Environment Conservation Journal 19 (1&2) 17-37, 2018
ISSN 0972-3099 (Print) 2278-5124 (Online)
Abstracted and Indexed

Soil quality and extent of soil-plant transfer of trace metals in areas adjoining the Benin-Ethiope fluvial system in the vicinity of Sapele, Nigeria

Samuel Omorovie Akporido, Onoriode Onos Emoyan and Ayo R. Ipeaiyeda ✉

Received: 15.09.2017 **Revised: 10.11.2017** **Accepted: 12.12.2017**

Abstract

Spillages of oil from processes of discharge of imported petroleum products and lubricating base oil and the process of production of lubricating oils can have adverse effect on water, sediments, soil, and biota of an environment. The study examined the effect of these spillages of oils on the soil by determining oil residues, physicochemical parameters of soils, and the concentrations of seven heavy metals in soil and plant of the area. Soil and plant samples were collected from areas around the Benin-Ethiope Fluvial system in the vicinity of Sapele Town and her satellite towns. Total petroleum hydrocarbons TPH and other physicochemical parameters of soil were determined by standard methods. Heavy metals in soil and plant were determined by atomic absorption spectrometry after appropriate wet acid digestion procedures. Average values of important parameters determined in soil were: pH, 6.5±1.0; TPH, 1930 mgkg^{-1}; Cr, 4.4±2.1 mgkg^{-1}; Cu, 7.0±4.3 mgkg^{-1}; Zn, 99±63 mgkg^{-1}; Pb, 35.5±9.0 mgkg^{-1}; Cd, 3.3±0.9 mgkg^{-1}; Ni, 7.6±5.5 mgkg^{-1} and Mn, 167±170 mgkg^{-1}. Results showed that the levels of pH and pollutant parameters (which include TPH and the heavy metals) were significantly higher in the study area than the control area. The average values of pH, Cd, Zn and TPH in most of the sampling stations exceeded soil guideline values (SGVs) (lower than guideline range in the case of pH). Transfer factors of most of metals indicated that they had been moderately transferred from soil to plant. Various indexes calculated in the study also showed that the soils in the study area were of low quality as a result of these pollutants.

Keywords: Benin-Ethiope Flavial System; Sapele Town; Total petroleum Hydrocarbons; Heavy metals; atomic absorption spectrometry; Transfer factor; soil guideline values

Introduction

The Niger Delta area is well known for petroleum prospecting and processing. Petroleum prospecting and processing activities were often accompanied by oil spillages, hence much attention by environmentalist have been focused on the activities in the upstream sector. The downstream sector of the petroleum industry had received much less attention which actually tends toward neglect by environmentalist. The neglect of the downstream sector has given much room to industries in these areas to dump dangerous waste in waters, sediments and soils of the Niger Delta. It had been shown that urbanization and industrialisation are important sources of pollutant to the environment (Forstner and Whittman, 1983; Yang *et al*., 2009; Bai *et al*., 2012, Haapala *et al*., 2012; Giri *et al*., 2013; Akporido and Kadiri, 2014; Akporido *et al*., 2015).The downstream sector of the petroleum industry in Nigeria especially in the Niger Delta consist of refineries (where crude oil is refined to petroleum products and production of petrochemicals), lubricating base oil importation, and production of lubricating oils. Petroleum products produced by local refineries in Nigeria were unable to meet the high demand for these commodities in Nigeria so that heavy importation of petroleum products was embarked upon. The production and importation of these commodities (i.e. petroleum products, lubricating oil and other petrochemicals) usually have effect on the environment (water, sediment, soil, biota) through spillage (during discharge from tankers) or during production (through the effluents) (Akporido and Kadiri, 2014). Effluents or spillages of petroleum products and lubricating oil have essentially the same effect as spillages from petroleum (crude oil). If large quantities are spilled, this can bring about elevated concentrations of petroleum hydrocarbons

Author's Address
[1]Department of Chemistry, Delta State University PMB 1, Abraka, Nigeria.
[2]Department of Chemistry, University of Ibadan Ibadan, Oyo state Nigeria
E-mail: *samaccess2006@yahoo.com*

and heavy metals in the receiving matrix (water, sediment, soil) and this can also lead to damage to, and loss of biodiversity, depletion of arable land, depletion of available potable water and affect the health of humans and higher animals which come into contact with the spilled oil (Luisseli, 2006; UNDP, 2006; Okereke *et al*., 2007; Perez *et al*., 2010; UNEP, 2011; Almeida *et al*., 2013). It had also been observed that the presence of heavy metals in materials (oil) spilled makes the biodegradation of hydrocarbon by micro-organisms more difficult (Kalita, 2009; Plaza *et al*., 2010; Nie *et al*., 2010). Spillages of petroleum products and lubricating oil cover more areas than spillages due to crude oil although the quantities spilled in most cases were very much less. This is so because of the many ways these products are spilled. They were mostly spilled during usage in transportation (i.e. during repair of boats, motor vehicles and electric generators), during production in factories and refineries (i.e. effluent from refineries) and during discharge from tankers and boats or at gasoline filling stations. Spilled materials at these points are often transferred by storm runoff water to a large area, into streams, rivers, lakes and the sea. Although much of the studies in the Niger Delta had been focused on the upstream sector of the petroleum industry especially on crude oil spillages, a number of studies had however been carried out in the downstream sector of the petroleum industry in which petroleum hydrocarbon residues (oil and grease, petroleum hydrocarbons, and polycyclic aromatic hydrocarbon), and trace heavy metals in the aquatic and terrestrial environment had been carried out (Olajire *et al*., 2005; Otukunefor and Obiuku, 2005; Awomeso, 2010; Adeniyi and Owoade, 2010; Anyakora *et al*., 2011; Akporido and Asagba, 2013, Akporido and IPeaiyeda, 2014).

The Benin-Ethiope fluvial system consists mainly of the Ethiope and Benin River. The Ethiope River takes its source in Umuaja village in Ukwuani Local Government Area of Delta State, Nigeria. The town is about 130 kilometres East of Sapele town in Sapele Local Government Area of the same Delta State. After Sapele, the River is officially known as the Benin River as shown in Fig. 1. It enters into the Gulf of Guinea in Warri North Local Government Area of Delta State. The activities occurring around the fluvial system at Sapele which may contribute to the lowering of the quality of the water, sediment, soil and biota include the following:

1) A fast growing urban centre at Sapele and her satellite towns. This growing urban centre houses several large markets.
2) Industries which releases their effluents into the river system. These industries include electricity generating plants (an example is the Power Holding Company of Nigeria generating plant), Agro industries- grain flour producing Mills and animal feeds producing companies (examples are the Flour Mills Ltd. And Top Feed Ltd), companies which import petroleum products, lubricating oil and lubricating base oils and store them in depots and those that produce lubricating oils from the imported lubricating base oil (examples are Asca oil PLC and Regandez Ltd.), and Ceiling and roofing sheets manufacturing companies (eg Eternit PLC)
3) Wood processing industries which process local timber for export and for local use. These industries push materials of high BOD into the waters of the fluvial system.
4) Large volume of transportation by means of engine boats occurs on the fluvial system. As a consequence of this, many boat-repair workshops are located along the river. These workshop release large quantities of used lubricating oils into waters of the river system and the soils of the area.

The activities which contribute by far more to the amount of spilled oil are the companies which import petroleum products and lubricating base oils and those companies that produce lubricating oils from the imported lubricating base oils. Spillages of oil occurs mostly during the discharge of the imported materials (petroleum products and lubricating base oil) from tankers and boats into their depots and during discharge of bilge, These processes of discharge of fuel and bilge contributes by far more spilled oil into the river systems. In addition these companies also release their effluents into the fluvial syste. Another important thing to note is that the area also houses petroleum (crude oil) prospecting and processing industries. The petroleum prospecting and processing industry in this area is however rather small. Some of the individual human activities in the area include subsistence farming in the land adjoining the river.

Some of the arable crops grown in the area include yam (*Diocorea sp*.), cassava (*Manihot esculanta*), tomatoes (*Solanum lycopascium*), maize (*Zea mays*), pineapple (*Annas comosus*), fluted pumpkin (*Telfera occidentalis*). The tree crops include mango (*Magnifera indica*), oil palm (*Eleais guineensis*), and coconut trees (*Cocus nucifera*). Fishing which is also of subsistence in nature is also one of the occupations of the people in this area. Those not in the two occupations already stated work in the Government service, the industries stated above and in the commercial sector. Report by Akporido and Kadiri (2014) has shown that the effluents from some of these industries are highly polluted since some of the tested effluents quality parameters exceeded guideline limitation values set by Department of Petroleum Resources (DPR) (DPR, 2002) and Federal Ministry of Environment Effluent limitation guideline (FMinEnv, 1987) and were actually able to pollute a receiving water body. The study also found that the concentrations of some of the trace heavy metals and petroleum hydrocarbons were very high in the waters of the River.

Akporido *et al*., (2015) found that the concentrations of all the trace heavy metals and total petroleum hydrocarbon in the sediments of study area very much exceeded corresponding ones in the control area and also that the average concentration of Cd and TPH of the study area exceeded guideline values of Environmental Guidelines and Standards of the Petroleum Industry in Nigeria (EGASPIN) (DPR, 2002) and National Oceanic and Atmospheric Administration (NOAA) (NOAA,1999) Sediment Quality Guidelines (SQGs).This study is a continuation of these two aforementioned studies, so it will be necessary to test the hypothesis – that since the waters and the sediments of the Benin-Ethiope fluvial system were polluted with trace metals and petroleum hydrocarbons probably brought into them by effluents from industries and spillages of oil from the activities of the industries along the river, the soils adjoining the river should also be polluted with trace metals and petroleum hydrocarbons.

This study examined the soil quality characteristics and the pollution status of the soils and vegetation of the area adjoining the Benin-Ethiope fluvial system and the extent of transfer of the observed pollutants (if any) to plants by determining the concentrations of two oil parameters (TOE and TPH), seven trace heavy metals (Cr, Cu, Cd, Zn, Pb, Mn, Ni) and determining the levels of selected soil physicochemical parameters (pH, TOC, TOM, soil texture (clay, silt and sand). Pollution indexes such as contamination/pollution (C/P) index, pollution load index (PLI), contamination factor were also used to determine the pollution status of the soil in the study area. The transfer factor was used to determine the extent of transfer of heavy metals to plants from soil.

Material and Methods

Description of Study Area:

The study area is localised around Sapele Town (i.e. the Benin-Ethiope Fluvial System). The area is bounded by four co-ordinates as follows: latitudes $5^0\ 52^1$ N and $5^0\ 57^1$N and longitudes $5^0\ 39^1$E and $5^0\ 45^1$E. As already stated, one of the component rivers in the fluvial system i.e. the Ethiope River takes its source at Umuaja 130 km East of Sapele Town. The other major component in the fluvial system (i.e. The Benin River) flowed in the South-West direction and finally entered the Gulf of Guinea in Warri North Local Government Area of Delta State, Nigeria. Seven sampling stations were established in the study area as shown in Fig. 1 (Map of study area showing a section of the Benin-Ethiope Fluvial System). Two sampling stations were also established at Edjeba (5^046^1N and 5^048^1E) and at Ovwori (5^047^1N and 5^047^1E).

