.00a
Soil1 F2	0.00ab	0.19ab	1.32g	0.00a
Soil2 F2	4.14d	0.00a	0.52cd	0.00a
Soil3 F2	5.09e	0.00a	0.00a	0.00a
Soil1 F3	3.11c	0.00a	0.00a	0.00a
Soil2 F3	0.77b	1.78f	0.98ef	0.00a
Soil3 F3	0.00a	0.03a	0.09a	0.00a
Soil1 F4	0.00a	0.58bcd	0.00a	3.24ab
Soil2 F4	0.00a	0.00a	0.00a	0.35ab
Soil3 F4	0.00a	0.00a	0.00a	0.00a
Soil1 F5	0.00a	0.00a	1.81h	19.73abc
Soil2 F5	0.00a	1.29e	0.75de	24.53cd
Soil3 F5	0.00a	0.00a	0.39bc	0.00a
Soil1 F6	0.00a	0.59bcd	0.38bc	40.13d
Soil2 F6	0.00a	0.64bcd	0.00a	36.44cd
Soil3 F6	0.00a	0.47abc	0.86e	20.07abcd
Soil1 F7	0.00a	0.90cde	1.44g	150.27fg
Soil2 F7	0.00a	0.23ab	0.00a	144.19f
Soil3 F7	0.00a	0.52bcd	0.74de	3.74ab
Soil1 F8	0.00a	0.96de	0.00a	38.25cd
Soil2 F8	0.00a	3.12g	0.15ab	60.42e
Soil3 F8	0.00a	2.75g	0.53cd	18.78abc
Soil1 F9	10.04f	9.70i	1.20fg	194.72h
Soil2 F9	5.46e	8.98h	0.26abc	166.80g
Soil3 F9	11.15g	9.16h	0.70de	149.15fg

Data are expressed as mean values; different letters along the column indicates significant variations ($P<0.05$) according to Tukey Honestly significant test statistics.

Chromium showed the most insignificant variation ($P>0.05$) for the oil contaminated soil, while iron depicted the metal fractions of most significant variation ($P<0.05$). In the oil contaminated soil, nickel was reportedly below measurable detection limit for most of the soil metal fractions. However, soil 3 (F2) and soil 2 (F9) showed no significant variation ($P>0.05$), while soil 1 (F2), soil 2 (F2), soil 1 (F3), soil 2 (F3), soil 1 (F9) and soil 3 (F9) were sources of significant variation($P<0.05$). Chromium levels in the oil contaminated soil showed that samples of [soil 1 (F1), soil 1 (F2), soil 2 (F7)], [soil 1 (F4), soil 1 (F6), soil 2 (F6), soil 3 (F7)], [soil 2 (F8), soil 3 (F8)], and [soil 2 (F9), soil 3 (F9)] depicted no significant variation ($P>0.05$), while sources of observed significant variations ($P<0.05$) were

samples of soil 2 (F3), soil 2 (F5), soil 3 (F6), soil 1 (F7), soil 1 (F8) and soil 1 (F9). All other soil fractions depicted chromium concentrations which were below measurable detection limit. Statistical assessment of copper showed significant difference (P<0.05) between six (6) soil samples, they included: soil 2 (F3), soil 1 (F5), soil 3 (F6), soil 2 (F8), soil 1 (F9) and soil 2 (F9). On the other hand, samples of [soil 3 (F5), soil 1 (F6)], [soil 2 (F2), soil 3 (F8)], [soil 1 (F2), soil 1 (F7)], and [soil 2 (F5), soil 3 (F7), soil 3 (F9)] were significantly different (P<0.05). All other samples were observed below equipment measurable limit. Finally, iron levels showed significant variation (P<0.05) for samples of soil 1 (F1), soil 1 (F6), soil 3 (F6), soil 2 (F7), soil 2 (F8), soil 1 (F9) and soil 2 (F9), while there was no significant difference (P>0.05) for samples of [soil 1 (F4), soil 2 (F4), soil 3 (F7)], [soil 2 (F5), soil 2 (F6), soil 1 (F8)], [soil 1 (F7), soil 3 (F9)] and [soil 1 (F5), soil 3 (F8)]. All other sample stations and metal fractions were below measurable limit (Table 2).

