



Full Length Research

## Comparative Study of Heavy Metals and Total Petroleum Hydrocarbon Concentrations in Remediated and Non-Remediated Crude Oil Contaminated Soil

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**Abstract:** The discharge of crude oil products to the environment (soil, water and air) has great negative impacts on the ecosystem. Most of these effects are from heavy metals, total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAH) among others. The aim of this research is to assess the effectiveness of the remediation on impacted soil through comparative analysis, and provide a recent data base on the pollution status of the soil. A stratified and random method of sample collection was adopted. From the three locations in Nkelleoken community, the result from the remediated soil showed that the greater amount of almost all the metals are bounded to F4 and F5 which are non-bioavailable to plants. Meanwhile the one from non-remediated soil is the opposite. The total petroleum hydrocarbon (TPH) results from the non-remediated soil samples were comparatively larger than that of the remediated soil (from 418.30±42.13 to 502.68 mg/kg). Whereas the TPH values from remediated site ranged from 193.65±37.20 to 207.0.4±70.14. Compared to the WHO standard (100-300 mg/kg) the TPH in the remediated soil were below the background limit. Microplasma Atomic Emission Spectroscopy and Total Petroleum Hydrocarbon Analyzer were used for the quantification of the inorganic and organic pollutants.

**Keywords:** Bioavailability: Contamination: Crude Oil: Heavy Metals: Metal Enrichment Factor: Bioavailability.

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## 1.0 Background of the Study

Soil is the thin layer of organic and inorganic materials that envelopes the Earth's surface (Essien & Antai, 2005; Abu & Chikere, 2006). The organic portion, which is gotten from the decayed remains of plants and animals, is concentrated in the dark uppermost topsoil. While the inorganic portion which is made up of rock fragments, is formed over thousands of years by physical and chemical weathering of bedrock (Dos & Maranhão, 2018). Soil is formed by a combination of depositional, chemical, and biological processes and plays an important role in the carbon, nitrogen, and hydrologic cycles. The chemistry of soil determines its ability to supply available plant nutrients and affects its physical properties and the health of its living population. In addition, soil's chemistry also determines its corrosivity, stability, and ability to absorb pollutants and to filter water. It is the surface chemistry of mineral and organic colloids that determines soil's chemical properties (Ihejirika *et al.*, 2019).

Crude oil is a complex mixture containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. We call crude oil and petroleum fossil fuels because they are mixtures of hydrocarbons that formed from the remains of animals and plants (diatoms) that lived millions of years ago in a marine environment before the existence of dinosaurs (Abdulkadir *et al.*, 2022). Over millions of years, the remains of these animals and plants were covered by layers of sand, silt, and rock. Heat and pressure from these layers turned the remains into what we now call crude oil or petroleum. The word petroleum means rock oil or oil from the earth (Anon, 2021). Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An average crude oil contains about 84% carbon, 14% hydrogen, 1% to 3% Sulphur, and less than 1% each of nitrogen, oxygen, metals, and salts. Petroleum exploration is largely concerned with the search for oil and gas, two of the chemically and physically diverse group of compounds termed the hydrocarbons. The hydrocarbon gases include dry gas (methane) and the wet gases (ethane, propane, butane, etc.). Condensates are hydrocarbons that are gaseous in the subsurface, but condense to liquid when they are cooled at the surface (Cohen, 2008; Essien & Antai, 2009).

Liquid hydrocarbons are termed oil, crude oil, or just crude, to differentiate them from refined petroleum products. Crude oils are customarily characterized by the type of hydrocarbon compound that is most prevalent in them. They are paraffins, naphthenes, and aromatics. Paraffins are the most common hydrocarbons in crude oil; certain liquid paraffins are the major constituents of gasoline (petrol) and are therefore highly valued (Anon, 2021). Naphthenes are an important part of all liquid refinery products, but they also form some of the heavy asphalt like residues of refinery processes. Whereas, aromatics generally constitute only a small percentage of most crude, the most common aromatic in crude oil is benzene, a popular building block in the petrochemical industry (Anon, 2021). The contamination of the environment (mainly terrestrial and aquatic) by crude oil is referred to as crude oil pollution and it is estimated that 80% of crude oil pollution is as a result of spillage. Extraction, processing, and transportation (pipe rupture) all contribute to the entry of petroleum into the soil environment.

