Evaluation of Crude Oil Contaminated Soils in Parts of Bayelsa State, Nigeria

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Abstract

The study evaluated crude oil contaminated soils in both central and eastern parts of Bayelsa State, Nigeria. Soil samples were collected by adopting a rectangular grid and drilling with the aid of a hand auger at the center (highest point of concentration) of the rectangle for proper representation of samples. Soil samples were collected at varying depths of top/bottom, 1m, 2m, and 3m, and were analyzed at Anal Concept Laboratory, Port Harcourt using standard methods as applicable. Results show acidity trend in all locations including control site with pH ranging from 3.6 to 4.9, except at ETE where a pH of 8.0 was obtained. Even this figure is slightly above the stipulated range of 6.0 to 7.0 pH for healthy plants growth. Mean values of EC range from 11us/cm to 59us/cm, whilst EC measurement at control location recorded very high value of 759us/cm showing negative influence of spill on soil nutrients. Seasonal variation was also noticed as mean EC levels dropped tremendously from 5.9 to 41.0us/cm during the wet season. Although HCO_3^{2-} and CO_3^- are not very important nutrients for soil because they react with soil calcium to form Ca(HCO3)2 or CaCO3., they act as organic matter stabilizers in calcareous soils. The result showed that both parameters had reduced concentrations for dry and wet seasons in all locations compared with control results of (4.1 and 2.0 mg/l) and (2.7 and 1.5 mg/l) for dry and wet seasons. SO_4^{2-} (mg/kg) values ranged from 2.0 to 14.0 mg/l in dry period and reduced further to 1.0 – 3.0mg/l in the wet season. Measurement in the control obtained a high level of 200 and 129mg/l for dry and wet season respectively. Chloride values ranged from 4.0 – 24mg/l for dry period and 2.0 – 9.0mg/l for wet period. Whilst control station recorded 31.0 and 62.0mg/l for wet and dry seasons respectively, depicting a drastic reduction in spill impacted areas. For organics, PAH recorded peak mean figure of 5.87mg/l at IKM top soil and a minimum mean value of 0.01mg/l at OTU top soil. PAH increased in concentration at different depths in all locations depicting a redistribution and infiltration of petroleum in the soil. On the contrary, OTU and IKM had very low values of PAH indicating low PAH concentration. Similarly, TPH peak for dry season was obtained at IkM T/B (539mg/l) followed by Orm 1-3 (318.26mg/l). But low levels were observed at ETE 1m and Oru 1-3m. The wet season had huge increase in concentration levels as maximum value of 2094.4mg/l was obtained at IKM T/B depicting crude redistribution aided by flood impact. High trend continued almost in all locations except for ETE 1 and ORU 1-3m. Cation such as Calcium showed increased concentration in the wet season at all locations, while, Na+, Mg2+ and K+ experienced drastic reduction during the wet season depicting dissolution on contact with water. For heavy metals, Arsenic recorded very low value of <0.01mg/l across the entire study area, Nickel had not much seasonal variations except for ETE 1 and ORM 1-3m where slight concentration levels were observed. Lead and Vanadium also behaved in similar manner as Ni2+ because increased levels were only encountered at ETE 1, ORM 1-3m and OTU 0-0.3m. On the contrary, Cadmium increased in levels at all locations in both seasons except for in ETE 1. Results from the control station also showed high values of 8.43mg/l and 4.57mg/l for Nickel and Lead respectively indicating natural existence of heavy metals in the earth which can be enhanced by anthropogenic activities. Deductions from the soil profile show predominance of sandstone across the study area indicative of high infiltration most likely the reason for the high level of crude oil observed in spill impacted samples.

Keywords: soils, contamination, crude oil, impacted area
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1. INTRODUCTION

Soil can be described as a collection of natural bodies on the earth's surface comprising of living matters which supports plants growth. The functions of soil depend largely on the features it possesses. Soil content is such that it comprises of mineral particles, organic matters, water and air which aids absorption and neutralization of pollutants into harmless substances through biochemical or chemical processes. Soil pollution occurs when the carrying capacity of a soil is exceeded. For instance, hydrocarbon spill blocks the air spaces between soil particles and destroys the fertility of the soil (Okiwelu, 2011). Soil pollutants are also capable of reducing soil water content, microorganisms and circulation of nutrients in the soil (Oliver, 2011).

The extent of migration of pollutants (that is, vertically or horizontally), is dependent on the soil porosity, ground slope and permeability (Abam, 2006). For instance, infiltration mechanism is a major determinant of subsurface water pollution because crude oil act as non-aqueous phase liquid (NAPLs) enabling the influence of air, water and oil migration in the vadose zone. According to Fingas (2004), evaporation is not strictly regulated by air boundary, but by temperature and time. The physical properties of soil that influence infiltration are soil texture, structure, consistency, Atterberg limit, colour, permeability and porosity. For example, soils in the Niger Delta area can be described as coarsening upward and comprising mainly of cretaceous sediments ranging from slight plasticity (inorganic silts) to high plasticity (organic clays) (Youdeowei et al., 2012). Grimaz et al (2007) attributes the extent of spill impact as a function of the following factors: surface spreading, evaporation and seepage mechanisms.

Sakshi *et al.* (2019) described "soil as a sink for a wide range of harmful pollutants and that these pollutants affect the physical, chemical, and biological properties of soil. They stated that soil is very sensitive to different contaminants, and it changes under different environmental conditions". Soil properties are affected by different activities happening on the land such as contaminants from heavy metals, crude oil spillage and leaking pipes.

Iyebor (2013) averred also that "soil fundamental functions are agricultural productivity, maintenance of environmental quality and provision of nutrients for plants, food for animals and human health". The capacity of the soil to carry out those crucial features describes its quality and health. Hence, Soil quality is the potential of a specific type of soil to function within natural or managed environment to preserve plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation (Iyebor, 2013; Karlen *et al.*, 1997). Samuel (2004) again, noted that soil or rock can be porous but quite impermeable, allowing the passage of small quantity of water. Expressing further, he explained pH as a key factor in determining the vulnerability of soil and groundwater to pollution. pH is a measure of the acidity or alkalinity in soils or water and defined it as the negative logarithm to base 10 of the movement of hydrogen ions (H^+) in solution with a scale of 0-14, with 7 being neutral. Accordingly, a pH below 7 is acidic while above 7 is basic. pH is considered as a key variable for soil as it affects the health, crop yields, crop suitability, plant nutrient availability, and the activity of soil microorganisms, which influences key soil processes (NRC, 2002). It specifically affects plant nutrient availability by controlling the chemical forms of the nutrients. The pH range for most plants is between 6.0 and 7.5. However, many plants have adapted to thrive at pH values outside this range.

Soukup *et al.* (2007) explained the important position soil texture plays in the migration of contaminants in the sub-surface. According to them, contaminants have the tendency to transport hastily through coarse-textured sands and gravel with high permeability and are concentrated in finer-textured silts and clays with low permeability. Stell (1998) claimed that clays and silts have higher floor location in step with unit quantity than coarse, greater permeable soils, contributing to better absorptivity of contaminants in clays. Van *et al.* (2001) noted that contaminants stick tightly to clay surfaces and hold securely to soil particles, contaminants are broken down by bacteria and other soil organisms and by means of chemical reactions with minerals and natural chemicals within the soil. According to Van *et al.* (2001), chemical and organic breakdown take place in loose cultivated surface layers where the soil tends to be warm, moist, high in organic matter and well aerated. They argued further that soil organic count is important in retaining contaminants. The implication of this is that soils with high organic matter provide an outstanding environment for chemical and biological breakdown of contaminants that reach groundwater level.

Genetically, soils are formed from weathering of rocks, their origin determine their composition, texture, structure and mechanical features. Genetically, soils are grouped into three; transported, residual and chemical/biological soils. Soil contamination can result from variety of factors, but the commonest are percolation from sanitary landfills, leakages from underground storage tanks, leachate and pesticides and oil spillage. In agriculture, petroleum pollutants retards soil fertility, the growth of forest trees and crops. Soil is regarded as the unit of agricultural environment in which the radical of planted seeds grows into plants. Although there are cases where the radical also survives in other units of the environment like air and water environment (breathing roots of mangrove plants and water or sea weeds respectively). Soil is a natural mineral which can be organic or inorganic forming a great part of the earth's surface. Little wonder some soil scientists reflects more on the composition, function and the formation processes of soils. They regard soil as a natural unconsolidated body of minerals and organic constituents that support plants growth and have properties in relation to the integrated effects of climate and living organisms acting on the parent material as conditioned by relief or topography over a long period of time. This may differ from the underlying materials in morphology (appearance), physical, chemical, biological and mineralogical properties as well as the way and manner it supports and reacts to plants growth.

