DETERMINATION OF THE PHYSICO-CHEMICAL PROPERTIES AND SELECTED HEAVY METAL CONCENTRATIONS IN SOIL AROUND A KOLO CREEK OIL WELL HEAD IN BAYELSA STATE, NIGERIA

*[1]Nwakife, C. N., Ndamitso, [1]M. M., [1]Ajai, A. I., [2]Amadi, A. N., [3]Unique, N. K. and [4]Akoma, A. O.

*[1]Department of Chemistry, Federal University of Technology Minna
[2]Department of Geology, Federal University of Technology Minna
[3]Department of Biological Sciences, Federal University of Technology Minna
[4]Science Laboratory Technology, Federal Polytechnic, Bida

*Corresponding author's email: nkechi.nwakife@futminna.edu.ng

ABSTRACT

Environmental impact of crude oil exploration and exploitation has become worrisome leading to the discharge of toxic elements into the environment. Soil samples obtained from Kolo Creek oil well head 22T in Bayelsa State, Nigeria were analysed for their physico-chemical properties using standard analytical methods while the heavy metals (Co, Cr, Ni, Pb, Fe and Cu) were analysed using the Atomic Absorption Spectrophotometer (AAS). The results obtained for the physico-chemical properties such as pH, electrical conductivity and total organic carbon ranged from 7.70 ± 0.06 to 8.20 ± 0.06, 24.00 ± 0.58 to 37.00 ± 0.58 µS/cm and 0.28 ± 0.01 to 0.39 ± 0.01 % respectively while the selected heavy metal levels (in mg/kg) ranged from BDL to 9.67 ± 0.33 (Co), 12.33 ± 0.33 to 38.66 ± 0.88 (Cr), 11.33 ± 0.33 to 15.66 ± 0.33 (Ni), 31.33 ± 0.33 to 173.66 ± 0.33 (Pb), 15123.67 ± 0.33 to 24211.33 ± 0.33 (Fe) and 11.33 ± 0.88 to 21.33 ± 0.88 (Cu). These results showed that iron had the highest concentration while cobalt had the lowest. The levels of these heavy metals in this study area were below the DPR maximum allowable limits for these heavy metals in Nigeria soils. However, the amounts of lead in the top and middle soil were higher than the Department of Petroleum Resources (DPR) target value but lower than the intervention value. Hence, there is need for regular monitoring of the crude oil exploration activities in Bayelsa State to prevent direct discharge of untreated effluents containing heavy metals into the environment. Furthermore, constant maintenance of the oil pipelines and well heads to prevent corrosion is recommended to help avert this environmental menace.

Keywords: Oil exploration, Well head, Heavy metals, Environmental Menace

INTRODUCTION

Exploration and exploitation of crude oil have been on the increase in Nigeria since 1956 when it was first discovered at Oloibiri in Bayelsa State (Ahmadu and Egbodion, 2013; Adati, 2012). Nigeria has abundant crude oil and natural gas deposits and attempts to delve into it have left the nation with

unique vulnerabilities (Uzoekwe and Oghosanine, 2011; Nduka and Orisakwe, 2009). Thus this has resulted in environmental degradation. The Niger Delta environment has been subjected to massive destruction due to oil exploration resulting to crude oil products spillage and other effluents discharged from operational activities (Mohammed *et al.*, 2013; Adeniyi and Afolabi, 2002). Chindah and Braide (2000) asserted that oil spillages can cause great harm to the soil of the host communities due to high retention time of oil in the soil which occurs as a result of its limited flow. This prevents proper soil aeration, affects soil temperature, structure, nutrient status and pH, which ultimately leads to crops, animals and aquatic lives destruction.

Furthermore, crude oil is a complex mixture of polycyclic aromatic hydrocarbons (PAH) and other hydrocarbons which may be branched, normal or cycloalkanes. Others include the aromatics, the isoprenoids and the polar ones containing mainly oxygen, sulphur and/or nitrogen compounds. Non-hydrocarbon compounds may also be present and these include porphyrins and their derivatives (Onwurah *et al.*, 2007; Callot and Ocampo, 2000). The metals obtained in the crude oils are mostly nickel, vanadium, lead, magnesium, copper, sodium, iron, molybdenum, cadmium, barium, zinc, silver, manganese, titanium, antimony, chromium, uranium, cobalt, tin, aluminium, gallium and arsenic (Ngwadinigwe and Nworgu, 1999). In addition, trace metals may be introduced to the crude oil as pollutants during transportation from oil wells to processing sites and storage tanks. They may also be naturally associated with crude oil during the process of its formation (Uno *et al.*, 2013). The concentrations of Zn, Na, Fe, K, V, Ca, Ni, Mg and higher V/Ni ratio in some crude oils from Bonny, Yorla, Imo River, Brass and Elwa oil fields within the Niger Delta region have been reported by Ngwadinigwe and Nworgu (1999).