Table 5: Heavy metal fractions in uncontaminated soils of Bdere community, Rivers State

Sample Identity	**Ni (mg/kg)**	**Cr (mg/kg)**	**Cu (mg/kg)**	**Fe (mg/kg)**
Soil Control F1	0.00a	0.00a	0.61bc	0.00a
Soil Control F2	0.00a	0.00a	0.05a	0.00a
Soil Control F3	0.08a	0.56b	0.39b	2.95a
Soil Control F4	0.00a	0.60bc	0.42b	22.11ab
Soil Control F5	3.15b	1.16d	0.45b	54.51b
Soil Control F6	0.00a	1.80e	0.88cd	192.94c
Soil Control F7	0.00a	1.11cd	1.08d	612.09e
Soil Control F8	0.00a	2.69f	1.31de	585.22e
Soil Control F9	9.43c	11.04g	0.93d	511.92d

Data are expressed as mean values; different letters along the column indicates significant variations (P<0.05) according to Tukey Honestly significant test statistics.

Nickel depicted the most insignificant difference (P>0.05) while chromium revealed the most significant difference (P<0.05) for metal fractions in uncontaminated (control) soil. Soils of the uncontaminated site predominantly depicted nickel levels below measurable detection limit. However, soil control (F3), (F5) and (F9) were sources of significant variation (P<0.05). For chromium, soil control (F1) and (F2) were the only sources of non-significance (P>0.05) while all other sampling points and metal fractions showed significant difference (P<0.05).Soil copper concentrations and fractions showed no significant variations (P>0.05) for [soil control (F3), (F4), (F5)] and [soil control (F7), (F9)]. All other samples showed significant variations (P<0.05). Finally, only samples of soil control (F7) and (F8) showed no significant difference (P>0.05) for iron in the different stations and fractions, while [soil control (F1), (F2), (F3)] and [soil control (F4), (F5), F6) and (F9)] were the sources of significant iron variation (P<0.05) in the uncontaminated soil environment (Table 3).