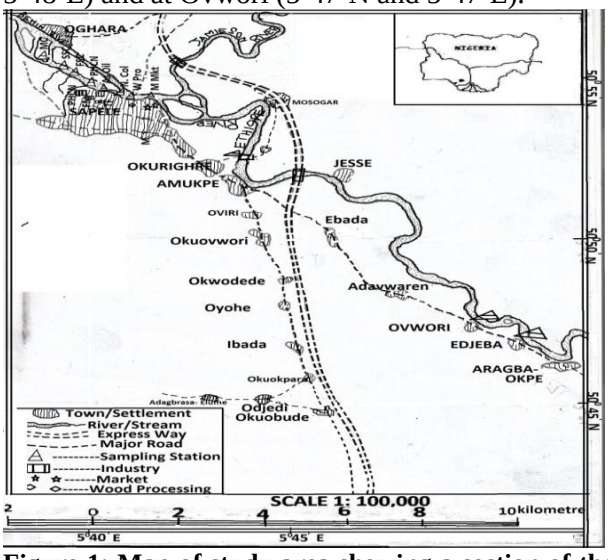

Figure 1: Map of study area showing a section of the Benin-Ethiope Fluvial system and the sampling stations

Design of Study

Seven sampling stations were established in the study area as given in the report by Akporido and Kadiri (2014) and Akporido *et al.*, (2015). The sampling stations are Okurighre located at one of the satellite towns to Sapele. The second sampling station was at the main market at Sapele about two kilometres from the first sampling station at Okurighre it was designated as "Main Market" sampling Station. From this point onwards the remaining sampling stations had a distance of 500 km between successive stations. The third sampling station was at the wood processing area along the river. Timber is processed here for export and local use. This sampling station was designated "Wood Processing Industry" sampling station. The next sampling station was at the Naval College also named "Naval College" sampling station. The fifth sampling station was at the Asca Oil company. This sampling station was named "Asca Oil". The sixth sampling station was at the Power Holding Company of Nigeria Ltd (PHCN) station, an electricity generating company and it was named "PHCN" sampling station. The last sampling station was located at the main confluence of the river with one of its tributaries very near to Oghara Town (Fig. 1) and it was named 'Main Confluence" sampling station. Soil and plant samples were collected twice every season for two dry seasons and two wet seasons for 2 years (i.e. every quarter of the year). Soil samples were collected for the following parameters: total organic extract (TOE), total petroleum hydrocarbons (TPH), heavy metals (Cr, Cu, Cd, Zn, Pb, Ni and Mn) and soil physicochemical parameters (pH, total organic carbon [TOC], total organic matter [TOM], soil texture [particle analysis – clay, silt and sand]). Plant samples were collected for heavy metal determination.

Sample Collection and Preservation

Sampling was carried out from July, 2010 to May, 2012. The sampling design consisted of delimiting in every sampling station, a sampling area of 60m x 60m. This sampling area was then divided into 100 grid plate of 6m x 6m area. Thus, thirty-three grid plates were randomly selected. From these plots, three replicates of pre-determined quadrates were established, and soil samples were taken from each. Soil samples were collected using a stainless steel auger from the different soil depths i.e. from the surface (0 – 15cm) and subsurface (15 – 30cm). Soil samples were stored in iced coolers for transfer to the laboratory. At the laboratory, samples for oil parameters were stored in deep freezers at -10^0C (as recommended by American Society for Testing and Materials (ASTM) (ASTM, 1982)). Soil samples were transferred from the field in polythene bags, samples for oil parameters were first wrapped in aluminium foil before being put into polythene bags. At the laboratory soil samples for trace metal analysis and physicochemical parameters were oven-dried at 80^0C for 2h. Plant samples were collected by cutting fresh shoots with a glass knife. Plant samples were kept in iced cooler for transfer to the laboratory. In the laboratory, they were oven-dried at 60 ^{0}C for two hours.

Analytical Procedures

pH was determined by adding 20 ml of water to 10 g of soil in a 200 ml beaker and sampling thoroughly with a clean glass rod and allowing soil to settle. The pH meter electrode was then dipped into the supernatant liquid and pH determined (International Institute for Tropical Agriculture Manual [IITA], Black, 1965). The % organic carbon or total organic carbon (TOC) was determined by the Walkley-Black method (Walkley and Black, 1934). % organic matter or total organic matter (TOM) was obtained by multiplying the value obtained for TOC by a factor 1.724 (Walkley and Black, 1934). Particle size analysis was carried out by the hydrometer method using a Boyoucos soil hydrometer (ASTM model) (Allen, 1989). The total organic extract (TOE) and total petroleum hydrocarbons (TPH) determination was carried out using the Reflux method. In this method which is a modification of the method used by Oudot *et al.*, (1981) and Berthou *et al.*, (1981), and used by Adekambi (1989). 200 g of partially thawed soil sample was measured into a 500 ml capacity round bottom flask. 150 ml of analar grade methanol, 1.5 g of KOH pellets, 5 pre-extracted boiling glass beads and 20 ml of pre-extracted distilled water were added to the contents of the round bottom flask. The flask was fitted to a clamped Liebig double surface reflux condenser. The content of the flask was refluxed for 2h in a steam bath. After cooling, the content was filtered into a 500 ml capacity glass separating funnel. Three 50 ml portion of redistilled hexane were used to re-extract the contents of the separating funnel. This was done

by shaking the contents of separating funnel vigorously for 5 mins with intermittent release of pressure by opening the cap. The organic layer (i.e. the hexane layer) was filtered each time through anhydrous sodium sulphate on a pre-extracted filter paper on a glass funnel into a fresh clean 500 ml capacity round bottom flask. At the end of the three extraction of the content of the separating funnel, the combined hexane extract in the round bottom flask was distilled to recover solvent (hexane). The residue from the hexane extract was transferred to a clean already weighed glass vial by using dicloromethane and the content was dried to constant weight in an oven at 45^0C. It was finally kept in a glass desicator. A blank determination was also carried out and the concentration of TOE was obtained from this by the equation.

$$\text{TOE}\left(\text{mgkg}^{-1}\right) = \frac{(\text{A-B})\text{x}10^6}{\text{Dry wt of experimental sample (g)}}$$

Where

A = weight of TOE observed for sample (g)

B = weight of TOE obtained for Blank (g)

The concentration of total petroleum hydrocarbon was determined from the TOE by re-dissolving TOE in hexane (100 mL) and 3 g. of activated silica gel (column chromatography silica gel) was added and this was stirred vigorously using a magnetic stirrer for 5 min. Silica gel was filtered out at the end of the process. The content of the beaker was poured into a round bottom flask and carried through the procedure as described for TOE hexane extract. Calculation of TPH is as done for TOE i.e. as in equation 1.

Trace heavy metals were determined by adding 50 mL of 2 M HNO_3 to 5 g of dried soil sample in a 200 mL beaker covered with a watch glass placed on a boiling water bath for 2h, with stirring at 15 min interval. The extracted material was filtered and the filtrate subsequently analysed using atomic absorption spectrometry (Perkin Elmer AA 200) (Anderson and Morel, 1978; Allens *et al.,* 1989).

Quality Assurance Programme for the Study:

Blanks were analysed for in all parameters determined and parameters were also analysed in duplicates. Recovery studies were carried out for the two oil parameters (i.e. TOE and TPH) and for all the trace heavy metals (Cr, Ca, Cd, Zn, Pb, Ni and Mn). The results for the determination of percentage recovery of seven trace heavy metals and two oil parameters (i.e. TOE and TPH) and given as Mean $\pm$ Standard Deviation of five determinations were as follows: Cu (4.5 $\pm$ 3.7%), Ni (95.5 $\pm$ 5.5%), Pb (93.2 $\pm$ 3.3%), Cd (91.7 $\pm$ 6.5%), Zn (98.8 $\pm$ 2.8%), Mn (93.5 $\pm$ 4.5%), TOE (99.5 $\pm$ 2.7%), and TPH (99.5 $\pm$ 3.5%).

Indexes Used

Enrichment Ratio (ER)

The Enrichment ratio (ER) (or enrichment factor [EF]) for each of the trace metals in each of the sampling stations was calculated using the average concentration of each of the metals in the four seasons studied and using the formula (Simon and Helz, 1981).

$$ER = \frac{C_X M_S \,/\, C_r M_S}{C_X M_b \,/\, C_r M_b} \text{---------(2)}$$

Where

$C_X M_S$ = Concentration of trace heavy metal in studied material

$C_r M_S$ = Concentration of reference heavy metal in studied material

$C_X M_b$ = Concentration of trace heavy metal in reference materials

$C_r M_b$ = Concentration of reference trace heavy metal in reference material

The background value of the trace heavy metal is that of the world surface average (Martin and Megbeyle, 1979). The background values of the studied trace heavy metals are, Mn = 720, Zn = 129, Cu = 32, Cr = 97, Ni = 49, Pb = 20, Cd = 10. Value for Cd was obtained from Puyate *et al*., (2007). Mn was chosen as the reference or conservative trace heavy metal as done in Akporido *et al*., (2015) since it is one of the most common elements in the area, its concentration was always higher than those of the other trace metals in sediment and soil samples of the study area. The status of each sampling station with respect to each trace heavy metal is as given in Sutherland (2000) and Loska *et al*., (2004). They are as follows: ER < 2 shows "deficiency" to "minimal enrichment". ER = 2 – 5, shows "moderate enrichment", ER = 5 – 20 shows "significant enrichment", ER = 20 – 40 shows "very high enrichment", and ER > 40 shows "extremely high enrichment".

Contamination/Pollution (C/P) index

The C/P index of each metal in each of the sampling stations was calculated using the average

value of each metal in the four seasons and employing the equation

$$\frac{C}{P}index = \frac{\text{Concentration of trace heavy metal}}{\text{tolerable level of metal in soil}}\text{-----(3a)}$$

The tolerable level of metal in soil used is the target value of the metal in EGASPIN (DPR, 2002).

$$C/P\ index = \frac{\text{Concentration of metal}}{\text{target value of metal in soil}}\text{-------(3b)}$$

The significance of interval of contamination/pollution (C/P) index by Lacatusu (Lacatusu, 1998) was used to interpret the observations and gave the status of the sampling stations with respect to each metal. The significance of interval as given by Lacatusu (1998) was as follows: C/P index < 0.1 shows "very slight contamination", C/P index = 0.10 – 0.25 shows "slight contamination", C/P index = 0.26 – 0.50 shows "moderate contamination", C/P index = 0.51-0.75 shows "severe contamination", C/P index = 0.76 – 1.00 shows "very severe contamination", C/P index = 1.1 – 2.0 shows "slight pollution"', C/P index = 2.1 – 4.0 shows "moderate pollution", C/P index = 4.1 – 8.0 shows "severe pollution", C/P index = 8.1 – 16.0 shows "very severe pollution" and C/P index > 16.0 shows "excess pollution".

Calculation of Contamination Factor (CF) and Pollution Load Index (PLI)

The contamination factor gives the relation of the concentration of metal in study area to its background value. The background value of an element is the maximum level of the element in an environment and beyond which the environment is said to be polluted by the element (Puyate *et al*., 2007). The background values of each metal were obtained as already stated above. The contamination factor (CF) is calculated as given in equation below:

$$CF = \frac{concentration\ of\ metal}{background\ value\ of\ metal}\text{-----(4)}$$

Where CF < 1 refers to low contamination, 1 $\leq$ CF $\leq$ 3 indicates moderate contamination, 3 $\leq$ CF $\leq$ 6 indicates considerable contamination, and CF > 6 indicates very high contamination (Puyate *et al*., 2007). The Pollution Load Index (PLI) was also calculated because of its averaging nature. It is capable of aggregating all the metal contaminants into one for each sampling station. The PLI is calculated as follows:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}\text{----- -(5)}$$

Where

CF = contamination factor

Calculation of Transfer Factor

Transfer factors (TF) are generally used in various models for predicting the concentrations of a given element in a given plant for a known level of soil contamination (Chojjnacka *et al.,* 2005; Mihali *et al.,* 2013). It is calculated as given below:

$$TF = \frac{Concentration\ of\ metal\ in\ plant}{Concentration\ of\ metal\ in\ soil}\text{----(6)}$$

Statistical procedures and packages employed

These included Bivarate correlation of concentrations of pollutant parameters and the soil physicochemical parameter by Pearson (2-tailed) correlation. This was employed from the statistical package of the Social Sciences (SPSS, 2007) (Version 17 SPSS Chicago). The comparison of the mean of the concentrations of a parameter in the study area with the mean of the concentrations of the corresponding parameter in the control area was carried out using t-test (two sample, assuming equal variances) with Microsoft Excel (2007 version). The comparison of the mean of concentrations of each parameter in the four seasons studied (first wet season, first dry season, second wet season and second dry season) and the mean of concentrations of each parameter in the seven sampling stations were carried out by using analysis of variance (ANOVA – single factor) with Microsoft Excel (2007 version) at 0.05 confidence level. The comparison of the mean of a set of values for two areas (i.e. the study area with the control area) was carried out using student t-test at 0.05 confidence level.