In view of the rapid urbanization and industrialization in Bayelsa State and its environment, crude oil polluted sites are prone to intense release of heavy metal via these activities which are detrimental to human beings in general (Olukunle, 2013). Soil and vegetation in the Niger Delta areas of Nigeria are affected by crude oil exploration and exploitation activities due to uncontrolled discharge of crude oil and its by-products (Oyem and Oyem, 2013). This results from operational errors, equipment failure, gas flaring and drilling of oil which affects the surrounding ecosystem (Adelana *et al.*, 2011). Studies have shown that high exploration activities increase the level of heavy metals in the environment and hence their toxicity (Asia *et al*, 2007). Among heavy metals lead, arsenic, nickel, chromium and cadmium are commonly considered as toxic to both plants and humans (Cheng *et al.*, 2006). The extent of soil pollution by heavy metals is very frightening (Chibuike and Obiora, 2014). It has been observed that the larger the urban area, the lower the quality of the environment (Eka and Udotong, 2003).

The exposure of a large population to toxic and non-biodegradable substances such as heavy metals has been reported to have high impact on human health and the ecosystem (Forsberg and Hans-Christen, 2005). Central nervous system destruction, cancers of various body organs and neurological disorders are some of the reported effects of human exposure to high dose of heavy metals (Alexander and Ubandoma, 2014; ATSDR, 1999). Severe mental retardation and low birth weight have been reported in some cases where the pregnant mother ingested high amounts of heavy

metals through direct or indirect consumption of fruits and vegetables (Mahaffey *et al.*, 1981). Airborne particulates and related trace metals have also been linked with both acute and chronic health effects which include heart diseases, lung cancer, respiratory diseases and damage to other organs (Wild *et al.*, 2009; Magas *et al.*, 2007; Prieditis and Adamson, 2002). Incessant crude oil spillage in the study area as evidenced in figure (1) below is associated with environmental degradation. This study is aimed at accessing the physico-chemical properties and the levels of the selected heavy metals in the soils around Kolo Creek oil well head 22T in Ogbia LGA, Bayelsa State so as to establish the contaminant status and compare them with the maximum allowable limits in order to establish the sustainability or otherwise of the environment.
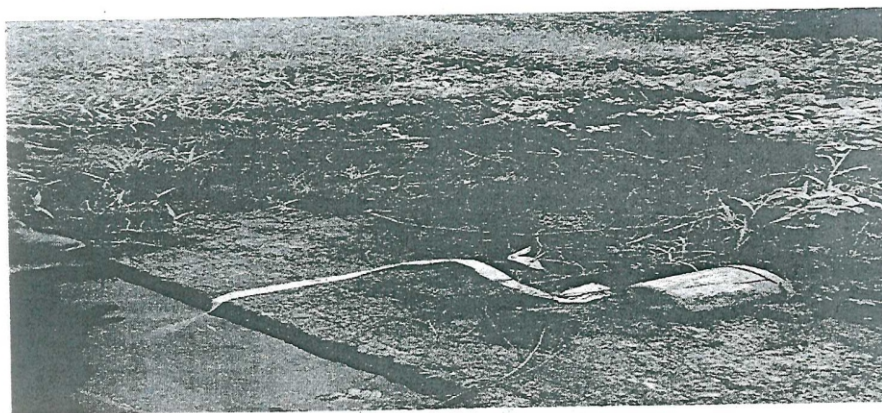