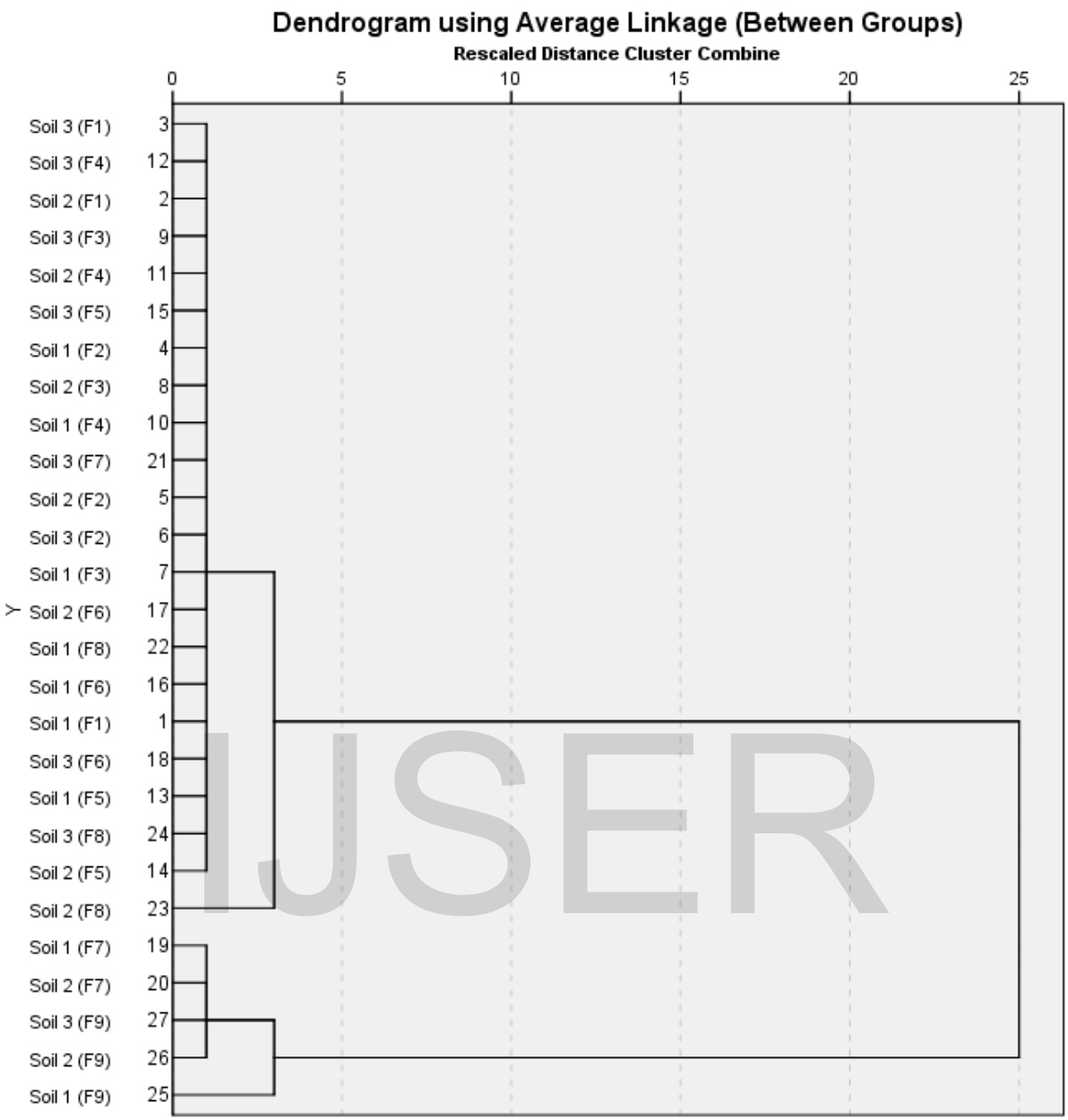

Fig 10: Hierarchical dendogram of the locations and different fractions of heavy metals in crude oil contaminated soil environment

