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Assessment of Physicochemistry of Crude Petroleum polluted Farm lands in Rivers State, Nigeria

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ABSTRACT

Assessment of Physicochemistry of crude Petroleum polluted Nweol community farm lands in Rivers State was evaluated, using standard analytical procedures. Mean values of physicochemical parameters in petroleum polluted soils and unpolluted/controls were: Polluted Baraol-Chara 1; Moisture contents 7.32%, pH 4.5, Conductivity 135.42µS/cm, Nitrate 8.52Mg/kg, Phosphorus 24.13mg/kg, Potassium 29.82mg/kg. Total Petroleum Hydrocarbon 293.58mg/kg, and heavy metals; Cadmium 6.33mg/kg, Chromium 269.60mg/kg, Lead 119.52mg/kg. Polluted Baraol-Chara 2; Moisture contents 7.24%, pH 4.5, Conductivity 201.64µS/cm, Nitrate 8.87mg/kg, Phosphorus 31.28 mg/kg, Potassium 50.28mg/kg, Total Petroleum Hydrocarbon 289.33mg/kg, and heavy metals; Cadmium 8.36mg/kg, Chromium 287.64mg/kg, Lead 114.11mg/kg. Polluted Baraol-Gor; Moisture contents 6.92%, pH 5.0, Conductivity 140.51µS/cm, Nitrate 8.91mg/kg, Phosphorus 26.51mg/kg, Potassium 32.80mg/kg, Total Petroleum Hydrocarbon 212.92mg/kg, and heavy metals were; Cadmium 8.04mg/kg, Chromium 313.93mg/kg, Lead 90.15mg/kg. In the unpolluted control from Gava area; Moisture contents 3.08%, pH 6.0, Conductivity 139.18µS/cm, Nitrate 14.95mg/kg, Phosphorus 51.55mg/kg, Potassium 31.07mg/kg, Total Petroleum Hydrocarbon 111.56mg/kg, and heavy metals; Cadmium 2.29mg/kg, Chromium 110.54mg/kg, Lead 85.35mg/kg. The studies revealed mean values for Total Petroleum Hydrocarbon at all sample sites, and were from the ranges of 119.26 to 296.27mg/kg which are beyond Environmental Protection Agency safe limits, making it unsuitable for farming and Agriculture. This is also evident that Nweol community affected farms soils are hazardous, and of health risk to anyone that consumes crops grown in these farms, including animals within the food chains. Comprehensive and total clean-up is therefore recommended, for safety of Nweol people, and others who depend on the affected farms.

Keywords: Petroleum spillage, Soil pollution, Total Petroleum Hydrocarbon, Heavy metals, Safe limits.

Introduction

Crude Petroleum is defined as a substance generally liquid, occurring naturally in the earth and composed mainly of mixtures of chemical compounds of carbon and hydrogen with or without non-metallic elements such as sulphur, oxygen and nitrogen (Akpor *et al*., 2007). The product is usually obtained beneath the earth surface by way of drilling wells. Colour of crude oil may be black, red, amber, or brown (Holliger *et al*., 2012).

Petroleum hydrocarbon can be introduced into the environment by way of oil spills, leakage of lose unplugged oil wells or disposal ponds of waste petroleum products, abandoned oil refinery sites, pipeline ruptures due to expiry or vandalism.

Other sources include accidental discharge during transportation in ship or vehicle, tanks failures, oil theft and bunkering activities (Ojumu and Ibe, 2004; Eze *et al*., 2014). Pollution of land and aquatic environments by Oil spillages are major environmental problems in Nigeria, and most especially in the Niger Delta region, and have caused continual threats to the resourceful water bodies, agricultural viable farmlands, forest tree species, vegetable or useful crop gardens, including animals and humans (Olukunle, 2013).

Oil spillage also destroys soil fertility, causing shifts and alterations in the microbiological and chemical properties of the soil, to pose damaging effects on both terrestrial and aquatic ecosystems (Olukunle, 2013).