Figure 1: Crude Oil Spillage around Kolo Creek Oil Well Head 22T

MATERIALS AND METHODS

Description of the Study Area

Kolo Creek oil well head 22T located within Elebele community in Ogbia Local Government Area of Bayelsa State was chosen for this study. Bayelsa State is located within the Niger-Delta region of Nigeria. It is geographically located within Latitude 04°02ʹ 30ʺ N to 05°34ʹ 00ʺ N and longitude 05°32ʹ 30ʺ E to 06°33ʹ 30ʺ E. It shares boundaries with Delta State in the North, Rivers State in the East and the Atlantic Ocean in the West and South (BDIC, 2013).
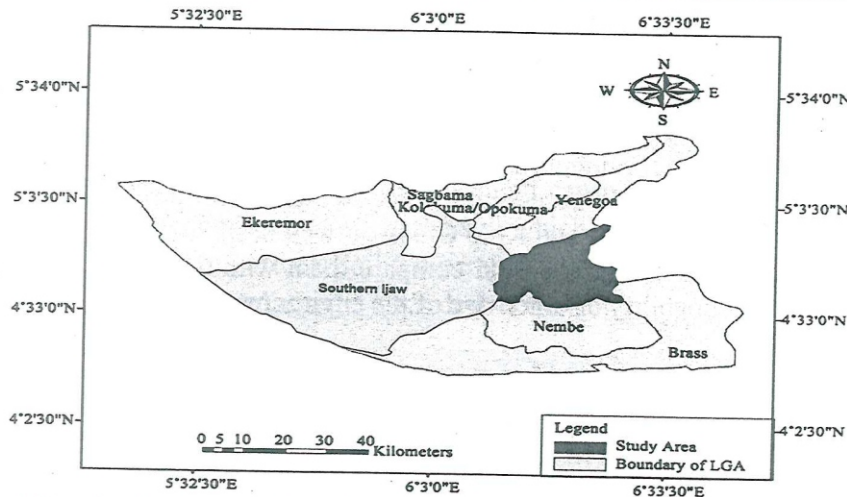
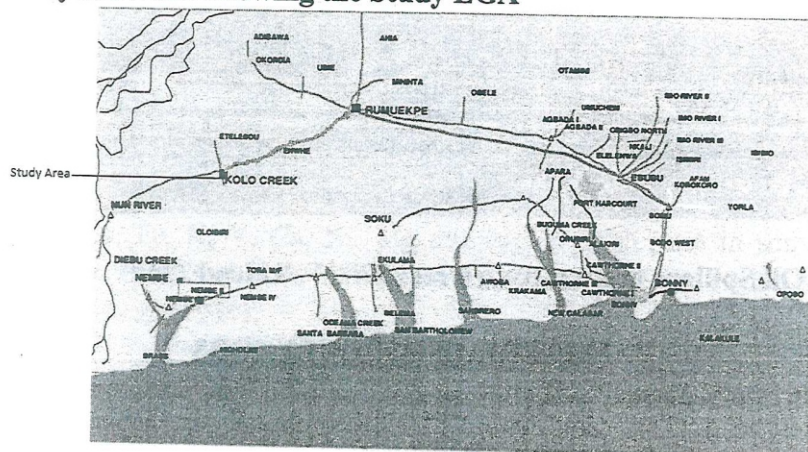Figure 2: Map of Bayelsa State Showing the Study LGA

Figure 3: Map of Study Area

Apparatus and Reagents

All the reagents used in this study were of analytical grades, the glass wares used were washed with 3.00 moldm^{-3} solution of HNO_3, rinsed with distilled water and air dried. Analysis of each heavy metal was carried out using the Atomic Absorption Spectrophotometer (AAS) model 210 VGD.

Table 1: List of Reagents used

Chemicals	Per cent (%) Purity	Manufacturer/Supplier
Conc. HNO_3	70%	BDH Limited, England
Conc. H_2SO_4	98.07%	E. MERCK, Darmstadt
Conc. HCl	35.5-37.5%	BDH Limited, England
H_2O_2	40%	E. MERCK, Darmstadt
$FeSO_4$	_____	KERMEL
$K_2Cr_2O_7$	_____	KERMEL

Sample Collection

Thirty-six (36) soil samples were collected from the four cardinal points around the oil well head at different distances (100 meters away) at 50 meters intervals between the sampling points and at three depths of 0-15 cm (top soil), 15-30 cm (middle soil) and 30-60 cm (bottom soil). The control samples were collected at a neutral point away from the oil well head. These were stored in clean polyethylene bags and transported to the laboratory.

Sample Preparation and Pre-treatment

The soil samples were air dried and were disaggregated into finely divided particles to increase the surface area laboratory mortar and pestle. After disaggregation, the soil samples were passed through a 2 mm sieve and further passed through a 45 μm sieve. 50.00 g of the 45 μm sized samples collected at four different cardinal points were weighed using an analytical weighing balance and then homogenised to obtain nine (9) composite soil samples. The composite samples were stored in polyethylene bags at 25°C prior to further analysis.

Soil Physico-Chemical Analysis

The soil samples were subjected to routine physico-chemical analysis using standard procedures as described for each of the physico-chemical parameters.

Determination of Soil pH

The pH measurement was determined using a 1:1 ratio of the soil sample to distilled water. This was achieved by weighing 10.00 g of the ground soil sample into a beaker after which 10.00 cm^3 of distilled water was added and the mixture stirred at regular intervals for about an hour. The pH of the soil sample was measured using a pH meter having glass-calomel electrode. Prior to the pH determination, the pH meter was calibrated using the prepared standard buffer solutions. The pH meter electrode was thoroughly rinsed with distilled water before and after immersing into each of the soil solution (Tijjani *et al.,* 2013).

