

# Spatiotemporal Dynamics in selected Physicochemical Properties, Metals, and Total petroleum hydrocarbons contents in Crude oil impacted Soil in Part of the Niger Delta Region of Nigeria

Grace E Obi-Iyeke\*

Department of Botany, Delta State University, Abraka, Nigeria

Received on January 12, 2025, Accepted on May 6, 2025

## Abstract

The Niger Delta of Nigeria has witnessed several oil spillages arising from oil production and transportation and oil pipeline vandalism. These activities might have caused continuous and remarkable changes in the structure and function of the ecosystem with resultant environmental impacts. Thus, this study aims to evaluate the spatio-temporal and seasonal changes in some physicochemical properties, metals, and total petroleum hydrocarbons contents in crude oil contaminated soils in part of the Niger Delta of Nigeria. Soil samples were collected from seven locations at a crude oil spillage site in Amukpe. Soil samples were analysed using standard chemical methods. The order of mean concentrations of the heavy metals in mg kg<sup>-1</sup> in the soil samples for dry seasons in descending orders were Fe (981) > Zn (270) > Pb (>74.1) > Mn (58.71) > Cu (48.2) > Cr (21.83) > Ni (12.6) > V (3.3) > Cd (0.41) > (0.04), and those of the wet season were Fe (1017) > Zn (230) > Pb (69.9) > Mn (51.6) > Cu (43) > Cr (19) > Ni (10.7) > Cd (0.83) > As (0.31). The concentrations of metals in this study were higher than their respective FAO/WHO permissible limits. Heavy metal enrichment factors follow the order Pb > Cd > Zn > Cu > Cr > Ni > Mn > As > V. The enrichment factor (EF) of Pb, Cu, Cd, Zn, and Cr were greater than 10 indicating anthropogenic origin. The result of correlation and principal component analysis indicates that there was a strong positive correlation between TPH and metals which indicate that TPH and metals from the same anthropogenic source, such as oil spillage and associated activities. The clean-up of the impacted site is recommended in order to restore the soil's fertility for productive agricultural activities which are the major source of economic survival of the inhabitants in the study area.

© 2025 Jordan Journal of Earth and Environmental Sciences. All rights reserved

**Keywords:** Amukpe; Contamination; Geoaccumulation index; Enrichment factor; Pollution load index

## 1. Introduction

The most visible activities in Nigeria's Niger Delta are oil exploration and exploitation, which are accompanied by a growing problem with oil contamination (Ogri, 2001). According to Yakubu (2007), oil pollution can have catastrophic effects, which is why Nigeria has seen several oil blowout disasters. Such blowouts and pipeline leakages have all resulted in pollution of land, freshwater swamps and the marine environment (Nwachukwu et al., 2010). Currently, there are eleven oil Corporations operating approximately 159 oil fields and 1,481 oil wells in the Niger Delta region of Nigeria (Wegwu et al., 2011). According to available data, the Niger Delta region of Nigeria is more susceptible to oil spills than any other place in the world, with an average of 273 oil spills occurring between 1983 and 2005, resulting in around 115,000 barrels of crude oil valued at US\$5.64 million annually (Agbogidi et al., 2009). Some notable recent oil spills recorded in Nigeria include Assa-Rumekpe pipeline at Elele Alumini (2014), Nkpoku-Bomu pipeline at Ekporo (2014), Nembe creek pipeline at Elem-Kalabari (2014), Bomu-Bonny pipeline at Dere (2013), Amukpe trunk line at Amukpe (2011), and Nun-river Kolo creek at Oporoma (2013) (Shell Petroleum Development Company (SPDC), 2014). It

appears that the amount of attention paid to oil spills on a global scale varies significantly depending on where they occur. For example, the 1989 Exxon Valdez oil spill (260,000 barrels) is highly referenced, likely because it happened in the United States. Still, there are many spills in developing nations that are larger, based on volume spilled and sensitivity of impact, than the aforementioned Exxon Valdez oil spill, but they are rarely used as benchmarks. Given that their regular sources of sustainable livelihoods—farming and fishing—are constantly disrupted, these spills and other environmental hazards related to the region's oil production have a significant impact on residents' fundamental right to exist (Agbogidi et al., 2009). Crude oil inundates the soil, a key component of agricultural productivity and a significant source of income for the communities that produce it, when it is accidentally released onshore for a variety of reasons, such as malfunctioning production machinery, operational errors, or deliberate damage to production facilities (Nkwocha and Duru, 2010; Yakubu, 2007; Odjuvwuederhie et al., 2006). Available records indicate that there is inadequate data to formulate or implement appropriate policies to manage some of the challenges of oil spillage, as most towns affected by crude oil spillage have not received any notable attention

\* Corresponding author e-mail: ekyobiyeke@gmail.com

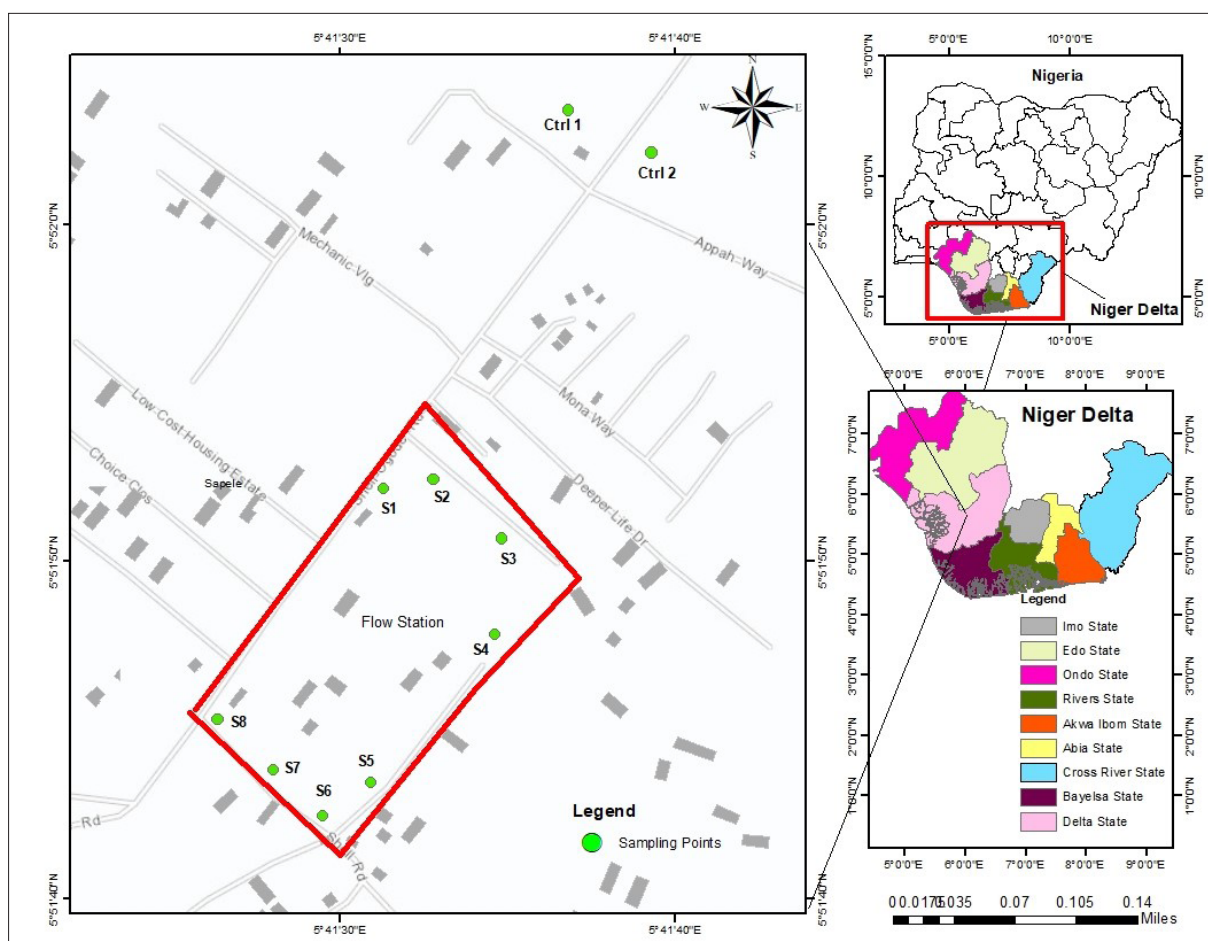
(Osuji et al., 2004; NEST, 1991). One such area is Amukpe, in Sapele Local Government Area of Delta State, the host community of Shell BP's oil well No. 25. This area has witnessed several oil spillages arising from oil production and transportation, as well as oil pipeline vandalism (SPDC, 2014). These activities have caused continuous and remarkable changes in the structure and function of the ecosystem with resultant environmental impacts. The desire to provide information on the effects of oil spillage on soil, food crops, and plant diversity in Amukpe becomes imperative, as their environment and socio-economic life have been threatened by the impact of the spillage. Thus, the aim of this study is to investigate the spatiotemporal dynamics of some physicochemical properties, metals and total petroleum hydrocarbons contents in crude oil- impacted soils from Amukpe in the Niger Delta of Nigeria.

**2. Materials and Methods**

**2.1 Description of Study Area**

The study area is Amukpe, located within Longitude E 5° 42' 55.76" and Latitude N 5° 51' 38.75" with elevation

above sea level being 11 meters. The area has a tropical equatorial climate. The area has an average annual rainfall of 1900 mm, with a temperature range of 23 °C to 37 °C and a relative humidity range of 75% to 89% (Erhayimwen et al., 2024; Tesi et al., 2020). The vegetation is typical of the rainforest except for drainage streams where swampy areas exist (Erhayimwen et al., 2024; Jaboro and Omonigho, 2019). The rich, silty soil, coupled with salt- and freshwater bodies, provided the necessary incentives for the people whose main occupations are farming and fishing (Obi-Iyeke, 2022). Amukpe is part of the Oben/ Sapele/Amukpe oil and gas field, which is operated by the Nigerian Petroleum Development Company. Amukpe has a flow station, a Liquid Treatment Facility, and crude storage tanks. Amukpe also hosts the commercial farm holding, which is an integrated farm registered as a company limited by the Delta State Government, modelled after the Songhai-Parakou of the Republic of Benin. The crude oil exploration has resulted in incidents of oil spillage in the study area. The study area map is shown in Figure 1.



**Figure 1.** Map of the study area

**2.2 Soil Sample Collection**

Soil sampling was done according to the FAO (2006) method. Eight (8) soil samples were collected from crude oil-impacted locations in the study area while two (2) soil samples were collected from a non-impacted area which served as control samples. Sampling points were geo-referenced using geographical positioning system (GPS)

to ensure consistency and are shown in Figure 1 and Table 1. The soil samples were collected at depths 0-15 cm and 15-30 cm using a stainless steel auger after foreign materials such as roots, gravel, pebbles, leaves and stones were removed. At each sampling point, three different samples were collected and pooled together. Thereafter, a single representative or composite sample was collected by

quartering and compartmentalization. Sampling was carried out during the dry season (January) and then the wet season (June) for two years. Soil samples for metal analysis were stored in polythene bags, while those for total petroleum hydrocarbons were stored in aluminum foil and kept in an ice chest. Samples were correctly labeled and transported to the laboratory. In the laboratory, the soil samples were air dried in the dark, sieved through a 2 mm mesh, and stored at -4 °C until analysis.

**Table 1.** Sample coordinates in decimal degrees

Sampling ID	Latitude	Longitude	Activities
S1	N 5.864468	E 5.692029	Farmland
S2	N 5.864559	E 5.692442	Farmland
S3	N 5.864057	E 5.693007	Farmland
S4	N 5.863282	E 5.692946	Farmland
S5	N 5.862064	E 5.691922	Farmland
S6	N 5.861775	E 5.691524	Farmland
S7	N 5.862156	E 5.691111	Farmland
S8	N 5.862582	E 5.690637	Farmland
Ctrl 1	N 5.867602	E 5.693558	Farmland
Ctrl 2	N 5.867237	E 5.694246	Farmland

### 2.3 Physicochemical Characterization of Soil Samples

Physical analysis was conducted on the composite soil samples, consisting of five random samples from each plot for the two profile layers (0-15cm and 15-30cm). Control samples were also collected 5km away from the polluted site, in the direction opposite to the drainage, with similar vegetation, using the same procedures. The background samples were collected 1000 m away from the polluted site. Particle size analysis was done by the Bouyoucas Method (1962). Total organic carbon was measured using the wet oxidation digestion method of Walkley and Black (1959). The exchangeable cations were extracted by the ammonium acetate extraction method (He et al., 2005). Available phosphorus was determined by the molybdenum blue colour method (Osuji et al., 2006). Nitrogen was determined by the modified Kjeldahl method (Bakker et al., 2000). A pH meter (Orion Digital pH / millivoltmeter 611) was used to determine the pH of the soil, following the procedures of Oluyemi et al. (2008). Total petroleum hydrocarbon (TPH) was determined using the method of Mihaly-Cozmuta et al. (2005).

### 2.4 Heavy metal analysis of the soil samples

Five grams of the air-dried soil sample were digested in an acid mixture prepared from 20 mL HNO<sub>3</sub>, 10 mL HCl, and 2 mL HF. The digest was placed on a hot plate (130 °C) for 2 hours with constant stirring. The filtered solution

was made up to 100 mL with distilled water. The solution was analyzed for heavy metals (Fe, Zn, Cr, Cd, Cu, Pb and Mn) using Flame Atomic Absorption Spectrophotometry (AAS) (PerkinElmer Analyst 200). Vanadium was analyzed using a nitrous oxide flame, whereas arsenic was analyzed by hydride generation AAS. The AAS was fitted with D2 background correction devices. All samples were analyzed in triplicate.

### 2.5 Data Analysis

Data collected were subjected to analysis of variance (ANOVA) and the means were compared using 'Duncan's new multiple range test (DNMRT) at p < 0.05 levels of significance. The Pearson correlation coefficient was used to assess the relationships between the metals in soil samples from polluted and unpolluted sites, while principal component analysis was applied to identify the sources of metals.

### 2.6 Determination of the extent of pollution

The extent of pollution and ecological risk was evaluated using various pollution indices including the contamination/pollution index, pollution load and geo-accumulation index.

**Contamination / pollution index:** The contamination/pollution index was computed using the equation:

$$CPI = \frac{\text{Concentration of metals in soil}}{DPR \text{ Target value}} \quad (1)$$

**Geoaccumulation index (I<sub>geo</sub>):** The geoaccumulation index was calculated by the equation:

$$I_{geo} = \text{Log } 2 \frac{C_n}{1.5B_n} \quad (2)$$

**Enrichment factor (EF):** The enrichment factor of metals in the soil was calculated following the equation:

$$EF = \frac{C_n (\text{test element})}{C_n (\text{Reference})} \div \frac{B_n (\text{test element})}{B_n (\text{Reference})} \quad (3)$$

**Pollution load index:** Pollution load index (PLI) was estimated using the equation:

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times CF4 \times \dots \times CFn} \quad (4)$$

The definition and values of variables in equations (1) to (4) are as given in Tesi et al. (2020) and Iwegbue et al. (2018).