Soil type depend largely on the composition (organic or inorganic) and can be differentiated by their separate nomenclatures such as loam, clay, sandy and silt naturally arranged or represented by the soil profile. It shows clearly various soil types and how they transform from one form to another following the action of pressure, temperature and varying climate over an extended period of time. Each soil type or sample has a standard mineral content as its natural embodiment aside introduction of alien substances as common soil pollutants. Idoniboye et al, (2003), stated that "oil pollution on land has far more hazardous impact on soil and microorganisms". The soil area affected by spill usually become oil bathed, the interstitial spaces of the soil becomes plugged which eventually prevents the diffusion of oxygen into the soil system and suffocates the soil. Inorganic processes under aerobiosis are halted preventing the generation of organic nutrients required by plants. Also, the dumping of radioactive materials on soil makes it potentially useless for the support of vegetation. These materials diffuse and permeate the soil to unimaginable depths depending on the potency of the waste materials and physical properties of the soil as earlier stated. Radioactive materials also affect living organisms in the soil.

The application of fertilizer during farming is another means that engender soil pollution. But due to population increase and high demand for food, fertilizers are still used for food production till date. Fertilizers and other chemicals like fungicides accompany run-off and subsequently get deposited as pollutants. Jansen et al. (1996) stated "sewage as another common soil pollutant". Nigeria lacks well-developed drilling waste treatment industries, commercial or governmentally operated incinerating plant, waste water treatment installations or sanitary land-fields. As a result, there are no proper disposal techniques and management of waste up till date. "Poor sanitary landfill practice contributes greatly to soil and groundwater pollution" (Akor et al, 2009). Soil plays a vital role by acting as sink for atmospheric pollutants. The heavy release of some dangerous fumes, affect the soil heavily which to an extent alters the physical composition of the soil in such areas. Effluents from machine parks and chemical stores alongside scrap metals constitute great level of contamination in soil, thus, altering its natural composition. Petroleum hydrocarbon exacts lasting effect on soils by manifesting in various forms like dissolution in water, absorption in soil solid particles and soil gas due to their low solubility characteristics. Other negative impacts of oil spill on soil include destruction of wild life, infertility in soil, pollution of host communities' ecosystem and destruction of the socio economy of the people.

2. DESCRIPTION OF STUDY AREA

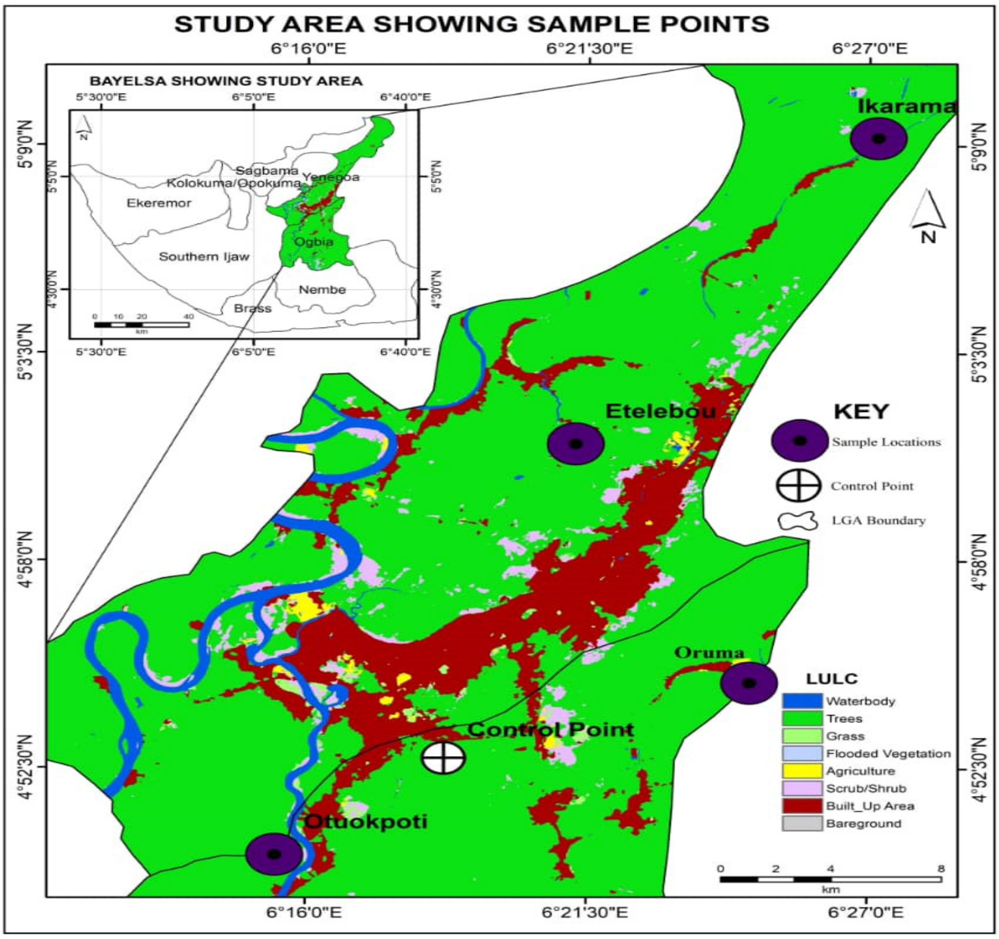


FIGURE 2.1: MAP OF STUDY AREA SHOWING SAMPLED LOCATIONS

Bayelsa state is situated at the southern part of Nigeria. It is in the center of the Niger Delta region, bordered on the west by Rivers State, on the east and south by Atlantic Ocean and on the north by Delta State. Bayelsa has one of the largest petroleum deposits in Nigeria as such, oil spill incidents are common occurrences in the area. Bayelsa is located within the inner delta plain and is composed of sedimentary deposits of the

Holocene and Quaternary periods. Bayelsa has many tributaries of River Niger hence, several changes still occur in terms of its geology till date. The Niger Delta which Bayelsa state is a part is composed of five (5) geomorphological units namely; Active abandoned beaches, Saltwater and mangrove swamps, Fresh water swamps, Dry deltaic plain and dry flat land and plain (Short and Stauble, 1966). Generally, Bayelsa has a relative humidity between 65-90% and a mean annual temperature of 25.7^{o}C. Its population as at the last national population census in 2006 is 1,704, 515 and 2,278,000 projected to 2021 at a growth rate of 3%.
This study was carried out in parts of Ogbia and Yenagoa Local Government areas:
(a) Ogbia Local Government Area is located at longitude 4^{0} 39’00”N and latitude 6^{0}16’00”E with a land area of 695km^{2} and a population of 179, 926. And the main occupation of the people is farming and fishing.
(b) Yenagoa Local government area is located at the central part of Bayelsa State at latitude 5^{o} 02’N and longitude 6^{o} 20’E. It has a land area of 1698km^{2}, an average annual rainfall of 2384.4mm, and mean annual evaporation of about 4.6mm per day.

3. RESEARCH DESIGN

The research is designed in such a way that sampling adequately represent the study area and the seasons the study was carried out. Soil sampling was done at two points in each location in order to obtain an average figure for both dry and wet seasons, also to evaluate temporal and spatial variation, and seasonal differences in spill impacted soils.

Two spill sites were sampled in Ogbia Local Government area namely Oruma (a.k.a Aya-ama) and Otuokpoti. Oruma (a.k.a Aya-ama) is situated along 16 Nun River-Kolo Creek pipeline and its coordinates are: 4 54’ 46.44’’N and 6 24’41.41’’E. The spill occurred in January 2020 due to Clamp failure (GIV records, Ministry of Environment, Bayelsa State). Otuokpoti location spill occurred in June 2018 during the flood as a result, the spread affected both farmlands and rivers around the area. Its coordinates are 4 50’58.84’’N 6 14’47.48’’E (Joint investigation report incident No: 2314360 JIV report S/N 0212). The report further showed that containment has been done in the location within the range of 0-0.3m depth and causative factor of spill was said to be clamp failure.

The two spill locations that were sampled in Yenagoa local government area are: Ikarama and Etelebou locations**.** Ikarama location is located along 14 Okordia-Rumuekpe pipeline. Its geographical coordinates are 5 9ˋ12.64¨N and 6 27ˋ10.33¨E. The spill occurred on the 28thof November, 2019 (GIV records, Ministry of Environment).Etelebou flow station is located along Gbaran-Kolo creek pipeline, few kilometers away from the Liquefied Natural Gas (L.N.G), Gbarain. Its geographical coordinates are 5 16’.03’’N and 621’16.0’ 0”E. The spill occurred on the 26th of August 2019 (Joint Investigation Report incident No: 2434200 JIV report S/N: 103012).