Oil contamination is one of the severe problems because it comprises of contaminants like heavy metals, toxic and hazardous cycloaliphatic and aromatic hydrocarbons (Ukonu *et al.*, 2022; Abbaspour *et al.*, 2020). They decrease the diversity of plants and microbes in the soil, deplete soil fertility, disrupt soil ecological balance, and even put human health at risk (Hassanshahian *et al.*, 2018). Oil pollution might affect soil physical properties. Pore spaces might be clogged, which could reduce soil aeration and water infiltration and increase bulk density, subsequently affecting plant growth. Oils that are denser than water might reduce and restrict soil permeability (Abosede, 2013). The exploration, transportation, refining and storage of petroleum has led to the spilling of the crude oil into the surrounding; especially Ogoni land. The oil so spilled has posed a great threat to the environment (soil, water, and even air). These impacts include the depletion of the ecosystem, total or partial annihilation of the indigenous living organisms, and have also caused so many problems to the

indigents of the affected area. Some of the problems associated with oil spillage to the inhabitants are; ill health, famine, pollution of water, soil and the air, among others.

Ukonu et al. (2022) argued that contaminated soil becomes unfit for agricultural purposes, less required for building constructions, and even difficult to walk upon. Mammals and other animals on the affected soil such as birds may suffer greatly; some die of hypothermia and suffocation, while soil microbes, worms as well as others such as insects become endangered species. As a result, there is great need for a clean up or remediation programs such as the ones discussed above. The United Nation Environmental Protection report in 2011 revealed that Ogoni land has been highly impacted. Recently, the Federal Government of Nigeria initiated the remediation of the impacted areas and the aftermath of the remediation has led to several questions on the quality of the remediation work by Hydrocarbon Pollution Remediation Project (HYPREP) in Rivers State. It's on this background that this research is carried out to assess the effectiveness of the remediation (Ukonu et al., 2022).

Crude oil utilization has improved our living standard, but it has also threatened the aquatic and terrestrial environment with its harmful effects (Joseph, 2023). It contains harmful substances such as polycyclic aromatic hydrocarbons (PAH) that can cause mutation and cancer. Soil contamination is of particular concern as it does not only affect human health, but also vegetation growth and biological environment (Chandran, 2011). Many remediation techniques have been devised but a quick, nature friendly and cost-effective method is required to remove and minimize the dangerous effects of crude oil (Ezeji *et al.*, 2007).

Chemical oxidation is an efficient method to remove dangerous wastes from the soil at the oil spilled sites. The efficiency of this method strongly depends on the soil matrix. Fenton's reagent, a mixture of Hydrogen peroxide and Ferric ion, is used for chemical oxidation. Germida (2002) found that hydrogen peroxide is a strong oxidizing agent that generates hydroxyl ions during Fenton's reaction while ferric ion acts as catalyst. Hydroxyl ions are very powerful and effective agents that destroy the contaminants present in the soil. Owhe-Ureghe et al. (2022) mentioned that another efficient oxidant that is used for the removal of crude oil from soil is ozone. It is easy to generate, store and handle for in situ treatment. Polycyclic aromatic hydrocarbons are more reactive with ozone in comparison to alkanes. Reactivity of poly aromatic hydrocarbons depends on the number of rings, heteroatoms presence or absence and alkylation level. Ozone also support microbial community present in the soil as it generates oxygen on its degradation, so it can be helpful in bioremediation method to aid microbial growth. Chemical method is a quick way to treat contaminated soil, but chemicals may pose a serious threat to the nearby soil and living beings due to leaching or side reactions (Kong *et al.*, 2018).