## 3. Results and Discussion

### 3.1 Soil physicochemical characteristics

The results of some physicochemical properties, including particle size distribution, pH, electrical conductivity, nitrate, phosphate, and total petroleum hydrocarbon contents in the crude oil-impacted soils for the two sampling years are presented in Table 1.

Table 1. Some physicochemical properties of soils of the study area

Sites	Depth	pH						TOC (%)						EC ( $\mu\text{S}/\text{cm}$ )					
		2013		2014		2014		2013		2014		2014		2013		2014			
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W		
1	0-15cm	6.06±0.05 <sup>c</sup>	6.14±0.04 <sup>d</sup>	6.52±0.43 <sup>b</sup>	6.54±0.04 <sup>d</sup>	1.80±0.09 <sup>d</sup>	1.60±0.12 <sup>c</sup>	1.72±0.03 <sup>b</sup>	1.51±0.39 <sup>d</sup>	62.7±0.05 <sup>c</sup>	60.9±0.06 <sup>b</sup>	58±0.05 <sup>e</sup>	42.4±2.05 <sup>d</sup>						
	15-30cm	6.76±0.17 <sup>b</sup>	6.9±0.67 <sup>a</sup>	6.79±0.57 <sup>b</sup>	6.99±0.61 <sup>c</sup>	1.52±1.05 <sup>d</sup>	1.46±1.04 <sup>c</sup>	1.51±0.00 <sup>b</sup>	1.31±0.05 <sup>c</sup>	54.4±0.70 <sup>d</sup>	42.1±1.90 <sup>d</sup>	57±0.21 <sup>c</sup>	41.7±0.03 <sup>d</sup>						
2	0-15cm	5.89±1.40 <sup>d</sup>	6.03±0.05 <sup>d</sup>	5.99±0.00 <sup>c</sup>	6.75±1.40 <sup>c</sup>	2.1±0.00 <sup>c</sup>	1.94±0.05 <sup>c</sup>	1.84±0.40 <sup>b</sup>	1.86±0.20 <sup>d</sup>	61.8±0.00 <sup>c</sup>	57.4±0.03 <sup>e</sup>	57.8±0.05 <sup>c</sup>	52.8±0.19 <sup>c</sup>						
	15-30cm	6.21±0.52 <sup>c</sup>	6.84±1.03 <sup>b</sup>	6.56±0.25 <sup>b</sup>	6.93±0.75 <sup>c</sup>	1.8±0.04 <sup>d</sup>	1.73±0.48 <sup>c</sup>	1.76±1.42 <sup>b</sup>	1.37±0.03 <sup>c</sup>	49±0.48 <sup>e</sup>	49.6±0.18 <sup>d</sup>	48.7±0.01 <sup>d</sup>	43±0.05 <sup>d</sup>						
3	0-15cm	6.06±0.60 <sup>c</sup>	5.97±0.09 <sup>c</sup>	6.74±0.39 <sup>b</sup>	5.98±0.00 <sup>c</sup>	3.1±0.18 <sup>b</sup>	3.8±1.36 <sup>a</sup>	2.9±0.01 <sup>a</sup>	3.3±0.15 <sup>b</sup>	49.3±0.06 <sup>c</sup>	53±0.04 <sup>c</sup>	49.3±1.07 <sup>d</sup>	53±1.13 <sup>c</sup>						
	15-30cm	6.74±0.65 <sup>b</sup>	6.43±1.05 <sup>c</sup>	6.94±0.01 <sup>b</sup>	6.75±1.28 <sup>c</sup>	2.9±0.05 <sup>c</sup>	3.0±0.00 <sup>a</sup>	1.6±0.50 <sup>c</sup>	1.8±2.30 <sup>c</sup>	36.1±0.10	35±0.16 <sup>c</sup>	36.1±0.90 <sup>c</sup>	35±0.02 <sup>c</sup>						
4	0-15cm	5.67±1.54 <sup>d</sup>	6.46±0.13 <sup>d</sup>	5.93±0.05 <sup>c</sup>	6.97±0.05 <sup>c</sup>	2.3±0.42 <sup>c</sup>	3.5±5.75 <sup>a</sup>	2.3±0.07 <sup>b</sup>	2.6±0.00 <sup>c</sup>	72.8±0.00 <sup>b</sup>	67±0.00 <sup>b</sup>	72.8±0.05 <sup>b</sup>	67±0.00 <sup>b</sup>						
	15-30cm	6.39±3.00 <sup>c</sup>	6.83±1.76 <sup>c</sup>	6.84±1.03 <sup>b</sup>	6.91±0.31 <sup>c</sup>	2.4±0.03 <sup>c</sup>	2.9±0.13 <sup>b</sup>	2.1±0.14 <sup>a</sup>	2.1±1.02 <sup>c</sup>	64±0.35 <sup>e</sup>	58.2±0.03 <sup>e</sup>	64±0.14 <sup>b</sup>	58.2±1.05 <sup>c</sup>						
5	0-15cm	5.94±0.95 <sup>d</sup>	6.05±0.94 <sup>d</sup>	6.98±0.05 <sup>b</sup>	6.99±1.52 <sup>c</sup>	1.61±0.00 <sup>d</sup>	1.83±0.00 <sup>c</sup>	1.83±0.70 <sup>b</sup>	1.87±0.44 <sup>d</sup>	51±0.92 <sup>d</sup>	46.4±0.12 <sup>d</sup>	51±1.80 <sup>c</sup>	46.4±0.00 <sup>d</sup>						
	15-30cm	6.03±2.17 <sup>c</sup>	6.74±2.01 <sup>b</sup>	7.02±0.09 <sup>a</sup>	7.2±0.93 <sup>b</sup>	1.51±0.72 <sup>d</sup>	1.63±0.25 <sup>c</sup>	1.21±0.20 <sup>c</sup>	1.01±0.05 <sup>c</sup>	38.2±0.04 <sup>f</sup>	31±0.07 <sup>e</sup>	38.2±0.04 <sup>c</sup>	31±0.48 <sup>c</sup>						
6	0-15cm	6.09±0.52 <sup>c</sup>	6.06±0.00 <sup>d</sup>	6.64±0.10 <sup>b</sup>	6.34±0.04 <sup>d</sup>	1.37±0.13 <sup>d</sup>	1.48±0.34 <sup>d</sup>	1.07±0.71 <sup>c</sup>	1.32±0.00 <sup>c</sup>	53.1±0.10 <sup>d</sup>	52±0.31 <sup>c</sup>	53.1±0.00 <sup>c</sup>	52±0.05 <sup>c</sup>						
	15-30cm	6.71±1.64 <sup>b</sup>	6.57±0.17 <sup>c</sup>	6.79±0.57 <sup>b</sup>	6.72±0.57 <sup>c</sup>	1.61±0.00 <sup>d</sup>	1.32±1.30 <sup>d</sup>	0.91±1.09 <sup>d</sup>	0.81±0.04 <sup>f</sup>	42.9±0.00 <sup>e</sup>	38.9±0.09 <sup>e</sup>	42.9±2.01 <sup>d</sup>	38.9±1.04 <sup>e</sup>						
7	0-15cm	4.9±1.57 <sup>c</sup>	5.7±0.45 <sup>f</sup>	5.34±1.04 <sup>d</sup>	5.93±2.48 <sup>c</sup>	3.73±0.01 <sup>a</sup>	3.46±0.04 <sup>a</sup>	2.41±0.00 <sup>a</sup>	3.71±0.05 <sup>b</sup>	86.1±2.08 <sup>a</sup>	72.5±0.05 <sup>b</sup>	86.1±0.17 <sup>a</sup>	72.5±0.18 <sup>a</sup>						
	15-30cm	5.1±0.05 <sup>e</sup>	6.08±2.71 <sup>d</sup>	5.82±0.00 <sup>c</sup>	6.45±0.64 <sup>d</sup>	3.24±0.25 <sup>b</sup>	3.21±0.21 <sup>a</sup>	2.41±0.68 <sup>a</sup>	2.8±0.36 <sup>c</sup>	48.3±0.18 <sup>e</sup>	44±0.03 <sup>d</sup>	48.3±0.04 <sup>d</sup>	44±2.53 <sup>d</sup>						
8	0-15cm	6.04±0.63 <sup>c</sup>	6.18±0.03 <sup>d</sup>	6.73±0.50 <sup>b</sup>	6.93±0.01 <sup>c</sup>	2.1±0.04 <sup>1c</sup>	2.1±0.01 <sup>b</sup>	1.9±0.21 <sup>c</sup>	1.0±0.00 <sup>c</sup>	32.5±1.04 <sup>f</sup>	31±0.00 <sup>c</sup>	32.5±0.38 <sup>c</sup>	31±0.19 <sup>c</sup>						
	15-30cm	6.56±0.98 <sup>b</sup>	6.03±0.51 <sup>d</sup>	6.81±0.07 <sup>b</sup>	6.98±1.00 <sup>c</sup>	1.9±0.00 <sup>d</sup>	1.8±0.05 <sup>d</sup>	0.7±0.53 <sup>c</sup>	0.8±0.71 <sup>b</sup>	23±0.05 <sup>b</sup>	20.6±0.02 <sup>f</sup>	23±0.45 <sup>f</sup>	20.6±0.05 <sup>f</sup>						
Control 1	0-15cm	7.01±0.00 <sup>b</sup>	7.06±0.07 <sup>b</sup>	7.13±0.03 <sup>a</sup>	7.06±0.00 <sup>b</sup>	0.7±0.05 <sup>f</sup>	0.61±0.03 <sup>c</sup>	0.51±0.03 <sup>d</sup>	0.61±0.05 <sup>f</sup>	21.9±0.00 <sup>g</sup>	18.5±0.04	22±0.05 <sup>f</sup>	17±0.04 <sup>h</sup>						
Control 2	15-30cm	7.56±0.11 <sup>a</sup>	7.73±1.34 <sup>a</sup>	7.21±0.51 <sup>a</sup>	7.62±1.30 <sup>b</sup>	0.81±0.63 <sup>c</sup>	0.71±1.00 <sup>c</sup>	0.74±0.50 <sup>d</sup>	0.80±0.00 <sup>f</sup>	17.8±2.01 <sup>h</sup>	17±0.04 <sup>h</sup>	18.6±1.46 <sup>g</sup>	18.3±0.56 <sup>g</sup>						
	0-15cm	6.94±0.00 <sup>a</sup>	7.01±2.04 <sup>b</sup>	6.89±0.32 <sup>b</sup>	7.01±0.00 <sup>b</sup>	0.92±0.01 <sup>e</sup>	0.83±0.04 <sup>c</sup>	0.88±1.34 <sup>d</sup>	0.67±1.46 <sup>f</sup>	22.7±0.16 <sup>g</sup>	21.7±1.03 <sup>f</sup>	22.9±0.61 <sup>f</sup>	22±0.01 <sup>f</sup>						
Control 2	15-30cm	7.25±0.10 <sup>a</sup>	7.53±1.80 <sup>a</sup>	7.04±1.60 <sup>a</sup>	7.27±0.52 <sup>b</sup>	0.83±1.07 <sup>e</sup>	0.81±0.00 <sup>c</sup>	0.37±0.56 <sup>d</sup>	0.34±0.29 <sup>g</sup>	20.3±0.05 <sup>g</sup>	19.9±0.05 <sup>g</sup>	21.1±0.00 <sup>f</sup>	21.5±0.06 <sup>f</sup>						

W=Wet season; D=Dry season; Means with different alphabets within the same column are significantly different at  $P \leq 0.05$  using Duncan's Multiple Range Tests

Continuing from Table 1. Some physicochemical properties of soils of the study area