Results and Discussion

Comparison of Concentrations of Parameters in Study Area with their Concentrations in Control Area

The concentrations of most pollutant parameters in soil were generally higher in the study area when compared with the control area (Table 1).

Table 1: Average values ($mgkg^{-1}$) of parameters of soil and plant in the study area and control area given in mean±standard Deviation ($n^{SS} = 54$; $n^{CS} = 16$; $n^{SP} = 28$; $n^{CP} = 8$)

Parameters	Study Area		Control Area	
	Soil	Plant	Soil	Plant
pH	6.5±1.0	-	6.78±0.11	-
TOM*	0.28±0.16	-	0.34±0.04	-
TOM *	0.49±0.27	-	0.58±0.07	-
Sand *	76.7±8.1	-	87.5±2.4	-
Silt *	7.0±4.2	-	1.9±0.4	-
Clay *	16.3±6.8	-	10.5±2.3	-
TOE	2710±1700	-	166±58	-
TPH	1930±1600	-	142±56	-
Cr	4.4±2.1	0.89±0.27	2.4±0.4	0.55±0.17
Cu	7.0±4.3	2.4±2.7	3.5±0.5	0.82±0.12
Zn	99±63	14.8±5.8	75±21	6.1±0.8
Pb	35.5±9.0	4.0±0.7	27.4±4.4	2.0±0.3
Cd	3.3±0.9	0.74±0.13	2.2±0.7	0.3±0.24
Ni	7.6±5.5	1.9±0.6	1.9±0.4	1.61±0.34
Mn	167±170	53±37	79.5±21	17.9±2.2

n^{SS} = total number os soil samples in study area
n^{CS} = total number of soil sample in control area
n^{SP} = total number of plant sample in study area
n^{CP} = total number of plant samples in control area
***= %**

The average concentrations of the two oil parameters,. TOE, 2710±1700 $mgkg^{-1}$ and TPH, 1930±1600 $mgkg^{-1}$ in soil of the study area were compared with the average concentrations of the two parameters in the control area, TOE, 166±58 $mgkg^{-1}$ and TPH, 142±56 $mgkg^{-1}$ (Table 1). It should be noted here that the concentrations of the two oil parameters in the control area does not give an indicate that the area is clean with respect to oil contamination. The reason for this is that both the study area and the control area are located in crude oil prospecting and processing region of the Western Niger Delta. The large differences between the values of these two oil parameters in the two areas showed the effect of these other factors i.e. industrialization and urbanization in these areas especially those due to the downstream sector of the petroleum industry. The average concentrations of the trace metals in soil were also generally higher in the study area compared with the control area. The average concentrations of the following trace metals were higher in the study than in the control area, Cr (total), Cu, Zn, Pb, Cd, Ni and Mn (Table 1). A comparison of the mean of the following pollutant parameters, TOE, TPH, Cr (total), Cu, Pb, Cd, Ni and Mn in soil of the study area with their mean in the control area using t-test (two sample, assuming equal variance) revealed that their mean in the study area were significantly different from their mean in the control area ($P < 0.5$). A student t-test comparison of the two locations (i.e. the study area and control area) using results in soil showed that both were significantly different from each other (∞ 0.05). The average concentrations of most heavy metals in plant in the study area were also generally higher than their corresponding average concentrations in the control area (Table 1) and followed the same pattern as obtained in soil.

Comparison of Concentrations of Parameters in the Sampling Stations.

Figure 2 to 19 showed the variation of concentrations of pollutant parameters with the sampling stations for surface (0 – 15 cm) and subsurface (15 – 30 cm) soils. It can be seen that the concentrations of most pollutant parameters (TOE, TPH, Cr (total), Cu, Ni and Mn) were higher between Wood Processing Industry station and PHCN station, and actually peaked at Naval College or Asca Oil sampling stations. This may be as a result of discharge of petroleum products and lubricating base oil to depots which brings about spillages of oil and the production of lubricating oil by companies in this stretch of the river. The mean of the concentrations of these pollutants (TOE, TPH, Cr (total), Cu, Ni and Mn) were compared in the seven sampling stations by

analysis of variance (ANOVA-single factor). It was found that they were statistically significantly different (with $p < 0.5$ in each case). Zn presents a different situation, the average concentration of Zn peaked at Okurighre (the first sampling station in the study area) and at Naval College with the concentration decreasing towards the last sampling station (i.e. Main Confluence). The behaviour of the average concentrations of Zn showed that it was not only the factor of oil being discharge from tankers or effluents from industries that is responsible for the high concentration. It is here suggested that property development has the effect of increasing the concentration of Zn in an area since Zn is an important component of roofing sheets (used for galvanising Iron i.e. coating on the surface of iron in roofing sheets) and other building materials. The average concentration was least where there is less property development. Urbanization has been described as a very important factor that increases the concentrations of pollutants in an environment (Wang *et al*., 2011; Yang *et al*., 2012; Akporido *et al*., 2015). A comparison of the mean of the concentrations of Zn in the seven sampling stations by analysis of variance (ANOVA – Single factor) showed that differences in the concentrations of Zn in the seven sampling stations are significantly different ($P < 0.5$). The concentrations of Pb (Figs. 12 and 13) and Cd (Figs. 14 and 15) did not vary much in the seven sampling stations. A comparison of the mean of their concentrations in the seven sampling stations using analysis of variance (ANOVA-single factor) showed that that they were not significantly different. Okurighre (130 $\pm$ 70 $mgkg^{-1}$), $mgkg^{-1}$), Navy College (160$\pm$21 $mgkg^{-1}$) and PHCN (127$\pm$37 $mgkg^{-1}$) were high and in the case of Navy College, sampling station (160$\pm$21 $mgkg^{-1}$) actually exceeded Norway Guideline values (150 $mgkg^{-1}$), SPDC Nig Ltd. EIA process guideline range (10.0 - 120 $mgkg^{-1}$) and Target value of EGASPIN (140 $mgkg^{-1}$). Zn is therefore a moderate pollutant in this area. The values of lead in all the sampling stations were also high although they did not exceed any soil guideline value.

Comparison of concentrations of Parameters in the Four Seasons

The concentrations of most of the pollutant parameters were highest in the second wet season (Table 2) (TOE, TPH, Cr, Cu, Zn, Pb, Cd and Ni). The high concentrations of these parameters in the second wet season may not be unconnected with the crude oil spillage that occurred in one of the crude oil flow stations as a result of the decapitation of an oil well by suspected saboteurs just before the beginning of the second wet season. This spillage appears to have masked the actual effect of industrialization and urbanization and seasonal variation on the measured parameters in this season.

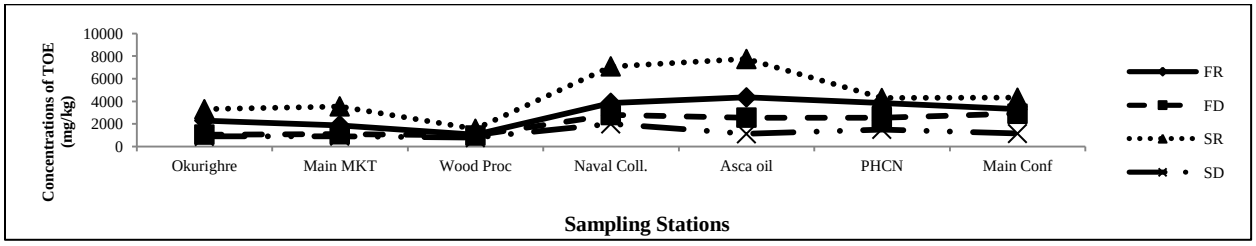

Fig.2: Variation of concentration of TOE of surface soil with the sampling Stations for each season

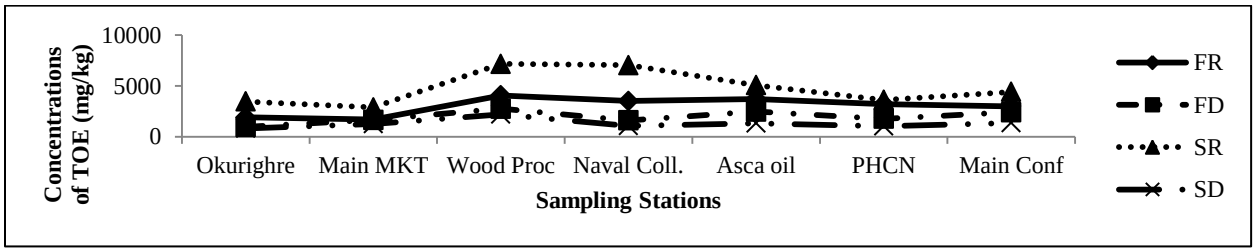

Fig 3: Variation of concentrations of TOE of subsurface soil with sampling stations for each season

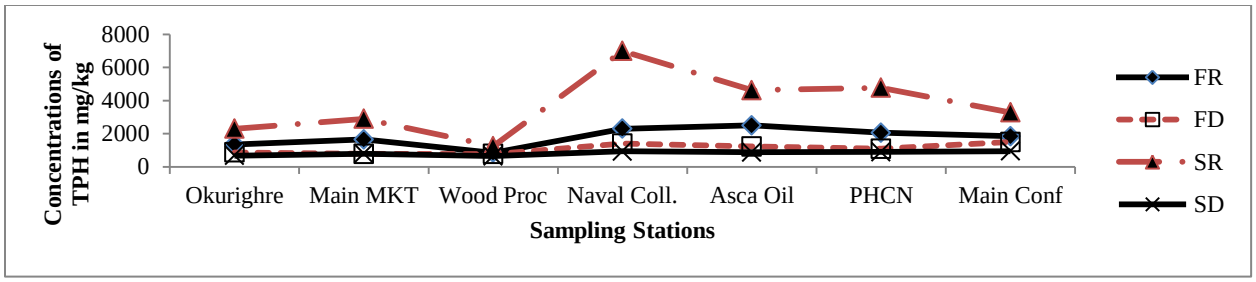

Fig. 4: Variation of concentrations of TPH of surface soil with Sampling stations for each season