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High strength petroleum pollutions are usually toxic to many things, particularly soil microorganisms and other soil dependent land organisms, including humans. Crude petroleum persistence on the ecosystem for long periods of time may accumulate in animals and plants tissues, passing from one to the next species through the food chain causing death or genetic mutations in both animals and humans (Chandra *et al*., 2013). Side effects of human exposure to these toxins in food chain may lead to serious health conditions. Lead poisoning destroys human nervous systems, and causes retardation, learning difficulties, bone marrow deficiencies and stunted growth in children. Chromium and arsenic can also cause cancer (Aya & Nwite, 2016).

Soil has been described as the upper layer of earth, a mixture of organic remains, clay and rock particles in which crops and other plants grow. Soil is further seen as a mixture of organic matter, minerals, gases, liquids and organisms that support life, such organisms described as the soil microorganisms (Ugboma, 2014). Soil also is a privileged habitat for microorganisms, harboring most biological environmental diversities on Earth. Soil microorganisms are very important part of the environmental ecosystems, which could adjust energy flow and cycle of matter by digesting animal, plant and oil residue, and play important role in growth and development of crops, balance of soil ecosystem, organic matter transfer and bioremediation (Mu *et al*., 2015). Soil Petroleum pollution significantly increases the soil pH up to 8.0, and also reduces available phosphorus concentration in the soil. Simple soil contaminations to a large extent can have natural recovery by attenuation over time, but high strength waste such as those of crude petroleum spillages may take a longer time to degrade (Aya and Nwite, 2016). Many high strength wastes may not biodegrade at all, depending on the ratio of chemical oxygen demand to the biological oxygen demand (Terrumun & Oliver, 2015). Normal values for pH, heavy metals, and total petroleum hydrocarbon of water and agricultural viable soils can be altered, by crude petroleum pollutants, to eventually pose many serious health challenges to users of such water, and farmlands where these occur (Olayiya *et al.*, 2016).

The physicochemical parameters of water and soil may include temperature, biochemical oxygen demand, dissolved oxygen, pH, alkalinity and conductivity. These are most often measured at the site of collection, and compared with the World Health Organization normal ranges for each of the parameters (Zigham *et al.*, 2012). Other parameters may be soil moisture contents, soil nutrients, heavy metals and total Petroleum hydrocarbon contents (Ruqia *et al.*, 2015). Excess amount of iron in the human body results to hypertension, drowsiness, red blood cells buckling. Zinc is important in the physiological and metabolic process of many organisms. It also plays important role in protein synthesis, and higher concentrations can be toxic and health risk (Zigham *et al.*, 2012; Ruqia *et al.*, 2015).

Farm soil environments are usually fragile, very susceptible, and especially vulnerable to oil and petroleum spillages much like the coastal regions also are poorly containable and mitigation is often very difficult (Onwurah *et al.*, 2007). Deleterious effects of soil pollutants especially the Petroleum hydrocarbon pollutants make it very compulsory to have mitigation, a counter measure to combat the pollutants in our environments. Decreased pH may be as a result of the growth of hydrocarbon degraders (Jackie *et al*., 2001; Timmerman *et al.*, 2003). Mitigation and controls in soil pollutions, may take many forms like, less use of chemical fertilizers in crop cultivation as these are more soil damaging than being beneficial, promoting reforestation and or afforestation of affected land, and by encouraging the use organic manures in planting.

Oil exploration was started in Oloibri community in present day Bayelsa State, Nigeria in January, 1956 by Shell British Petroleum (now SPDC). Shell Petroleum Development Company started yet another Oil operation by 1958 in Ogoni Kingdom of Rivers State, drilling a total of 96 Oil wells in Ogoniland alone to bring nine Oil fields on stream (Friends of the Earth International, 2019).

Far above three decades ago Ogoni-land in Rivers State, Nigeria has been on spotlights for environmental pollutions with Petroleum spillages and crude oil pollution, unguardedly perpetrated by multinational oil producing companies as a result of oil extraction activities (Friends of the Earth International, 2019; Kolawole, 2022). Few communities in Gokana may still experience more recent pollutions due to proximity to abandoned flow stations, and fresh oil-pipe outbursts.