	Nitrate (mg kg <sup>-1</sup> )						Phosphate (mg kg <sup>-1</sup> )						CEC (mg kg <sup>-1</sup> )					
	2013		2014		2013		2014		2013		2014		2013		2014			
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W		
1	0-15cm	28.5±0.07 <sup>c</sup>	26.6±3.10 <sup>f</sup>	31.4±3.05 <sup>d</sup>	29.8±0.57 <sup>e</sup>	12.4±0.73 <sup>g</sup>	11.9±3.61 <sup>h</sup>	14.6±0.02 <sup>f</sup>	14±0.04 <sup>f</sup>	22.1±0.05 <sup>c</sup>	20.1±3.01 <sup>b</sup>	23.8±2.40 <sup>d</sup>	22.4±0.00 <sup>e</sup>	20.6±3.10 <sup>e</sup>	19.4±0.05 <sup>c</sup>	30.4±1.00 <sup>b</sup>	22.7±0.05 <sup>de</sup>	
	15-30cm	32.9±0.05 <sup>b</sup>	34.3±0.16 <sup>c</sup>	34.9±0.09 <sup>c</sup>	35.2±6.01 <sup>c</sup>	14±1.90 <sup>e</sup>	13.6±0.03 <sup>f</sup>	15.9±1.60 <sup>e</sup>	14.7±2.48 <sup>f</sup>	15±1.21 <sup>e</sup>	20.1±4.00 <sup>d</sup>	21.5±0.09 <sup>b</sup>	19.4±0.05 <sup>c</sup>	20.6±3.10 <sup>e</sup>	30.4±1.00 <sup>b</sup>	22.7±0.05 <sup>de</sup>	22.7±0.05 <sup>de</sup>	
2	0-15cm	29±1.13 <sup>c</sup>	29.8±2.50 <sup>e</sup>	29.5±2.10 <sup>c</sup>	30±1.93 <sup>d</sup>	13.8±0.05 <sup>f</sup>	12±0.05 <sup>g</sup>	14.7±2.48 <sup>f</sup>	14±0.05 <sup>f</sup>	33.4±1.10 <sup>b</sup>	29.4±0.01 <sup>a</sup>	30.1±0.09 <sup>b</sup>	22.3±3.28 <sup>d</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	33.6±0.93 <sup>b</sup>	34.9±0.04 <sup>c</sup>	34.9±0.50 <sup>c</sup>	36±0.06 <sup>c</sup>	16±2.74 <sup>c</sup>	14.6±0.38 <sup>c</sup>	17±0.05 <sup>c</sup>	16.7±4.79 <sup>d</sup>	16.9±0.05 <sup>d</sup>	18.3±0.50 <sup>d</sup>	20.4±0.95 <sup>b</sup>	20.8±0.40 <sup>d</sup>	21.4±2.77 <sup>e</sup>	20.4±0.95 <sup>b</sup>	20.4±0.01 <sup>b</sup>	20.4±0.18 <sup>e</sup>	
3	0-15cm	25.4±3.60 <sup>d</sup>	27.5±2.58 <sup>f</sup>	25.4±2.93 <sup>f</sup>	28.7±0.13 <sup>c</sup>	12.7±0.59 <sup>g</sup>	13±2.00 <sup>f</sup>	14.6±2.53 <sup>f</sup>	16.9±0.05 <sup>d</sup>	18.3±0.16 <sup>d</sup>	20.4±0.95 <sup>b</sup>	20.8±0.40 <sup>d</sup>	21.4±2.77 <sup>e</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	30.4±0.94 <sup>b</sup>	31.7±5.90 <sup>d</sup>	30.4±0.04 <sup>d</sup>	35.1±2.46 <sup>c</sup>	14±3.02 <sup>e</sup>	13.8±3.15 <sup>f</sup>	16.1±0.05 <sup>d</sup>	14.7±2.01 <sup>f</sup>	18.3±0.50 <sup>d</sup>	20.4±0.01 <sup>b</sup>	20.4±0.01 <sup>b</sup>	22.3±3.28 <sup>d</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
4	0-15cm	28.5±0.01 <sup>c</sup>	26±1.01 <sup>f</sup>	29.5±0.92 <sup>c</sup>	27±0.05 <sup>c</sup>	12±0.01 <sup>g</sup>	12.1±0.02 <sup>g</sup>	11.1±0.34 <sup>f</sup>	13.8±0.00 <sup>g</sup>	27.4±4.20 <sup>b</sup>	30.1±0.41 <sup>a</sup>	26.3±0.05 <sup>c</sup>	23.4±0.55 <sup>d</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	34.2±4.00 <sup>b</sup>	30±2.00 <sup>d</sup>	32.3±3.78 <sup>cd</sup>	30±0.29 <sup>d</sup>	13.4±1.93 <sup>f</sup>	13.6±0.00 <sup>f</sup>	15.3±0.05 <sup>e</sup>	14.7±0.25 <sup>f</sup>	21.5±0.00 <sup>cd</sup>	32.1±3.59 <sup>a</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
5	0-15cm	32.6±1.72 <sup>c</sup>	30.3±1.10 <sup>d</sup>	34.7±0.03 <sup>bc</sup>	31.3±0.04 <sup>d</sup>	15.7±5.20 <sup>d</sup>	14.7±3.46 <sup>e</sup>	18±2.00 <sup>b</sup>	16.9±1.63 <sup>d</sup>	28.7±1.03 <sup>b</sup>	29.8±0.02 <sup>a</sup>	27.3±0.30 <sup>c</sup>	26.4±0.06 <sup>c</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	38.7±2.00 <sup>b</sup>	36.5±0.04 <sup>e</sup>	37.1±2.71 <sup>b</sup>	37.2±0.92 <sup>c</sup>	16.9±0.06 <sup>c</sup>	15±1.03 <sup>d</sup>	18±1.04 <sup>b</sup>	18.7±0.05 <sup>b</sup>	24.4±0.01 <sup>c</sup>	26.4±5.34 <sup>b</sup>	25.2±2.90 <sup>c</sup>	26.1±0.30 <sup>c</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
6	0-15cm	26.3±0.18 <sup>e</sup>	29.8±3.50 <sup>d</sup>	28.3±1.39 <sup>e</sup>	31±4.01 <sup>d</sup>	11.5±2.80 <sup>h</sup>	12±4.10 <sup>g</sup>	13.6±2.85 <sup>g</sup>	15±3.04 <sup>e</sup>	15.3±4.10 <sup>e</sup>	15.3±0.01 <sup>c</sup>	17.8±0.03 <sup>f</sup>	15.7±0.01 <sup>f</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	31.6±0.05 <sup>b</sup>	31.1±1.03 <sup>d</sup>	32±2.78 <sup>cd</sup>	36.4±0.64 <sup>c</sup>	12.9±0.03 <sup>g</sup>	13.4±0.35 <sup>f</sup>	12.9±0.30 <sup>h</sup>	17.6±1.90 <sup>e</sup>	16.4±0.34 <sup>c</sup>	13.2±0.05 <sup>d</sup>	16.3±0.00 <sup>f</sup>	12.3±2.45 <sup>g</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
7	0-15cm	25.7±3.80 <sup>e</sup>	26.2±0.05 <sup>f</sup>	24.4±0.43 <sup>f</sup>	29.4±5.10 <sup>c</sup>	11.1±0.46 <sup>h</sup>	10.3±1.48 <sup>i</sup>	13.5±3.96 <sup>g</sup>	12.9±0.00 <sup>h</sup>	38.4±0.52 <sup>a</sup>	29.1±1.46 <sup>a</sup>	36.8±1.56 <sup>a</sup>	32.4±0.00 <sup>a</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	28.9±0.64 <sup>c</sup>	29±2.83 <sup>c</sup>	28.9±0.05 <sup>e</sup>	32.8±0.02 <sup>d</sup>	12.9±3.70 <sup>g</sup>	12.9±2.80 <sup>g</sup>	15±0.73 <sup>c</sup>	13.81±0.52 <sup>g</sup>	13.81±0.52 <sup>g</sup>	38.3±3.11 <sup>a</sup>	33.7±0.05 <sup>a</sup>	20.6±1.10 <sup>e</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
8	0-15cm	30.6±0.05 <sup>b</sup>	31.7±0.07 <sup>d</sup>	33.9±2.69 <sup>c</sup>	34.2±2.18 <sup>c</sup>	13±1.40 <sup>f</sup>	13.4±0.05 <sup>f</sup>	14.3±0.05 <sup>f</sup>	14.2±1.04 <sup>f</sup>	19.8±0.44 <sup>d</sup>	16.8±0.21 <sup>c</sup>	21.4±0.62 <sup>d</sup>	22.3±0.44 <sup>e</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	35.7±1.93 <sup>b</sup>	33.9±4.10 <sup>d</sup>	35.4±0.48 <sup>b</sup>	35.5±0.03 <sup>c</sup>	14.7±0.06 <sup>c</sup>	14±0.20 <sup>e</sup>	16±0.03 <sup>d</sup>	13.1±0.02 <sup>g</sup>	16.1±0.50 <sup>e</sup>	16.6±2.00 <sup>e</sup>	16.0±0.07 <sup>f</sup>	13.0±0.00 <sup>g</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
Control 1	0-15cm	42.3±0.26 <sup>a</sup>	40.6±0.02 <sup>b</sup>	43.7±5.01 <sup>a</sup>	41.6±0.72 <sup>b</sup>	17.3±0.34 <sup>b</sup>	15±0.74 <sup>d</sup>	18.6±0.05 <sup>b</sup>	17.8±0.70 <sup>c</sup>	10.3±0.01 <sup>f</sup>	7.8±0.02 <sup>f</sup>	7.3±0.00 <sup>h</sup>	7.00±0.97 <sup>i</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	46.7±3.40 <sup>a</sup>	45±1.46 <sup>a</sup>	47±0.15 <sup>b</sup>	47.4±0.00 <sup>b</sup>	18±1.05 <sup>a</sup>	16.8±2.03 <sup>c</sup>	19.7±3.19 <sup>a</sup>	18.1±0.05 <sup>b</sup>	10.7±0.00 <sup>f</sup>	9.80±1.41 <sup>e</sup>	8.60±3.10 <sup>e</sup>	8.20±2.40 <sup>h</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
Control 2	0-15cm	43.2±0.18 <sup>a</sup>	39.5±0.05 <sup>b</sup>	44.6±0.02 <sup>a</sup>	40±1.78 <sup>b</sup>	15.3±0.00 <sup>d</sup>	17±0.00 <sup>b</sup>	17.9±0.03 <sup>c</sup>	18.5±0.00 <sup>b</sup>	8.7±1.53 <sup>f</sup>	7.20±0.00 <sup>f</sup>	7.30±2.41 <sup>h</sup>	6.80±0.01 <sup>i</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	
	15-30cm	45.9±0.05 <sup>a</sup>	42.6±2.48 <sup>b</sup>	45.7±0.97 <sup>a</sup>	43±5.02 <sup>b</sup>	17.5±1.94 <sup>b</sup>	18.4±1.02 <sup>a</sup>	19.7±0.50 <sup>a</sup>	19.1±0.52 <sup>a</sup>	9.8±0.91 <sup>f</sup>	10.3±2.11 <sup>e</sup>	9.4±0.01 <sup>g</sup>	8.50±0.00 <sup>h</sup>	20.4±0.18 <sup>e</sup>	26.3±0.05 <sup>c</sup>	20.1±1.00 <sup>d</sup>	23.4±0.55 <sup>d</sup>	

W=Wet season; D=Dry season; Means with different alphabets within the same column are significantly different at  $P \leq 0.05$  using Duncan's Multiple Range Tests

Continuing from Table 1. Some physicochemical properties of soils of the study area

	Clay (%)						Silt (%)						Sand (%)					
	2013			2014			2013			2014			2013			2014		
	D	W		D	W		D	W		D	W		D	W		D	W	
1	0-15cm	11.6 <sup>e</sup>	12 <sup>d</sup>	12.6 <sup>e</sup>	12.9 <sup>d</sup>		14.2 <sup>f</sup>	13.6 <sup>f</sup>		14.9 <sup>e</sup>	14 <sup>e</sup>		41.7 <sup>d</sup>	38.2 <sup>e</sup>		38 <sup>f</sup>	33.3 <sup>h</sup>	
	15-30cm	13.4 <sup>e</sup>	13.8 <sup>c</sup>	14.3 <sup>c</sup>	14 <sup>b</sup>		15 <sup>e</sup>	14.3 <sup>e</sup>		15 <sup>d</sup>	15.2 <sup>d</sup>		38.9 <sup>e</sup>	34.6 <sup>f</sup>		36.5 <sup>g</sup>	32.9 <sup>h</sup>	
2	0-15cm	12.7 <sup>d</sup>	13.6 <sup>e</sup>	12.8 <sup>e</sup>	14.4 <sup>b</sup>		18.4 <sup>b</sup>	18.1 <sup>b</sup>		17 <sup>b</sup>	19 <sup>a</sup>		38.7 <sup>e</sup>	42.1 <sup>c</sup>		38 <sup>f</sup>	35.6 <sup>g</sup>	
	15-30cm	13.7 <sup>c</sup>	13.1 <sup>c</sup>	14.4 <sup>c</sup>	13.9 <sup>e</sup>		19.6 <sup>a</sup>	18.9 <sup>a</sup>		18.5 <sup>a</sup>	19 <sup>a</sup>		41 <sup>d</sup>	36.7 <sup>f</sup>		35 <sup>h</sup>	33 <sup>h</sup>	
3	0-15cm	10.1 <sup>f</sup>	12.1 <sup>d</sup>	11.5 <sup>f</sup>	12.9 <sup>d</sup>		12.4 <sup>b</sup>	12.8 <sup>g</sup>		13 <sup>f</sup>	13.2 <sup>f</sup>		38.4 <sup>e</sup>	31 <sup>g</sup>		34.6	29.7 <sup>i</sup>	
	15-30cm	11.9 <sup>e</sup>	12.4 <sup>d</sup>	12.7 <sup>e</sup>	13.4 <sup>e</sup>		13 <sup>g</sup>	11.1 <sup>h</sup>		14 <sup>e</sup>	14.4 <sup>e</sup>		35.1 <sup>f</sup>	28.7 <sup>h</sup>		31.6	26 <sup>i</sup>	
4	0-15cm	10 <sup>f</sup>	8.2 <sup>g</sup>	10 <sup>g</sup>	9 <sup>f</sup>		14.3 <sup>f</sup>	12.3 <sup>g</sup>		14.1 <sup>e</sup>	13 <sup>f</sup>		54.6 <sup>a</sup>	55.3 <sup>a</sup>		46.3 <sup>c</sup>	46.9 <sup>e</sup>	
	15-30cm	11.7 <sup>e</sup>	10 <sup>f</sup>	12 <sup>e</sup>	11.2 <sup>e</sup>		14.8 <sup>f</sup>	13.1 <sup>f</sup>		15.3 <sup>d</sup>	13.9 <sup>f</sup>		49.1 <sup>b</sup>	51.6 <sup>b</sup>		42.6 <sup>d</sup>	48.1 <sup>b</sup>	
5	0-15cm	11.3 <sup>e</sup>	10.4 <sup>f</sup>	12.5 <sup>e</sup>	11.6 <sup>e</sup>		17.5 <sup>c</sup>	15.8 <sup>d</sup>		18 <sup>a</sup>	16.2 <sup>c</sup>		42.1 <sup>d</sup>	38.6 <sup>e</sup>		38.8 <sup>f</sup>	31 <sup>i</sup>	
	15-30cm	12.8 <sup>d</sup>	11.7 <sup>e</sup>	13.3 <sup>d</sup>	12 <sup>d</sup>		18.1 <sup>b</sup>	12.2 <sup>g</sup>		18.9 <sup>a</sup>	13.7 <sup>f</sup>		41 <sup>d</sup>	39.3 <sup>e</sup>		34.5 <sup>i</sup>	32 <sup>i</sup>	
6	0-15cm	10.8 <sup>f</sup>	11.7 <sup>e</sup>	11 <sup>f</sup>	12.1 <sup>d</sup>		15.2 <sup>e</sup>	14.4 <sup>e</sup>		16.1 <sup>c</sup>	14.2 <sup>e</sup>		48.3 <sup>b</sup>	42.5 <sup>c</sup>		42.1 <sup>d</sup>	39.8 <sup>e</sup>	
	15-30cm	11.5 <sup>e</sup>	11 <sup>e</sup>	12.5 <sup>e</sup>	13.1 <sup>c</sup>		15.1 <sup>e</sup>	14 <sup>e</sup>		15.9 <sup>d</sup>	15.4 <sup>d</sup>		45.1 <sup>e</sup>	40.1		40.4 <sup>e</sup>	38.2 <sup>e</sup>	
7	0-15cm	9.7 <sup>g</sup>	11.6	10.4 <sup>g</sup>	11.1 <sup>e</sup>		13.6 <sup>g</sup>	12 <sup>g</sup>		13.8 <sup>f</sup>	12.6 <sup>g</sup>		58.3 <sup>a</sup>	52.4 <sup>b</sup>		57 <sup>a</sup>	51.9 <sup>a</sup>	
	15-30cm	10.7 <sup>f</sup>	12.4 <sup>d</sup>	12 <sup>e</sup>	12.9 <sup>d</sup>		18.9 <sup>b</sup>	12.8 <sup>g</sup>		15 <sup>d</sup>	13.2 <sup>f</sup>		50.6 <sup>b</sup>	51.7 <sup>b</sup>		51.4 <sup>b</sup>	48.9 <sup>b</sup>	
8	0-15cm	12.5 <sup>d</sup>	11.6 <sup>e</sup>	13.2 <sup>d</sup>	11.8 <sup>e</sup>		16.8 <sup>d</sup>	15.8 <sup>d</sup>		16.4 <sup>c</sup>	15.5 <sup>d</sup>		45.7 <sup>c</sup>	42.6 <sup>c</sup>		40.7 <sup>c</sup>	40.3 <sup>d</sup>	
	15-30cm	13.1 <sup>c</sup>	12.9 <sup>d</sup>	14.5 <sup>c</sup>	13 <sup>c</sup>		16.6 <sup>d</sup>	16.4 <sup>c</sup>		17 <sup>b</sup>	16.9 <sup>c</sup>		42 <sup>d</sup>	40.9 <sup>d</sup>		37.9 <sup>f</sup>	37.4 <sup>f</sup>	
Control 1		14 <sup>b</sup>	13.2 <sup>c</sup>	15.6 <sup>b</sup>	13.2 <sup>c</sup>		15.3 <sup>c</sup>	16.3 <sup>c</sup>		15.9 <sup>d</sup>	16.1 <sup>c</sup>		30.6 <sup>g</sup>	28.3 <sup>b</sup>		29.1 <sup>j</sup>	25.1 <sup>j</sup>	
Control 2	0-15cm	15 <sup>a</sup>	15 <sup>a</sup>	16 <sup>a</sup>	15 <sup>a</sup>		15.5 <sup>c</sup>	17 <sup>b</sup>		15.8 <sup>d</sup>	17.1 <sup>b</sup>		26.3 <sup>h</sup>	24		28.4 <sup>k</sup>	22.7 <sup>m</sup>	
	15-30cm	13.8 <sup>e</sup>	13.4 <sup>c</sup>	14.8 <sup>c</sup>	13.4 <sup>e</sup>		17.5 <sup>c</sup>	14.8 <sup>e</sup>		17.1 <sup>b</sup>	15.3 <sup>d</sup>		31 <sup>g</sup>	38.3 <sup>b</sup>		29.5	32.1 <sup>j</sup>	
	15-30cm	14.5 <sup>b</sup>	14.6 <sup>b</sup>	16.5 <sup>a</sup>	14.6 <sup>b</sup>		18 <sup>b</sup>	15.4 <sup>d</sup>		18.3 <sup>a</sup>	15.9 <sup>d</sup>		27.1 <sup>b</sup>	26.9 <sup>i</sup>		28.8 <sup>k</sup>	27.2 <sup>k</sup>	