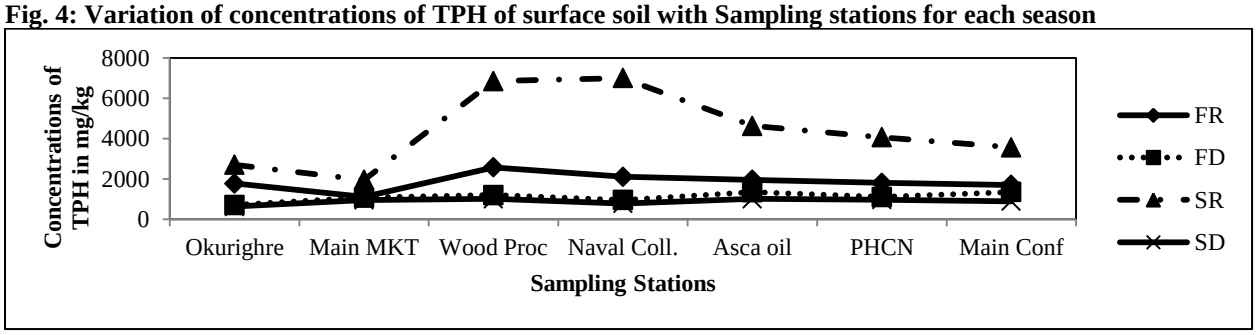

Fig. 5: Variation of concentrations of TPH of subsurface soil with sampling stations for each season

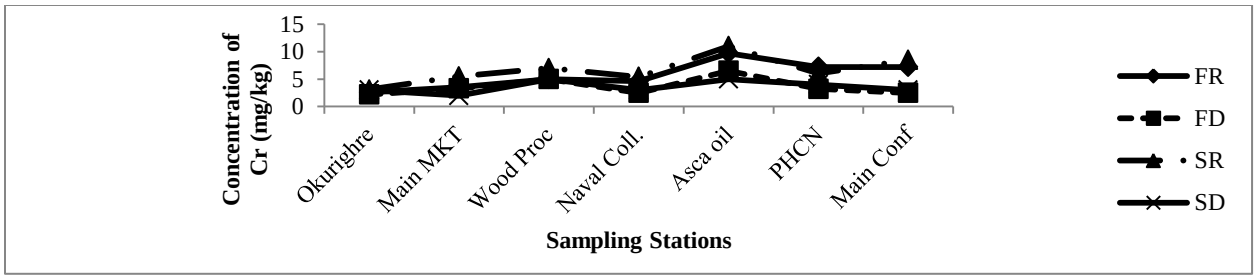

Fig. 6: Variation of concentrations of Cr (total) of surface soil with sampling stations for each season

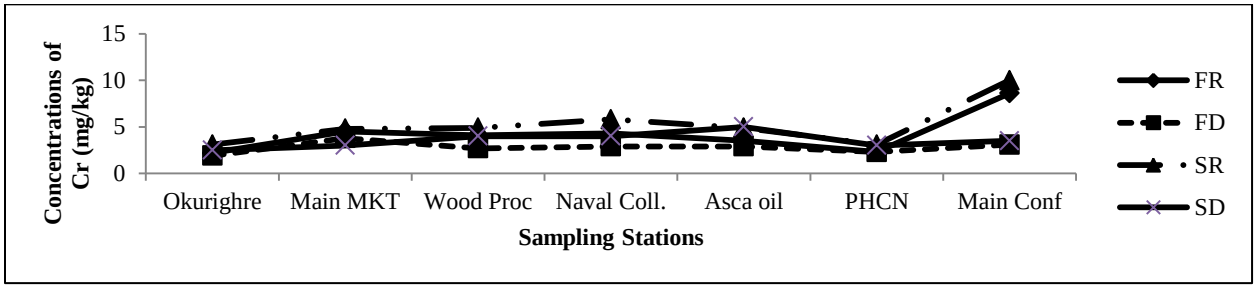

Fig. 7: Variation of concentrations of Cr (total) of subsurface soil with sampling stations for each season.

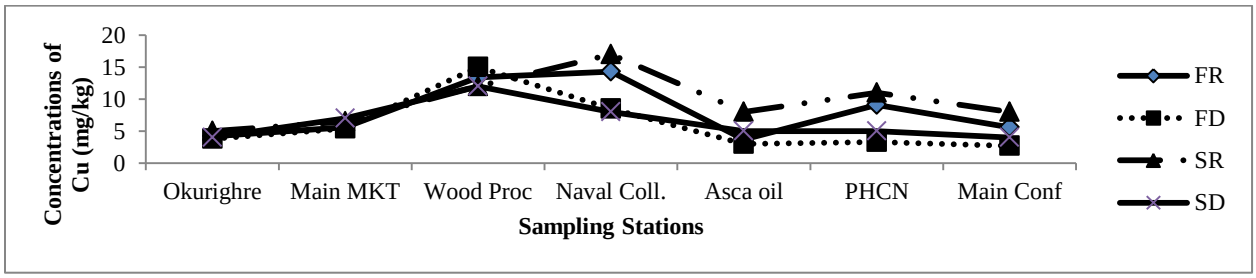

Fig. 8: Variation of concentrations of Cu of surface soil with sampling stations for each season

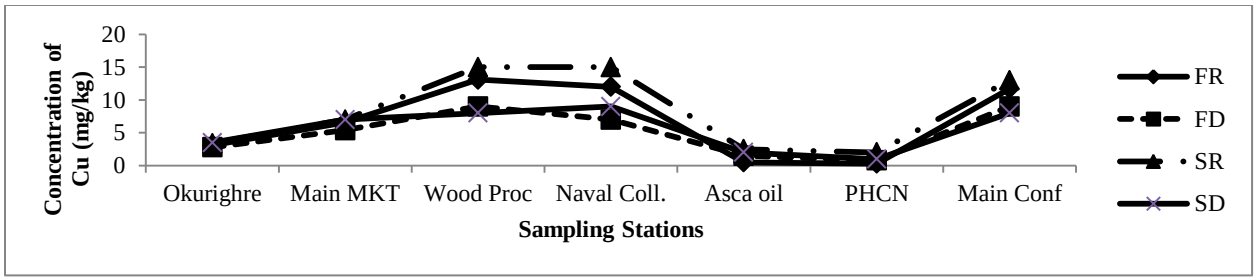

Fig. 9: Variation of concentrations of Cu of subsurface soil with sampling stations for each season.

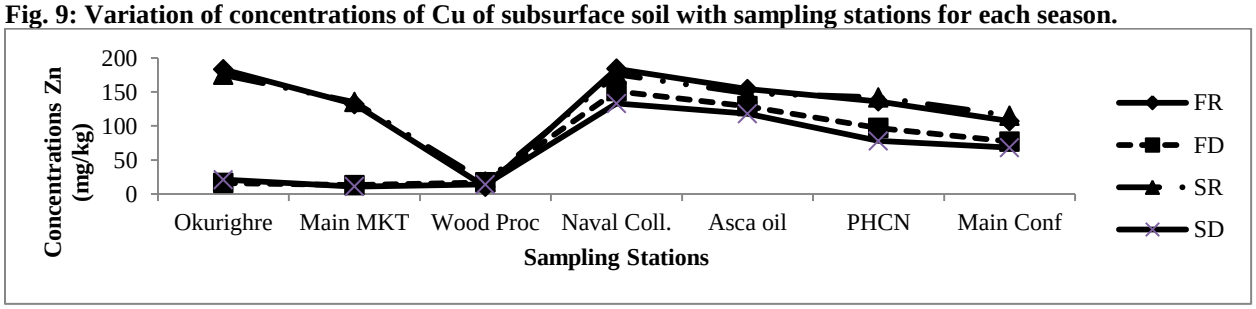

Fig. 10: Variation of concentrations of Zn of surface soil with sampling stations for each season

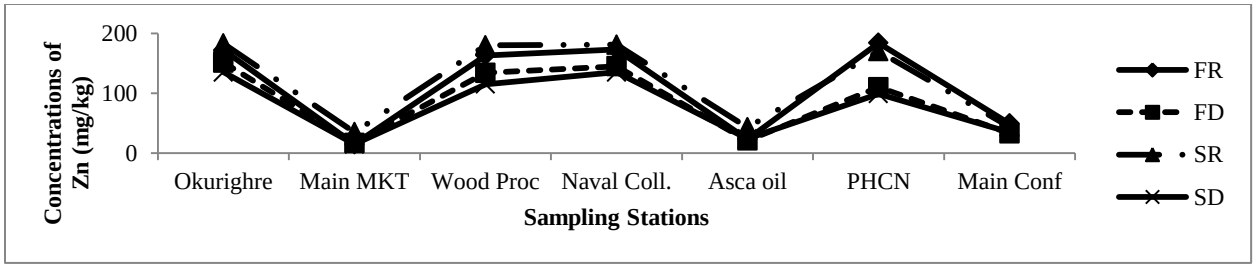

Fig. 11: Variation of concentrations of Zn of subsurface with sampling stations for each season.

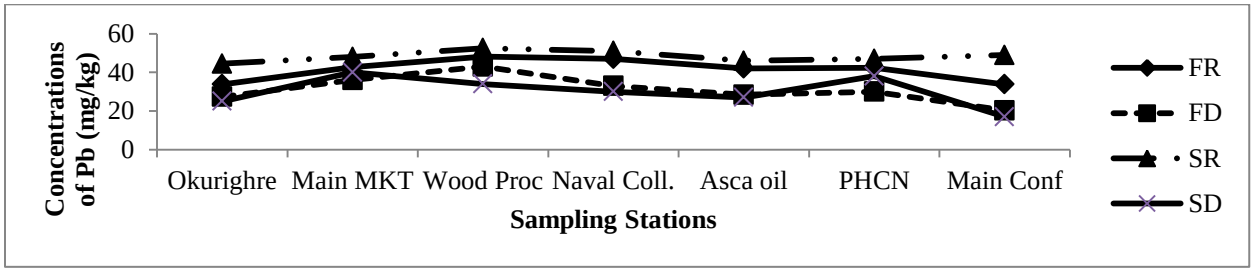

Fig. 12: Variation of concentrations of Pb in surface soil with sampling stations for each season

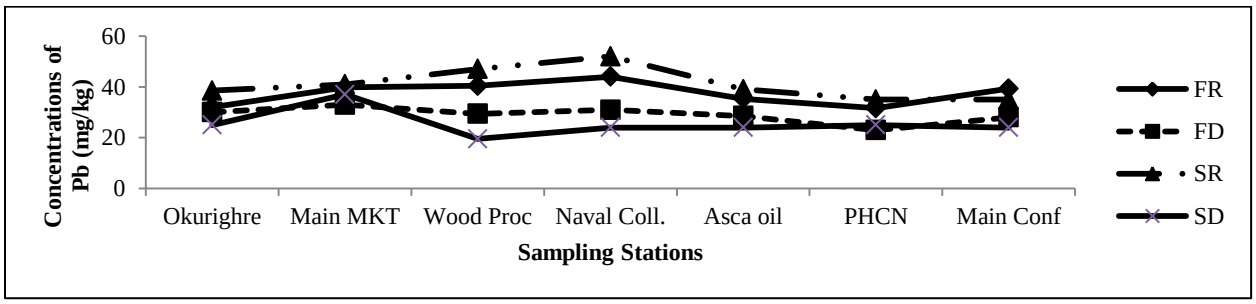

Fig. 13: Variation of concentrations of Pb in subsurface soil with sampling stations for each season.

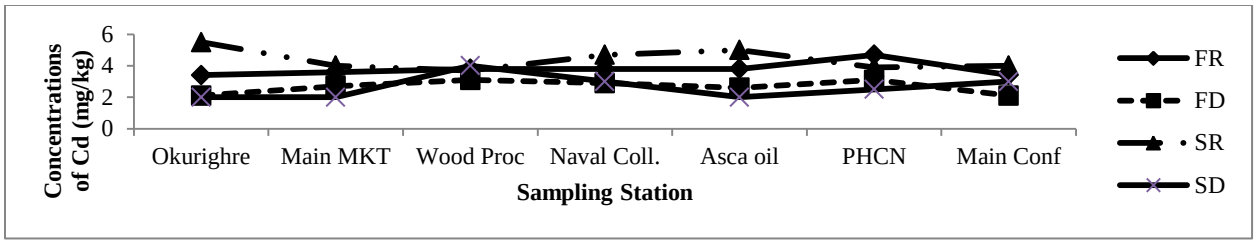

Fig. 14: Variation of concentrations of Cd in surface soil with sampling stations for each season.