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While others had experienced it in the past and the affected environments have not fully recovered for basic agricultural activities (Friends of the Earth International, 2019). In 1958 Shell Petroleum Development Company started Oil operations in Ogoni Kingdom of Rivers State, drilling a total of 96 Oil wells in Ogoniland alone to bring nine Oil fields on stream (Friends of the Earth International, 2019). Between 1976 and 1991, more than two million barrels of oil polluted Ogoni land alone in 2,976 separate oil spills. Shell has always insisted that most of the spills were cause by saboteurs. Yet Amnesty International claims its researchers have found at least eighty nine (89) spillages which deliberately might have been mislabelled as theft or sabotage (Friends of the Earth International, 2019). More than twenty three (23yrs) years ago oil pipe lines that passed through Nweol community farmlands at Baraol-Chara, and Baraol-Gor were vandalized by disgruntled persons following oil-pipe abandonment and outburst of facilities on expiry, resulting to crude petroleum spillages in the community farms.

The aim of this study was to assess physicochemistry of crude Petroleum polluted soils in Rivers State, Nigeria, so as to verify usefulness in Agriculture as safe farm soils.

Materials and Methods

Description of the Study Area

The study area are some farmlands contaminated with crude oil that resulted from an oil spillage about twenty-three (23) Years ago in Nweol, Gokana Local Government area, Rivers State, Nigeria.

Two sampling stations**,** Baraol-Chara and Baraol-Gor that experienced oil spillages served for the three soil sampling locations namely; Baraol-Chara1, Baraol-Chara 2, and Baraol-Gor. While Gava Area where no oil spillage occurred served as unpolluted/control soil. These are two major farm areas that sustain farming activities and livelihood in Nweol. Major crops cultivated within these locations are; various species of Yams, Cocoyam, Cassava, three leaves yams, and different kinds of vegetables, including Pumpkins, garden eggs, Pepper, maize, melon, and tomatoes. Apart from other forest trees, such as Indian bamboo (*Panicum maximum*) which occupied part of the polluted sampling locations, all food crops cultivated within the area have root zones which thrive within 0-1meter, whereas oil spillages may go deeper below the rhizosphere of these vegetable or food crops. The Google Earth map .showing positions of the study area are as shown in Plate 1.