W=Wet season; D=Dry season; Means with different alphabets within the same column are significantly different at  $P \leq 0.05$  using Duncan's Multiple Range Tests

The pH value for the crude oil-impacted soil ranged from 4.9 to 7.2 across the two sampling years. The results obtained from this study indicated that the pH values in the crude oil-impacted soils were acidic to near-neutral in nature, which corresponds to the typical pH of anaerobic soils in the Niger Delta. The pH values, reported in this study, were within the range of 6.0 to 7.5, as set by FAO (2011) for agricultural soils. The pH recorded in the study also corresponds to pH value previously reported for Niger Delta soils (Nkwocha and Duru, 2010; Abii and Nwosu, 2009; Iwegbue et al., 2009; Iwegbue et al., 2006. pH is an important soil property, having great effect on solute concentration and sorption/adsorption of contaminants in soils (Ambo et al., 2013). High pH value might reduce the mobility of some metal species down the soil strata, while low pH value usually enhances metal distribution and transport in soil (Ogboi, 2012; Osuji and Nwoye, 2007). The pH values in this study agree with the results obtained by Ideriah et al. (2013) from soil in the Niger Delta region and with those reported by Wegwu et al. (2011) in a post-impact assessment of a crude oil-spilled site four years after the recorded incidence. When evaluating the movement of most metals, soil pH is crucial because precipitation as insoluble organic complexes, carbonates, and hydroxides, as well as enhanced sorption to oxide surfaces, reduces mobility as the soil pH rises (Osuji and Udoetok, 2008). As the pH value decreases, the concentration of soluble metals increases (Abii and Nwosu, 2009). The acidic or alkaline status of the soil determines the availability of many nutrients for plant growth. pH thus plays a key role in soil microbial reactions (Edema et al., 2009).

Total organic matter (TOC) in the sampled plots ranged from 0.37 to 3.8%. The total organic matter at the polluted site was significantly higher ( $p < 0.05$ ) than that of the control site. The amount of organic matter in soils affects numerous chemical and physical processes. It is a key indicator of the soil as a rooting environment, even though soil organic carbon is not necessary for plant growth (Tesi et al., 2020).

The electrical conductivity (EC) varied between 17 and 86.1  $\mu\text{S cm}^{-1}$ . The highest EC value was observed at Site 7 during both sampling periods. The electrical conductivities of the impacted soils were significantly higher ( $p < 0.05$ ) than those of the control sites.

Cation exchange capacity (CEC) in the sampled plots ranged from 6.80 to 38.4  $\text{mg kg}^{-1}$ . The cation exchange capacity at the polluted site was significantly higher ( $p < 0.05$ ) than that of the control site. Additionally, there was significant variation in responses to sites and depth. The higher values of CEC were observed at sites 7, 4, and 1 in comparison to other sites. A similar range of CEC (9.41-48.31  $\text{mg kg}^{-1}$ ) was reported by Iwegbue et al. (2013) in the soil surrounding cassava processing mills in southern Nigeria. The values of CEC obtained in this study were significantly higher than those reported in soils from an oil field in the Niger Delta, Nigeria, by Iwegbue et al. (2006). The soil's ability to absorb metals is correlated with its CEC. The more exchange sites on the soil minerals that are accessible for metal retention, the higher the CEC value.

The concentrations of nitrate in the crude oil-impacted soil were lower than the levels found in the control sites, ranging from 24.4 to 47.4  $\text{mg kg}^{-1}$  for the two sampling periods. The phosphate concentration in the soil impacted by crude oil varied from 10.3 to 18.7  $\text{mg kg}^{-1}$ . There were no significant spatial and seasonal changes in the levels of phosphate in these soils. The concentration of nitrates and phosphates was very low and coupled with the fact that the spill was an extensive one that has lasted for about 3 years (in a low oxygen state). Metabolic activities have depleted the nitrates and phosphates in the soil, which may retard hydrocarbon degradation. Soil N and P levels were lower at the two depths in the polluted plots than in the control sites. The reduction in phosphorus could be attributed to the effect of the oil spill on the soil, which affected the activity of the enzyme phosphatase and, therefore, inhibited the release of phosphorus from the organic materials in the soil. The acidic/alkaline status of the soil determines the availability of many nutrients for plant growth. pH thus plays a key role in soil microbial reactions (Edema et al., 2009). It has been noted that contamination from crude oil lowers the soil's nutritional content (Nwadinigwe and Onyeidu, 2012). Osuji and Nwoye (2007) reported that the soil ecosystem is limited by organic matter, such that the presence of nitrogen-free substrates (crude oil), N and P become limiting. The low levels of phosphorus and nitrogen is indicative of a stressed environment.

Analysis of the soil samples showed that the proportion of soil particles varied as follows: sand (22.7%-58.3 %), clay (8.2%-16.5 %), and silt (12.0%-19.6%). The particle size pattern indicates the dominance of the sand fraction. The clay fraction of the soil was less than 18%. There is a significant spatial variation in particle size distribution. The sand fraction forms the predominant fraction at all sites and depths, while the clay fraction is low compared to the sand and silt. The sandy loam nature of the soil may have been responsible for an extensive vertical and horizontal migration of oil in the environment. This observation agrees with that of Akani et al. (2009), who reported that the sandy-loam nature of soils enhances oil migration in crude oil-polluted soil. There is no regular trend in particle size distribution with depth.

### 3.2 Metals and TPH concentrations in the soils

The results of the heavy metal and TPH analyses of the examined soils for the two sampling years are presented in Table 2. The results showed that impacted sites generally had higher concentrations of metals than the control site. The concentrations of metals in the crude oil-impacted soil were several times higher than those of the uncontaminated control sites throughout the different sampling seasons and periods, except for vanadium. This result indicates that the crude oil spillage had a significant impact on the environment due to the presence of metals. The spatial difference in the concentrations of crude oil-impacted soil is related to the background concentration of metals, topography, surface processes, and the magnitude of the crude oil spillage's impact.

Table 2. Seasonal variation of metals concentrations (mg kg-1 dry weight) in soils of the study area

Sites	Depth	As						Cd						Pb						Cr					
		2013		2014		2013		2014		2013		2014		2013		2014		2013		2014					
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W				
1	0-15cm	1.02	0.75	0.94	0.74	1.6	1	1.43	1.1	88.0	81.0	75.7	72.2	33.7	26.4	15.5	20.5								
	15-30cm	0.36	0.21	0.03	0.01	0.8	0.96	0.21	0.52	49.0	40.0	38.9	38.8	24.1	21.7	15.6	17.9								
2	0-15cm	1.04	0.68	0.45	0.28	0.6	0.52	0.64	0.83	94.0	89.0	82.9	65.8	21.4	18.7	18.3	19.0								
	15-30cm	0.2	0.15	0.04	0.05	0.2	0.06	0.83	0.02	56.0	69.0	50.5	44.3	20.9	18.9	18.0	16.0								
3	0-15cm	0.93	0.56	0.83	0.46	0.6	0.48	0.57	0.97	96.0	91.0	70.2	72.7	18.6	19	16.8	14.6								
	15-30cm	0.07	0.09	0.02	0.01	0.2	0.16	0.21	0.24	42.0	44.0	38.5	28.5	13.5	15.8	15.1	10.4								
4	0-15cm	0.36	0.56	0.3	0.45	2.8	2.08	2.2	2.43	107	98.0	94.2	72.0	34.8	28.3	27.6	22.1								
	15-30cm	0.05	0.01	0.06	0.01	1.2	1.13	1.32	1.17	86.0	47.0	72.8	33.3	30.7	22.6	29.8	23.7								
5	0-15cm	0.64	0.32	0.91	0.74	1.5	1.16	1.21	1.02	89.0	97.0	68.0	81.3	16.7	13.9	14.5	11.1								
	15-30cm	0.08	0.05	0.04	0.03	0.1	1.02	0.56	0.83	38.0	42.0	29.6	35.7	16	11.7	10.3	9.7								
6	0-15cm	0.72	0.64	0.74	0.75	1.3	0.86	1.29	0.48	92.0	85.0	78.6	69.5	22.4	20	19.0	16.9								
	15-30cm	0.08	0.03	0.05	0.02	0.6	0.62	0.4	0.13	48.0	58.0	32.7	42.4	19.6	18.7	19.0	17.3								
7	0-15cm	0.83	0.31	0.43	0.83	2.4	1.74	2.04	1.05	126	116	93.0	94.5	29.7	24.4	22.5	20.1								
	15-30cm	0.06	0.06	0.05	0.064	0.6	0.52	0.31	0.1	72.3	48.0	54.7	41.6	20	21.7	20.2	19.2								
8	0-15cm	0.42	0.49	0.53	0.95	0.9	0.76	0.13	0.51	66.0	68.0	46.1	41.6	14.9	15.6	11.0	13.8								
	15-30cm	0.05	0.02	0.03	0.06	0.4	0.23	0.26	0.17	37.0	44.0	24.7	27.4	11.8	9.43	9.5	12.0								
Control 1	0-15cm	0.03	0.02	0.05	0.04	0.01	0.05	0.05	0.09	23.0	23.0	21.1	20.3	0.78	ND	0.94	0.02								
	15-30cm	ND	0	0.006	ND	0.02	0.03	0.03	0.01	16.0	7.8	13.4	15.0	0.1	1.31	0.06	ND								
Control 2	0-15cm	0.06	0.02	0.01	0.02	0.09	0.12	0.09	0.11	20.0	16.0	23.5	22.8	0.34	0.1	0.15	0.10								
	15-30cm	0.01	ND	ND	ND	0.02	0.04	0.06	0.04	19.0	16.0	14.9	13.0	0.98	0.56	0.20	0.01								

W=Wet season; D=Dry season

Continuing from Table 2. Seasonal variation of metals concentrations (mg kg-1 dry weight) in soils of the study area

Sites	Depth	Ni						Cu						V						Mn					
		2013		2014		2013		2014		2013		2014		2013		2014		2013		2014		2013		2014	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1	0-15cm	11	8.94	9.75	7.18	54.0	47.0	41.5	39.0	5.61	2.31	3.97	2.01	58.7	56.9	50.0	48.5								
	15-30cm	9.6	7.93	6.13	6.98	24.0	21.0	19.5	18.6	4.21	0.94	3.04	2.41	50.2	53.5	43.7	42.3								
2	0-15cm	13.7	11.9	10.45	10.54	42.0	40.0	39.7	43.0	7.32	3.59	7.16	2.23	67.4	53.7	53.6	51.4								
	15-30cm	10.5	9.02	8.89	7.93	32.0	29.0	19.9	25.7	4.23	0.36	4.04	0.52	46.7	25.7	37.0	32.5								
3	0-15cm	9.8	6.94	7.23	5.87	77.0	70.0	54.2	54.7	3.44	1.89	3.01	1.73	63.5	66.8	56.2	52.0								
	15-30cm	9.34	5.61	8.75	3.42	33.0	27.0	31.0	24.5	1.32	0.6	2.76	1.42	64.3	60.3	42.1	35.9								
4	0-15cm	16.5	11.6	12.3	9.65	62.0	59.0	41.6	39.1	5.82	3.26	3.42	2.41	96.4	98.6	57.0	68.7								
	15-30cm	10.9	11.8	9.05	10.65	46.0	36.0	29.9	17.9	2.34	1.42	3.06	0.95	63.9	60.4	40.4	48.0								
5	0-15cm	9.72	9.01	7.95	8.63	94.0	88.0	58.7	61.1	1.06	0.96	1.01	1.04	56.4	58.7	45.0	42.1								
	15-30cm	8.16	8.82	8.04	7.93	47.0	35.0	23.4	33.1	0.01	0.2	0.82	0.36	48.8	49.2	30.5	28.6								
6	0-15cm	23.7	20.1	18.64	17.34	59.0	43.0	30.8	28.0	1.7	2.14	1.95	1.64	58.7	48.9	42.9	40.7								
	15-30cm	20.6	16.7	15.45	13.52	34.0	34.0	17.6	12.8	0.89	0.31	1.21	0.96	40.4	38.6	27.2	31.3								
7	0-15cm	17.4	15.7	13.04	10.63	49.0	41.0	29.5	19.5	5.03	5.09	3.12	2.94	98.7	64.6	61.0	54.7								
	15-30cm	15.4	14.2	10.62	11.49	38.0	31.0	15.9	9.4	4.86	3.94	3.31	3.01	54.9	38.8	45.6	29.3								
8	0-15cm	7.41	7.09	8.64	8.31	52.0	46.0	42.0	33.3	3.01	2.54	2.41	1.06	39.6	30.0	42.3	32.1								
	15-30cm	7.03	6.44	7.97	7.52	29.0	33.0	27.8	11.8	1.97	0.95	0.85	1.23	31.0	20.4	26.7	18.5								
Control 1	0-15cm	1.21	0.12	1.14	0.18	10.0	13.0	9.6	11.4	0.18	0.26	0.11	0.47	13.6	9.9	11.8	7.1								
	15-30cm	2.09	0.91	1.01	0.9	12.0	12.0	9.2	10.8	0.0	0.23	0.003	0.13	8.4	6.7	6.6	4.4								
Control 2	0-15cm	0.47	0.42	0.09	0.49	11.0	11.0	10.3	11.6	0.26	0.19	0.07	0.19	15.2	11.4	12.3	8.6								
	15-30cm	1.18	1.06	1.02	1.01	9.0	7.9	8.3	8.6	0.04	0.07	ND	0.04	9.6	5.0	6.7	3..23								