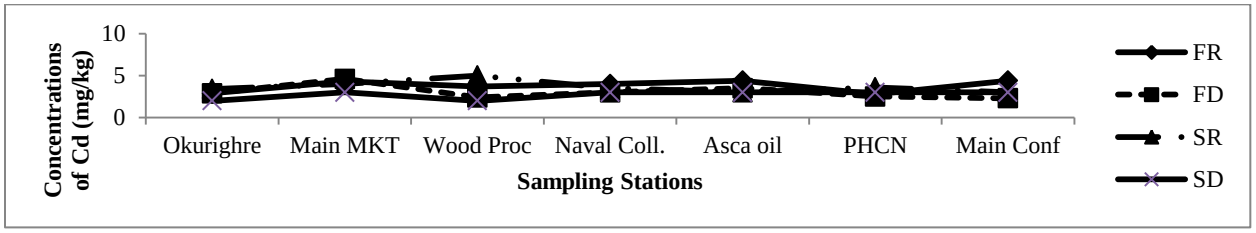

Fig: 15: Variation of concentrations of Cd of subsurface with sampling stations for each of the four seasons

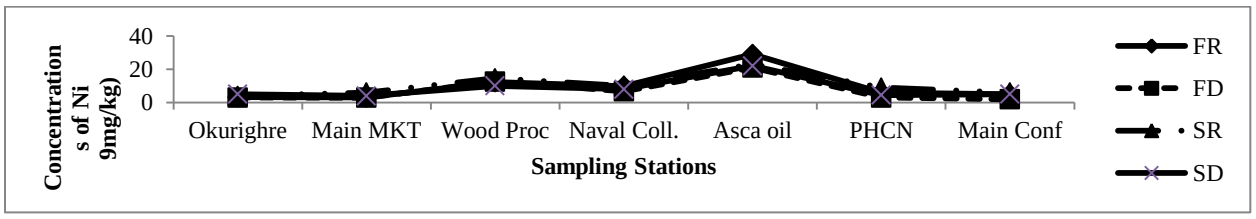

Fig. 16: Variation of concentrations of Ni in surface soil with sampling stations for each season.

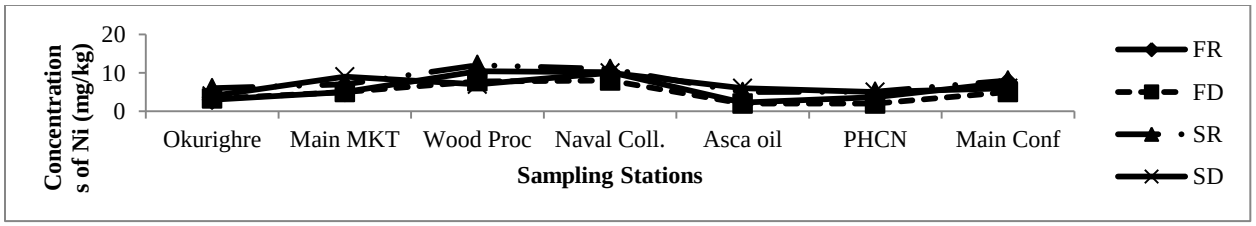

Fig. 17: Variations of conn. of Ni in subsurface soil with sampling stations for each of the four seasons

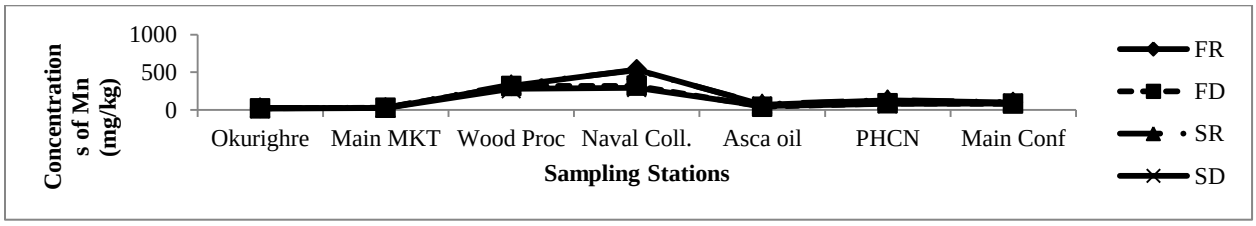

Fig. 18: Variation of concentrations of Mn of surface soil with sampling stations for each of the four seasons

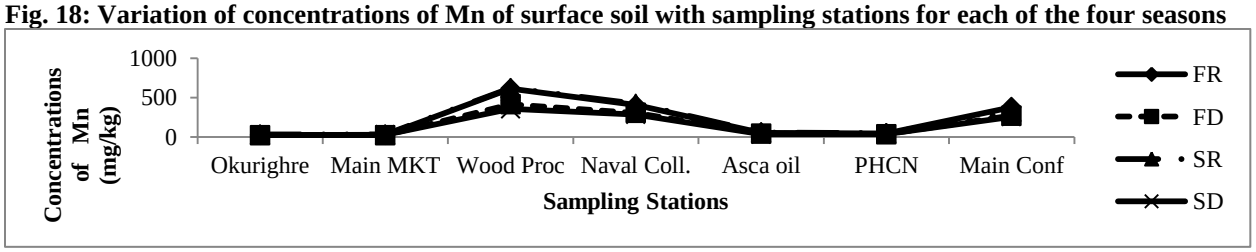

Fig. 19: Variation of concentrations of Mn of subsurface soil with sampling stations for each of the four seasons.

A comparison of the mean of the following parameters in the four seasons by analysis of variance (ANOVA-single factor) showed that the differences in their means were significant – TOE (P = 1.46E-09), TPH (P = 5.04E-11), Cr (P = 0.0088), Zn (p = 0.04), Pb (P = 5.01E-10) and Cd (P = 3.87E-07). The variation of the heavy metals in plant in the four seasons studied (Table 2) is similar to that in soil although the suspected effect of the crude oil spill in the second wet season was less pronounced.

Comparison of concentrations of parameters with soil guideline values (SGVs).

Assessment of pollution effects of trace metals on soil can be carried out by comparing the concentrations of metals in soils of an environment with soil guideline values (SGVs). SGVs are intended as helpful tools for land authorities to use in determining that land is contaminated on the basis that there is a significant harm being caused in relation to human health (Department of Environment, Food and Rural Affaires [DEFRA] [Britain], 2006). They are also "trigger values" for screening-out low risk areas of land contamination, and give an indication of representative average levels of chemicals in soil below which the long-term health risk are likely to be minimal (Environment Agency, 2013). The average concentrations of each metals and the pH of each sampling station were first compared with soil guidelines values (SGVs) for four land uses of the Canadian Environmental Quality Guidelines (CEQG) (Canadian Council of Ministers of the Environment [CCME], 1999) (Table 3). The average pH of three sampling stations, Navy College (5.83±0.34), Asca Oil (5.29±0.30), and PHCN (5.36±0.22) were lower than guideline range for the four land uses (i.e. agricultural, Residential /parkland, Commercial, and industrial land uses) which is 6 - 8. It will be recalled that the concentrations of TOE and TPH and a few of the heavy metals peaked in this region (i.e. around these three sampling stations which successively follow each other). This was also a suggested reason for the high acidity in the soils of these sampling stations. High acidity of soil is not good for growth of crops. High acidity also increases mobility of heavy metals by making them more readily available for plant uptake. This is not good for the health of would-be users of products from such farms. Another implication of high acidity for the health of the people in this area is that most people in the area depend on ground water (through boreholes) for drinking and other domestic activities. This could bring about ulceration in the people consuming this water or worsen the health conditions of ulcer patients. Out of the seven trace heavy metals, it is only Cd Cd that had average concentrations higher than the SGVs for Agricultural land use in all the sampling stations. The implication of this was that the health of those eating The average values of the seven heavy metals and TPH were also compared with six other soil guideline values (Table 3). They are the Norway (guideline values), Netherland (Acton Levels), Switzerland (Guideline values), Accompanying Guideline for Shell Petroleum Development Company Nigeria Limited (SPDC Nig. Ltd) Environmental Impact Assessment (EIA) Process (Acceptable Ranges), EGASPIN's target and intervention values. It can be seen that the average concentration of Cd in the seven sampling stations exceeded the EGASPIN target value of 0.80 $mgkg^{-1}$, and since the target value of EGASPIN are the ultimate values aimed for in the environment, the soils of the seven sampling stations cannot be said to be of good quality with respect to Cd.. The average concentrations of Cd in the soil in each of the seven sampling stations also exceeded the Norway Guideline value (1.00 $mgkg^{-1}$), and the accompanying Guideline for SPDC Nig. Ltd EIA process Acceptable range (0.70 – 3.00 $mgkg^{-1}$). This confirmed that the seven sampling stations were polluted with Cd. Another trace metal of importance is Zn. Its average values in the following sampling stations,It can also be seen from Table 3 that the average values of total petroleum hydrocarbons (TPH) were high in all the sampling stations. The average concentrations of TPH in each of the seven sampling stations actually exceeded the target value of EGASPIN (50 $mgkg^{-1}$) for mineral oil showing that the area is moderately polluted with petroleum hydrocarbons. The increasing concentrations of petroleum hydrocarbons which comes mainly from the discharging of petroleum products and lubricating oil base oil, and from the production of lubricating oils by the Oil companies in this area should be checked by environmental authorities by monitoring the activities of these oil and lubricant

Table 2: Average values (mgkg^{-1}) of soil parameters given in mean±SD deviation four four seasons (n^{SeS} 14; n^{SeP} = 7)

Parameters	First Wet Season		First Dry Season		Second Wet Season		Second Dry Season	
	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant
pH	6.4±1.2	-	6.5±1.0	-	6.4±1.1	-	6.62±0.91	-
TOC*	0.24±0.17	-	0.29±0.16	-	0.29±0.14	-	0.32±0.15	-
TOM*	0.42±0.30	-	0.49±0.28	-	0.51±0.24	-	0.54±0.25	-
Sand*	76.0±9.6	-	75.4±8.5	-	77.9±7.5	-	77.5±7.5	-
Silt*	6.5±5.8	-	6.6±3.9	-	7.8±4.4	-	7.1±2.4	-
Clay*	17.6±8.0	-	18.5±6.8	-	14.4±6.2	-	14.7±5.9	-
TOE	2970±1030	-	1960±740	-	4670±1900	-	1240±420	-
TPH	1830±490	-	1100±250	-	3950±1900	-	859±130	-
Cr (total)	5.0±2.4	0.9±0.3	3.2±1.2	0.8±0.3	5.9±2.4	1.1±0.2	3.6±1.0	0.8±0.3
Cu	7.4±4.9	2.6±3.5	5.5±3.9	2.1±2.3	9.0±4.9	2.8±3.0	6.0±3.0	2.1±2.3
Zn	120±67	14.8±6.4	79±58	14.1±5.4	125±62	16.1±6.4	72±57	14.2±6.1
Pb	39.4±5.4	4.2±0.7	30.1±5.4	3.7±0.6	44.7±6.0	4.6±0.7	27.8±7.0	3.6±0.5
Cd	3.8±0.6	0.7±0.1	2.8±0.6	0.7±0.1	4.0±0.8	0.9±0.1	2.7±0.6	0.7±0.1
Ni	7.9±6.9	2.1±0.6	6.0±5.3	1.7±0.5	9.0±5.0	2.3±0.7	7.5±4.7	1.6±0.5
Mn	198±210	56±37	143±150	57±37	197±210	53±44	132±130	51±38

companies before the situation degenerates any further.