The control site was Bayelsa Palm, a government owned lowland estate located at the borders of Bayelsa state capital and its coordinates are 4 52’.46’’N and 6 18’.84’’E. The area can be described as intertwine of swamp and plain land. The selection of control location was done with consideration to its non-spill impacted nature, accessibility, safety, cost and proximity.

4. MATERIALS AND METHOD

4.1 SAMPLE COLLECTION

Soil samples were collected at intervals of 0 – 0.3m, 1m, 2m, and 3m (Fig 4.1). Polyethene bags were used for packaging of samples for physicochemical parameters before storing in ice-chest. Samples for the analysis of organics (PAHs and TPH) were collected in foil papers, properly wrapped and stored in the ice-chest. All samples were appropriately labelled indicating the location, date and time of sampling and the type and condition of the sample. On-site experimentation was conducted for soil parameters that changes quality at varying time and weather conditions such as pH and EC. Time interval in investigation (February - September) was done to observe spatial and temporal variation of natural attenuation processes in crude oil contaminated sites.

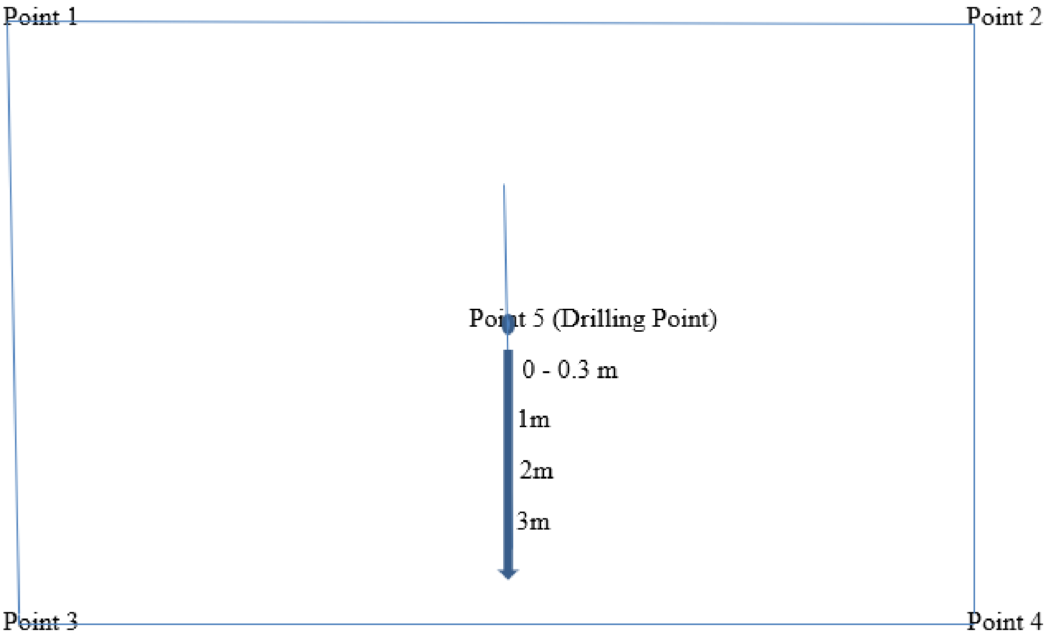


Figure 4.1: Illustration of Drilling Point and Sample Collection Method.

5. LABORATORY ANALYSIS

Laboratory analytical experimentation of soil samples was carried out at Anal concept in Port Harcourt. In order to obtain accurate and results and ensure data integrity, samples were sent to the laboratory within a period of 48 hours.

Soil pH determination was carried out with the aid of glass electrode, pH meter and reagents, 0.01M of calcium Chloride, distilled water and 1N of potassium chloride. The experiment involved the use of 1:1 ratio of soil to water mixture (APHA 1995).

Soil Sulphate (Turbidimetric method): A Bausch and Lomb Spectronic-70 Electrophoto-colorimeter was used and 10ml of sample aliquot pipette into 25ml volumetric flask. Distilled water was added to bring volume to approximately 20ml and 1ml of gelatin-$BaCl_2$ was again added to make up volume and mixed thoroughly, then allowed to stand for 30 minutes (AHPA, 1995).

Soil Nitrate Determination (APHA, 1995): Soil Nitrate Determination was prepared by dissolving 2.5g of brucine or brucine sulphate in 100 ml of glacial acetic acid and stored in the dark because of its highly toxic nature. Concentrated H_2SO_4 and standard NO_3^- were poured into 500ml of extracting solution with 0.5ml of chloroform added as a preservative with Nitrate standard solution diluted (0-2g NO_3^-N per ml). This procedure was done simultaneously with each set of soil extract and 1ml aliquot of standards solution. Transmittance of these solutions were measured and a calibration curve constructed by plotting on semi-log graph paper the transmittance against concentration. The scaled colorimeter was read directly in kg of NO_3^-N.

Determination of Soil Electrical Conductivity: Soil electrical conductivity was measured with the aid of a Conductivity Meter and Potassium Chloride as reagent. 0.7456g of dry KCL was dissolved in water then it was made it up to 1 litre at 25C. This is an electrical conductivity of 1413mhos/cm. It's related to the concentration of dissolved mineral salts. This provides a rapid and convenient means of estimating the concentration of electrolytes (APHA, 1995).)

Determination of Soil Chloride (Silver nitrate method): Reagents used include

(i.) Silver nitrate standard solution - Dissolve 4.791g Silver nitrate in water and dilute to 1 litre, store in a brown bottle (1.0ml = 0.1mg CI).

(ii.) Sodium chloride standard solution

(iii.) Potassium chromate indicator - Dissolve 5g K_2CrO_4 in 100ml water. Silver nitrate solution drop-wise was added to produce a light red precipitate of silver chromate and filter. Soil sample of 100ml was measured into a conical flask and a small amount of $CaCO_3$ was added and stirred. A separate portion of 0.1ml of HNOs was added to discharge the colour of Phenolphthalein. Appropriate quantity of HCl acid was added to the sample under test and stirred (APHA, 1995).

Determination of Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+ and Mn^{2+}) in Soil:

Required apparatus for this analysis include Centrifuge, 100-m volumetric flask, Flame photometer and Atomic Absorption Spectrophotometer and the used reagents include Acetic acid, glacial, NH_4OH (concentrated) and ammonium acetate solution. In pH7.0, was added 58ml of glacial acetic acid to about 600ml of distilled water in a 2-liter beaker. A concentrated NH_4OH of 70ml (specific gravity= 0.9) was added. The NH_4OH is best added under a fume hood through a long stemmed glass funnel so that it is introduced into the bottom or the acid solution. Solution was cooled or adjusted to pH 7.0 with acetic acid or NH_40H using a pH meter. The solution was transferred into a 1-liter volumetric flask, diluted to volume and mixed with Pyrex reagent bottle.

Determination of Heavy Metals in Soil: Determination of heavy metals in soil was done using AQUA-REGIA DIGESTION and FLAME ATOMIC ABSORPTION SPECTROMETRIC METHOD:

Soil sample of 5g of air-dried 2mm mesh size sieved soil was used for sample weighing, the sample was transferred into 100ml glass beaker. A mixture of 2ml of nitric acid, 6ml of hydrochloric acid, and about 20ml of distilled water was added to the soil sample. The mixture was heated and allowed to digest to 5ml then filtered into 50ml volumetric flask through filter paper fitted in filter funnels. Using a distilled water, the filtrate was made up to 50ml mark of volumetric flask followed by calibration of atomic absorption spectrophotometer using 0.5, 1.0, 2.0, 5.0, 10.0, and 100.0 mg/g (APHA, 1995).

Determination of TPH, and PAH in Soil:

Step 1: Extraction: “Soil sample weighing 2g was put into a clean extraction container, 20ml of extraction solvent (hexane) was then added into sample, mixed thoroughly and allowed to settle. The mixture was filtered carefully into solvent-rinsed extraction bottles using filter paper fitted into Buchner funnels. The extract was concentrated to 2ml and transferred for clean-up and separation” (APHA, 1995).

Step 2: Clean-Up and Separation: Glass wool measuring 1cm was placed at the bottom of 10mm internal diameter x 250 mm long chromatographic column. Activated slurry of 2g silica and 10ml dichloromethane was prepared and placed into chromatographic column with 0.5 cm of sodium sulphate added to top of the column and rinsed with additional 10ml of dichloromethane. The column was pre-eluted with 20ml of hexane and allowed to flow through for a period of time until the liquid in the column was just above sodium sulphate layer with1ml of extracted sample transferred into the column. Extraction bottle was rinsed with 1ml of hexane before adding dissolved extract. Eluent was collected using 10ml calibrated measuring cylinder by the opening of stop cork of the column.