Determination of Soil Electrical Conductivity

From the ground samples, 10.00 g of the soil was weighed into a beaker, 10.00 cm^3 of distilled water was added to the soil sample and the mixture stirred thoroughly for about an hour. The electrical conductivity of the soil suspension was measured at 25°C using a conductivity meter. The conductivity meter probe was thoroughly rinsed with distilled water before and after every reading (Tijjani *et al.,* 2013).
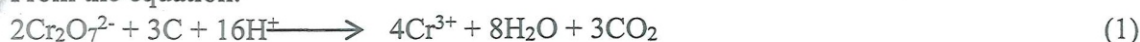
Determination of Total Organic Carbon

From the pre-treated soil sample, 1.00 g was weighed and transferred into a 250 cm^3 Erlenmeyer flask and 10.00 cm^3 of 1.00 moldm^{-3} K$_2$Cr$_2$O$_7$ was added, swirled gently to disperse the soil in the solution. To this mixture, 20.00 cm^3 of concentrated H$_2$SO$_4$ was added and the flask was immediately swirled to ensure thorough mixing. A thermometer was inserted into the flask and heated with the aid of a hot plate. The mixture was swirled over the hot plate until the thermometer reading attained a temperature of 135°C and was allowed to cool on an asbestos sheet in a fume cupboard. Two blanks were prepared in the same way to standardize the FeSO$_4$. After cooling for about 20-30 minutes, the mixture was diluted to 200.00 cm^3 with distilled water and titrated against 0.40 moldm^{-3} FeSO$_4$ solution. Three (3) drops of Ferroin indicator was added to the sample solution until dark green

on was obtained. At this end point, the iron(II) tetraoxosulphate(VI) solution was added in til the colour changed from blue-green to reddish-grey (Iyabo *et al.*, 2015).

alculation

From the equation:

$$2Cr_2O_7{}^{2-} + 3C + 16H^{\pm} \longrightarrow 4Cr^{3+} + 8H_2O + 3CO_2 \tag{1}$$

2 cm^3 of 1 M dichromate solution is equivalent to 3 mg of carbon

The percentage organic carbon (OC) was determined using the equation below:

$$OC\ (\%) = \frac{0.003\ g \times M \times 10\ cm^3 \times \left(1 - \frac{T}{s}\right) \times 100}{\text{weight of sample}} \tag{2}$$

Where:

M = concentration of $K_2Cr_2O_7$ solution in moldm^{-3}
T = volume of $FeSO_4$ used in sample titration (cm^3)
S = volume of $FeSO_4$ used in blank titration (cm^3)

Digestion of Soil Sample

The procedure recommended by Environmental Protection Agency (EPA, Method 3050B) was used as the conventional acid extraction method (US EPA, 1996).

With the aid of an analytical balance, 1.00 g of the soil sample was weighed into a 250 cm^3 beaker for digestion. The soil samples were, firstly, heated at 95°C with 10 cm^3 of 50 % HNO_3 without allowing it to boil. After cooling, it was refluxed with repeated addition of 65 % HNO_3 until no brown fumes were given off by the sample. Then the solution concentrated by reducing its volume to 5 cm^3 by evaporating on a water bath, then allowed to cool. After cooling, 10 cm^3 of 30 % H_2O_2 was added slowly and the mixture was refluxed with 10 cm^3 of 37 % HCl at 95°C for 15 minutes. The digest obtained was filtered through a No. 110 Whatman filter paper, diluted to 100 cm^3 in a volumetric flask with distilled water and transferred into a clean polyethylene container, capped and stored at 4°C for analysis.

Determination of Heavy Metal

The heavy metal concentrations of the various soil samples were determined using the Buck Scientific atomic absorption spectrophotometer, AAS, Model 210 VGP.

Data Analysis

The parameters were determined in triplicate and the results obtained were subjected to one way analysis of variance (ANOVA) at 95 % confidence level using the statistical software, SPSS.