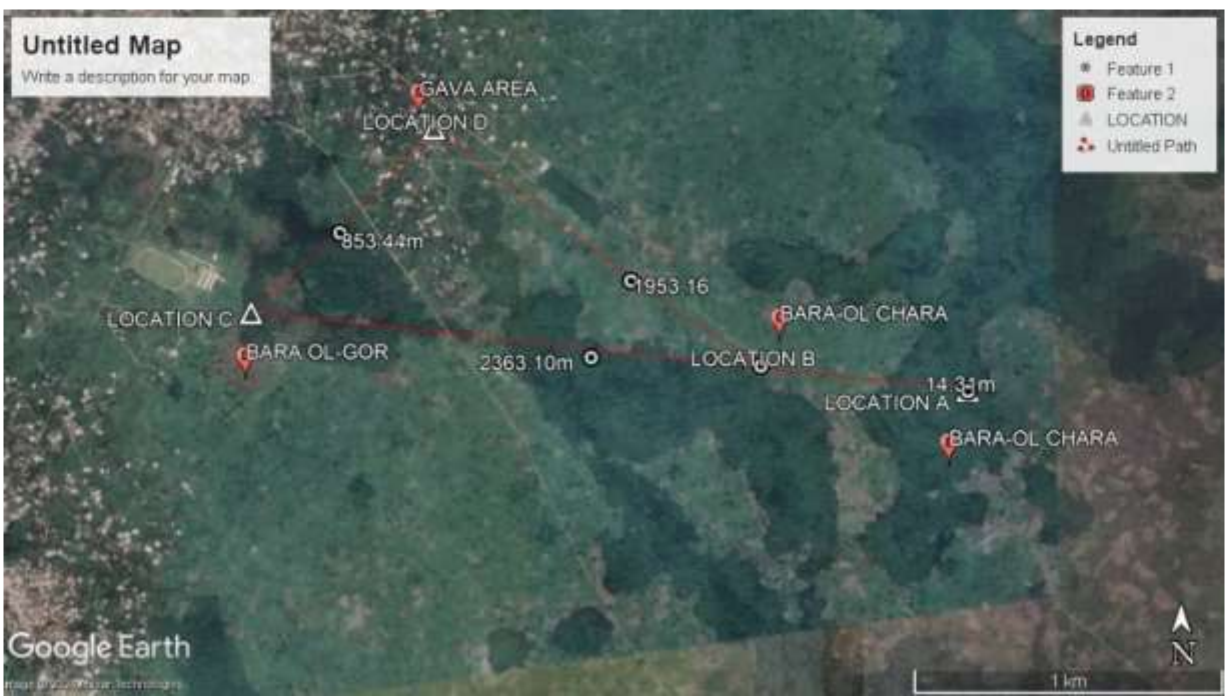

Plate 1: Google Earth Map Showing Positions of the Study Area and Sampled Locations

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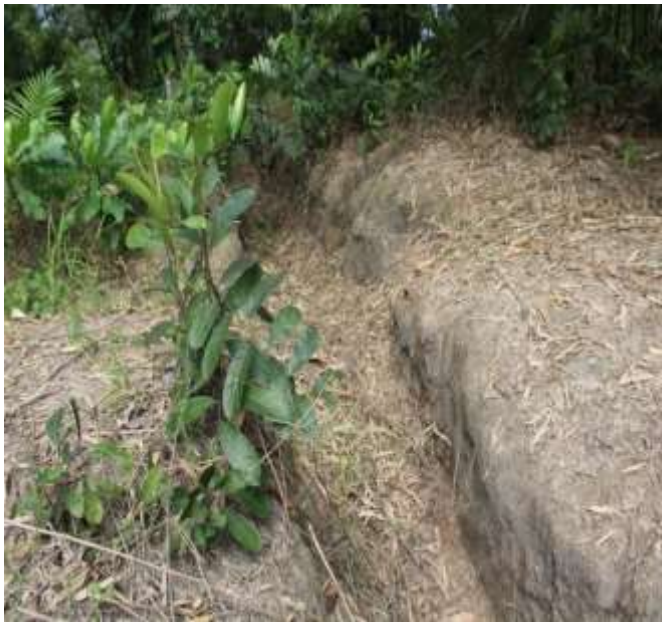

Plate 2: Farmland at Baraol-Chara 1

Plate 3: Farmland at Baraol-Chara 2

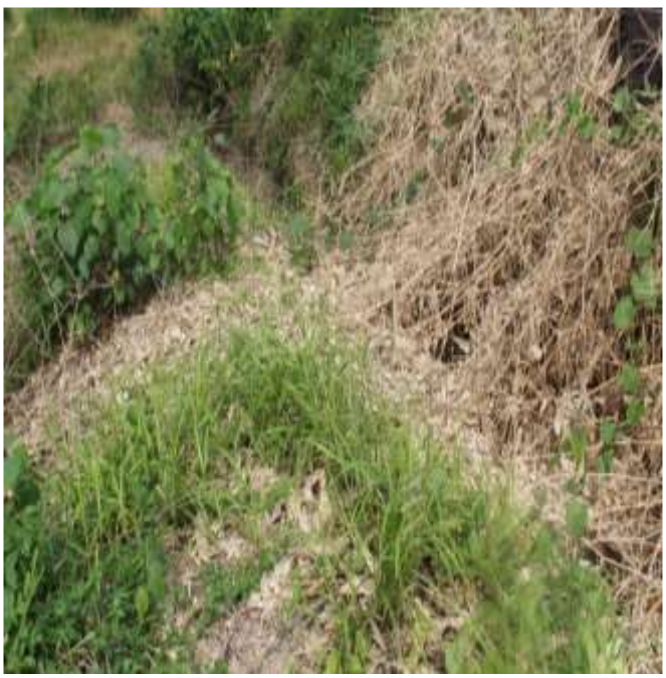

Plate 4: Farmland at Baraol-Gor

Plate 5: Gava Area/unpolluted soil (Control)

Distances between these soil sampling locations are known. Distance between Baraol-Chara 1 and Baraol-Chara 2 is 14.31m, between Baraol-Gor and Baraol-Chara is 2363.10m. The distances between Gava area or unpolluted control location and the polluted sites are 1953.16m Baraol-Chara and 853.44m from Baraol-Gor. The Google Earth map Coordinates of Baraol-Chara 1: Latitude 514513N and Longitude 314651E, Baraol-Chara 2: Latitude 514514N and Longitude 314665E, Baraol-Gor: latitude 514773N and longitude 312302E, and Unpolluted Gava Area (Control): latitude 515381N and longitude 31290E.