Note: Before exposure of sodium sulphate layer to air, hexane was added to column in 1-2ml increments, accurately measured volume of 8-10ml of the eluent was collected and labelled aliphatices (TPH), poly aromatics (PAH) or volatile aromatics (BTEX) as applicable.

Step 3: Gas Chromatographic Analysis: “The concentrated aliphatic or aromatic fractions were transferred to labelled glass vials with rubber crimp caps for GC analysis. 1ul of the concentrated sample was injected by means of hypodermic syringe through a rubber septum. Separation occurred as vapour constituent separated gas and liquid phases. The sample was automatically detected as it emerged from the column by the FID detector whose response is dependent upon the composition of the vapour, hydrometer reading to compensate for the added dispersing agent” (APHA, 1995).

Soil sulphate, chloride and nitrate were determined using colorimetric method (APHA, 1995). Exchangeable cations such as Ca, Mg, K, and Na were determined with spectrophotometric method. Whilst, heavy metals were analyzed by adopting flame atomic absorption spectrophotometer. Organics (PAH and TPH) were analyzed through gas chromatography, permeability was determined using particle size distribution and moisture content of soil samples was done through continuous oven drying of samples in order to obtain a constant weight.

6. RESULTS AND DISCUSSSION

Table 6.1: Seasonal Variation in the Physicochemical Properties of Soil for Dry and Rainy Seasons

Parameters	**Dry season**		**Rainy season**		**Standard soil limit (DPR, 2018)**
	Mean $(\overline{X})$ (Control location)	**Mean $(\overline{X})$ (Impacted area)**	**Mean $(\overline{X})$ (Control location)**	**Mean $(\overline{X})$ (Impacted area)**	
pH	3.7	4.6 ± 1.0	4.3	4.8 ± 0.4	6.5-8.0
Conductivity (μS/cm)	758	33 ± 16	428	20.7 ± 14.8	-
Bicarbonate (mg/kg)	4.2	0.4 ± 0.1	2.5	1.4 ± 2.0	-
Carbonate (mg/kg)	2.3	0.3 ± 0.1	1.4	1.6 ± 2.7	-
Sulphate (mg/kg)	240	8 ± 5	133	1.3 ± 1.2	-
Nitrate (mg/kg)	2.5	0.7 ± 0.4	1.3	0.2 ± 0.2	-
Phosphate (mg/kg)	1.14	0.30 ± 0.09	0.55	0.17 ± 0.12	-
Chloride (mg/kg)	66	14 ± 9	29	5 ± 4	-
PAH (mg/kg)	0.04	1.52 ± 2.17	0.031	5.611 ± 11.452	1

TPH (mg/kg)	5.87	142.62 ± 12.17	3.94	505.13 ± 13.86	50
Sand (%)	63.68	74.02 ± 7.14	64.12	71.29 ± 5.33	-
Silt (%)	12.32	5.20 ± 2.71	11.4	5.11 ± 2.72	-
Clay (%)	24	20.78 ± 5.81	24.48	23.60 ± 3.85	-
Particle size distribution, (PSD)	CH	SS, LS, SL, CH, SC	CH	SL, CH, SC	-
Permeability (cm/s)	0.00018	0.00173 ± 0.00121	0.00015	0.00021 ± 0.00005	-
Water content (%)	46.8	24.9 ± 7.4	34.55	21.56 ± 6.99	-
Sodium (mg/kg)	165.6	129.7 ± 42.5	116.41	62.60 ± 13.17	-
Magnesium (mg/kg)	564.1	532.3 ± 107.3	204.6	112.7 ± 39.7	-
Calcium (mg/kg)	35.81	44.74 ± 9.16	335.98	431.39 ± 147.87	-
Potassium (mg/kg)	613.2	538.6 ± 148.9	362.2	201.3 ± 87.5	-
Lead (mg/kg)	18.5	12.4 ± 4.5	8.43	6.47 ± 5.05	0.05
Cadmium (mg/kg)	0.45	0.16 ± 0.11	0.5	0.5 ± 0.3	0.005
Nickel (mg/kg)	7.56	7.49 ± 2.85	4.57	6.22 ± 1.97	0.07
Vanadium (mg/kg)	0.36	0.35 ± 0.13	0.25	0.30 ± 0.09	-
Arsenic (mg/kg)	0	0 ± 0	0	0 ± 0	29

Graphical presentation of physiochemical parameters concentration in soil for dry and rainy seasons at sample locations namely; Elelebou (ETE), Ikarama (IKM), Oruma (ORU) and Otuokpoti (OTUO) is shown below:

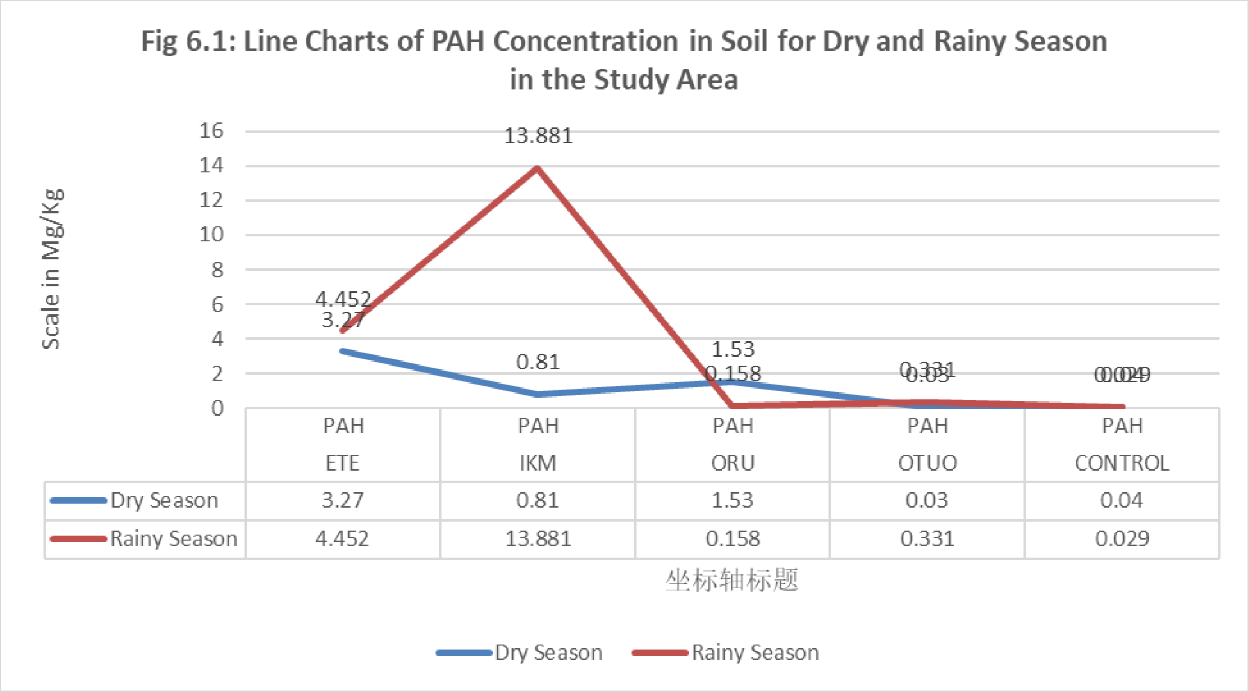


Fig 6.1: Line Charts of PAH Concentration in Soil for Dry and Rainy Season in the Study Area

Fig 6.2: Line charts of TPH concentration in soil for Dry and Rainy seasons in the study area