Pearson (2-tailed) Correlation of Concentrations of Soil Parameters

A Pearson (2-tailed) correlation of all parameters (with the exception of pH) in the soil of the study area (Table 4) showed that the following pair of parameters were very strongly positively correlated (their correlation coefficient were significant at 0.01 confidence level), they were TOM and Sand (0.826), TOE and TPH (0.929), TOE and Cr (0.529), TOE and Zn (0.497), TOE and Pb (0.670), TOE and Cd (0.561), TOE and Mn (0.377), TPH and Cr (0.417), TPH and Cu (0.417), TPH and Zn (0.447), TPH and Pb (0.607), TPH and Cr (0.513), TPH and Mn (0.373), Cr and Cu (0.401), Cr and Pb (0.493), Cr and Cd (0.461), Cr and Ni (0.633), Cu and Pb (0.590), Cu and Cd (0.389), Cu and Ni (0.357), Cu and Mn (0.842), Pb and Cd (0.676). The following pair are strongly correlated, and their correlation coefficients are significant at 0.05 confidence level, TOE and Ni (0.312), silt and Cu (0.294), clay and Cu (0.334), Pb and Ni (0.362), Pb and Mn (0.317), Ni and Mn (0.274).

A strong correlation between members of a pair may be as a result of the following reasons:

(i) One is an integral part of the other e.g. TPH is a part of TOE and

(ii) Both members arise from the same source.

The later reason best explains the very strong and strong correlation between members of the pairs in most of the cases. It can be seen that most of the heavy metals were significantly correlated withTOE and TPH (the two oil parameters). It may therefore be reasoned that they had their sources in the oil industry i.e Petroleum products and lubricating oils that were continually spilled in the area as a result of the activities of the petroleum products and lubricating oil companies and from the effluents of these companies.

Discussion of result of calculation of transfer factor

Table 5 presents the transfer factors of the heavy metals in the seven sampling stations. It was only in Mn that the transfer factors exceeded the value of unity. The sampling stations where the transfer factor of Mn exceeded unity were Okurighre (1.36), Main market (2.067) and PHCN (1.43). The implication of this was that plants in the areas around these sampling stations such as vegetables must have been contaminated with Mn. Although Mn is beneficiary to man at lower concentrations, it has adverse effect at higher concentrations. The transfer factors of the other metals did not exceed unity in any of the sampling stations. The value of the transfer factor of Zn in main market sampling station is 0.451 which indicates that Zn had been reasonably transferred from soil to plant. Cd a metal that has been observed to be an important pollutant in this area have moderately high transfer factor values in all the sampling station which indicated that its concentration in plants will soon be a cause for health concern. The values of transfer factor of Cr, Cu and Ni in Okurighre

sampling station were also relatively high (Table 5). Soil to plant transfer of heavy metals is one of the main ways of human exposure to soil contamination (Cui *et al.,* 2004; Chojnacka *et al.,* 2005; Kashif *et al.,* 2009; Big *et al.,* 2012; Mihali *et al.,* 2013). The transfer factor of heavy metals from soil to plant depend on the metal chemical character, on the plant species as well as on several soil characteristics such as pH, cation exchange capacity, soil moisture, total organic matter, interference of other metals, texture (clay, silt and sand) (Cui *et al.,* 2004; Mihali *et al.,* 2013; Martin and Meybeck, 1979). There are many vegetable farms in Okurighre area and if the pollution of the water, sediments, soil and biota from the aforementioned sources is not abated very soon, it will result in very severe consequences for the health of the people in these areas and especially those who depend on vegetables obtained from these areas for food.

Discussions of Results of Calculation of Enrichment Ratio

in each of the sampling stations are presented in Table 6. A look at this table showed that most of the sampling stations have high enrichment factors for Pb. The enrichment factors for Pb in Okurighre and Main Market stations were 48.6 and 52.1 respectively. The status of these two stations with respect to Pb was "extremely high" enrichment ratios. Pb in Asca Oil sampling station had enrichment factor of 22.8, this falls into the class of "very high" enrichment ratio with Pb. PHCN and Main Confluence sampling stations with enrichment factors of 16.4 and 5.54 respectively both fall into the status of "significant" enrichment with Pb. Another substance that had fairly high enrichment in the sampling stations is Zn. The enrichment ratio of Zn in Okurighre station was 30.9 which make it to have a status of "very high enrichment". It also have enrichment ratios of 8.22, 8.72 and 9.61 in Main Market sampling station, Asca Oil station, and PHCN respectively, which showed that the three stations fell into the class of "significant" enrichment with Zn. Cd has enrichment ratios of 9.14 and 8.71 in Okurighre and Main Market respectively. Cu has an enrichment ratio of 5.48 in Main Market station. One important thing to note here was that Okurighre and Main Market sampling stations suffered much from the enrichment of the four metals (i.e. Pb, Zn, Cd and Cu). These observations have shown that there was high anthropogenic input of these metals into these two sampling stations. The enrichment of these sampling stations with these metal must have been as a result of activities of oil companies in the downstream sector of the petroleum industry though the spillage of petroleum products and lubricating oil in the waters and soils of the area. These activities which are a consequence of industrialisation and urbanization should be properly monitored by environmental authorities.

Discussion of Results of Calculation of Contamination/Pollution (C/P) Index

The contamination/pollution (C/P) indexes for each metal in each of the sampling stations are given in Table 6. Using the significance of interval by Lacatusu (1998) already given, it can be seen that most of the sampling stations were contaminated with all the trace metals. The C/P index of Cd in Okurighre station (3.75), Main market (4.125), Wood Processing Industry (4.38) and PHCN (4.125) which showed that they were severely polluted with Cd. Zinc had a C/P index of 1.143 in the Navy College soil showing that this station was slightly polluted with Zn. These observations agreed with observations earlier made when the average values of Cd and Zn in these sampling stations were compared with soil guideline values (SGVs). There were also various levels of contamination by these two metals and the other metals in the different sampling stations in the study area (Table 6).

Discussion of Results of Calculation of Contamination Factor (CF) and Pollution Load Index (PLI)

The results of the calculation of contamination factor (CF) showed that only in Zn and Pb that average CF values were above unity. These average CF were calculated for the four seasons, first wet (FW) seaso, First dry (FD) season, second wet (SW) season and second dry (SD) season. The results for Zn for SW season are, Okurighre (1.89), Navy College (1.35), PHCN (1.21); results for Zn in FW season are, Okurighre (1.38), Navy college (1.39) and PHCN (1.22). The results for Pb in the FW season are, Okurighre (1.0), Main Market(2.07), Wood proc. (2,22), Navy College (2.19), Asca oil (1.94), PHCN (1.85) and MC (1.83); resultsfor Pb in the FD season are,

Table 3: Average concentration of TPH and the heavy metals in the sampling stations compared with Soil Guideline Values (SGVs)

Country/name of sampling station	pH	TPH (mg/kg)	Cr (Total) (mg/kg)	Cu ($mgkg^{-1}$)	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Mn ($mgkg^{-1}$)	References
CEQG Agric. Land Use	6 – 8	-	6.40	63.0	200	70	1.40	50	-	CCME,1999
CEQG Residential/Parkland Land Use	6 – 8	-	6.40	63.0	200	140	10.0	50	-	CCME, !999
CEQG Commercial Land use	6 – 8	-	87.0	91.0	360	260	22	50	-	CCME, !999
CEQG Industrial Land Use	6 – 8	-	87.0	91.0	360	600	22	50	-	CCME, 1999
Norway (Guideline Value)	-	-	100	100	150	50	1.00	30.0	NS	Reimann et al., 1997
Netherlands (Action level)	-	-	380	190	720	530	12.0	210	NS	Reimann et al., 1997
Switzerland (Guideline values)	-	-	-	50.0	200	50	0.80	-	NS	FOEFL, 1987
SPDC Nig. Ltd. EIA Process (Acceptable range)	-	-	10.0-100	5.00 – 50.0	10.0-120	5.00-50.0	0.70-3.00	5.00-50.0	NS	SPDC Nig Ltd., 2004
EGASPIN Soil/Sediment Target Values	-	50.0	100	36.0	140	85.0	0.80	35.0	NS	DPR, 2002
EGASPIN soil/sediment intervention values	-	5000	380	190	720	530	12.0	210	NS	DPR, 2002
Okurighre	7.63±0.24	1380±800	2.6±0.5	3.7±0.7	130±70	32.0±6.8	3.0±1.2	3.9±1.1	23.5±4.1	Present Study
Main Market	7.61±0.17	1290±690	3.5±1.1	6.5±0.7	40±50	39.5±4.1	3.3±0.9	5.5±2.2	27.0±2.5	Present Study
Wood Processing Industry	6.0±0.3	1890±2100	4.7±1.2	12.2±2.6	81±74	39±11	3.5±0.9	10.8±2.5	337±140	Present Study
Navy College	5.83±0.34	2810±2600	4.1±1.2	11.4±3.7	160±21	39±11	3.5±0.6	9.2±1.4	386±100	Present Study
Asca Oil	5.29±0.30	2290±1600	6.1±2.9	3.3±2.3	83±60	33.8±8.0	3.4±1.0	14±11	53±14	Present Study
PHCN	5.56±0.22	1910±1200	3.9±1.8	4.1±4.0	127±37	34.0±8.3	3.3±0.8	4.8±2.1	74±35	Present Study
MC	7.48±0.47	1850±950	5.8±3.1	7.7±3.6	66±32	31±11	3.2±0.8	5.6±1.8	200±120	Present Study

FOEFL = Federal Office of Environment, Forest and Landscape;
CEQG = Canadian Environmental Quality Guidelines
SPDC= Shell Petroleum Development Company (Nigeria);
EGASPIN= Environmental Guidelines And Standards for the petroleum industry in Nigeria
DPR = Department of Petroleum Resources (Nigeria);
CCME = Canadian Council of Ministers of the Environment;
SPDC = Shell Petroleu Development Company

Table 4: Pearson (2-tailed) correlation of all parameters (with the exception of pH) in the soil matrix of the study area.