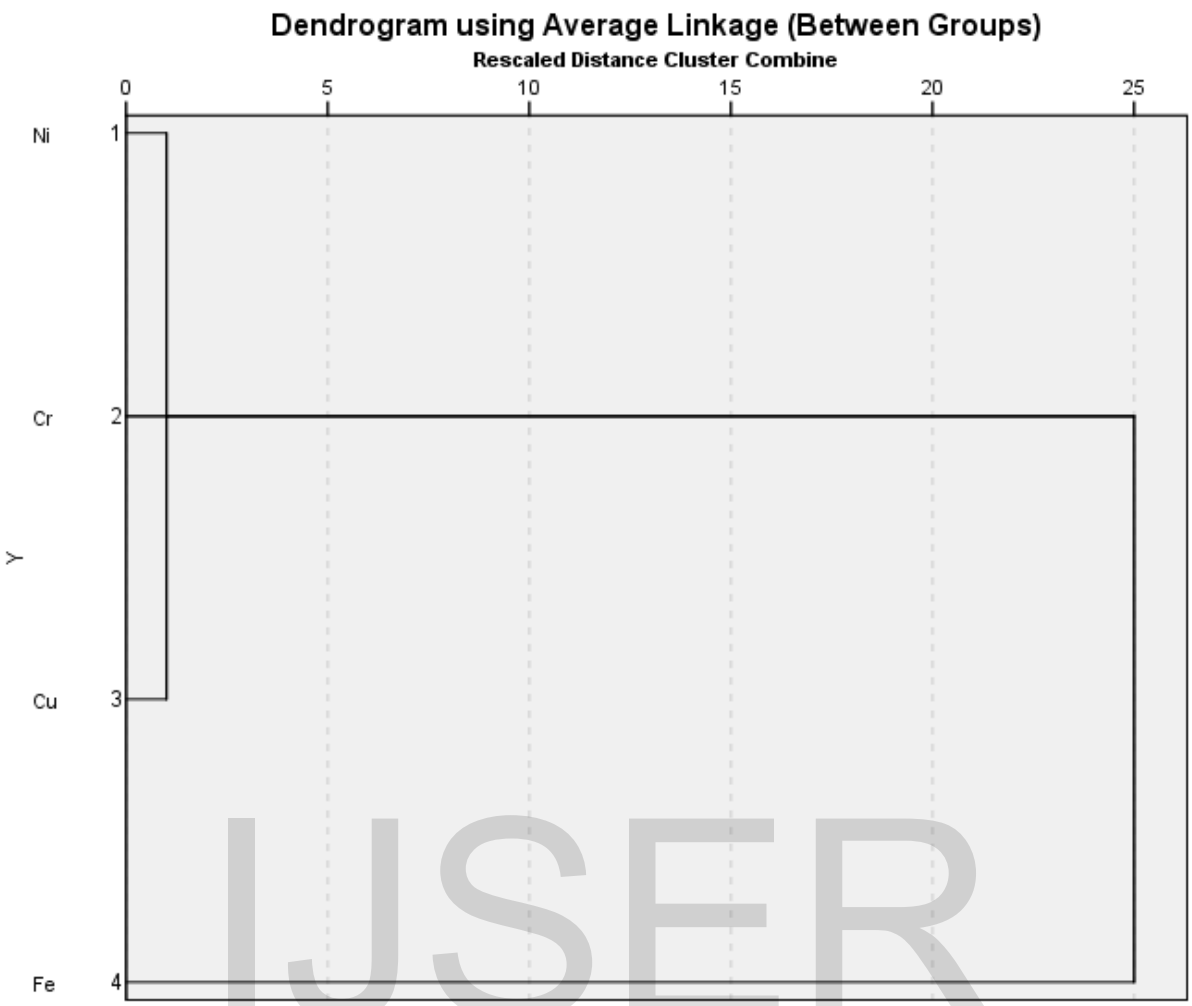

Fig 11: Hierarchical dendogram of the variables (heavy metals) in crude oil contaminated soil environment

3.5 Mutually dependent and independent heavy metal associations in crude oil contaminated soil (using cluster analysis)

Oil contaminated soil data revealed the strongest mutual dependence for (Ni-Cu) and (Cr-Fe). Also, Fe and Ni were the most mutually independent heavy metal variables (Fig 11). The sample locations revealed strongest mutual dependence for the residual fractions (F9) of soil locations 1 and 3. The strongest mutual independence was revealed between the carbonate bound fraction (F3) of soil site 1 and the organic matter fraction (F8) of soil site 2. All other sample sites and the metal fractions were closely interlinked (Fig 10).