Excavation of crude oil contaminated soil is the quickest and safe way but not a sophisticated and cheap method. The contaminated soil is removed and transported to appropriate landfill for the disposal. The samples are collected from bottom and sidewalls of the excavated area to check if the site is clean or not (Santos, 2018; Ukonu et al., 2022). Another physical method is the washing of contaminated soil. Washing with organic solvents such as ethanol- water mixture and ethyl acetate-acetone-water mixture exhibited significant removal of hydrocarbons from the contaminated soil. Soil washing does not only treat the oil contaminated soil but also remove the heavy metals from the soil. The efficiency of washing can be enhanced by the addition of surfactants (Santos, 2018).

In Thermal stripping/low temperature thermal desorption/soil roasting contaminated soil is heated to very low temperature (200- 1000 °F) to increase the vaporization and separation of low boiling point contaminants from the soil (Germida, 2002). By this process organic contaminants can be completely or partially decomposed depending upon the thermal stripping temperature and organic compounds present in the soil. This method can remove approximately 90% of the contaminants but it is very costly and not eco-friendly. Another way to remove crude oil from the soil is incineration. The contaminated soil is burned by using fire at high

temperature (1600-2500 °F). This method is also not environmentally friendly as volatile and flammable compounds present in crude oil will cause environmental pollution (Smith, 2017).

Bioremediation is a traditional method that involves the use of living organisms (bacteria, fungi and plants) to degrade harmful substances present in the environment. Bioremediation of crude oil from the soil is very efficient, cheap and environmentally friendly solution. The effectiveness of this method is dependent on hydrocarbon concentration, soil characteristics and composition of pollutants (Gentry *et al.*, 2004). Soil is a diverse ecosystem as it inhabits various microbial populations. The composition of naturally residing microbes change with the composition and concentration of contaminants, so only resistant consortium of microbes survive and work actively in the cleaning of polluted soil. Hydrocarbon degrading microbes are extensively present naturally in the contaminated soil and breakdown complex hydrocarbons into simple form by the use of their enzymatic systems (Barnes *et al.*, 2002).

Phytoremediation is an effective, solar driven and low-cost strategy that uses plants for the removal of contaminants from the soil of large contaminated area. Plants have the ability to grow in polluted soil by metabolizing or accumulating the harmful compounds in their roots or shoots (Germida *et al.*, 2002). It requires such plants that can grow in oil contaminated soil and also provide favorable environment to contaminants degrading microbes by exudates secretion or aeration. Plant-microbe strategy not only increases the metabolic activity of rhizosphere microbes, but it also improves the soil physical and chemical properties and increases microbial access to the contaminants present in the soil (Santos, 2018).

Although the concept of speciation is now widely appreciated in many fields, there have been few efforts to provide a formal definition. Its usage varies among different fields, ranging from evolutionary changes to distinctions based on chemical state ion (Bernhard *et al.*, 1986). Speciation refers to aspects of the chemical and physical form of an element. Oxidation state, stoichiometry, coordination (including the number and type of ligands), and physical state or association with other phases all contribute to define speciation. These properties govern the chemical behavior of elements, whether in environmental settings or in human organs, and play a crucial role in determining toxicity (Olusesi & Joshua, 2022; Gebeyehu *et al.*, 2022).

Metals such as iron and zinc are essential for metabolic function, but can be toxic in excess. Others, like cadmium and lead, have no known beneficial function and pose health risks even at low levels of exposure and uptake. The amount of exposure or uptake is obviously a key factor in assessing adverse health impacts, and defines the field of toxicology (Yerima *et al.*, 2019). However, the metal speciation is also a critical factor in determining toxicity. For example, inorganic dissolved mercury ( $\text{Hg}^{2+}_{(\text{aq})}$ ) and methyl mercury chloride ( $\text{CH}_3\text{HgCl}_{(\text{aq})}$ ) are both considered to be toxic, but the properties and behavior of the latter make it a significantly greater health threat (NRC, 2000). Another example is illustrated by the two common oxidation states of chromium in soils and water.