RESULTS AND DISCUSSION

Table 2, shows the physico-chemical parameters of soil around Kolo Creek Oil Well Head 22T. The pH of the soil is a vital parameter that directly influences metals mobility. It also plays significant role in solute concentration and in sorption and desorption of contaminants in soil. The pH values of the samples ranged from 7.70 ± 0.06 to 8.20 ± 0.06 indicating slight alkalinity while the corresponding control samples were within the range of 6.70 ± 0.06 to 7.90 ± 0.06 indicating slightly acidic to slightly alkaline. The pH values are very close at each soil profile which may suggest that, all other factors being equal, pH effects on the metal's bioavailability is insignificant. These values were in the same range as that reported by Akpoveta et al. (2010); Osakwe and Otuya (2008), but higher than the values reported by Laurent et al.(2011); Tukura et al. (2007); Iwegbue et al.(2009); Oviasogie and Ofomaya (2007). Slight alkalinity in pH values observed in this study is common to reduced (anerobic) soils in the environment (Akpoveta et al., 2010). The range of pH values as was obtained in the study area was higher than the 4.8 ± 0.00 to 6.8 ± 0.00 range reported by Nduka and Orisakwe (2009) for some soils around Warri Refinery Petrochemical Company (WRPC) in Delta State. The top soils had lower pH values when compared with the sub soils which are consistent with work carried out at some industrial sites in Akure (Iyabo et al., 2015; Oguntimehin, 2002). The pH values increased from the top soil to the middle soil with a decrease from the middle to the bottom soil which is as a result of partial infiltration or leaching of the metal ions that lowers the pH value in the soil. The sampling points 1 and 2 of the top and bottom soils were not significantly different ($p\leq0.05$) but differed from those of the control. Soil serves as repository and has the ability to immobilise chemicals like heavy metal ions when deposited on it. The immobilisation of the heavy metals was mainly due to sorption properties which are determined by physico-chemical properties of the soil such as: amount of clay and organic matter, soil pH, water content, temperature of the soil and properties of the particular metal ion. Soil pH ultimately determines the amount of negatively-charged adsorption sites in many soil constituents, including Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. Thus, as pH increases (more alkaline), so does the amount of negatively charged sites, which in turn attracts the cationic metals. Over a relatively short range of pH from intermediate to alkaline, heavy metal adsorption increases from near zero to near complete adsorption. Soil pH also strongly controls precipitation of heavy metals, which occurs under alkaline conditions. Precipitation also effectively immobilizes heavy metals within a soil profile. This process was further explained by USDA which reported that alkaline soil pH (6.5 and above) decreases the mobility and bioavailability of cationic heavy metals such cadmium, mercury and lead in soils.

Table 2: Physico-Chemical Parameters of Soil around Kolo Creek Oil Well Head 22T

Parameters	Soil Profile	Sampling Points		
		Point 1	Point 2	Control
	TS	7.70 ± 0.06^a	7.70 ± 0.06^a	6.70 ± 0.06^b
pH	MS	8.20 ± 0.06^a	8.00 ± 0.06^b	$7.90\pm0,06^b$
	BS	7.90 ± 0.06^a	7.90 ± 0.06^a	7.50 ± 0.06^b

Conductivity µS/cm	TS	29.00 ± 0.58^b	37.00 ± 0.58^a	19.00 ± 0.58^c
	MS	26.00 ± 0.58^a	27.00 ± 0.58^a	16.00 ± 0.58^b
	BS	37.00 ± 0.58^a	24.00 ± 0.58^b	12.00 ± 0.58^c
TOC %	TS	0.39 ± 0.01^a	0.37 ± 0.01^a	0.27 ± 0.01^b
	MS	0.33 ± 0.01^a	0.30 ± 0.01^b	0.22 ± 0.01^c
	BS	0.31 ± 0.01^a	0.28 ± 0.01^a	0.20 ± 0.01^b

Key

BS = Bottom Soil, TS = Top Soil, MS = Middle Soil, TOC = Total Organic Carbon
All Values are Means ± Standard Errors of Triplicate Determinations
Values in the same rows having same superscript are not significantly different at $p\geq0.05$

The Electrical conductivity presented in Table 2 above ranged from 24.00 ± 0.58 to 37.00 ± 0.58 µS/cm while its corresponding controls ranged from 12.00 ± 0.58 to 19.00 ± 0.58 µS/cm. The electricity conductivity of a soil sample is due to the presence of ionic substance and soluble salts. High electrical conductivity will lead to toxic effect on the plants that are grown in the soil. However, in the present study, the electrical conductivity was low an indication of low concentration of the ionic substance and soluble salts. This low electrical conductivity can be adduced to the high rainfall in the region which causes dissolution or runoff of the soluble salts. The range of values obtained in this study are higher than the 12.67 to 12.91 µS/cm range reported by Cristiana et al. (2013) for some soil samples from the Navodari region of Romania but lower than the 108 to 201 µS/cm range of values reported by Akpoveta et al. (2010) for soil samples around metal scrap dumps in some parts of Delta State. The electrical conductivity values of the control soil samples could be as a result of the lower concentration of the soluble salt/metal ions in the control sampling point.