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Collection of soil Samples

Randomized samples of crude oil polluted farm soil samples were obtained from Baraol-Chara 1, Baraol-Chara 2 and Baraol-Gor. Unpolluted soil controls were obtained at the distances of 1953.16m and 853.44metres from the sites of pollution. Samples were scoped at three sampling times from surface, subsurface and deep-soil from petroleum polluted farm-sites, and an unpolluted site using a soil auger borer at depths of 0-15cm for surface samples, 16-30cm for subsurface samples, and 31-45cm for deep-soil samples, and composed into 12 sets of composite bulk. All samples were aseptically put into sterile plastic bags, labeled accordingly, and transported in cooled box with ice blocks to the laboratory for analysis.

Physicochemical Parameters Analyzed for the Soil Samples

The Physicochemistry of all polluted soils, and the unpolluted/controls were conducted as to evaluate the following parameters: temperature, pH, conductivity, moisture contents, Petroleum hydrocarbon contents, nutrients status, and heavy metal contents.

The pH values of the various soil samples were measured in situ with the use of a portable pH metre. The probe of the metre was dipped into the sample and values were obtained as displayed on the metre screen, ranging between the values of 0-14 (Yetisen *et al*., 2013).

The various ambient temperature levels were measured instantly at site of sample collection at each sample with the use of a thermometer. The probe of the thermometer was dipped into the sample and values were obtained as displayed on the thermometer stem in centigrade. The results obtained were recorded in degree centigrade (^{o}C) (Chrystie *et al*., 2017).

Soil moisture content was obtained by weighing all the wet soil samples from the field, drying them separately in an oven, and then weighing each dry soil. Then moisture contents of the soil were calculated by subtracting the weight of the dry soil from the weight of the moist soil, and then dividing each by the weight of the dry soil. Gravimetric water content equals the weight of moist soil minus weight of dry soil, divided by the weight of dry soil (Meisami-asi *et al*., 2013). By this method two aluminum dishes were weighed. Fifty grams (50g) of moist soil were put into each aluminum dish and reweigh. Hence, the weights of the moist soil samples were then known. The moist soil samples were all subsequently dried overnight at 105°C in the oven. All the dishes together with dried soil samples were finally removed from the oven and allowed to cool, and both the dishes plus the oven dried soils were all reweighed. By this technique the weight of the dry soil samples also became known. By percentage, the soil moisture contents in percentage (%) for each of the tested samples were calculated using the following equation:

$$\%\ MC = \frac{M - D}{D} \times \frac{100}{1}$$

Where: % = percentage, MC= moisture content,
M = weight of moist soil, D= weight of dry soil

Conductivity of the soil samples was determined by the use of a conductivity meter (Hanna conductivity meter model EC215). The probe was immersed into the sample carefully until a stable reading was recorded in micro-Siemens per centimetre (µS/cm) (Oven *et al*., 2014).

Soil nutrients; nitrate (N), phosphorus (P) and potassium (K) were analyzed by an optical transducer to detect their presence in the soil. Such transducer was needed to decide how much extra contents of these nutrients are to be added to the soil to increase soil fertility, to improve quality of soil and reduce undesired use of fertilizers added to the soil. The N, P, K values in the samples was determined by light absorption rate of each nutrient as described by Singh & Shaligram (2014), and Marianah *et al*, (2017).

The optical transducer implemented as a detection sensor consisted of three LEDs as light source and a photodiode as a light detector. The wavelength of LEDs was chosen to fit the absorption band of each nutrient. The nutrient absorbed the light from LED and the photodiode converted the remaining light that was reflected by reflector to current. The system utilizes an Arduino microcontroller for data acquisition therefore the output from the transducer was converted into a digital display reading (Marianah *et al*, 2017).