	TOC	TOM	Sand	Silt	Clay	TOE	TPH	Cr	Cu	Zn	Pb	Cd	Ni	Mn
TOC	1.000													
TOM	0.107	1.000												
Sand	0.106	0.538**	1.000											
Silt	-0.163	-0.276*	0.387*	1.000										
Clay	-0.079	-0.408**	-0.825**	0.132	1.000									
TOE	0.122	-0.163	-0.110	0.139	0.121	1.000								
TPH	0.139	-0.102	-0.052	0.094	0.016	0.929**	1.000							
Cr	0.258	-0.094	-0.296*	0.236	0.234	0.529**	0.417**	1.000						
Cu	0.037	0.118	-0.511**	0.294*	0.334*	0.365**	0.415**	0.401**	1.000					
Zn	0.028	-0.194	-0.044	-0.031	0.068	0.497**	0.447**	0.011	0.073	1.000				
Pb	0.198	-0.197	-0.285	0.280*	0.162	0.570**	0.607**	0.493**	0.590**	0.196	1.000			
Cd	0.101	-0.128	-0.128	0.226	0.056	0.561**	0.513**	0.461**	0.359**	0.202	0.676**	1.000		
Ni	-0.050	-0.320*	-0.584**	0.250	9.524	0.312*	0.236	0.633**	0.351**	0.184	0.312*	0.187	1.000	
Mn	-0.048	0.036	-0.521**	0.124	0.456	0.377**	0.373**	0.197	0.842**	0.237	0.317*	0.213	0.274*	1.000

** correlation coefficient significant at 0.01 confidence level, *Correlation coefficient significant at 0.05 confidence level

Table 5 :Transfer factors of heavy metals in each sampling station

Heavy Metals	Transfer Factors in Sampling stations						
	Okurighre	Main Market	Wood Processing	Naval College	Asca Oil	PHCN	Main Confluence
Cr	0.483	0.186	0.127	0.280	0.119	0.205	0.15
Cu	0.372	0.188	0.701	0.216	0.235	0.35	0.126
Ni	0.478	0.395	0.088	0.19	0.137	0.432	0.489
Pb	0.152	0.089	0.083	0.092	0.128	0.124	0-143
Mn	1.36	2.067	0.056	0.277	0.491	1.43	0.12
Cd	0.253	0.199	0.171	0.201	0.217	0.261	0.267
Zn	0.148	0.451	0.107	0.109	0.088	0.181	0.151

Table 6 : Enrichment ratio (ER) and contamination/pollution (C/P) indexes of each metal in each sampling station

Sampling Stations	Enrichment Ratios(ER) and Contamination/ Pollution (C/P) Indexes													
	Cr		Cu		Zn		Pb		Cd		Ni		Mn	
	ER	C/P	ER	C/P	ER	C/P	ER	C/P	ER	C/P	ER	C/P	ER	C/P
Okurighre	8.46	0.026	3.57	0.103	30.9	0.929	48.6	0.376	9.14	3.75	2.44	0.111	1.00	-
Main Market	1.00	0.036	5.48	0.153	8.27	0.286	52.1	0.465	8.71	4.125	3.00	0.157	1.00	-
Wood Proc.Industry	0.11	0.042	0.82	0.339	1.34	0.579	4.14	0.459	0.71	4.38	0.15	0.309	1.00	-
Navy College	0.08	0.041	0.68	0.317	2.29	1.143	3.61	0.459	0.014	4.38	0.13	0.263	1.00	-
Asca Oil	0.88	0.061	1.41	0.092	8,77	0.593	22.8	0.42	4.57	0.425	0.94	0.40	1.00	-
PHCN	0.41	0.039	1.25	0.114	9.61	0.907	16.4	0.40	3.21	4.125	0.66	0.137	1.00	-
Main Confluence	0.22	0.058	0.89	0.214	1.84	0.471	5.54	0.365	1.14	0.40	0.24	0.160	1.00	-

Okurighre (1.44) , Main Main Market (1.73), Wood Proc. (1.81), Navy College (1.30), Asca Oil (1.45), PHCN (1.33) and MC (1.21); results for Pb in the SW season are, Okurighre (2.08), Main Market (2.23), Wood proc. (2.19), Navy College (2.58), Asca Oil (2.13), PHCN (2.05) and MC (2.10); results for Pbin ths SD season are, Okurighre (1.25), Main Market (1.93), Wood Proc. (1.34), Navy College (1.35), Asca Oil (1.28), PHCN (1.60) and MC (1.03). The results showed that most of the sampling stations were moderately polluted with Zn and Pb. The aggregated pollution loads of all the metals for each sampling station were given by the pollution load index (PLI). The average pollution load indexes (PLI) of each of the sampling stations (i.e. average for surface and subsurface) were, Okurighre (0.0008), Main Market (0.0009) Wood Processing Industry (0.0177), Navy College (0.0198), Asca Oil (0.0033), PHCN (0.0027), and Main Confluence (0.0033). Although these value were generally low, it can however be seen that the pollution load indexes are relatively higher at the Wood Processing Industry, Navy College and Asca Oil sampling stations which confirmed the earlier observation made about the average values of TPH and most of the heavy metals having their peak values at these stations.

Comparison of Results of study with Results Obtained for the same parameters in Similar Studies Elsewhere

A comparison of results obtained for various parameters in soil for the present study area with results obtained for similar studies elsewhere (Table 8) revealed that most values obtained in the study area for the pollutant parameters (i.e. the trace metal and the two oil parameters) were comparably with results obtained for corresponding parameters in other studies done elsewhere. Some of the values were however higher. The average concentration of Cd in study area, 3.3$\pm$ 0.9 mgkg^{-1} (2.0 – 5.5 mgkg^{-1}) was comparable with values obtained for the refinery in India (3.00 mgkg^{-1}) by Jasmine and Mukherji (2015), zinc deposit area in China (5.19 $\pm$ 0.3 mgkg^{-1}) by Yi *et al*., (2007), Warri River, Steel production (9.2±6.4 mgkg^{-1}) by Akporido *et al*., (2014), mine and ore processing area of Baie Mare (Femeziu section) area of Romania (0.15 – 113 mgkg^{-1}) by Mihali *et al.*, (2013) and Niger Delta area (1.3 $\pm$ 1.0 mgkg^{-1}) by Olawoyin *et al*., (2012). These areas were adjudged to be polluted areas. The average value for Cd in the study area was however much less than values obtained for mechanic village in Effurun (35$\pm$10 mgkg^{-1}) by Akporido *et al.,* 2015 and Lead/zinc smelting area in South West China(75.4 mgkg^{-1}) by Li *et al*., (2014); Langston,1990. These two cases are examples of extremely high pollution with Cd. The study involving mechanic village Effurun had to do with the determination of total metal (i.e the value of Cd includes Cd in the residual fraction or Cd in the soil crystal lattice) and the one involving lead/zinc smelting area is naturally expected to be of high concentration of Cd as a result of the accumulation of the metal with time. The average concentration of Pb in study area, 35.5 $\pm$ 9.0 (17-52.5mgkg^{-1}) was comparable with values obtained for refinery in India (49.0

Table 7: Average values obtained in soil for study area compared with with results obtained in similar studies in other places

Country	River/Location	pH	TPH ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	Cr ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Mn ($mgkg^{-1}$)	References
Nigeria (Niger Delta)	Agbada Oil field		124-38600	-	-	-	-	-			Osuji *et al.,* 2005
Nigeria	Mechanic Village, Effurun	6.40±0.58	-	35±10	-	68.5±9.9	-	121±51	102±18	-	Akporido *et al.,* 2015
India	A refinery in India	-	-	3.00	91.0	49.0	-	ND	55.0	66.0	Jasmine and Mukherji, 2015
China	Zinc deposit			5.19±0.03	859±18	-	-	9.90±0.08	73.2±1.8	-	Yi *et al.,* 2007
Nigeria	Niger Delta Area	-	-	0.04-0.95	11.1-27.4	3.40-99.4	1.30-165	1.60-13.6			Asia *et al.,* 2007
China	Gudao Oil-polluted Region	7.3 – 8.05	0.51 – 28400	0.19	78.2	20.8	56.6	26.3	18.4	-	Fu *et al.,* 2014
Pakistan	Urban soil of karachi	-	-	-	99.5±37	42.1±56	9.6±4.2	-	33.3±13	-	Karim and Qureshi, 2014
Nigeria	Warri River	5.85± 0.32	-	9.2 ± 6.4	112 ± 41	126 ± 40	-	44±50			Akporido *et al.,* 2014
Romania	Baia Mare Area (Femeziu section)	5.7 – 7.5	-	0.15 - 113	100 - 3791	115 - 19195	0,2 – 50.5	0.2 – 29.3	6.5 - 1730	4.25 - 2124	Mihali et al., 2013
Nigeria	Niger Delta	6.2±0.7	-	1.3±1.0	58.3±37	895±420	13.2±5.5 (Cr IV)	42.7±20	28.3±32	202±78	Olawoyin *et al.,* 2012
China	Lead/Zinc Smelter in S.W. China	-	-	75.4	8078	2485	-	-	-	-	Li *et al.,* 2014
Nigeria	Benin-Ethiope Fluvial System	6.5±1.0 (4.8 – 8.1)	1930± 1600 (630 –7000)	3.3±0.9 (2.0 – 5.5)	99±63 (11 – 184)	35.5±9.0 (17 -52.5)	4.4±2.1 (1.9 – 11)	7.6±5.5 (2.0 – 23)	7.0±4.3 (0.3 – 17)	167±170 (17 – 620)	Present study

Gudao oil polluted region in China (20.8 $mgkg^{-1}$) by Fu *et al*., (2014), Urban soil of Kerachi, Pakistan (42.1 $\pm$ 56$mgkg^{-1}$) by Karim and Qureshi, 2014 and Niger Delta area (3.40 – 99.4 $mgkg^{-1}$) by Asia *et al*., (2007). These areas are also known to be polluted areas. The average value of Pb obtained for study area is however less than values obtained for Effurun mechanic village (68.5±9.9 $mgkg^{-1}$) by Akporido *et al.,* (2015), steel production area of Warri River (126±40 $mgkg^{-1}$) by Akporido *et al*., (2014), Mine and ore processing area of Baie Mare area of Romania (115 – 19195 $mgkg^{-1}$) by Mihali *et al*., (2013), Niger Delta area by Olawoyin *et al*., (2012) (895±420 $mgkg^{-1}$), and Lead/zinc smelting area in SW China (2485 $mgkg^{-1}$) by Li *et al*., (2014). As already observed in some of these studies, it was the total Pb that was determined in Effurun mechanic village. The three others areas have intensive polluting activities such as mining and metal ore smelting, These may be the reason why the concentrations of Pb were very high. The high concentration in Niger Delta (895 $mgkg^{-1}$) by Olawoyin *et al*., (2012) can however not be rationalised on the basis of any of the explanations given above. It is here suggested that the areas in which samples were taken in the Niger Delta in that study should have activities which polluted the area with Pb examples these are waste dumpsite where car and other vehicle batteries are dumped. The other parameters studied showed similar trend as those already discussed for cadmium and lead.

Conclusion

The study has found that the quality of soil of the study area was generally low. (i.e. not good enough). The pH of the soil of some of the sampling stations were lower than guideline values which invariably means that the acidity of these sampling stations were high, and this had the undesired consequence of increasing the mobility of the trace metals in the environment thus making them readily available for uptake by plants. The study also found that Cd, Zn and Pb were of pollutant status in the soil of the study area. The transfer of trace metals to plant was on the increase but had not got to an alarming level. The level of petroleum hydrocarbons in the soil had also been found to be above guideline values. It had also been observed that these pollutants have their sources in the activities of companies which import petroleum products, lubricating base oil, and factories which produce lubricating oils and release their effluents in the waters and soils of the area. The waters and soils get polluted by them through spillages during discharge from tankers in the case of petroleum products and lubricating base oils and through effluents in the case of factories producing lubricating oils.

Acknowledgement

Environmental authorities in Nigeria which include the Department of petroleum Resources (DPR), Federal Ministry of Environment (FMEnv) and the Nigerian Environmental standards Regulatory and Enforcement Agency (NESREA) should do more work in monitoring and ensuring that standards are complied with in this area. This will help in no small way in bringing about abatement to pollution of waters and soils of this area

References

Adekambi, O.E. 1989. *Petroleum hydrocarbons pollution of the Nigerian waters and sediments around Lagos and Niger Delta area of Nigeria.* A Ph.D Thesis of the University of Ibadan, Ibadan.

Adeniyi, A. A. and Owoade, O. J. 2010. Total petroleum hydrocarbons and trace heavy metals in roadside soils along the lagos-Badagry expressway, Nigeria. ***Environ. Monit. and Assess.,*** 167 (1 – 4): 625 – 6308.