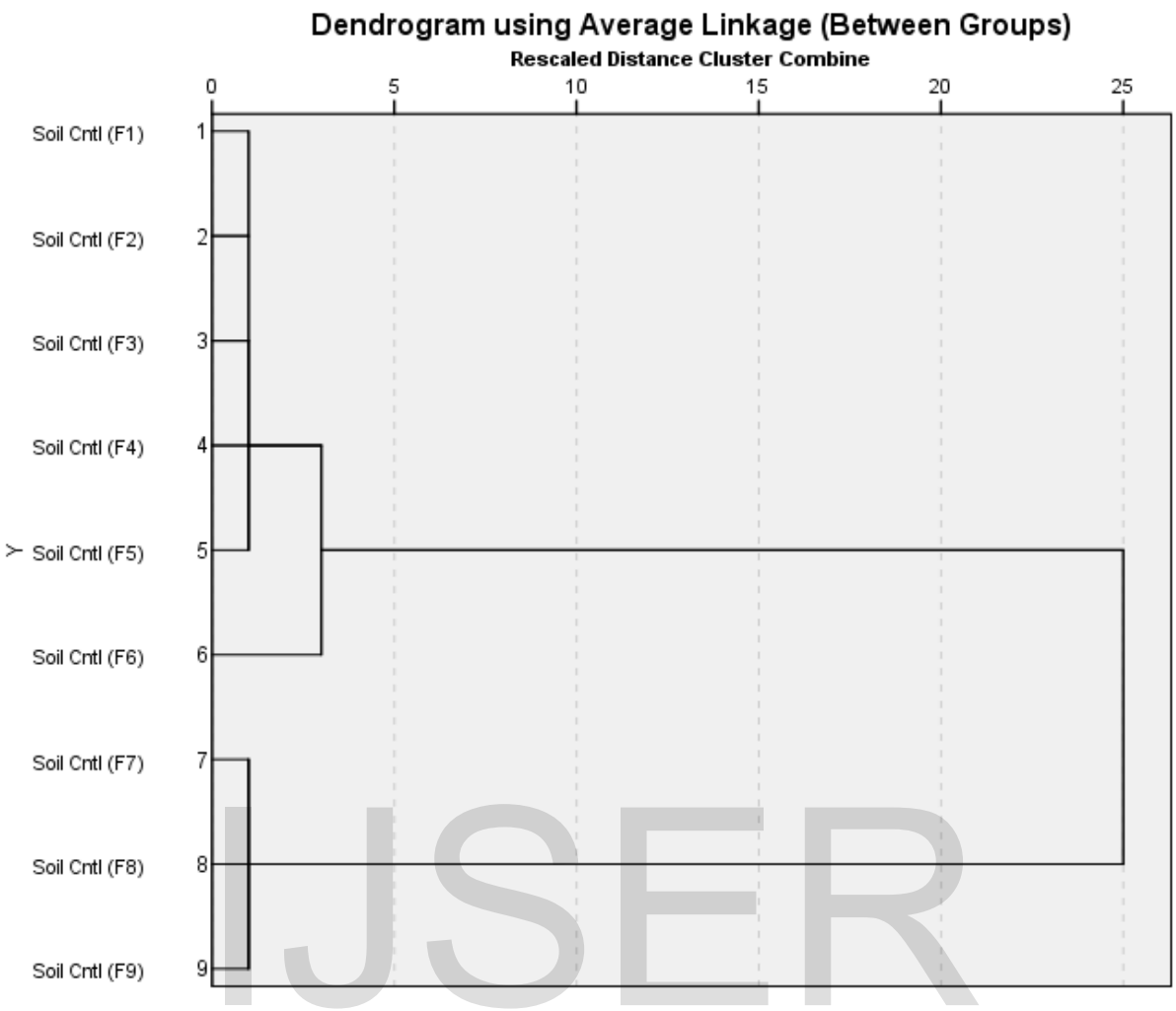

Fig 12: Hierarchical dendogram of the locations and different fractions of heavy metals in uncontaminated (control) soil environment