The total organic carbon (TOC) contents of the soil samples around the oil well head ranged from 0.28 ± 0.01 to 0.39 ± 0.01 % while the corresponding controls were from 0.20 ± 0.01 to 0.27 ± 0.01 % and this range is an indication of low organic matter content which will likely affect the ability of the soil to absorb heavy metals released to it through cation exchange and chelate formation (Kassir et al., 2011). Thus, heavy metals would be poorly bound to these soil surfaces thereby making them highly mobile and available for plant uptake and underground water contamination (Erick et al. 2013). The low values of TOC in the study area indeed reflect a depletion of this parameter by wastes which are indiscriminately disposed during the exploration and exploitation activities. The amounts of the TOC decreased down the soil profile. This is attributed to the fact that the top soil usually contains more plant residue and vegetation leading to greater plant productivity than lower layers of the soil. This range, however, compares favourably with the 0.38 to 0.54 % reported by Akpoveta et al. (2010) for soil samples around metal scrap dumps in some parts of Delta State but is lower than the 0.66 to 6.25 % reported by Kassir et al. (2011) for some contaminated soil zones in Baghdad. The TOC values for all the middle soils of all the sampling points were all significantly

different at 95 % confidence limit while the values for the top and bottom soils of sampling points 1 and 2 were not significantly different but differed from the control.

The results in table 3 showed that heavy metals were present in considerable amount in the soil. This is so because of the wide use of chemicals containing heavy metals being discharged into the environment as a result of petroleum exploration and production activities. The primary sources of the observed heavy metals were drilling fluids and pipe dope. Pipe dope is used to make up the drill string. Its purpose is to prevent damage to the threads of the drill pipe and it is almost always used in excess. The excess pipe dope is then washed into the drilling fluid as the well is drilled. Pipe dope generally has high concentrations of lead. Other sources of heavy metals in oil spills include: produced water, waste oils, air pollutants from combustion engines, completion fluids, drilling mud and drill cuttings. The drill cuttings produced from the formation are also covered with the drilling fluid containing heavy metals. Drilling mud contains a number of metals, including arsenic, cadmium, and lead.

The cobalt values of the samples ranged from BDL to 9.67 ± 0.33 mg/kg while those of the controls ranged from BDL to 5.00 ± 0.58 mg/kg. These values were lower than the DPR maximum allowable limits for cobalt in Nigeria soils. The low amount of cobalt can be said to have occurred as a result of leaching of the cobalt down into deeper soil horizons where it became inaccessible. It could also have been as a result of soil surface run-off which involves the removal of soil particles or sediment by flowing water, wind or raindrop splash. The highest cobalt value in this study (9.67 ± 0.33 mg/kg for the top soil) is lower than the highest value (10.54 mg/kg) reported by Akpoveta et al. (2010). For the top soil samples, the cobalt values increased with distance except that the control had the lowest value. The middle soil of this site had the cobalt content that was below the detection limit and the concentration of this metal at the bottom soil decreased with increase in the distance from the oil well head. The levels of cobalt in both the top and bottom soils respectively from this well head were not significantly different ($p \geq 0.05$) but differed from those of the control.

Table 3: Heavy Metal Contents (mg/kg) of Soil around Kolo Creek Oil Well Head 22T

Heavy Metals	Soil Profile	Sampling Points		
		Point 1	Point 2	Control
Co	TS	8.33 ± 0.33^a	9.67 ± 0.33^a	5.00 ± 0.58^b
	MS	BDL	BDL	BDL
	BS	7.67 ± 0.33^a	6.67 ± 0.33^a	1.00 ± 0.58^b
Cr	TS	31.33 ± 0.88^a	27.33 ± 0.33^b	7.67 ± 0.88^c
	MS	38.66 ± 0.88^a	15.33 ± 0.33^b	2.66 ± 0.33^c
	BS	25.33 ± 0.33^a	12.33 ± 0.33^b	2.33 ± 0.33^c
Ni	TS	14.67 ± 0.33^a	13.33 ± 0.33^b	3.67 ± 0.33^c
	MS	11.33 ± 0.33^b	15.66 ± 0.33^a	2.66 ± 0.33^c
	BS	11.33 ± 0.33^b	14.67 ± 0.67^a	4.67 ± 0.33^c