W=Wet season; D=Dry season

Continuing from Table 2. Seasonal variation of metals concentrations (mg kg<sup>-1</sup> dry weight) in soils of the study area

Sites	Depth	Zn						Fe						TPH					
		2013		2014		2013		2014		2013		2014		2013		2014			
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W		
1	0-15cm	262	248	209	202.1	1031	968	956	764	128	113	106	98.7						
	15-30cm	211	197	196	183.3	976	697	634	514	79	67	75.5	59.0						
2	0-15cm	218	206	185	179.9	1207	1184	994	974	137	105	92.1	75.9						
	15-30cm	221	212	154	146.4	1053	3988	630	605	82	69	54.1	47.0						
3	0-15cm	249	203	192	178	843	706	594	474	175	138	125	110						
	15-30cm	236	187	185	160.5	758	643	502	387	91	99	78.3	67.2						
4	0-15cm	437	352	286	235.4	1463	1127	1194	1014	219	201	155	133						
	15-30cm	454	329	224	194	1211	948	1005	922	99	93.1	89.5	76.9						
5	0-15cm	214	202	195	175.6	764	678	646	532	113	101	89.7	84.9						
	15-30cm	219	207	186	159.8	501	587	574	398	69	63	43.1	39.1						
6	0-15cm	226	196	188	164.9	1125	797	973	903	154	139	128	94.4						
	15-30cm	233	206	151	148.5	853	534	730	848	83.5	79	71.9	58.2						
7	0-15cm	449	327	327	272.8	1583	1252	1208	994	231	215	138	115						
	15-30cm	433	354	274	238	1144	977	972	682	97.7	93	92.5	81.0						
8	0-15cm	133	120	104	84.75	698	683	627	601	108	96	68.0	51.8						
	15-30cm	129	128	87	72.63	487	503	483	548	58.3	52	38.3	30.7						
Control 1	0-15cm	33.1	30.6	28	32.75	79	69	54	56	12.9	11.6	10.3	13.9						
	15-30cm	32.6	31.3	19	24.02	74	57	50	42	8.01	7.93	6.7	9.5						
Control 2	0-15cm	27.3	25.4	26	20.57	82	84	65	59	9.35	10.2	8.4	12.7						
	15-30cm	28.9	22.8	21	18.42	64	73	56	44	9.03	9.64	7.7	11.2						

W=Wet season; D=Dry season

In this study, higher concentrations of metals were observed in the dry season than in the wet season, which may be influenced by the leaching action of rainwater during the wet season. Moreover, the elevated levels of metal during the dry season may be related to the fact that atmospheric deposition of metal-contaminated dust is highest during the dry season. This result is similar to that of Nwadinigwe et al. (2014) and Nwajei (2011), who also reported a higher concentration of metal during the dry than during the wet season. In this study, the distribution patterns of metals followed the order  $Fe > Zn > Mn > Pb > Cu > Cr > Ni > V > Cd > As$  in both seasons.

The concentrations of As ranged from 0.01 to 1.04 mg kg<sup>-1</sup> at all sites and depths and were lower than the DPR target value of 1.0 mg kg<sup>-1</sup> for As in soil (DPR, 2018). The concentration of As found in the impacted sites was higher than that found in the soils of oil fields in Nigeria (Iwegbue et al., 2006).

The concentration of Cd ranged from 0.02 to 2.8 mg kg<sup>-1</sup> at all sites and depths. The Cd contents found in these oil-impacted soils were above the DPR target value of 0.8 mg kg<sup>-1</sup> for Cd in soil. The Cd levels found in this study were comparable to the range of 0.05-3.01 mg kg<sup>-1</sup> (Iwegbue et al., 2009), < 0.2 mg kg<sup>-1</sup> (Osuji and Onojake, 2005), 2.2-11.0 mg kg<sup>-1</sup> (Fatoba et al., 2015), 0.10-0.18 mg kg<sup>-1</sup> (Bada and Olarinre, 2012), and 0.001-0.20 mg kg<sup>-1</sup> (Nwaichi et al., 2016) previously reported for crude oil-impacted soils in the Niger Delta of Nigeria.

The concentrations of Pb in the crude oil impacted sites varied from 24.7 to 723 mg kg<sup>-1</sup>. The concentrations of Pb decreased with depth during the two sampling periods. There were significant ( $P \leq 0.05$ ) spatial and seasonal differences in the concentrations of Pb in crude oil-impacted sites. The results of these studies indicated that the topsoil had a higher concentration of Pb than the subsoil, which may be attributed to the fact that most anthropogenic activities are typically restricted to the surface horizons. The concentration of Pb reported in this study exceeded the permissible limit of 0.35 mg kg<sup>-1</sup> set by FAO/WHO (2011). The concentrations of Pb in the majority of the sites exceeded the 85 mg kg<sup>-1</sup> maximum allowable concentration of Pb in soil (DPR, 2018). Pb concentrations in the range of 14.32 to 37.98 were found in soil contaminated with crude oil at Aboh-Abalagada, Delta State (Iwegbue et al., 2009). Osuji and Onojake (2004) reported Pb levels of 10.0 to 10.8 mg kg<sup>-1</sup> in soil samples collected 6 months after the Ebocha-8 oil spill in River State. Iwegbue et al. (2006) reported Pb levels of 2.0 to 58.0 mg kg<sup>-1</sup> in soils of an oil field in Delta State, Nigeria. The concentrations of Pb in soil profiles collected within a 30m distance of crude oil-contaminated sites were found to be 0.08 to 0.44 mg kg<sup>-1</sup>. The concentrations of Pb observed in these sites were higher than the concentration of Pb previously reported for some crude oil contaminated sites in the Niger Delta (Iwegbue et al., 2009; Iwegbue et al., 2006) but were similar to those values found in rural/urban soils under different land uses (Iwegbue, 2014) and in the vicinity of Shell Petroleum Development Company operating area (Nwajei, 2009). Pb concentrations above regulatory control limits call for concern, given the

toxicity and health effects associated with human exposure to Pb. Therefore, these sites need remediation to reduce the risk of human exposure to Pb.

The concentrations of Cr in the crude oil impacted site range from ND to 34.8 mg kg<sup>-1</sup>. The concentrations of Cr in the impacted sites were significantly higher ( $P \leq 0.05$ ) than those in the control sites. Particularly when exposed to moderate redox settings at a pH close to neutral, chromium exhibits little mobility. The adsorption of Cr<sup>6+</sup> diminishes as the pH rises. Cr<sup>6+</sup>, however, is harmful to biological systems (Hu et al., 2011). The concentrations of Cr in the crude oil-impacted sites were higher than the control site which suggests the impact of the oil spillage. The concentration of Cr reported in this study was higher than the permissible limit of 0.5 mg kg<sup>-1</sup> set by FAO/WHO (2011). The concentrations of Cr observed in these sites were below the maximum permissible limit of 100 mg kg<sup>-1</sup> specified by the DPR (2018). Iwegbue et al. (2006) reported Cr levels in the range of 1.0 to 62.0 mg kg<sup>-1</sup> in the soil of an oil field in the Niger Delta. Similarly, Iwegbue et al. (2009) found Cr concentrations of 2.19 to 44.07 mg kg<sup>-1</sup> in Delta State. Ikhajiagbe et al. (2014) found Cr concentrations, ranging from 0.09 to 2.19 mg kg<sup>-1</sup> in waste oil-polluted sites in the Benin metropolis. The concentrations of Cr in the present study correspond to the range reported for the crude oil impact zone in the Niger Delta (Iwegbue et al., 2006), but were lower than those reported for waste oil-impacted sites (Ikhajiagbe et al., 2014).

The concentration of Ni varied between 3.42 and 23.7 mg kg<sup>-1</sup>. There are no significant seasonal or temporal changes in the concentrations of Ni in the crude oil-impacted soil. There is a significant difference ( $P \leq 0.05$ ) in the concentrations of Ni observed between the control sites and those of the impacted sites. The concentration of Ni obtained in this study was above the maximum permissible limit set by FAO/WHO (0.20 mg kg<sup>-1</sup>). The concentration of Ni observed in the crude oil-impacted sites was below the Department of Petroleum Resources' maximum allowable limit of 35 mg kg<sup>-1</sup> for Ni in soil. A wide concentration range of nickel (Ni) has been reported for crude oil-impacted soils in the Niger Delta. Iwegbue et al. (2009) found Ni concentrations of 11.87 to 42.25 mg kg<sup>-1</sup> in crude oil-impacted soils. Osuji and Onojake (2004) reported Ni concentration in the range of 12.6 to 12.8 mg kg<sup>-1</sup> in soil samples collected 6 months after the Ebocha-8 oil spillage in the Niger Delta.

The concentrations of Cu in the crude oil impacted site range from 0.01 to 61.1 mg kg<sup>-1</sup>. Higher concentrations of Cu were observed during the dry season than during the wet season. The concentration of Cu obtained in this study were above the maximum permissible limit set by FAO/WHO (0.20 mg kg<sup>-1</sup>). The concentrations of Cu in the majority of sites during the first sampling period exceeded the 36 mg kg<sup>-1</sup> maximum allowable limit for Cu set by the Department of Petroleum Resources in soil (DPR, 2018). A wide range of Cu in soils has been reported in the literature. Osuji and Onojake (2004) reported lower Cu levels in the range of 4.1 to 5.2 mg kg<sup>-1</sup> in soil samples collected six months after the Ebocha-8 oil spillage in the Niger Delta, Nigeria. The concentrations of Cu found in this study were higher than those previously

reported for crude oil-impacted sites in the Niger Delta (Ideriah et al., 2013) but similar to the Cu concentration reported in soil in the Niger Delta (Aniekan et al., 2014). The concentrations of Cu in most of the samples were above the permissible limits of 36 mg kg<sup>-1</sup> set by DPR (2018).

The concentrations of V in the crude oil impacted soil ranged from ND to 7.32 mg kg<sup>-1</sup>. The mean concentration of manganese at the studied site ranged from 3.23 to 98.7 mg kg<sup>-1</sup> for the two sampling years. There is no guide specifying the permissible limit of vanadium in soil by the Nigerian regulatory authorities. However, the concentration of vanadium observed in these sites was generally higher in comparison with vanadium concentration observed in farm land in Ibeno (Nwadinigwe et al., 2014b), crude oil impacted sites (<0.2mgkg<sup>-1</sup>) in Nigeria (Osuji and Onoyake, 2004) but was comparable to vanadium levels reported for an oil field in the Niger Delta (Iwegbue et al., 2006).

High contents of Mn in soils are of concern due to the high mobility of Mn. It can be easily mobilized and contaminate water sources, such as surface and groundwater. Its precipitation and oxidation are more effective at higher pH values (Lloyd and Solomon, 2002). The concentrations of Mn in the crude oil impacted site range from 18.5 to 98.7 mg kg<sup>-1</sup>. The concentration of Mn reported in this study exceeded the permissible limit of 0.2 mg kg<sup>-1</sup> set by FAO/WHO (2011). However, the content of Mn in the soils was lower than the CAV of 850 mg kg<sup>-1</sup>. Nwadinigwe et al. (2014b) reported the mean concentrations of Mn in soil from farmland in Ibeno, Nigeria, as 9.66 to 10.37 mg kg<sup>-1</sup>. Iwegbue et al. (2006) reported Mn concentrations in the range of 12.3 to 539.4 mg kg<sup>-1</sup> in crude oil-impacted soil in Delta State. The concentrations of Mn observed in these sites were similar to the range reported for crude oil-impacted soil (2009) and in soil in the vicinity of Shell Development Company, Delta State (Nwajei, 2009).

The concentration of Zn during the study period varied from 18.42 to 454 mg kg<sup>-1</sup>. There are significant differences ( $P \leq 0.05$ ) in the spatial and seasonal characteristics of Zn in the impacted soils. The concentrations of Zn were higher than during the dry season than in the wet season and also higher in the first sampling year than in the second sampling year. Although zinc is essential for humans, animals, and plants, prolonged exposure to soil contaminated with zinc can cause a variety of toxicities and health problems, including anemia (Chibowski, 2000). The concentrations of Zn in all sites were above the regulatory control limit of Zn in soil, except for site 8 and control sites. The concentration of Zn reported in this study was higher than the permissible limit of 2.0 mg kg<sup>-1</sup> set by FAO/WHO (2011) and also higher than the values (4.47 to 49.55 mg kg<sup>-1</sup>) reported by Iwegbue et al. (2006) in crude oil contaminated soil at Abalagada in Delta State and Nwadinigwe et al. (2014b) who reported mean Zn concentrations of 0.066 mg kg<sup>-1</sup> in soil samples in farm lands in Ibeno coastal area, Nigeria.

Fe in the sites varied from 42 to 1583 mg kg<sup>-1</sup> for the sampling years. The concentration of Fe in the surface horizon was higher than that of the subsoil (15- 30 cm). There was a significant reduction in the mean concentration of Fe during the second sampling year. Iron has no specified

permissible limit in soil in the legislation of most countries. The concentration of Fe reported in this study exceeded the allowable limit of 5.0 mg kg<sup>-1</sup> set by FAO/WHO (2011). However, the crustal abundance value for Fe is 4.7% (47000 mg kg<sup>-1</sup>). The levels of Fe observed at the crude oil-impacted sites were far below the crustal abundance values. A wide concentration range of Fe has been reported in the literature for contaminated soils. For example, Iwegbue (2014) reported Fe concentrations of 4388.2 to 31891 mg kg<sup>-1</sup> under different land uses in the Niger Delta. Similarly, Iwegbue et al. (2015) reported Fe concentrations ranging from 58.0 to 257mg kg<sup>-1</sup> in soils around asphalt plants in Delta State. Nwadinigwe et al. (2014b) found mean Fe levels between 12.09 and 15.5 mg kg<sup>-1</sup> in soils of cropland in the Ibeno coastal area, Nigeria.

The quantifiable quantity of petroleum-based hydrocarbons in an environmental medium is known as total petroleum hydrocarbon, or TPH. It represents a large family of substances that originated from crude oil (Tse and Nwankwo, 2013). Total petroleum hydrocarbon (TPH) varied from 6.7 to 231 mg kg<sup>-1</sup>. Significant and apparent variability exists when the concentration of TPH on various sites and profiles is compared. The concentration of TPH decreased with depth in all sites. This signifies that higher TPH accumulates in the topsoil in relation to the subsoil. TPH was significantly ( $P < 0.05$ ) higher at the polluted sites compared with the control site within the two sampling years. The high TPH content in polluted sites confirms the presence of petroleum pollution. The level of TPH in the dry season was higher than in the wet season. This difference could be due to the higher temperature values in the dry season, which resulted in the melting of the sunken oil, causing it to resurface again at sites. The significant reduction in the concentration of TPH and heavy metals, during the second sampling year, may be attributed to the biodegradation process which is controlled not only by its speciation, changes in pH and salinity but also by unknown factors (Essienn et al., 2010). A similar range of mean TPH (104.5 mg kg<sup>-1</sup>) has been reported in soils impacted with crude oil in the Niger Delta (Iwegbue et al., 2007). Higher TPH content (317.43 mg kg<sup>-1</sup>) was also observed in Nigeria from Niger Delta soils (Aniekan et al., 2014); 1276 mg kg<sup>-1</sup> observed in crude oil spill site in Kpean community in Rivers State, Nigeria (Gighi et al., 2012), and 5251.99 mg kg<sup>-1</sup> recorded in soils impacted with petroleum in Olomoro, Delta State, Nigeria by Idodo-Umeh and Ogbeibu (2010). Although the initial concentration of hydrocarbon at the time of spillage was not known, natural degradation of the spilled oil by microbes over the period might have also affected the result of the amount of TPH recorded.