The method of Gas chromatography (GC) or mass spectrometric detector (MSD) was employed in the estimation of total petroleum hydrocarbon of the test soil samples as described by Okop and Ekpo (2012).

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Gas chromatography is the most common technique for quantitative analysis of total petroleum hydrocarbon (TPH) in water, soil, and sediment. This standard method describes measurement of TPH in soil with flame ionization detector. The technique has the capacity to reveal the type of hydrocarbons present and its applicable to both volatile and semi volatile samples (Okop and Ekpo, 2012). By this method, the GC column was directly fitted into the ion source of the mass spectrometer by way of transfer line. Results were interpreted by visualizing the separated components on the paper, and the distance travelled by each component was measured.

Heavy metal contents of the polluted soil samples obtained from the study area were examined by the Atomic Absorption Spectrophotometer (AAS) technique as described by Uneka *et al*., (2015).

The AAS is an analytical technique used to determine how much of certain elements are in a sample. It uses the principle that atom can absorb light at a specific, unique wavelength. Atomic absorption spectrophotometry detects elements in either liquid or solid samples through the application of characteristic wavelengths of electromagnetic radiation from light source. Individual elements will absorb wavelengths differently, and absorbencies are measured against standards in Mg/kg (Walsh *et al*., 2006; Uneka *et al*., 2015).

Results

Result of the mean values of the physicochemical parameters of petroleum polluted soils at Baraol-Chara 1, Baraol-Chara 2, Baraol-Gor, and the control soils from Gava area are as presented in Table 1.

Table 1: Mean values of physicochemical parameters in polluted and unpolluted/control soils samples

Parameter	**Soil Treatment**				**EPA Maximum limits**
	Polluted Baraol Chara 1	**Polluted** Baraol Chara 2	**Polluted** Baraol-Gor	**Control** Gava area	
Moisture Content (%)	7.32	7.24	6.92	3.08	3- 4
pH	4.5	4.5	5.0	6.0	7-8.9
EC(µS/cm)	135.42	201.64	140.51	139.18	150-500
Nitrate (mg/kg)	8.52	8.87	8.91	14.95	10-50
Phosphorus (mg/kg)	24.13	31.28	26.51	51.55	30-50
Potassium (mg/kg)	29.82	50.28	32.80	31.07	40-80
TPH (mg/kg)	293.58	289.33	212.92	111.56	<100
Cadmium (mg/kg)	6.33	8.36	8.04	2.29	0.8*
Chromium (mg/kg)	269.60	287.64	313.93	110.54	100*
Lead(mg/kg)	119.52	114.11	90.15	85.35	85*

Legend: EPA = Environmental Protection Agency; * = Target values for heavy metals specified to indicate desirable maximum levels in unpolluted soils EC= Electrical Conductivity, TPH =Total Petroleum Hydrocarbon, Control= Unpolluted soil.

The mean value of parameters in polluted soils at Baraol-Chara 1, were; MC 7.32%, pH 4.5, EC 135.42µS/cm, Nitrate 8.52mg/kg, Phosphorus 24.13mg/kg, and Potassium 29.82mg/kg. Mean value Baraol-Chara 2 soils, were; MC 7.24%, pH 4.5, EC 201.64µS/cm, Nitrate 8.87mg/kg, Phosphorus 31.28mg/kg, and Potassium 50.28mg/kg. Mean value for polluted soils of Baraol-Gor, were; MC 6.92%, pH 5.0, EC 140.51µS/cm, Nitrate 8.91mg/kg, Phosphorus 26.51mg/kg, and Potassium 32.80mg/kg. Values for Control were; MC 3.08%, pH 6.0, EC 139.18µS/cm, Nitrate 14.95mg/kg, Phosphorus 51.55mg/kg, and Potassium 31.07mg/kg.

Mean values of Total Petroleum Hydrocarbon in the polluted soils; Baraol-Chara 1 was 293.58mg/kg, Baraol-Chara2 was 289.33mg/kg. Baraol-Gor was 212.92mg/kg and Control soil was 111.56mg/kg.