Pb	TS	132.67 ± 0.33^{a}	54.33 ± 0.33^{b}	10.33 ± 0.33^{c}
	MS	173.66 ± 0.33^{a}	31.33 ± 0.33^{b}	5.33 ± 0.66^{c}
	BS	63.33 ± 0.33^{a}	33.33 ± 0.67^{b}	7.33 ± 0.33^{c}
Fe	TS	18321.33 ± 0.33^{b}	24211.33 ± 0.33^{a}	7566.00 ± 1.00^{c}
	MS	15525.66 ± 0.33^{b}	19847.66 ± 0.33^{a}	8800.00 ± 0.00^{c}
	BS	21055.67 ± 0.88^{a}	15123.67 ± 0.33^{b}	7455.67 ± 0.67^{c}
Cu	TS	20.33 ± 0.88^{a}	14.67 ± 0.88^{b}	3.33 ± 0.33^{c}
	MS	21.33 ± 0.88^{a}	11.33 ± 0.88^{b}	2.33 ± 0.33^{c}
	BS	13.67 ± 0.88^{a}	11.33 ± 0.88^{a}	2.33 ± 0.33^{b}

Key

BS = Bottom Soil , TS = Top Soil, MS = Middle Soil, BDL = Below Detection Limit

All Values are Means ± Standard Errors of Triplicate Determinations

Values in the same rows having same superscript are not significantly different at $p\geq0.05$

The concentrations of chromium in soils as shown in Table 3 ranged from 12.33 ± 0.33 to 38.66 ± 0.88 mg/kg while those of the corresponding controls are from 2.33 ± 0.33 to 7.67 ± 0.88 mg/kg and these were found to be below the DPR maximum allowable limits for chromium in Nigeria soils. The amount of chromium presence could be as a result of water based muds which consist of natural clays, organic and inorganic additives for the achievement of proper density, viscosity and lubrication characteristics. Additives of particular pollution concern are those of Ferro chrome lignosulphate which tends to cause chromium pollution. The levels of chromium in this study were within the range of 1.30 to 165.00 mg/kg reported by Asia et al. (2007) for some soil samples from some oil producing communities in the Niger Delta. These values are higher than all the values reported by Cristiana et al. (2013) for soils in Navodari region. The highest chromium value of 38.66 ± 0.88 mg/kg obtained in this study is also higher than the 18.72 mg/kg reported for soil samples from Agbor by Akpoveta et al. (2010). The amounts of chromium in this study decreased with increase in the distance from the oil well head and were all significantly different at 95% confidence limit ($p\leq0.05$). The control had the least concentration although for samples from sampling point 2 and the control, the concentrations of this metal decreased down the soil profile. For sampling point 1, it was found to increase from top to the middle with a subsequent decrease at the bottom. This could be adduced to gradual infiltration into the sub soil.

Table 4: DPR Values of Maximum Allowable Limits for Heavy Metals in Soil used in Nigeria

Metals	Target value (mg/kg)	Intervention values (mg/kg)
Chromium	100.00	380.00
Copper	36.00	190.00
Lead	85.00	530.00
Nickel	35.00	210.00
Cobalt	20.00	240.00
Iron	—	—

Source: DPR Guidelines, 1991; Iyabo *et al., 2015*

The amounts of nickel for this site ranged from 11.33±0.33 to 15.66±0.33 mg/kg while its corresponding control samples ranged from 2.66±0.33 to 4.67±0.33 mg/kg. The observed amounts could be as a result of crude oil spillage which naturally contains variable concentrations of heavy metals, including vanadium and nickel (Ngwadinigwe and Nworgu, 1999). These values found in this study were, however, below the DPR maximum allowable limits for nickel in Nigeria soils. The contents of nickel in the control soil samples were the lowest because of its distance away from the source of anthropogenic activities. The top soils showed decrease in these values with increase in the distance from the oil well head which is due to the crude oil spillage around the oil well head. The range of values obtained in this study is higher than the 0.64 to 13.80 mg/kg nickel as given by Asia *et al.* (2007) for soil and ground water samples in the Niger Delta. The nickel concentrations in the samples are higher than the 3.10 to 5.12 mg/kg as reported by Akpoveta *et al.* (2010).

The amounts of lead in this study decreased with increase in distance at all points from the oil well head and were significantly different from one another. This could be due to the waste products from the use of chemicals like pipe lax, lube 106 and other lubricants like diesel oil which are used in the production of petroleum. The control had the lowest concentrations of this metal at all the sampling points indicating lower pollution of the soil in that vicinity. There was no regular variation in the concentrations of this metal down the soil profile. The lead concentrations in the soil as shown in Table 3 ranged from 31.33±0.33 to 173.66±0.33 mg/kg while those of the corresponding controls were from 5.33±0.66 to 10.33±0.33 mg/kg. When compared with the DPR maximum allowable limit for lead, it was found that the top soil and middle soil were above the target value although below the intervention value for lead in Nigeria soil which indicates that the soil in the vicinity was contaminated with lead. The highest lead concentration obtained in this study (173.66±0.33) is higher than the highest value (47. 88 mg/kg) reported for some soil in Navodari region by Cristiana *et al.* (2013) because lead are contained in paints used to protect equipment and in lube oil in the engines to run drilling and production equipment. This value is also higher when compared to the 99.4 mg/kg reported by Asia *et al.* (2007) for some soils and groundwater samples in the Niger Delta.