### 3.3 Assessment of the extent of pollution

#### 3.3.1 Contamination/Pollution Index

The contamination/pollution index (CPI) indicates the relationship between the measured concentration of metals in the soil and the background concentration (Lacutus, 2002). The computed CPIs are shown in Tables 3 and 4. The CPI of metals in the crude oil impacted soils indicates that the majority of the studied metals (Fe, Zn, Cu, Cr, V, Pb, and Ni) had CPI values greater than 16 in all sites and depths, indicating excessive pollution, while the CPI for As and Mn were < 1, indicating slight contamination.

Table 3. Contamination/pollution index of metals for the first sampling year

Location	Depth	Pb		Cu		Cd		Mn		Fe		Zn		Ni		Cr		V		As	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1	0-15cm	149	137	360	313	400	250	0.27	0.28	14.2	13.3	689	728	57.9	47.1	37.9	29.7	4.68	1.93	0.13	0.10
	15-30cm	83	68	160	140	200	240	0.26	0.24	13.4	9.6	547	586	50.5	41.7	27.1	24.4	3.51	0.78	0.05	0.03
2	0-15cm	159	151	280	267	150	130	0.26	0.32	16.6	16.3	572	606	72.1	62.6	24.0	21.0	6.10	2.99	0.14	0.09
	15-30cm	95	117	213	193	50	15	0.12	0.22	14.5	54.8	589	614	55.3	47.5	23.5	21.2	3.53	0.30	0.03	0.02
3	0-15cm	163	154	513	467	150	120	0.32	0.31	11.6	9.7	564	692	51.6	36.5	20.9	21.3	2.87	1.58	0.12	0.07
	15-30cm	71	75	220	180	50	40	0.29	0.31	10.4	8.8	519	656	49.2	29.5	15.2	17.8	1.10	0.50	0.01	0.01
4	0-15cm	181	166	413	393	700	520	0.47	0.46	20.1	15.5	978	1214	86.8	61.1	39.1	31.8	4.85	2.72	0.05	0.07
	15-30cm	146	80	307	240	300	283	0.29	0.31	16.6	13.0	914	1261	57.4	62.1	34.5	25.4	1.95	1.18	0.01	0.00
5	0-15cm	151	164	627	587	375	290	0.28	0.27	10.5	9.3	561	594	51.2	47.4	18.8	15.6	0.88	0.80	0.08	0.04
	15-30cm	64	71	313	233	25	255	0.24	0.23	6.9	8.1	575	608	42.9	46.4	18.0	13.1	0.01	0.17	0.01	0.01
6	0-15cm	156	144	393	287	325	215	0.28	0.28	15.5	11.0	544	628	124.7	105.8	25.2	22.5	1.42	1.78	0.09	0.08
	15-30cm	81	98	227	227	150	155	0.19	0.19	11.7	7.3	572	647	108.4	87.9	22.0	21.0	0.74	0.26	0.01	0.00
7	0-15cm	214	197	327	273	600	435	0.31	0.48	21.8	17.2	908	1247	91.6	82.6	33.4	27.4	4.19	4.24	0.11	0.04
	15-30cm	1225	81	253	207	150	130	0.19	0.26	15.7	13.4	983	1203	81.1	74.7	22.5	24.4	4.05	3.28	0.01	0.01
8	0-15cm	112	115	347	307	225	190	0.14	0.19	9.6	9.4	333	369	39.0	37.3	16.7	17.5	2.51	2.12	0.05	0.06
	15-30cm	63	75	193	220	100	58	0.10	0.15	6.7	6.9	356	358	37.0	33.9	13.3	10.6	1.64	0.79	0.01	0.00

Table 4. Contamination/pollution index of metals in the second sampling year

Location	Depth	Pb		Cu		Cd		Mn		Fe		Zn		Ni		Cr		V		As	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1	0-15cm	128	122	277	260	358	275	0.23	0.24	13.1	10.5	581	561	51.3	37.8	17.4	23.1	3.31	1.68	0.12	0.10
	15-30cm	66	66	130	124	53	130	0.20	0.21	8.7	7.1	546	509	32.3	36.7	17.6	20.1	2.53	2.01	0.00	0.00
2	0-15cm	140	112	265	287	160	208	0.25	0.26	13.7	13.4	513	500	55.0	55.5	20.6	21.3	5.97	1.86	0.06	0.04
	15-30cm	86	75	132	171	208	5	0.18	0.16	8.7	8.3	427	407	46.8	41.7	20.2	18.0	3.37	0.43	0.01	0.01
3	0-15cm	119	123	361	365	143	243	0.27	0.25	8.2	6.5	533	495	38.1	30.9	18.8	16.4	2.51	1.44	0.11	0.06
	15-30cm	65	48	206	163	53	60	0.20	0.17	6.9	5.3	514	446	46.1	18.0	16.9	11.7	2.30	1.18	0.00	0.00
4	0-15cm	160	122	277	260	550	608	0.27	0.33	16.4	13.9	795	654	64.9	50.8	31.1	24.8	2.85	2.01	0.04	0.06
	15-30cm	123	56	199	119	330	293	0.19	0.23	13.8	12.7	621	539	47.6	56.1	33.4	26.6	2.55	0.79	0.01	0.00
5	0-15cm	115	138	391	407	303	255	0.22	0.20	8.9	7.3	541	488	41.8	45.4	16.3	12.4	0.84	0.87	0.12	0.10
	15-30cm	50	61	156	220	140	208	0.15	0.14	7.9	5.5	518	444	42.3	41.7	11.6	10.9	0.68	0.30	0.01	0.00
6	0-15cm	133	118	206	187	323	120	0.21	0.20	13.4	12.4	521	458	98.1	91.3	21.3	19.0	1.63	1.37	0.10	0.10
	15-30cm	55	72	117	85	100	33	0.13	0.15	10.0	11.7	421	413	81.3	71.2	21.4	19.5	1.01	0.80	0.01	0.00
7	0-15cm	158	160	197	130	510	263	0.29	0.26	16.6	13.7	907	758	68.6	55.9	25.2	22.6	2.60	2.45	0.06	0.11
	15-30cm	93	70	106	62	78	25	0.22	0.14	13.4	9.4	762	661	55.9	60.5	22.7	21.6	2.76	2.51	0.01	0.01
8	0-15cm	78	71	280	222	33	128	0.20	0.15	8.6	8.3	288	235	45.5	43.7	12.4	15.4	2.01	0.88	0.07	0.12
	15-30cm	42	46	185	79	65	43	0.13	0.09	6.6	7.5	243	202	41.9	39.6	10.7	13.5	0.71	1.03	0.00	0.01

The CPI values for the metals did not show a remarkable seasonal difference. However, the CPI value for the metals during the second sampling year was lower than that obtained in the first sampling period. A similar range of CPI has been reported in contaminated environmental media (Etchie et al., 2011), while higher CPI values have been reported in polluted sediments (Fagbote and Olanipekun, 2010) and at an industrial contaminated site in Pakistan (Malik et al., 2010).

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

The  $I_{geo}$  values of the metals in the soils are shown in Tables 5 and 6 for the first and second sampling years, respectively. The  $I_{geo}$  sequence was as follows: Zn > Cu > Cd > Pb > Ni > Cr > Fe > V > As > Mn for both years. The  $I_{geo}$  of Cu, Cd, Zn, Ni, and Pb falls into  $I_{geo}$  class 7 (i.e., > 5) in both years, which indicates that the soils were extremely polluted with Cu, Cd, Zn, Ni, and Pb. However, the  $I_{geo}$  values of As, V, and Mn fall into  $I_{geo}$  class 1 (i.e., < 0), indicating that the soils were not polluted with As, V, and Mn at any site or depth in either year.

### 3.3.3 Enrichment factor

The computed enrichment factors (Er) for the studied metals are displayed in Tables 7 and 8. Heavy metal enrichment factors follow the order Pb > Cd > Zn > Cu > Cr > Ni > Mn > As > V for the two sampling years. Generally, the EF of metals was higher in the dry season than in the wet season. Also, higher EFS were obtained for the metals in the first sampling year compared with the second sampling year. As the EF values increase, the contributions of the anthropogenic origins also increase. Metal enrichment in these soils may be due to oil spills and related anthropogenic activities in this area.

### 3.3.4 Pollution load index (PLI)

PLI provides a comparative means of assessing site quality, where a value of PLI < 1 denotes perfection; PLI = 1 presents a baseline level of pollutant; and PLI > 1 indicates deteriorating site quality. The computed PLI for this study is shown in Tables 9 and 10. The pollution load index in the first year ranged from 5.72 to 30.8 and 0.00 to 24.8 for dry and wet seasons, respectively. While the PLI for the second year ranged from 6.48 to 21.7 and 6.02 to 19.6, corresponding to the dry and wet seasons, respectively. The PLI of most sites and depths was more than 1, indicating deteriorating site quality. The result of the pollution load index (PLI) also indicates that site 7 with PLI mean value of 30.8 and 23.1 for dry and wet season, respectively, in the first sampling year has the highest heavy metal load. In contrast, site 8 with a PLI mean value of 9.01 and 0.00 for the dry and wet seasons, respectively, the first sampling year recorded the least metal load.

### 3.3.5 Correlation Analysis

The 'Pearson's correlation coefficients of metals and TPH studied are shown in Tables 11 and 12. The results of the correlation analysis showed similar patterns between the parameters investigated in this study for the first and second years. In both years, a negative correlation was observed between pH and metals. This observation indicates that pH has no effect on metals in the soils. However, there was a strong positive correlation between TPH and metals in both years which indicate that TPH and metals originate

from the same anthropogenic source, such as oil spillage and associated activities. Also, there was positive strong correlation between Cu/Pb, Cd/Pb, Mn/Cd, Fe/Pb, Fe/Mn, Zn/Cd, Zn/Mn, Zn/Fe, Cr/Pb, Cr/Cd, Cr/Mn, Cr/Fe, Cr/Zn, V/Pb, V/Fe, V/Zn, V/Mn, As/Pb, As/Cu, and As/Mn. The correlation pattern of these metals in this study, observed in both years, suggests that they exist in the soils in the Fe and Mn oxide phases. This result agrees with that of Osam et al. (2011) who reported a positive correlation between TPH and metals at an oil-polluted site in Omoko, Nigeria.

Table 5. Geoaccumulation index of metals during the first sampling year

Location	Depth	Pb		Cu		Cd		Mn		Fe		Zn		Ni		Cr		V		As	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1	0-15cm	6.64	6.52	7.91	7.71	8.06	7.38	-2.41	-2.45	3.24	3.15	8.92	8.84	5.27	4.97	4.66	4.31	1.64	0.36	-3.50	-3.94
	15-30cm	5.79	5.50	6.74	6.54	7.06	7.32	-2.63	-2.54	3.16	2.68	8.61	8.51	5.07	4.80	4.17	4.02	1.23	-0.94	-5.00	-5.8
2	0-15cm	6.73	6.65	7.55	7.47	6.64	6.44	-2.21	-2.54	3.47	3.44	8.66	8.58	5.59	5.38	4.00	3.81	2.02	1.00	-3.47	-4.08
	15-30cm	5.98	6.29	7.15	7.01	5.06	3.32	-2.74	-3.60	3.27	5.19	8.68	8.62	5.20	4.98	3.97	3.82	1.23	-2.32	-5.85	-6.27
3	0-15cm	6.76	6.68	8.42	8.28	6.64	6.32	-2.29	-2.22	2.95	2.69	8.85	8.56	5.10	4.61	3.80	3.83	0.93	0.07	-3.63	-4.36
	15-30cm	5.57	5.64	7.20	6.91	5.06	4.74	-2.28	-2.37	2.80	2.56	8.77	8.44	5.03	4.30	3.34	3.57	-0.45	-1.59	-7.37	-7.0
4	0-15cm	6.92	6.79	8.11	8.04	8.87	8.44	-1.69	-1.66	3.75	3.37	9.66	9.35	5.86	5.35	4.70	4.41	1.69	0.86	-5.00	-4.36
	15-30cm	6.60	5.73	7.68	7.32	7.64	7.56	-2.29	-2.37	3.47	3.12	9.72	9.25	5.26	5.37	4.52	4.08	0.38	-0.34	-7.85	-10.2
5	0-15cm	6.65	6.78	8.71	8.61	7.97	7.60	-2.47	-2.41	2.81	2.64	8.63	8.55	5.09	4.98	3.65	3.38	-0.76	-0.91	-4.17	-5.17
	15-30cm	5.42	5.57	7.71	7.28	4.06	7.41	-2.68	-2.66	2.20	2.43	8.66	8.58	4.84	4.95	3.58	3.13	-7.49	-3.17	-7.17	-7.85
6	0-15cm	6.70	6.59	8.04	7.58	7.76	7.16	-2.41	-2.67	3.37	2.87	8.71	8.50	6.38	6.14	4.07	3.91	-0.08	0.25	-4.00	-4.17
	15-30cm	5.76	6.03	7.24	7.24	6.64	6.69	-2.95	-3.01	2.97	2.29	8.75	8.58	6.18	5.87	3.88	3.81	-1.02	-2.54	-7.17	-8.59
7	0-15cm	7.15	7.03	7.77	7.51	8.64	8.18	-1.66	-2.27	3.86	3.52	9.70	9.24	5.93	5.78	4.48	4.19	1.48	1.50	-3.80	-5.22
	15-30cm	9.68	5.76	7.40	7.11	6.64	6.44	-2.51	-3.01	3.39	3.16	9.65	9.36	5.76	5.64	3.91	4.02	1.43	1.13	-7.59	-7.59
8	0-15cm	6.22	6.26	7.85	7.68	7.23	6.99	-2.97	-3.38	2.68	2.65	7.95	7.80	4.70	4.64	3.48	3.55	0.74	0.50	-4.78	-4.56
	15-30cm	5.39	5.64	7.01	7.20	6.06	5.26	-3.33	-3.93	2.16	2.20	7.90	7.89	4.62	4.50	3.14	2.82	0.13	-0.92	-7.85	-9.17
<b>Mean</b>		<b>6.39</b>	<b>6.29</b>	<b>7.74</b>	<b>7.58</b>	<b>7.42</b>	<b>7.11</b>	<b>-2.41</b>	<b>-2.59</b>	<b>3.17</b>	<b>3.22</b>	<b>8.97</b>	<b>8.74</b>	<b>5.47</b>	<b>5.23</b>	<b>4.03</b>	<b>3.83</b>	<b>0.87</b>	<b>0.07</b>	<b>-4.85</b>	<b>-5.22</b>