Mean of heavy metals at Baraol-Chara 1 were; Cadmium 6.33mg/kg, Chromium 269.60mg/kg, and Lead 119.52mg/kg. Baraol-Chara 2 were; Cadmium 8.36mg/kg, Chromium 287.64mg/kg, and Lead 114.11mg/kg. At Baraol-Gor were; Cadmium 8.04mg/kg, Chromium 313.93mg/kg, and Lead 90.15mg/kg. Control were; Cadmium 2.29mg/kg, Chromium 110.54mg/kg, and Lead 85.35mg/kg.

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Discussion

Analysis of Physicochemistry in polluted, and unpolluted/control soils revealed deviations in values from normal for all parameters except for the soil moisture contents and soil conductivity which were within acceptable values. Excessive soil phosphorus reduces the plant's ability to take up required micronutrients, particularly iron and zinc, even when soil tests show there are adequate amounts and availability of those nutrients in the soil. Potassium is a major plant nutrient that is less directly impacted by soil pH. However, still to some extent especially when the soil pH drops below 5.5 the impacts of soil potassium are felt. Healthy levels of potassium in soil range from 40 to 80 mg/kg. These results agrees with previous reports that Petroleum Hydrocarbons tend to seep into the ground, where they persist, reducing the quality and productivity of the soil, making it unsuitable for cultivation (Ou *et al*., 2004). High soil potassium is indicative for farms that do not have an adequate land base for the amount of manure generated (Umass Extension, 2019).

Studies revealed that the Mean Total Petroleum Hydrocarbon values in the polluted soils were; Baraol-Chara 1 293.58mg/kg, Baraol-Chara 2 289.33mg/kg, Baraol-Gor 212.92mg/kg, and the unpolluted Gava area/control soils 111.56mg/kg which were all above the safe limits by Environmental Protection Agency (EPA) which are clear indications for the lingering presence of Petroleum pollutants in the farmland soils, making the soils unsuitable for farming and Agriculture. By this result it is evident that Nweol community affected farm soils at Baraol-Chara and Baraol-Gor sample stations, even the Gava area control are hazardous, and of health risk to anyone that consumes crops grown in the farms, including animals within the food chains. This statement is in agreement with previous reports that Crude petroleum persistence on the ecosystem for long periods of time, may accumulate in animals and plants tissues, passing from one to the next species through the food chain causing death or genetic mutations in both animals and humans (Chandra *et al*., 2013). This study also agrees with other reports that possible consequence of soil pollution results to untold environment damages, affecting animals and microbial life. Oil spills have degraded most agricultural lands and have turned productive areas into waste lands.

With this increasing soil infertility by the destruction of natural soil inhabiting microorganisms, and dwindling agricultural productivity, and resulting to farmers been forced to abandon their land, to seek non-existent alternative means of livelihood (Amadi *et al*., 1996; Odjuvwuederhie *et al.*, 2006).

High concentration levels of heavy metals present in contaminated sites could pose health risk to humans, plants and animal lives (Okop and Ekpo, 2012). Lead naturally is present in all soils, as Lead occurs naturally within the range of 15 to 40 parts lead per million parts of soil (ppm), or simply recorded as 15 to 40 milligrams lead per kilogram of soil (mg/kg). Soil Pollutions by petroleum and Oil spillages can increase soil heavy metal levels to several thousand milligrams lead per kilogram. This reported fact is in agreement with research on heavy metal concentrations, as high concentrations in the soils, including the control samples are show of dangers. More so, pollution by heavy metals in soil and aquatic environments is a universal out growing problem, and currently is becoming alarming as it is contributing greatly to the heavy metal contents of most agricultural products, including food crops, vegetables, fish and other sea food and aquatic products (Ene *et al.*, 2009).

In conclusion, the Total Petroleum Hydrocarbon values in the polluted soils and the unpolluted (control) soils were all above the safe limits by Environmental Protection Agency (EPA) which are indications for still lingering presence of Petroleum pollutants in the farmland soils, making it unsuitable for farming and Agriculture. It is also a remarkable evidence for health risk in any person who consumes crops grown in the affected farms, including animals in the food chain within Nweol community.

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