Hexavalent chromium in the form  $\text{CrO}_4^{2-}$  is soluble in water, making it mobile, and readily taken up by organisms. This form is also a known carcinogen (ATSDR 2000). Trivalent chromium tends to be insoluble, often forming hydroxide solids, and is considered an essential element in small amounts (Olusesi & Joshua, 2022; Gebeyehu *et al.*, 2022). There are at least five aspects important for defining speciation: element identity, physical state, oxidation state, chemical formula, and detailed molecular structure (DOE, 1995). It has been recommended that the usage of speciation in chemistry should be restricted to distribution of chemically distinct species: Chemical compounds that differ in isotopic composition, conformation, oxidation or electronic state, or in the nature of their complexes or covalently bonded substituents, can be regarded as distinct chemical species (Templeton *et al.*, 2000).

The chemical and physical aspects that define speciation of a metal control its reactivity, including its solubility and uptake behavior, and in many circumstances, toxicity (Olusesi & Joshua, 2022; Gebeyehu *et al.*,

2022). Solubility and uptake behavior, in turn, influence mobility of the metal in the environment, and therefore constrain pathways of exposure to organisms, including humans. During exposure the metal speciation directly influences absorption across a physiological membrane, which allows entry into systemic circulation. A transformation in speciation may occur in biological fluids (e.g. lung or gut fluids) prior to any absorption, however, which may affect absorption and subsequent toxicity. Within organ systems detoxification processes may further alter speciation and toxicity, and also influence transportation, excretion, and storage. This oversimplified description illustrates the importance of metal speciation over the entire spectrum of process impacting the metal's fate from weathering to human impact (Plumlee & Ziegler, 2003). The dependence of toxicity on speciation is now well known. The behavior of a metal may be completely changed by its oxidation state or its association with specific ligands, as exemplified by the contrasting toxicities of methylmercury and inorganic mercury specie.

The metalloid tin also shows markedly different health threats depending on its association with specific ligands. Neither metallic nor inorganic forms of tin present a health problem in small amounts; in fact, SnF<sub>2</sub> is a common additive of toothpaste. However, many organotin compounds, which are predominantly created by human industrial processes, are highly toxic (ATSDR, 2005). Tributyltin, widely used as a biocide and antifouling agent for seagoing vessels since the 1970s, is a potent ecotoxicant which persists in marine environments, and accumulates in tissue of fish and shellfish thereby causing adverse health effects in humans (Dopp *et al.*, 2004). One of the complicating aspects of speciation is that each species exhibits a distinct behavior, making generalizations about stability and reactivity difficult. As noted already, the total concentration of a particular element in any system, environmental or human, is not necessarily a good indicator of its potential health impact (Plumlee *et al.*, 2006). Although this concept has been widely embraced by the research community and acknowledged by regulatory agencies, its impact on development of regulatory standards has been limited.

The fate of a metal in an environment is determined by the ease of availability, the higher the level of bioavailability, the higher the impact on the target system (Adekola, 2010). However, the ease of extraction is related to the degree of solubility and bioavailability of metal form which has been discussed above. Therefore, the degree of pollution caused by the metals in the soil can be determined through metal enrichment factor (EF) of the metals and the pollution load index (PLI) (Hikon *et al.*, 2018);

$$\text{Enrichment Factor (EF)} = \frac{\text{Concentration of metals in non-remediated site}}{\text{Concentration of metals from remediated site}} \dots\dots\dots (ii)$$

$$\text{Pollution Load Index (PLI)} = \frac{\text{Concentration of metal}}{\text{Permissible limit of the metal}} \dots\dots\dots (iii)$$

Total Petroleum Hydrocarbons (TPH) are the fractions of the components of the petroleum substance that are found as pollutants on the soil.