The concentrations of iron in this study calls for concern because of the relatively high values, it ranges from 15123.67±0.33 to 24211.33±0.33 mg/kg while the corresponding control samples were

from 7455.67±0.67 to 8800.00±0.00 mg/kg. Iron toxicity rarely creates problems in the field. Although the aquifers in the area is shallow and the iron could find its way to the groundwater thereby polluting it. Iron was found to have infiltrated up to the bottom soil. The high iron values of the samples in this study revealed that over the years there has been high accumulation of this metal since these values were much higher than 536.00 to 12872.00 mg/kg reported by Asia *et al.,* (2007). The contents of this iron in the top and middle soils were not regularly distributed but those of the bottom soil samples decreased with increase in the distance from the well head. These values differed significantly and the control samples had the lowest values. Down the profile, there was no regular variation of this metal except for samples from point 1 whose values decreased. The 1428 mg/kg iron content reported for soil samples from Abraka by Akpoveta *et al.* (2010) is lower than even the lowest value (15123.67±0.33 mg/kg) obtained in this study. However, the highest value of iron content (53130 mg/kg) of soil around the spoiled heap of an abandoned lead ore treatment plant in South East Congo-Brazzaville reported by Laurent *et al.* (2011) was higher than the highest value (24211.33±0.33 mg/kg) obtained in this study. These high iron contents of the samples in this study could be adduced to its natural occurrence in the soil, from chemical wastes such as D76 (weighting agent) which is one of the chemicals used for drilling operations, leaching of the rusted pipelines into the soil during run-offs or rainfall and iron contained in the laterite soil used in sand filling the waste pits after completion of the drilling operations (Asia *et al.*, 2007).

Copper is an essential element, but may be toxic to both humans and animals when its concentration exceeds the safe limits. The copper contents of the soil around Kolo Creek oil well head 22T ranged from 11.33±0.88 to 21.33±0.88 mg/kg while those of the corresponding controls were from 2.33±0.33 to 3.33±0.33 mg/kg. The results showed a low concentration of copper and were also below the acceptable limits set by DPR. This indicates that the study area was not polluted in terms of copper contamination. However, the amounts of copper as shown in Table 3 decreased with increase in distance from the oil well head indicating the presence of considerable amount of copper around the oil well head. The concentrations of this metal in the top and middle soils of all the sampling points were all significantly different while those of the bottom soils for sampling points 1 and 2 did not differ significantly. In all cases, control samples had the least values of this metal which were significantly different from those of the other points, an indication that the considerable amount was as a result of heavy metals being components of crude oil. Down the soil profile, the amounts of copper in sampling point 2 and the control decreased while those of sampling point 1 had no regular distribution pattern. Copper is generally higher in soil derived from igneous rocks and tends to be lower in extreme acid and alkaline soil. This range of values in this study was lower than the 24.221 to 51.396 mg/kg range reported for some soil samples from Navodari region by Cristiana *et al.* (2013) but higher than the 0.47 to 1.140 mg/kg range reported for soils around metal scrap dumps in some parts of Delta State by Akpoveta *et al.* (2010). The 90 to 210 mg/kg copper contents reported by Laurent *et al.* (2011) are higher than the values obtained in this study. Mwegoha and Kihampa (2010) reported that the amount of copper in some agricultural soils and water in Dares Salaam city, Tanzania ranged from 4.51±1.71 to 21.07±2.88 mg/kg and this range is almost the same as the range obtained in this study. However, the 2.20 to 6.60 mg/kg copper content of some soil

samples from highly industrialized Lagos environment as reported by Chimezie *et al.* (2013) is lower than the range of this metal obtained in this study.

CONCLUSION

It is evident that the heavy metals analysed were present in considerable amounts when compared with their corresponding control samples. This could have been induced by the direct discharge of toxic elements containing heavy metals into the environment during petroleum exploration, exploitation and production activities which involve the use of too many chemicals. However, these concentrations were below the DPR values of maximum allowable limits for heavy metals in soil used in Nigeria with the exception of lead in the top and middle soil which were higher than the target value but lower than the intervention value.

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