Table 6. Geoaccumulation index of metal during the second sampling year

Location	Depth	Pb		Cu		Cd		Mn		Fe		Zn		Ni		Cr		V		As	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1	0-15cm	6.42	6.35	7.53	7.44	7.90	7.52	-2.64	-2.68	3.13	2.81	8.60	8.55	5.10	4.66	3.54	3.94	1.14	0.16	-3.62	-3.96
	15-30cm	5.46	5.45	6.44	6.37	5.13	6.44	-2.83	-2.88	2.54	2.24	8.51	8.41	4.43	4.61	3.55	3.74	0.76	0.42	-8.59	-10.2
2	0-15cm	6.55	6.22	7.46	7.58	6.74	7.11	-2.54	-2.60	3.19	3.16	8.42	8.38	5.20	5.21	3.78	3.83	1.99	0.31	-4.68	-5.36
	15-30cm	5.83	5.65	6.47	6.84	7.11	1.74	-3.07	-3.26	2.53	2.47	8.15	8.08	4.96	4.80	3.75	3.58	1.17	-1.79	-8.17	-7.85
3	0-15cm	6.31	6.36	7.91	7.93	6.57	7.34	-2.47	-2.58	2.45	2.12	8.47	8.37	4.67	4.36	3.65	3.46	0.74	-0.06	-3.80	-4.65
	15-30cm	5.44	5.01	7.11	6.77	5.13	5.32	-2.89	-3.12	2.20	1.83	8.42	8.22	4.94	3.59	3.50	2.96	0.62	-0.34	-9.17	-10.2
4	0-15cm	6.73	6.35	7.53	7.44	8.52	8.66	-2.45	-2.18	3.45	3.22	9.05	8.77	5.44	5.08	4.37	4.05	0.93	0.42	-5.27	-4.68
	15-30cm	6.36	5.23	7.06	6.32	7.78	7.61	-2.95	-2.70	3.20	3.08	8.70	8.49	4.99	5.22	4.48	4.15	0.77	-0.92	-7.59	-10.2
5	0-15cm	6.27	6.52	8.03	8.09	7.66	7.41	-2.79	-2.89	2.57	2.29	8.50	8.35	4.80	4.92	3.44	3.05	-0.83	-0.79	-3.66	-3.96
	15-30cm	5.06	5.34	6.70	7.20	6.54	7.11	-3.35	-3.44	2.40	1.87	8.43	8.21	4.82	4.80	2.95	2.86	-1.13	-2.32	-8.17	-8.59
6	0-15cm	6.47	6.30	7.10	6.96	7.75	6.32	-2.86	-2.94	3.16	3.05	8.44	8.26	6.03	5.93	3.83	3.66	0.12	-0.13	-3.96	-3.94
	15-30cm	5.21	5.58	6.29	5.83	6.06	4.44	-3.52	-3.32	2.74	2.96	8.13	8.10	5.76	5.57	3.83	3.70	-0.57	-0.91	-7.85	-9.17
7	0-15cm	6.72	6.74	7.04	6.44	8.41	7.45	-2.35	-2.51	3.47	3.19	9.24	8.98	5.52	5.22	4.07	3.91	0.79	0.71	-4.75	-3.80
	15-30cm	5.95	5.55	6.15	5.38	5.69	4.06	-2.77	-3.41	3.15	2.64	8.99	8.78	5.22	5.33	3.92	3.85	0.88	0.74	-7.85	-7.49
8	0-15cm	5.70	5.56	7.55	7.21	4.44	6.41	-2.88	-3.28	2.52	2.46	7.59	7.29	4.92	4.87	3.05	3.36	0.42	-0.76	-4.44	-3.60
	15-30cm	4.80	4.95	6.95	5.72	5.44	4.82	-3.54	-4.07	2.14	2.33	7.34	7.07	4.81	4.72	2.84	3.17	-1.08	-0.55	-8.59	-7.59
<b>Mean</b>		<b>6.07</b>	<b>5.93</b>	<b>7.18</b>	<b>7.04</b>	<b>7.15</b>	<b>6.93</b>	<b>-2.83</b>	<b>-2.92</b>	<b>2.87</b>	<b>2.68</b>	<b>8.51</b>	<b>8.34</b>	<b>5.16</b>	<b>5.02</b>	<b>3.73</b>	<b>3.63</b>	<b>0.64</b>	<b>-0.15</b>	<b>-5.08</b>	<b>-4.89</b>

Table 7. Enrichment factor of As, Cd, Pb, Cr and Ni during the study period

Depth	As						Cd						Pb						Cr						Ni																	
	2013			2014			2013			2014			2013			2014			2013			2014			2013			2014														
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W														
1	0-15cm	3.58	2.8	3.55	3.5	248	162	234	226	201	196	186	222	171	14.2	8.48	14	7.44	6.38	7.05	6.5	15-30cm	1.33	1.09	0.17	0.07	130	216	52	158	119	136	144	177	12.9	16.3	12.9	6.8	7.87	6.68	9.38	
	0-15cm	3.12	2.08	1.64	1.04	72.7	68.8	101	133	182	177	196	159	9.2	8.2	9.6	10.2	7.85	6.95	7.27	7.48		15-30cm	0.69	0.14	0.23	0.3	28.3	2.4	207	5	124	40	188	172	10.4	2.5	14.9	13.8	6.89	1.56	9.76
3	0-15cm	3.99	2.87	5.05	3.51	113	106	150	320	267	301	277	360	11.6	14	14.7	16.1	8.09	6.79	8.41	8.55	15-30cm	0.33	0.51	0.14	0.09	49.6	39	65.5	97.1	129	160	180	173	9.3	12.8	15.7	14	8.51	6.03	12	6.1
	0-15cm	0.89	1.8	0.91	1.6	296	289	289	376	171	206	185	167	12.4	13.1	12.1	11.4	7.8	7.11	7.15	6.58		15-30cm	0.15	0.04	0.23	0.04	150	187	206	199	167	117	170	85	13.2	12.4	15.5	13.4	6.22	8.6	6.22
5	0-15cm	3.03	1.71	5.15	5.03	314	268	293	300	275	335	247	359	11.4	10.7	11.7	10.8	8.79	9.18	8.5	11.2	15-30cm	0.58	0.31	0.23	0.27	215	272	153	327	176	168	121	211	16.7	10.4	9.38	12.8	11.2	10.4	9.68	13.8
	0-15cm	2.31	2.9	2.75	3	182	169	208	83.3	193	250	190	181	10.4	13.1	10.2	9.8	14.6	17.4	13.2	13.3		15-30cm	0.34	0.2	0.25	0.09	108	182	85.9	24	134	253	105	118	12	18.3	13.6	10.7	16.7	21.6	14.6
7	0-15cm	1.9	0.9	1.29	3.02	234	218	264	165	188	219	181	223	9.8	10.2	9.7	10.5	7.6	8.67	7.46	7.39	15-30cm	0.19	0.22	0.02	0.34	87.6	83.4	50	23	149	117	132	143	9.1	11.6	10.8	14.7	9.3	10.1	7.55	11.6
	0-15cm	2.17	2.59	3.06	5.71	209	174	32.5	133	220	234	173	163	11.2	11.9	9.2	11.9	7.33	7.18	9.53	9.55		15-30cm	0.37	0.14	0.22	0.4	132	71.6	84.4	48.6	179	205	120	118	12.7	9.8	10.3	11.5	9.98	8.85	11.4
8	MIN	0.15	0.04	0.02	0.04	28.3	2.36	32.5	5.18	119	40	105	84.8	9.1	2.5	8.48	9.77	6.22	1.56	6.22	6.1	MEAN	3.99	2.9	5.15	5.71	314	289	293	376	275	335	277	360	17.1	18.3	15.7	18.1	16.7	21.6	14.6	13.8
	MEAN	1.56	1.27	1.56	1.75	161	157	155	164	180	195	175	189	11.8	11.9	11.8	12.7	9.07	9.04	9.16	9.31																					

Table 8. Enrichment factor of Cu, V, Mn and Zn during the study period

Sites	Depth	Cu						V						Mn						Zn															
		2013			2014			2013			2014			2013			2014			2013			2014												
		D	W		D	W		D	W		D	W		D	W		D	W		D	W		D	W											
1	0-15cm	54.6	50.2	45.4	53.4	1.97	0.86	1.5	0.95	3.15	3.25	2.89	3.51	126	127	108	131	15-30cm	25.4	31.3	32.1	37.7	1.56	0.49	1.73	1.69	2.84	4.24	3.81	4.54	107	140	153	176	
	0-15cm	36.6	35.8	41.7	46.1	2.19	1.1	2.6	0.83	3.09	2.51	2.98	2.92	89.4	86.4	91.9	91.3		15-30cm	31.6	7.8	33	44.3	1.45	0.03	2.32	0.31	2.45	0.36	3.25	2.97	104	26.3	121	120
3	0-15cm	94.9	104	95.3	120	1.48	0.97	1.83	1.32	4.16	5.23	5.23	6.07	146	143	160	186	15-30cm	45	45.1	64.4	66	0.63	0.34	1.99	1.33	4.69	5.18	4.63	5.13	154	143	182	205	
	0-15cm	44.5	54.3	36.4	40.2	1.44	1.05	1.04	0.86	3.64	4.84	2.64	3.75	148	154	119	115		15-30cm	39.4	40	31.1	20.3	0.7	0.54	1.1	0.37	2.92	3.52	2.22	2.88	185	172	110	104
5	0-15cm	128	135	94.9	120	0.5	0.51	0.57	0.71	4.08	4.79	3.85	4.37	139	147	149	163	15-30cm	97.2	62.1	42.6	86.8	0.01	0	0.52	0.33	5.37	4.63	2.94	3.98	216	174	160	199	
	0-15cm	54.4	57.3	33.1	32.4	0.55	0.97	0.72	0.66	2.89	3.4	2.44	2.49	99.4	122	95.3	90.4		15-30cm	41.7	66.7	25.2	15.7	0.38	0.21	0.6	0.41	2.62	4	2.06	2.04	135	191	103	86.7
7	0-15cm	32.8	34.2	25.5	20.5	1.15	1.47	0.93	1.07	3.45	2.85	2.79	3.04	140	129	134	136	15-30cm	34.7	33.7	17.1	14.3	1.54	1.46	1.23	1.59	2.65	2.2	2.6	2.37	187	179	140	173	
	0-15cm	77.3	70.8	70	57.9	1.56	1.34	1.39	0.64	3.14	2.43	3.73	2.95	94.2	87.2	81.8	69.7		15-30cm	63.3	68.5	60.2	22.5	1.46	0.68	0.64	0.81	3.52	2.25	3.06	1.87	127	89.5	65.6	
	MIN	25.4	7.8	17.1	14.3	0.01	0	0.52	0.31	2.45	0.36	2.06	1.87	89	26	81.8	65.6	MAX	128.5	135	95.3	120	2.19	1.47	2.6	1.69	5.37	5.23	5.23	6.07	216	191	182	205	
	MEAN	56.4	56.1	46.7	49.9	1.16	0.75	1.29	0.87	3.42	3.48	3.2	3.43	138	134	125	132		MEAN	56.4	56.1	46.7	49.9	1.16	0.75	1.29	0.87	3.42	3.48	3.2	3.43	138	134	125	132

Table 9. Pollution Load Index of metals during the first sampling year

Location	Depth	DRY SEASON											WET SEASON										
		Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	PLI	Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	PLI
1	0-15cm	149	360	400	0.28	14.2	728	57.9	37.9	4.68	0.13	24.7	137	313	250	0.27	13.3	689	47.1	29.7	1.93	0.1	19.3
	15-30cm	83	160	200	0.24	13.4	586	50.5	27.1	3.51	0.05	16.1	68	140	240	0.26	9.6	547	41.7	24.4	0.78	0.03	12.2
2	0-15cm	159	280	150	0.32	16.6	606	72.1	24	6.1	0.14	22.4	151	267	130	0.26	16.3	572	62.6	21	2.99	0.09	18.4
	15-30cm	95	213	50	0.22	14.5	614	55.3	23.5	3.53	0.03	13.9	117	193	15	0.12	54.8	589	47.5	21.2	0.3	0.02	9.77
3	0-15cm	163	513	150	0.31	11.6	692	51.6	20.9	2.87	0.12	20.3	154	467	120	0.32	9.7	564	36.5	21.3	1.58	0.07	16.3
	15-30cm	71	220	50	0.31	10.4	656	49.2	15.2	1.1	0.01	10.3	75	180	40	0.29	8.8	519	29.5	17.8	0.5	0.01	8.46
4	0-15cm	181	413	700	0.46	20.1	1214	86.8	39.1	4.85	0.05	29.4	166	393	520	0.47	15.5	978	61.1	31.8	2.72	0.07	24.8
	15-30cm	146	307	300	0.31	16.6	1261	57.4	34.5	1.95	0.01	17.9	80	240	283	0.29	13	914	62.1	25.4	1.18	0	0
5	0-15cm	151	627	375	0.27	10.5	594	51.2	18.8	0.88	0.08	18.2	164	587	290	0.28	9.3	561	47.4	15.6	0.8	0.04	15.8
	15-30cm	64	313	25	0.23	6.9	608	42.9	18	0.01	0.01	5.72	71	233	255	0.24	8.1	575	46.4	13.1	0.17	0.01	9.31
6	0-15cm	156	393	325	0.28	15.5	628	125	25.2	1.42	0.09	21.6	144	287	215	0.24	11	544	105.8	22.5	1.78	0.08	18.4
	15-30cm	81	227	150	0.19	11.7	647	108	22	0.74	0.01	12.1	98	227	155	0.19	7.3	572	87.9	21	0.26	0	0
7	0-15cm	214	327	600	0.48	21.8	1247	91.6	33.4	4.19	0.11	30.8	197	273	435	0.31	17.2	908	82.6	27.4	4.24	0.04	23.1
	15-30cm	122.5	253	150	0.26	15.7	1203	81.1	22.5	4.05	0.01	21	81	207	130	0.19	13.4	983	74.7	24.4	3.28	0.01	14.2
8	0-15cm	112	347	225	0.19	9.6	369	39	16.7	2.51	0.05	14.7	115	307	190	0.14	9.4	333	37.3	17.5	2.12	0.06	13.8
	15-30cm	63	193	100	0.15	6.7	358	37	13.3	1.64	0.01	9.01	75	220	58	0.1	6.9	356	33.9	10.6	0.79	0	0
<b>Mean</b>		<b>125</b>	<b>320</b>	<b>258</b>	<b>0.28</b>	<b>13.5</b>	<b>750</b>	<b>66.3</b>	<b>24.5</b>	<b>2.75</b>	<b>0.05</b>	<b>19.1</b>	<b>117</b>	<b>287</b>	<b>208</b>	<b>0.25</b>	<b>14</b>	<b>639</b>	<b>56.3</b>	<b>21.3</b>	<b>1.58</b>	<b>0.04</b>	<b>16.1</b>