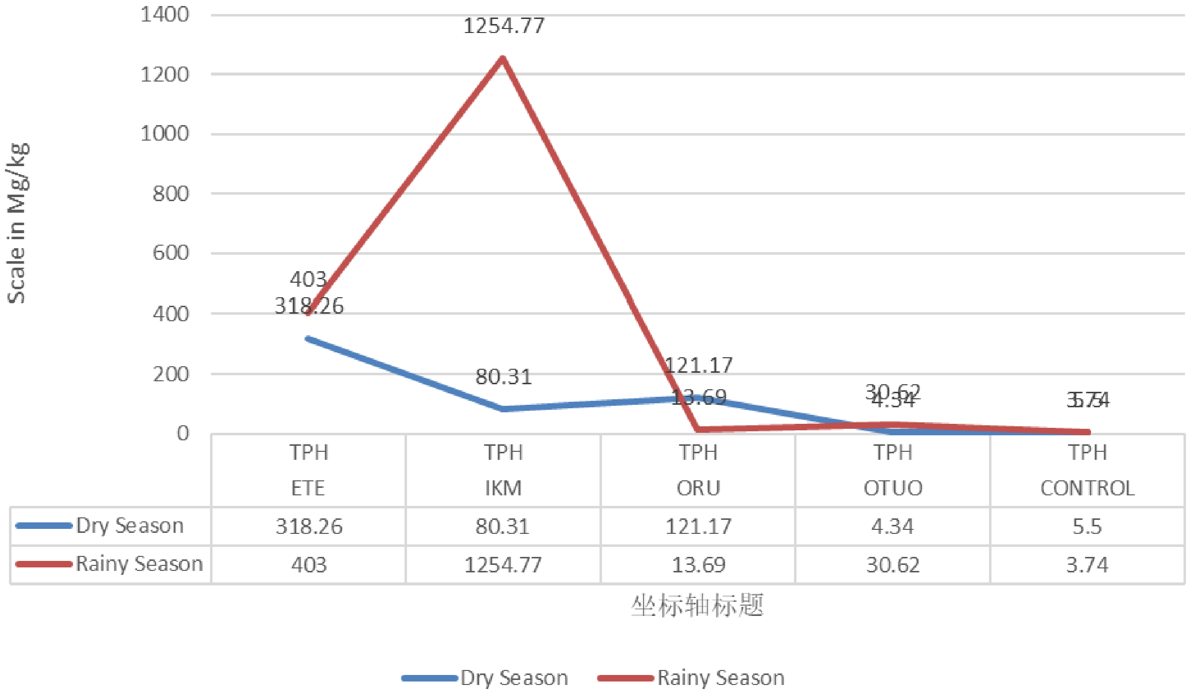
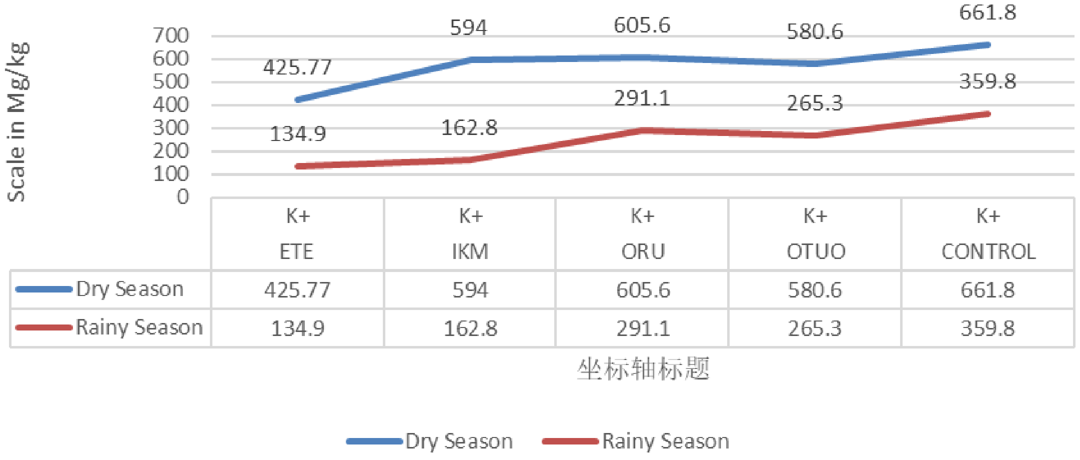


Fig 6.3: Line Charts of K+ concentration in soil for Dry and Rainy seasons in the Study Area



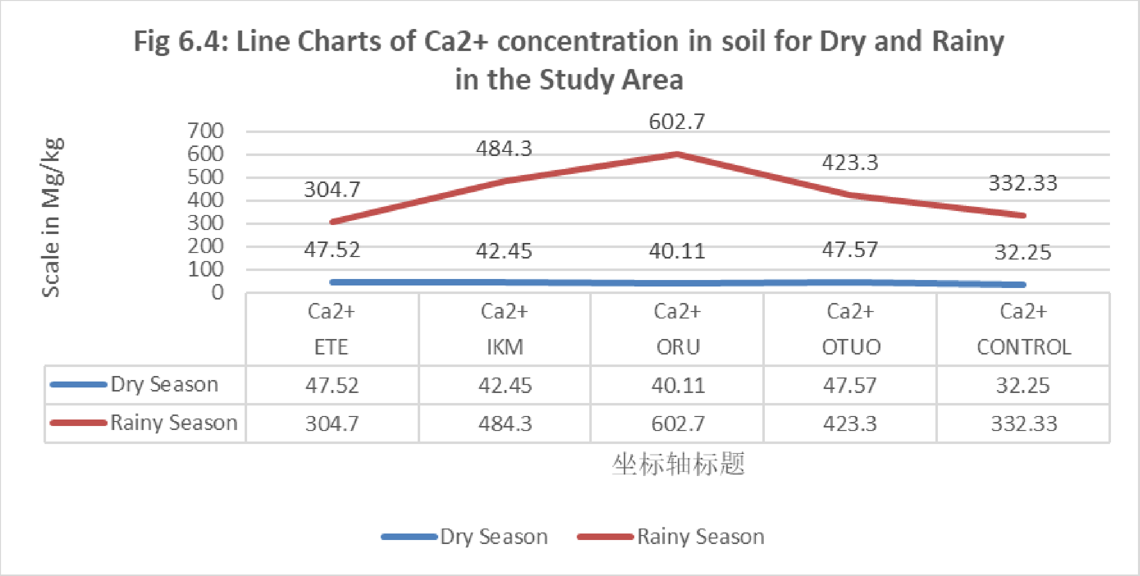


Fig 6.4: Line Charts of Ca2+ concentration in soil for Dry and Rainy in the Study Area

	Ca2+ ETE	Ca2+ IKM	Ca2+ ORU	Ca2+ OTUO	Ca2+ CONTROL
Dry Season	47.52	42.45	40.11	47.57	32.25
Rainy Season	304.7	484.3	602.7	423.3	332.33

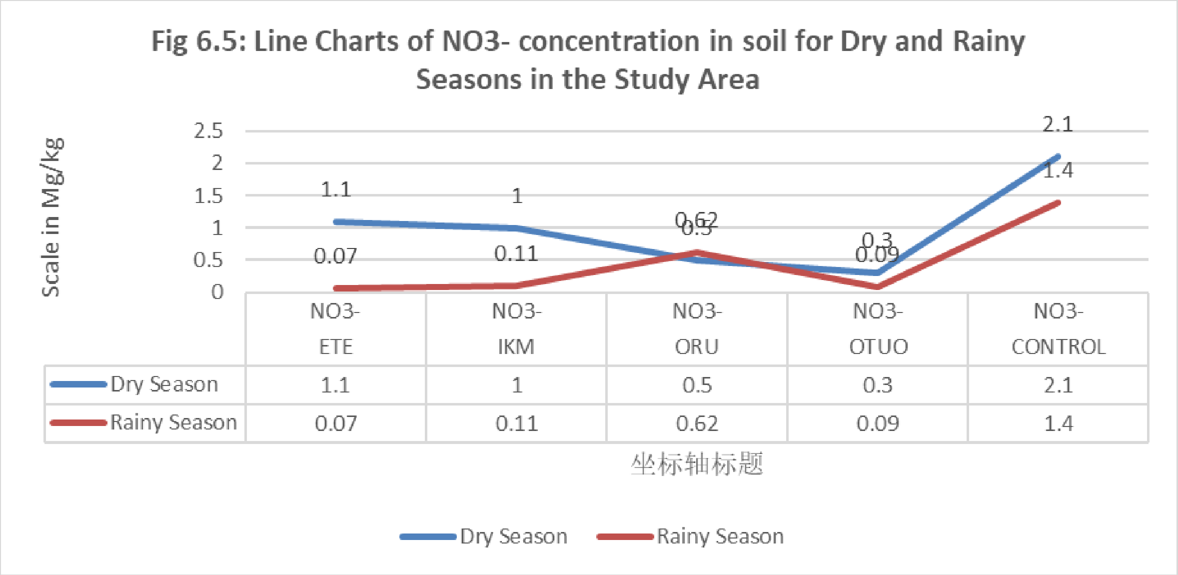


Fig 6.5: Line Charts of NO3- concentration in soil for Dry and Rainy Seasons in the Study Area

	NO3- ETE	NO3- IKM	NO3- ORU	NO3- OTUO	NO3- CONTROL
Dry Season	1.1	1	0.5	0.3	2.1
Rainy Season	0.07	0.11	0.62	0.09	1.4