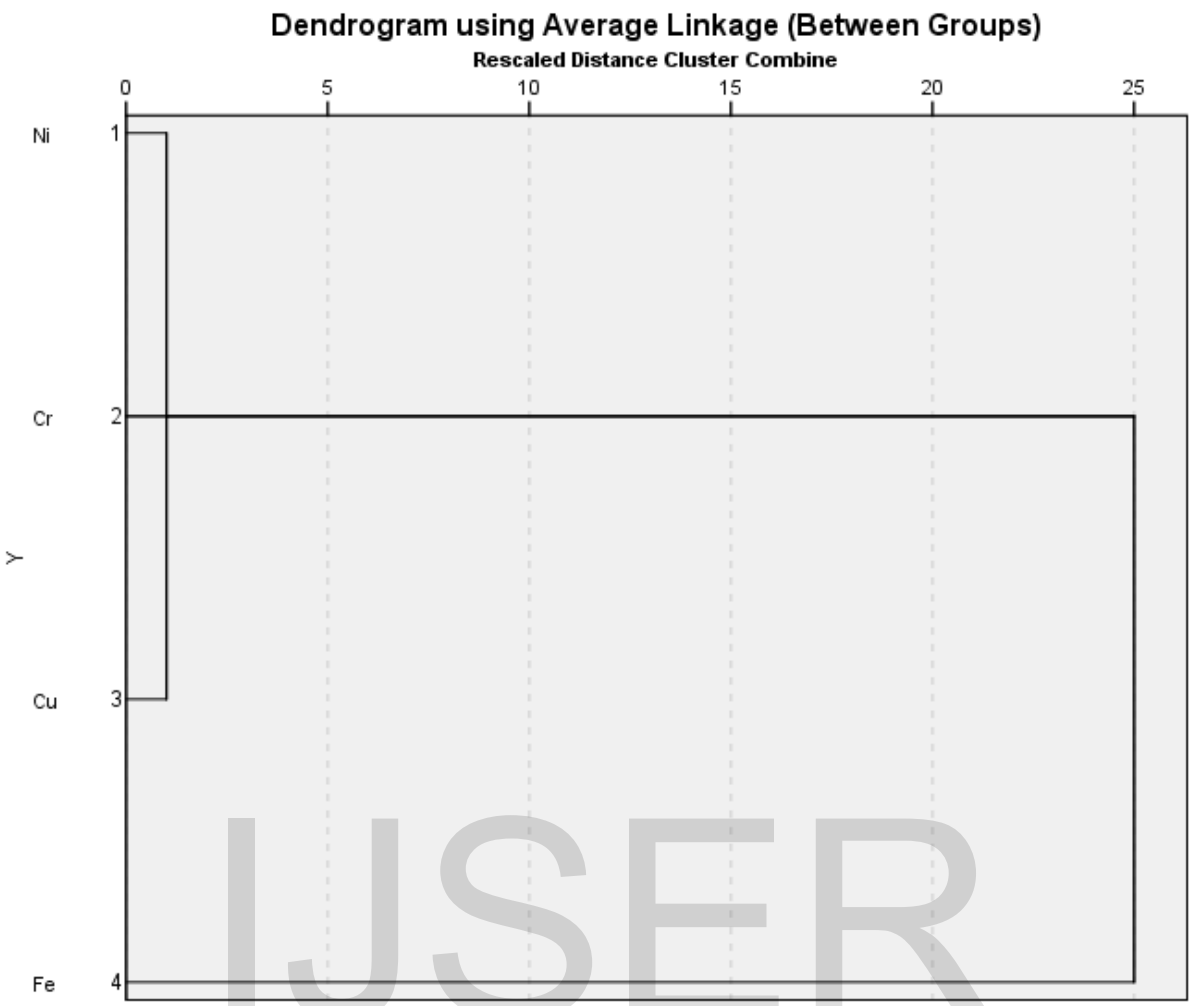

Fig13: Hierarchical dendogram of the variables (heavy metals) in the uncontaminated (control) soil environment

3.6 Mutually dependent and independent heavy metal associations in uncontaminated (control) soil

Cluster analysis was used to identify variables (sample location and heavy metals retention) of close association across the uncontaminated (control) soil site. Heavy metals of mutual dependence reflected similarity or closeness in characteristics while those of mutual independence depicted differing characteristics. In terms of heavy metals, there was similarity with soils emanating from the crude oil contaminated environment. Hence, uncontaminated (control) soil data revealed the strongest mutual dependence for (Ni-Cu) and (Cr-Fe). Also, Fe and Ni were the most mutually independent heavy metal variables (Fig 13). The control locations revealed strongest mutual dependence between plant available fractions (F4) and amorphous Fe-oxide fractions (F6) of the uncontaminated (control) soil. Also, the crystalline Fe-oxide fractions (F7) and residual fractions (F9) of the control site were mutually dependent. All other heavy metal fractions of the uncontaminated (control) site were closely interlinked (Fig 12).

4.0 CONCLUSION

Despite the relatively high concentration of iron and chromium in the control site (farmlands), they remained poorly mobile and non-bioavailable when compared to metals of the oil contaminated site (along the SPDC right of way (ROW)). This study shows that crops cultivated from farmlands in Bdere and sold in local markets will most likely be enriched with copper. On the other hand, crops which may sprout along the SPDC ROW are likely to be enriched with nickel. Even though, the level of copper in this study poses no public health concern. The significant affiliation of Ni (32.27%) and Cu (23.61%) to the easily mobile and bioavailable fractions of oil contaminated soils (along the SPDC ROW) portends high toxicity potential for both metals if there concentrations increase. Periodic monitoring of the soil environment for heavy metal contamination is therefore important. Because of the occasional flooding in this area, water-soluble metals can be transported, thereby resulting in the cross-contamination of less impacted farmlands over time and heavy metal enrichment in soil. Hence, spilt crude oil in soil may have been responsible for the elevated toxicity potential of metals. Cr revealed the most significant variation in oil contaminated soil. Cluster analysis showed the strongest mutual independence between the carbonate bound fraction (F3) of soil station 1 and the organic matter fraction (F8) of soil station 2. The concentrations of potentially mobile and bioavailable heavy metals in the soil were below DPR limit. Hence, the potential bioavailability of residual metals in soil posed no immediate threat to the environment.

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Conflict of Interest
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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