Table 10. Pollution Load Index of metals during the second sampling year

Location	Depth	DRY SEASON											WET										
		Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	PLI	Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	PLI
1	0-15cm	128	276.9	357.5	0.241	13.1	580.6	51.3	17.45	3.31	0.12	19.6	122.4	260.2	275	0.23	10.5	561.3	37.79	23.07	1.68	0.1	16.7
	15-30cm	65.8	129.7	52.5	0.21	8.71	545.8	32.3	17.57	2.53	0	8.71	65.68	123.9	130	0.2	7.07	509.2	36.74	20.07	2.01	0	8.27
2	0-15cm	140	264.8	160	0.258	13.7	512.6	55	20.61	5.97	0.06	18.3	111.6	286.7	207.5	0.25	13.4	499.6	55.47	21.31	1.86	0.04	15.6
	15-30cm	85.6	132.5	207.5	0.178	8.65	427.1	46.8	20.17	3.37	0.01	11	75.08	171.2	5	0.16	8.32	406.5	41.74	17.99	0.43	0.01	6.11
3	0-15cm	119	361.3	142.5	0.271	8.17	532.6	38.1	18.82	2.51	0.11	16.4	123.2	364.7	242.5	0.25	6.52	494.6	30.89	16.45	1.44	0.06	14.4
	15-30cm	65.2	206.5	52.5	0.203	6.9	513.7	46.1	16.94	2.3	0	8.66	48.27	163.2	60	0.17	5.32	445.9	18	11.71	1.18	0	6.02
4	0-15cm	160	277.3	550	0.274	16.4	794.6	64.9	31.06	2.85	0.04	21.3	122.1	260.4	607.5	0.33	13.9	653.9	50.79	24.8	2.01	0.06	18.7
	15-30cm	123	199.4	330	0.195	13.8	621.4	47.6	33.43	2.55	0.01	14.6	56.41	119.5	292.5	0.23	12.7	538.8	56.05	26.57	0.79	0	9.29
5	0-15cm	115	391.3	302.5	0.217	8.88	540.9	41.8	16.31	0.84	0.12	15.8	137.7	407.1	255	0.2	7.32	487.6	45.42	12.43	0.87	0.1	14.7
	15-30cm	50.1	156.1	140	0.147	7.89	517.6	42.3	11.6	0.68	0.01	8.06	60.53	220.4	207.5	0.14	5.47	443.8	41.74	10.92	0.3	0	7.4
6	0-15cm	133	205.5	322.5	0.207	13.4	520.9	98.1	21.3	1.63	0.1	18.3	117.8	186.9	120	0.2	12.4	458.1	91.26	18.97	1.37	0.1	15.2
	15-30cm	55.4	117.2	100	0.131	10	420.8	81.3	21.39	1.01	0.01	9.15	71.88	85	32.5	0.15	11.7	412.6	71.16	19.46	0.8	0	7.27
7	0-15cm	158	196.7	510	0.294	16.6	907.4	68.6	25.24	2.6	0.06	21.7	160.2	130.1	262.5	0.26	13.7	757.7	55.95	22.55	2.45	0.11	19.6
	15-30cm	92.8	106.2	77.5	0.22	13.4	762.3	55.9	22.65	2.76	0.01	11.5	70.44	62.4	25	0.14	9.38	661.2	60.47	21.62	2.51	0.01	8.75
8	0-15cm	78.1	280.1	32.5	0.204	8.62	287.9	45.5	12.4	2.01	0.07	11.1	70.56	222.1	127.5	0.15	8.26	235.4	43.74	15.45	0.88	0.12	11.6
	15-30cm	41.9	185.3	65	0.129	6.63	242.5	41.9	10.72	0.71	0	6.48	46.44	78.8	42.5	0.09	7.53	201.8	39.58	13.52	1.03	0.01	6.24
Mean		101	218	212.5	0.211	10.9	545.6	53.6	19.89	2.34	0.04	15.2	91.27	196.7	182.5	0.2	9.59	485.6	48.63	18.54	1.35	0.05	13.4

A similar correlation pattern among metals in soils in the Niger Delta, Nigeria, was reported by Aniekan et al. [43].

**Table 11.** Correlation Analysis First Sampling Year, 2013

	Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	TPH	pH
Dry season												
Pb	1.00	0.60*	0.76**	0.80**	0.78**	0.59*	0.44	0.66*	0.55*	0.70**	0.88**	-0.72**
Cu		1.00	0.49	0.33	0.06	0.09	0.05	0.12	-0.08	0.53*	0.52*	-0.34
Cd			1.00	0.75**	0.64*	0.58*	0.38	0.74**	0.32	0.37	0.76**	-0.54*
Mn				1.00	0.81**	0.74**	0.38	0.67*	0.49	0.41	0.84**	-0.53*
Fe					1.00	0.78**	0.60*	0.81**	0.69*	0.36	0.77**	-0.56*
Zn						1.00	0.40	0.70**	0.36	-0.05	0.61*	-0.52*
Ni							1.00	0.39	0.13	0.18	0.58*	-0.44
Cr								1.00	0.58*	0.34	0.67*	-0.30
V									1.00	0.52*	0.47	-0.44
As										1.00	0.58*	-0.44
TPH											1.00	-0.64*
pH												1.00
Wet season												
Pb	1.00	0.67*	0.52*	0.49	0.16	0.26	0.33	0.43	0.61*	0.70**	0.76**	-0.77**
Cu		1.00	0.36	0.43	-0.17	0.02	-0.07	0.01	0.14	0.48	0.53*	-0.46
Cd			1.00	0.73**	-0.22	0.59*	0.32	0.57*	0.46	0.28	0.65*	-0.35
Mn				1.00	-0.21	0.57*	0.09	0.61*	0.34	0.40	0.82**	-0.30
Fe					1.00	0.14	0.00	0.20	-0.03	-0.02	-0.07	0.01
Zn						1.00	0.44	0.75**	0.55*	-0.04	0.64*	-0.05
Ni							1.00	0.40	0.40	0.11	0.36	-0.19
Cr								1.00	0.57*	0.42	0.76*	-0.40
V									1.00	0.47	0.65*	-0.59*
As										1.00	0.60*	-0.77**
TPH											1.00	-0.56*
pH												1.00

\*\*Pearson Correlation is significant at the 0.01 level (1-tailed)\*Pearson Correlation is significant at the 0.05 level (1-tailed)

**Table 12.** Correlation Analysis Second Sampling Year, 2014

	Pb	Cu	Cd	Mn	Fe	Zn	Ni	Cr	V	As	TPH	pH
Dry season												
Pb	1.00	0.49	0.83**	0.85**	0.83**	0.68*	0.37	0.66*	0.53*	0.58*	0.88**	-0.59*
Cu		1.00	0.30	0.51*	0.02	-0.01	-0.20	-0.06	0.08	0.82**	0.42	-0.17
Cd			1.00	0.57*	0.78**	0.68*	0.41	0.65*	0.15	0.38	0.74**	-0.43
Mn				1.00	0.63*	0.70**	0.06	0.44	0.59*	0.53*	0.84**	-0.64*
Fe					1.00	0.78**	0.56*	0.78**	0.46	0.19	0.75**	-0.64*
Zn						1.00	0.25	0.69*	0.28	0.07	0.73**	-0.63*
Ni							1.00	0.39	-0.04	0.14	0.47	-0.37
Cr								1.00	0.36	-0.09	0.64*	-0.27
V									1.00	0.10	0.31	-0.17
As										1.00	0.52*	-0.38
TPH											1.00	-0.64*
pH												1.00
Wet season												
Pb	1.00	0.58*	0.55*	0.70**	0.47	0.58*	0.25	0.29	0.45	0.75**	0.80**	-0.78**
Cu		1.00	0.50*	0.47	-0.13	0.04	-0.25	-0.23	-0.12	0.52*	0.40	-0.53*
Cd			1.00	0.85**	0.44	0.51*	-0.02	0.43	0.27	0.37	0.72**	-0.31
Mn				1.00	0.58*	0.68*	0.05	0.61*	0.49	0.39	0.88**	-0.52*
Fe					1.00	0.49	0.68*	0.82**	0.43	0.28	0.55*	-0.31
Zn						1.00	0.18	0.62*	0.69*	0.13	0.76**	-0.35
Ni							1.00	0.42	0.13	0.20	0.20	-0.10
Cr								1.00	0.54*	0.07	0.55*	-0.19
V									1.00	0.22	0.63*	-0.41
As										1.00	0.52*	-0.82**
TPH											1.00	-0.56*
pH												1.00

\*\*Pearson Correlation is significant at the 0.01 level (1-tailed)\*Pearson Correlation is significant at the 0.05 level (1-tailed)

3.5.6 Principal Component Analysis (PCA)

PCA is a reduction method that correlates attributes and identifies orthogonal linear recombinations of the attributes that summarize the principal sources of variability in the data (Kaplunovsky, 2004). PCA was used to determine the sources of metals in the soil impacted by crude oil. The factors obtained were rotated using a Varimax-normalized algorithm, which facilitates easy interpretation of the principal component loadings and maximization of the variance explained by the extracted components. The PCA results for metals in crude oil-impacted soils are displayed in Figures 2-5.

In the first year (dry season), three components or factors were extracted, accounting for 80.49% of the total variance. Factor 1 accounted for 57.48% of the total variance and was heavily dominated by Cd, Cr, NI, Mn, Zn, Fe, and TPH. The association of metals in the factor with TPH suggests that the concentration of these metals in the soil arises from the crude oil spillage. Additionally, this association indicates that Cd, Cr, Ni and Zn are present in the Fe-Mn oxides phase in the crude oil, and Zn are present in the Fe-Mn oxide phase of the crude oil. Furthermore, Zn is present in the Fe-Mn oxide phase of the crude oil-impacted soil. Factor 2 accounts for 13.80% of the total variance and has positive loadings in Pb, Cu and As. The factor indicates that Pb, Cu, and As in the impacted soil are from a common source. As and Cu pollution can result from agricultural activities such as the application of organic manure and pesticides. Factor 3 accounts for 9.21% of the total variance and was dominated by V. This indicates that the source of V in the crude oil-impacted soils was different from that of the other metals. In the wet season of the first sampling year, four components were extracted, accounting for 83.34% of the total variance. Factor 1 accounts for 44.94% of the total variance and has positive loadings for Cd, Cr, Mn, Zn, and TPH. This factor indicates that Cd, Cr, Mn, and Zn in these soils are associated with crude oil spillage. Factor 2 accounted for 17.44% of the total variance with high positive loadings in Pb, Cu, and As.

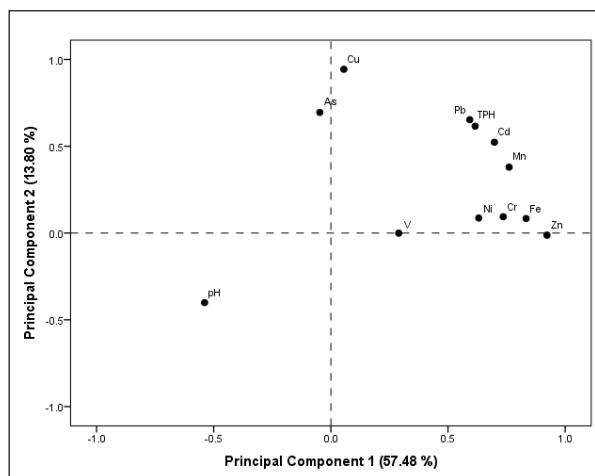


Figure 2. The loading plot of PCA of heavy metals for the first year in the dry season.

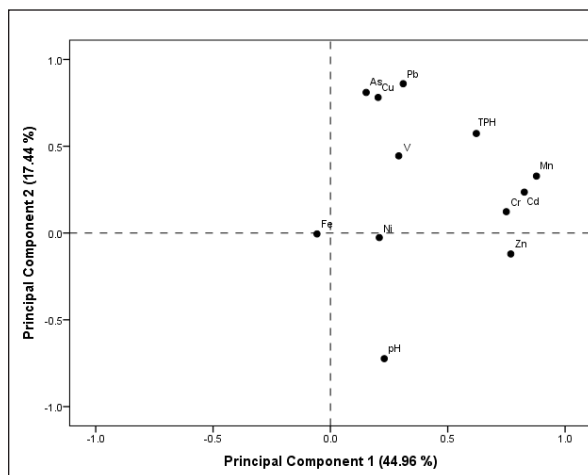


Figure 3. The loading plot of PCA of heavy metals for the first year in the wet season.

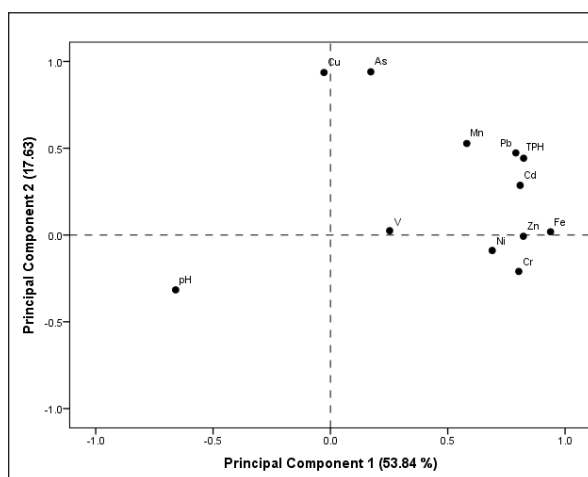


Figure 4. The loading plot of PCA of heavy metals for the second year in the dry season.

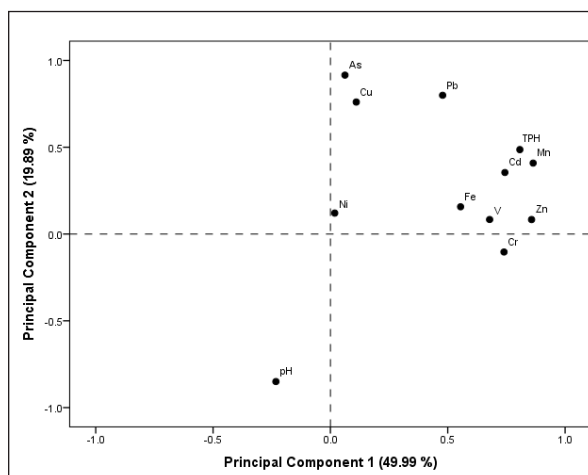


Figure 5. The loading plot of PCA of heavy metals for the second year in the wet season

The sources of Pb, Cu, and As have been previously described above. Factor 3 accounted for 11.39% of the total variance and was dominated by Ni and V. The Ni/V ratio has been used as an indicator for differentiating the origins of crude oil. Factor 4 accounted for 9.55% of the total variance