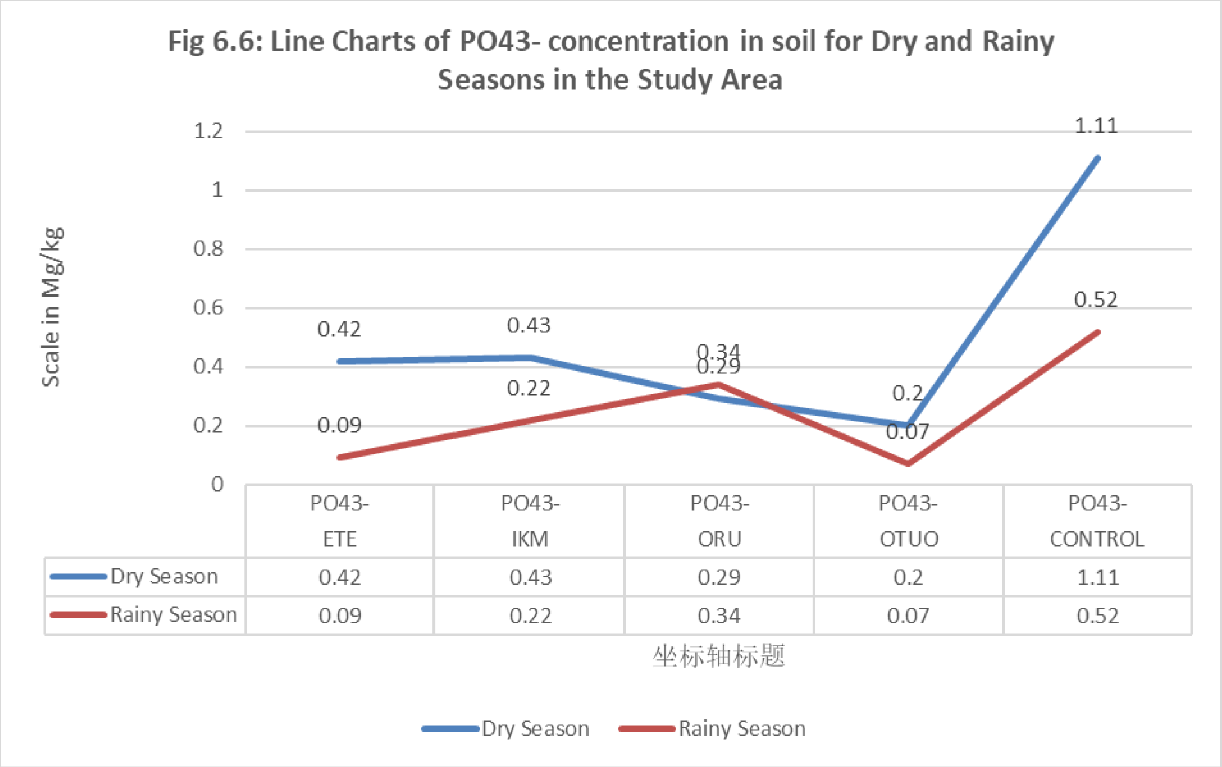


Fig 6.6: Line Charts of PO43- concentration in soil for Dry and Rainy Seasons in the Study Area

	PO43- ETE	PO43- IKM	PO43- ORU	PO43- OTUO	PO43- CONTROL
Dry Season	0.42	0.43	0.29	0.2	1.11
Rainy Season	0.09	0.22	0.34	0.07	0.52

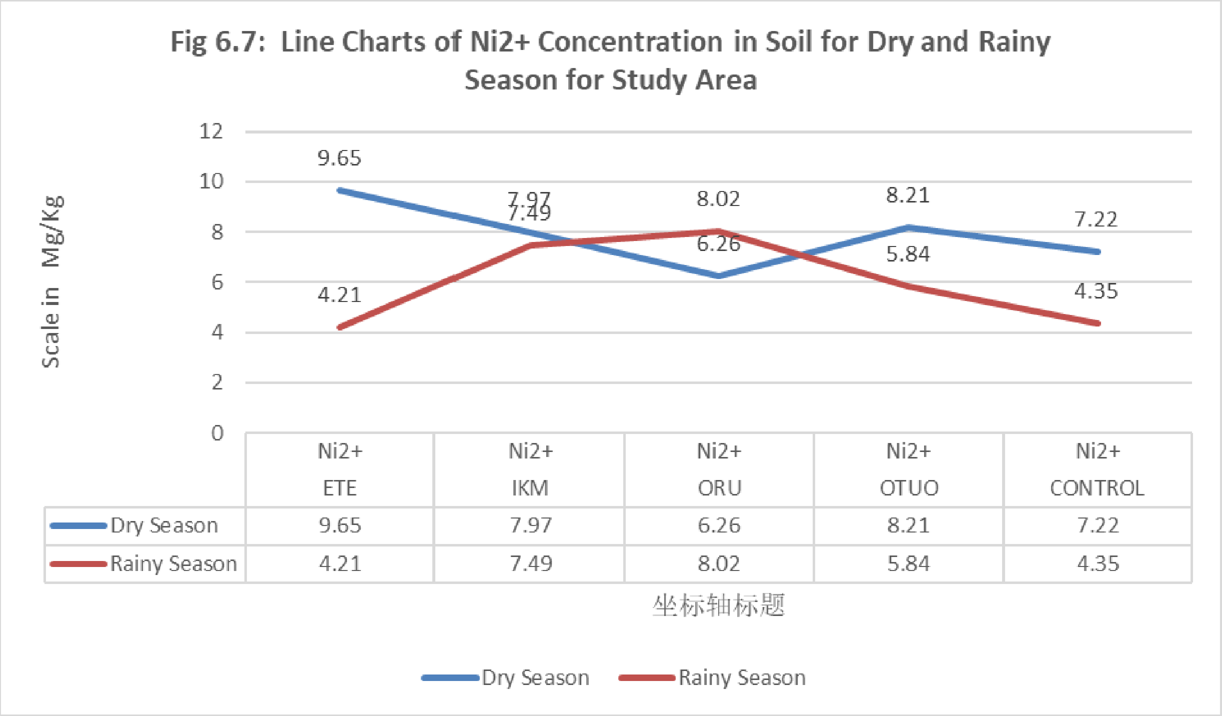


Fig 6.7: Line Charts of Ni2+ Concentration in Soil for Dry and Rainy Season for Study Area

	Ni2+ ETE	Ni2+ IKM	Ni2+ ORU	Ni2+ OTUO	Ni2+ CONTROL
Dry Season	9.65	7.97	6.26	8.21	7.22
Rainy Season	4.21	7.49	8.02	5.84	4.35

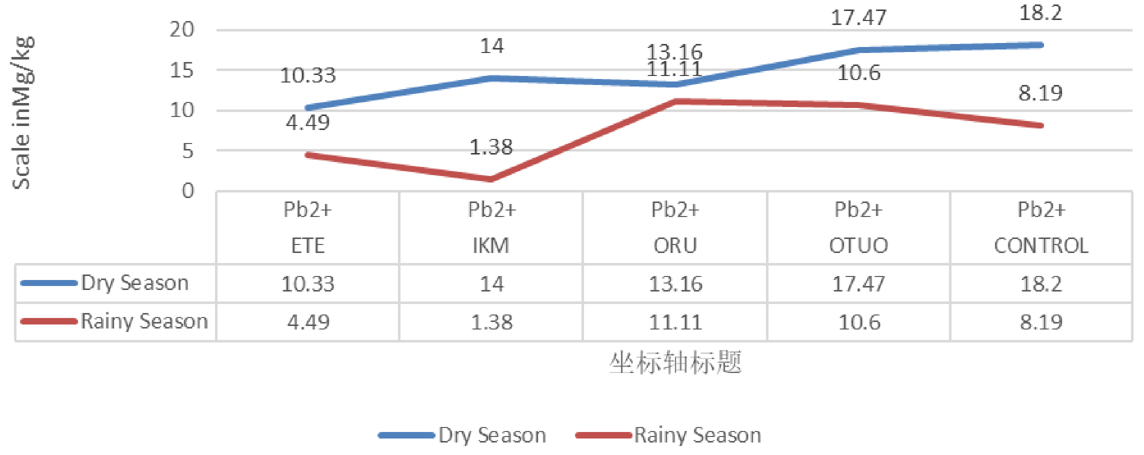


Fig 6.8: Line Charts of Pb2+ Concentration in Soil for Dry and Rainy Seasons in the Study Area

	Pb2+ ETE	Pb2+ IKM	Pb2+ ORU	Pb2+ OTUO	Pb2+ CONTROL
Dry Season	10.33	14	13.16	17.47	18.2
Rainy Season	4.49	1.38	11.11	10.6	8.19