Akporido, S. O. and Asagba, S. O. Quality characteristics of soil close to the Benin River in the vicinity of a lubricating oil producing factory, Koko, Nigeria. ***Int. J. Soil Sci***., 2013, 8 (1), 1 – 16

Akporido, S. O. and kadiri, H. E. 2014. Effect of urbanization and industrialization on the waters of the Benin river-Ethiope River System around Sapele, Nigeria. ***Global Advanced J. of phys. and Appl. Sci.,*** 2014, 3 (3): 035 . 050

Akporido, S. O., Agbaire, P.O., and Ipeaiyeda, A. R. (2014). Effect of steel production on the quality of soil aroundUdu section of Warri River in the vicinity of a steel plant, Nigeria. ***Asian Journal of Applied Science,*** 7 (7): 552 – 562. Doi: 10.3923/ajaps.2014.552.567.

Akporido, S. O., Emoyan, O. O. And Otobrise, C. 2015. Sediment pollution of the Benin – Ethiope fluvial system around Sapele (Nigeria) from industrial and Urban waste. ***International Research Journal of public and Environmental Health***, 2 (1): 4 – 15

Akporido, S.O. and Ipeaiyeda, A. R. (2014). An assessment of the oil and heavy metal profile of sediments of the Benin River adjacent to a lubricating oil producing factory, Delta

state Nigeria. ***International Research Journal of public and Environmental Health,*** 1 (2), 40 – 53

Allens, S.E., Davison, W., Grimshaw, H. M. , Perkinson, J.A., Quarulby, C. and Rowland, A. P. 1989. ***Chemical analysis of ecological materials,*** Oxford, Blackwell Scientific Publications,

Almeida, R., Mucha, A. P., Teixeira, C., Burdalo, A. A., and Almeida, C. M. 2013. Biodegradation of petroleum hydrocarbons in estuarine sediments: metal influence. ***Biodegr.,*** 24 (1), 111 – 123

Anderson, D. M. And Morel, F. M. 1978. Copper sensitivity of *Gonyaulax tanarensis.* ***Limnol. Oceanogr.,*** 23: *283 – 295*

Anyakora, C., Coker, H. and Arbabi, M. 2011. Application of polynuclear aromatic hydrocarbons in chemical finger printing: the Niger Delta case study. *Iranian Journal of* ***Environmental Health Science and Engineering,.*** 8 (1), 75 – 84

Asia, I.O., Jegede, S. I., Jegede, D. A. Ize-Iyamu O. K. and Akpasubi, E. B. 2007 The effect of Petroleum exploration and production operation on heavy metals contents of soil and groundwater in the Niger Delta. ***Int. J. of Phys. Sci.,.*** **2**(10): 271-275.

Awomeso, J. A., Taiwo, A. M., Gbadebo, A.M. and Adenowo, J. A. (2010) 'Studies on the pollution of waterbody by Textile industry effluent in Lagos, Nigeria' ***Journal of Appl. Sci. in Environ. Sanit.,*** 5 (4), 353 – 359.

Bai, J. F., Zhang, C. L., Wang, J. W., Xu, J. Q., Zhou, Y. And Wu, W. J. 2012.Environmental risk and recoverable potential, evaluation of heavy metals in the sludge from the industrial wastewater in China, ***Adv. Mater. Res.,*** 508: 196 – 199.

Black, C. A. Methods of soil Analysis Agronomy No 9 Part 2 Amer. Soc. Agronomy. Madison. Wisconsin.

Berthou, F., Gourmolun, Y., Dreano, Y. and Friocourt, P. 1981. Application of gas chromatography on glass capillary column to the analysis of hydrocarbon pollutants from the Amoco Cadiz oil spill. ***Journal of chromatography*** 203, 277-292

Big, C. L., Lacatus, R. And Damian, F. 2012. Heavy metals in soil – plant system around Baia Mare city, Romania. ***Carpathian Journal of Earth and Environmental sciences***, 7 (3): 219 - 230

CCME (Canadian Council of Ministers of the Environment), 1999 Canadian soil quality guidelines for the protection of environmental and human health. In:Canadian Environmental Quality Guidelines, 1999. Canadian Council of Ministers of the Environment Winnipeg, .

Chojnacka, K., Chojnacka, A., Gorecka, H. and Gorecki, H. (2005). Bioavailability of heavy metals from polluted soils to plants. ***Science of the Total Environment***, 337, 175 – 182

Cui, Y.-J., Zhu, Y. G., Zhu, R. H., Chen, D. Y., Huang, Y.-Z., Qui, Y. Liang, J.-Z (2005). Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. ***Environment International,*** 30, 785 – 791

Department for Environment, Food and Rural Affaires (DEFRA), 2006. Assessing risk from land contamination – a proportionate approach. Soil guideline values: the way forward. www.defra.gov.uk. (accessed 02-01-2014)

DPR (Department of Petroleum Resources), 2002. Environmental guidelines and standards for the petroleum industry in Nigeria. Department of Petroleum Resources (DPR), Victoria Island Lagos, Nigeria,.

Environment Agency, 2013. Soil guideline values. Environment Agency, http://www.ems-asbestos.co.uk/glossary/soil.guideline values-sgv/.

Federal Office of Environment, Forest and Landscape (FOEFL),1987. Commentary on the ordinance Relating to pollutants in soil (VSBO of June 1986),FOEFL, Bern, Switzerland,

Forstner, U. and Whitman, G. T. W. 1983. Metals in the aquatic environment, New York. Springer-Verlag

Fu, X-W., Wang, D – G., Ren, X – H. And Cui, Z – J. 2014. Spatial distribution patterns and potential sources of heavy metals in soils of a crude oil – polluted region in china. ***Pedosphere,*** 24 (4): 508 - 518

Giri, S,. Singh, A. K. And Tewary, 2013. Source and distribution of metals in bed sediments of Subarnarekha River, India. Environ. ***Earth Sci.,*** 70: 3381 – 3392

Haapala, K. R. Catalina, A. V., Johnson, M. L. And Sutherland, J. W. 2012. Development and application of models for steel making and casting environmental performance. ***J. Manuf. Sci. Eng.,*** vol 134. 10.1115/1.4007463

Jasmine, J. and Mukherji, S (2015). Characterization of oil sludge from refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia. ***Journal of Environmental Management***, 149, 118 – 125.

Kalita, M., Bhattacharyya, K. G. and Devi, A. (2009). Assessment oil field soil with special references to the presence of heavy metals: a case study in agricultural soil of Rudrasagar oil field , Assam. ***India J. Environ. Prot***., 29 (12): 1065 – 1071

Karim, Z. and Qureshi, B. A. 2014. Health risk Assessment of heavy metals in urban soil of Karachi, Pakistan. ***Humanand Ecological Risk Assessment: An international Journal, 20 (3): 658 – 667.***

Kashif, S.R., Akran, M., Yaseez, M. andAli, S. (2009). Studies on heavy metals status and their uptakes by vegetables in adjoining areas of Hudiara drain in Lahore. ***Soil and Environment,*** 28 (1), 7 – 12

Lacatusu, R. 1998 Appraising levels of soil contamination and pollution with heavy metals. European Soil Bureau – Research Report No. 4.

Langston, W. J. 1990 Toxic effects of metals and the incidence of metals pollution in marine ecosystems. In Furness, R. W. and Rainbow, P. S. (eds). Heavy Metals in the marine environment. CRS ress Boca Ration FL pp. 101-122.

Li, P., Lin, C., Cheng, H., Duan, X. and Lei, K. 2014. Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. Ecotoxicol. and Environ. Safety, 113: 391 – 399

Loska, K., Wiechula, D. and Korus, I. 2004. Metal contamination of farming soils affected by industry. ***Environ. Int.,*** 30 (2): 159 – 165

Luiselli, L., G.C. Akani and E. Politano, 2006. Effects of habitat alteration caused by petrochemical activities and oil spills on the habitat use and interspecific relationships among four species of afrotropical freshwater turtles. ***Biodiversity and Conservation,*** 15(11), 3756-3767.

Martin, J. M. and Meybeck, 1979. Elemental mass balance of materials carried by major rivers. ***Mar. Chem.,*** 7: 175 – 206

Mihali, C., Oprea, G. Michnea, A., Jelea, S., Jelea, M., Man, C., Senila, M. and Griger, L. 2013. Assessment of heavy metal content and pollution and pollution level in soil and plant in Baia mare area, NW Romania***. Carpathian J. of Earth and Environ. Sci.,*** 8 (2): 143 – 152.

Nie, M., Xian, N., Fu, X., Chen, X. and Li, B, 2010. The Interactive effect of petroleum-hydrocarbon spillage and plant rhizosphene on concentrations and distribution of heavy metals in sediments in the Yellow River Delta, ***China. J. Hazard. Mater.*** 174 (1 – 3), 156 – 161

Okereke, J.J., S.O. Obiekezie and K.O. Obasi, 2007. Microbial flora of oil-spilled sites in Egbema, Imo State Nigeria. ***African J. of Biotech.,*** 6(8): 991-993

Olajire, A. A., Altenburger, R., Kuster, E. and Brack, W. 2005. Chemical and ecotoxicological assessment of polycyclic aromatic hydrocarbon contaminated sediments of Niger Delta, Southern Nigeria. ***Science of the Total Environment*** 340(1-3): 123-136.

Olawoyin, R., Oyewole, S. A. and Greyson, Robert L.20123 Potential risk effect from elevated levels of soil heavy metals on human health in the Niger Delta. ***Ecotoxicol. Environ. Safety,*** 85 (1): 120 – 130.

Otokunefor, T.V. and Obiukwu, C. (2005). Impact of Refinery effluent on the physicochemical properties of awater body in the Niger Delta. ***Appl. Ecol. and Environ.*** Res., 3(1): 61 – 72

Oudot, J., Fusey, P., Van Praat, M., Feral, J. P. And Gaill, F. 1981. Hydrocarbon weathering in seashore invertebrates and sediments over a two year period following the Amoco Cadiz Spill: Influence of microbal metabolism. ***Environmental Pollution Series*** A. 26, 93-110.

Perez-Casanova, J. C.,Hamontere, D., Samuelson, S., Burt, K., King, T. L. and Lee, K. 2010. The immune response of juvenile Atlantic cod (Gadus morhua L.) to chronic exposure to produced water. ***Mar. Environ. Res.*** 70 (1), 26 – 34.

Plaza, G. A., Nalecz-Jawecki, G., Pinyakong, O., Illmmer, P. And Margesin, R. 2010. Ecotoxicological and microbiological characterization of soils from heavy-metal and hydrocarbon – contaminated sites. ***Environmental Monitoring and Assessment,*** 163 (1 – 4), 477 – 488.

Puyate, Y. T., Rim-Rukeh and Awatefe, J. K. 2007. Metal pollution assessment and particle size Distribution of bottom sediment of Orogodo River, Agbor, Delta State, Nigeria. ***J. Appl. Sciences Res.,*** 3 (12): 2056 – 2061.

Sutherland, R. A. 2000. Bed sediment – associated trace metals in an urban stream, Oahu, Hawaii. ***Environ. Geol.,*** 39 (6): 611 – 627.

United Environment Programme (UNEP). 2011. Environmental assessment of Ogoniland. United Nation Environment Programme (UNEP), Nairobi.

United Nation Development Programme (UNDP). 2006 *Niger Delta Human Development.* http://hdr.undp.org/en/reports/nationalreports/africa/nigeria/name,3368,en.html.Accessed 19 June, 2011.

Wang, P. –J., Liu, L., Li, F. –S., Hu, Z. –Q. and Bai, L. –P. 2011. Characteristic distribution of typical contaminants in the soil of a coking plant site in the southwest of china. Meitan Xuebao/***Journal of the China Coal Society*** 36 (9), 1587 – 1592.

Yang, T., Liu, Q., Zeng, Q. and Chan, L. 2009. Environmental Magnetic responses of Urbanization processes: Evidence from Lake sediments in East Lake, Wuhan, China. ***Geophys. J. Int.,*** 179 (2), 873 – 886.