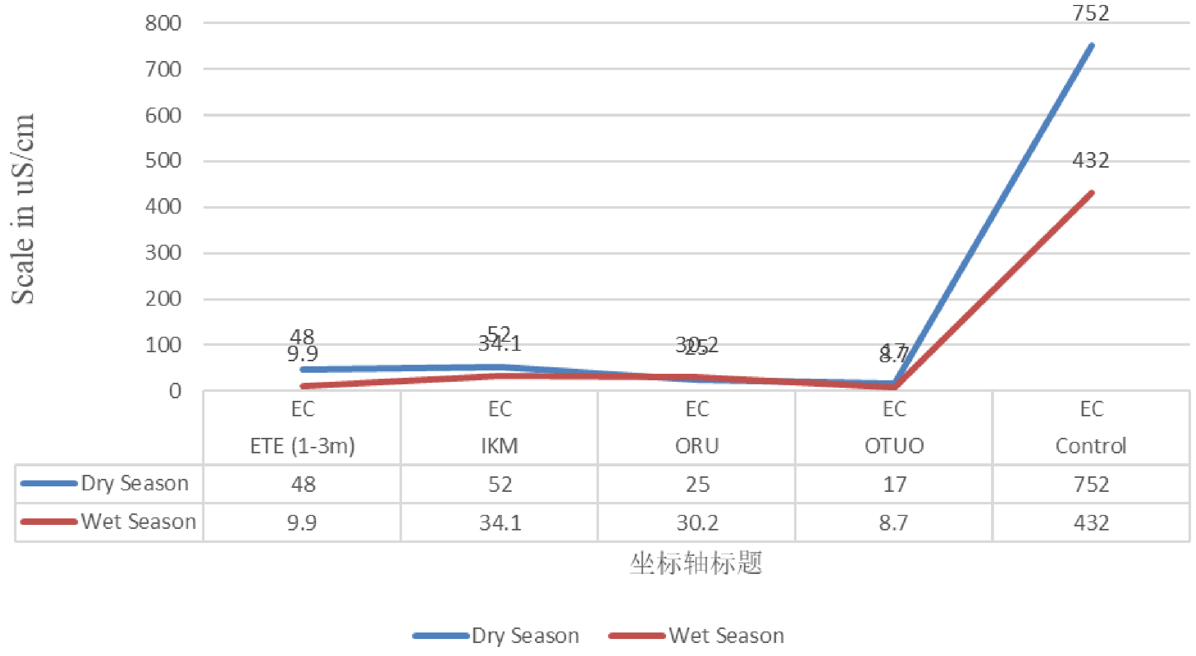


Fig 6.9: Line Chart of Electrical Conductivity (EC) in Soil for Dry and Rainy Season in the Study Area

	EC ETE (1-3m)	EC IKM	EC ORU	EC OTUO	EC Control
Dry Season	48	52	25	17	752
Wet Season	9.9	34.1	30.2	8.7	432

6.1 PHYSICOCHEMICAL PROPERTIES OF SOIL (Dry Season)

pH

pH defines the acidity and alkalinity trend of a soil. The pH meter is scaled in such a way that 0-6 is acidic, 8-14 is alkaline and 7 is neutral. From the results shown on table 6.1, the four impacted locations showed acidity with pH values ranging from 3.6 to 4.9. The control site also recorded acidic value of 3.7 confirming acidity in soil samples. From the results it can be inferred that soil acidity is determined mostly by soil type rather than oil spill.

Electrical Conductivity (EC)

Electrical conductivity values across study area range from 10uS/cm to 59uS/cm. The minimum value was recorded at 3 meter depth in Otuokpoti location while the maximum value was obtained at 5 meter depth at Ikarama location. The control location recorded very high electrical conductivity value 759uS/cm which is indicative of negative impact of spill on soil nutrient availability

Anions and Cations

Anions and cations also trended differently as illustrated in figures 6.1 - 6.8 above. Amongst analyzed heavy metals, Lead and Cadmium had peak values of 22.19mg/l and 0.46mg/l at Otuokpoti location. Whereas, Vanadium and Nickel had peak values of 0.67mg/l and14.06mg/l at Etelebou location. Minimum values of heavy metals in sediments across the four sampled locations was recorded in Etelebou location and it range from <0.001mg/l to 2.16mg/l. Contrarily, Arsenic recorded very low value of <0.01mg/l in all locations during the dry season.

PAH and TPH

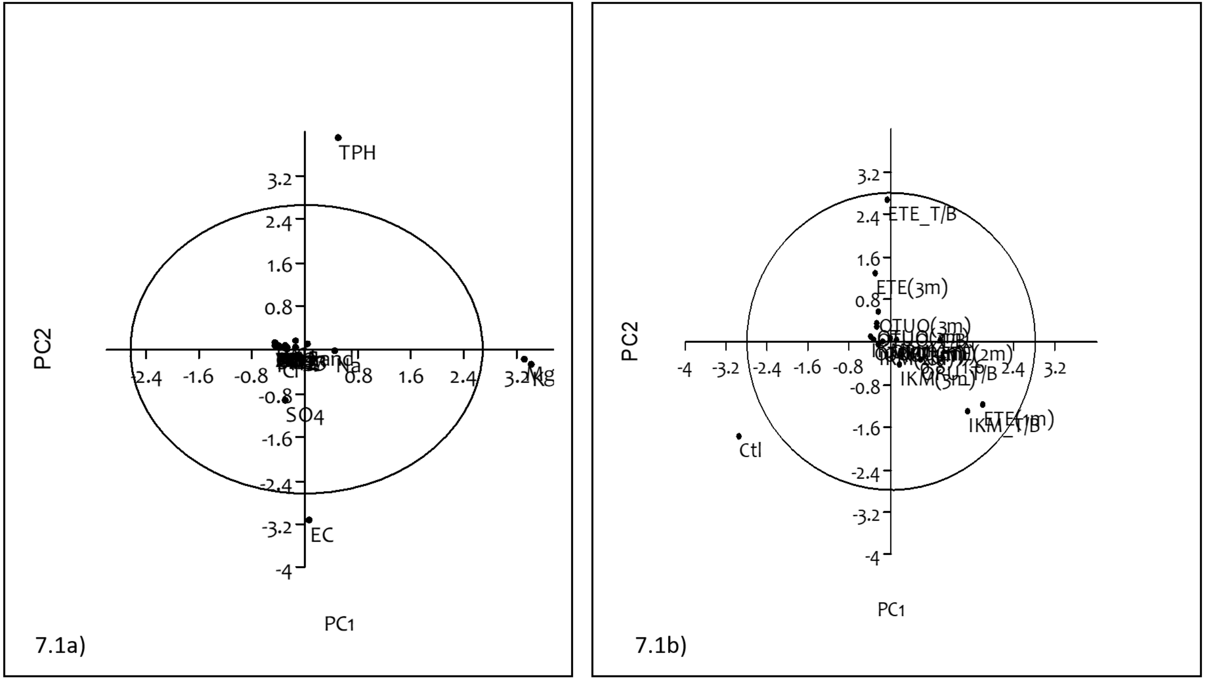
Total petroleum hydrocarbon had a peak value of 602.78mg/l and it was obtained at 1m depth in Etelebou location. Second peak value (234.54mg/kg) was obtained at Oruma location and the least value 1.31mg/l was obtained at Otuokpoti. Results across the study area showed highest hydrocarbon concentration at 0-0.3m depth but a notable decrease at greater depths (1-3m) during the dry season. Polycyclic Aromatic hydrocarbon showed highest concentration at Ikarama location with peak values of 5.78mg/kg and 23.62mg/kg for dry and rainy seasons respectively.

6.2: PHYSICOCHEMICAL PROPERTIES OF SOIL (RAINY SEASON)

Seasonal variations in concentration was observed for PAH and TPH. Both parameters increased in concentration during the rainy seasons compared to the dry season. This implies a redistribution of spilled crude oil from more concentrated areas in dry season to other areas of less concentration due to the effect of moisture caused by the rain. It was observed that heavy metals like Nickel decreased in concentration at deeper depths. The least value of Nickel (2.9mg/l) was obtained at Etelebou location. Lead obtained maximum values of 13.78mg/l, 18.95mg/l, and 7.11mg/l at Otuopkoti, Oruma and Etelebou locations respectively. On the contrary, arsenic was within low concentration levels on the average (<0.01mg/l) in all locations across the study area. The control location also showed high figures of (8.43mg/l and 4.57mg/l) for Nickel and Lead implying that heavy metals exist naturally on the earth crust but can be enhanced by anthropogenic activities such as oil spillage. Seasonal variation was minimal for pH at all impacted locations. Control site obtained pH value of 3.7 which is more acidic than that of impacted locations. This implies that soil pH is mostly influenced by soil type other than crude oil impact.

7. PRINCIPAL COMPONENT ANALYSIS OF SOIL PARAMETERS

Figures 7.1a and 7.1b: Principal component analysis of soil parameters and locations (dry season).



7.1a)

7.1b)

Applying principal component analysis (PCA) on soil analytical results as shown in figs 7.1a and 7.1b, the rainy season showed less dispersion amongst test parameters and at different locations when compared with the dry period. For instance, TPH and Ca were the only significantly isolated parameters in the study area during the rainy season. The dispersion of TPH and Ca from other parameters is largely due to their outlier values across the study area. Evidently, there was upward trend in TPH and Ca concentration in the rainy season (Table 6.1). The rise in concentration of TPH and Ca could be attributed to effect of flooding and redistribution of hydrocarbon contaminants. The seasonal shift in TPH concentration observed in this study conforms to the study by (Keller et al. 2005) at Idoha U.S.A. But it is contrary to the findings of Aigberua et al. (2016a) where a "reduction in soil residual TPH was observed during the wet season. The rise in TPH concentration during the rainy season may have contributed to the observed varying concentration levels at different soil depths in the study area. Results from this study also conforms to the "predominant distribution of hydrocarbon at shallower depths as reported for oil-contaminated soils of Rumuolukwu" (Aigberua *et al*., 2016*a).*

An isolation of EC was noticed which is likely due to the relatively lower EC values was obtained at impacted areas. Magnesium (Mg^{2+}) and potassium (K^{+}) had some dispersion which may have emanated from their outlier concentrations when compared with other test parameters. Aigberua *et al*. (2016a) also reported a positive correlation trend for electrical conductivity and available soil nutrients.

8: Particle Size Distribution and Lithology Logs of Sampled Locations in Study Area

The severity of crude oil contamination and the subsequent pollution of soil is dependent on the soil properties and thickness of the vadose zone (unsaturated zone) overlying the saturated zone. For instance, infiltration rate defers for different soil types, soils with larger grains possess higher infiltration rate than those of smaller grains. The hydraulic system and soil properties either retard or improve transportation of contaminants from surface to the sub-surface (Tombul, 2003). Thus, permeability or hydraulic conductivity of sub-soil plays vital role in the prediction of infiltration and intensity of contamination. Therefore, it can be inferred that well sorted sediments like sand and gravel have higher fluid conductivity, though this can be influenced negatively at longer time.

Table 8.1: Mean percentage Particle Size Distribution for Dry and Wet seasons in Sample Locations

Location/seasons	SOIL TYPE			Permeability	Water Content%
	Sand %	Silt %	Clay%		
Ete Dry	76.56	5.36	18.08	2.05 x10-3	21.56
Wet	71.56	4.63	23.80	1.78 x10-4	17.04
Oru Dry	66.02	6.50	27.48	1.55 x10-4	34.69
Wet	68.76	7.09	24.16	2.25 x 10-4	24.42
Ikm Dry	74.54	5.94	19.52	1.8 x 10-3	25.59
Wet	72.93	3.92	23.15	2.3 x 10-4	29.12
Otu Dry	78.94	3.01	18.05	3.0 x 10-3	17.83
Wet	71.90	4.82	23.29	2.18 x 18-4	15.69
Ctrl Dry	63.68	12.32	24.00	1.8 x 10-4	46.80
Wet	64.12	11.40	24.48	1.5 x 10-4	34.55

Table 8.1 shows mean values of sand, silt and clay percentages in the study area. High percentage of sand was obtained for Etelebou, Ikarama, and Otuokpoti stations indicative of high infiltration and percolation of crude oil from surface to subsurface. Oruma station experienced slightly lower values of sand than other locations depicting sand/clay mixture. Seasonal changes in particle size distribution was mild or almost absent in the study area.. Water content (WC) trended negatively from dry to wet season at Etelebou, Oruma, Otuokpoti and Control locations but an opposite trend was obtained at Ikarama. On the other hand, permeability had a positive shift across sampled locations from dry to wet season in exception of Oruma location where the reverse was the case.

A soil formation heterogeneity or homogeneity is a function of the depositional history. For example, silt and clay possess high porosity but are impermeable in nature. Particle size distribution result was constant for both seasons in the study area, while water content (WC) trended negatively from dry to wet season at Etelebou, Oruma, Otuokpoti and Control locations. Permeability had a positive shift moving from dry to wet season at all locations except Oruma location which has a lower percentage of sand.

The unified soil classification (USC) system was adopted for the illustration of soil stratigraphy in sampled locations as shown on Fig 5.1 below.

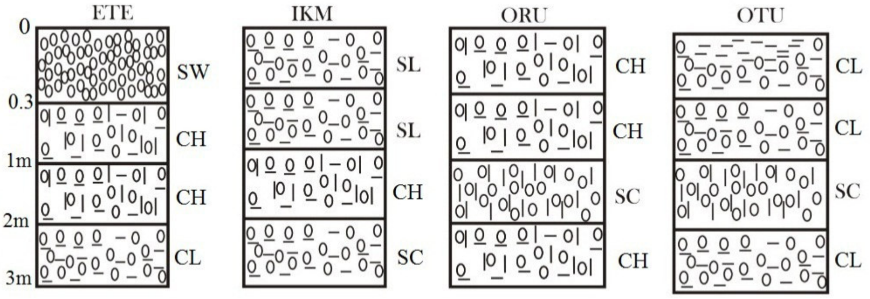


Figure 8.1: Lithology logs of sampled locations across the study area

Note: ETE – Etelebou, IKM – Ikarama, ORU – Oruma or Ayaba-ama, OTU – Otuopkoti

Soil type and the grain distribution are essential factors that determine the movement of crude oil from surface to sub-surface. Deductions from the profile shows predominance of sand across the area indicative of high infiltration hence, the high level of deterioration noticed in soil and sub-surface water samples in the study area.

10: Conclusion

The characterization of soil in crude oil contaminated sites at Ogbia and Yenagoa local government areas was carried out. Soil pH maintained a constant trend with only slight influence by crude oil contamination as shown on the results. Etelebou and Oruma showed most impacted judging from the highest levels of TPH values obtained for soil samples in the dry season. But a redistribution of spilled crude was observed at Ikarama location for soil with a peak value of 3595.05mg/kg and 41.108mg/kg at 1m depth for TPH and PAH respectively during the rainy season Table 6.1). **Additionally, at Oruma location, soil samples in dry season showed highest concentration of EC, HCO_3^{2-}, TDS, SO_4^{2-} and Cl^- depicting negative impact of spilled oil (Table 6.1). Soil nutrients concentration such as K^+, PO_4^{3-}, NO_3^-, Ca^{2+} and Mg^{2+} was drastically lowered in spill impacted areas due to the reduced values obtained. Amongst analyzed heavy metals in soil samples, only Lead (Pb) and nickel (Ni^{2+}) showed rise in concentration, while Cd an V concentration levels were relatively low but similar with that of the control location. Meanwhile, Arsenic was undetected in both impacted and non-impacted locations. TPH concentration was higher in oruma than otuokpoti while PAH had lower concentration at both impacted and non- impacted locations. Generally, soil physicochemical parameter showed decline in anions concentration especially during the dry season whilst, an increase was observed during the wet season. Contrarily, cations showed a rise in concentration during the dry season but relatively reduced in rainy season. The study area is made of predominantly sandstones (fig 5.1) depicting high infiltration and seepage phenomena.** Summarily, organics, influence on heavy metals (Pb, Ni, V, Cd, As) concentration was minimally low as was clearly illustrated in results. While organics influence on soil nutrients was relatively high. In conclusion, the results showed hydrocarbon contamination as the primary cause of soil nutrients (HCO_3^{2-} and CO_3^-, NO_3^- and Cl^-, PO_4^{3-}) decline and reduced oxygen concentration in the soils of impacted areas capable of causing distorted growth and low yields in crops.

11: Recommendation

The study revealed high level of deterioration in the sampled locations due to exposure to crude oil pollution. Based on the findings of the study, the following recommendations are proffered for the sustainability of our environment.

1. The government should ensure total compliance to laws and regulations enacted towards attaining a more sustainable environment.
2. Multinationals and servicing companies whose activities are crude oil related should be monitored regularly for adequate maintenance of their oil facilities to avoid accidental discharges of crude oil.
3. Government, in collaboration with the ministry of environment should carry out sensitization programs geared towards instilling on our youths the dangers of sabotage and other ill practices that are crude oil related.
4. Spillages should be reported to appropriate quarters for swift containment in order to prevent spread and damages to our eco-system.

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