TPH can be calculated in terms of its percentage removal. (Fagbote, et al 2010).

$$\% \text{Removal of TPH} = \frac{X1-X2}{X1} \times 100 \dots\dots\dots (iv)$$

Where X1 is the concentration of total petroleum in the contaminated or non remediated soil, X2 is the concentration of total petroleum in the remediated or unpolluted soil.

The knowledge of crude oil spill behavior is of the utmost importance for the evaluation and risk assessment of mineral oil contamination and its effects (Seitinger *et al.*, 1994). An oil spill can affect the environment in numerous ways. The magnitude of the impact could be dependent on the type of accident (blowouts,

explosions, pipeline ruptures), the region of the spill and the clean up and control techniques (Katusiime, 2009). Advanced technology notwithstanding, accident in the form of blow-outs of production well and pipeline leaks have continued to occur in the Niger Delta region of Nigeria and other oil-producing parts, destroying farmland, crops, fish, and other wildlife (such as snails, mushrooms, and non-woody resources), thereby causing hardship to the subsistent farmers in the area (Edwin-Wosu & Kinako, 2004; Agbogidi *et al.*, 2005). Also seriously contaminated are streams, ponds, rivers and lakes, which serve as sources of drinking water.

The exploitation of natural gas deposits of the Niger Delta region of Nigeria had not been economically viable until recently. As a result, much of it has been burnt-off to allow access to the underlying oil (NDDC, 2006; Platform, 2006). The burning gas (flares) produces gases such as nitrogen oxide and sulphur dioxide which are released into the air. These air-borne pollutants are highly toxic, and the growth of plants (especially crops) was particularly inhibited by the hot sooty emissions (Edwin-Wosu & Kinako, 2004). Accidents could also occur due possibly to vandalization of the pipelines leading to enormous loss of crude oil and/or refined petroleum products (Onwuka, 2005). Crude oil spillages in this article will include oil spillages in heavy, medium, and light degrees of occurrences on farmland in Rivers State of Nigeria.

## 2.0 Methodology of the Study

The study adopted a stratified and random method of sample collection. About six (6) sampling points were mapped for sampling in the study areas. Each point was divided into three portions and samples were collected randomly from the points. The three samples were thoroughly mixed together to obtain a representative sample. Remediated soil samples were collected with the aid of a stainless steel hand dug soil auger (2.50 cm in diameter) from three (3) sampling points at the depth of 0-30 cm and were labelled A, B and C while the non remediated soil samples was also collected from three (3) points labelled X, Y and Z at the depth of 5 meters with manual stainless steel auger. The soil samples were collected into a prewashed polyethylene bottle which was previously rinsed with 0.1M HCl. The samples were immediately transported to the laboratory. Physical sorting was done by removing debris, stones and organic matter and samples were air dried. Similar method was used for the collection of samples for organic contaminant determinations but the samples were collected into a glass sampling bottle containing 5 mL methanol as preservative and stored at 4°C in a refrigerator.

### 2.1 Determination of Total Metals Concentrations

For each dried sieved soil sample 1.0g was weighed in to a 100cm<sup>3</sup> beaker (pyrex), and digested with a mixture of 3cm<sup>3</sup> concentrated HNO<sub>3</sub> and 2cm<sup>3</sup> of HClO<sub>4</sub> for 1hour at 100°C in a fume cupboard. After cooling, the mixture was filtered and made up to 50cm<sup>3</sup> with deionized water (Hikon *et al.*, 2018). It was analyzed using Microwave Plasma Atomic Emission Spectrophotometer (MY 17380004) and the results reported in parts per million (ppm). Triplicate determinations were made.

### 2.2 Determination of Metal Species

Heavy metals in the soil were extracted using the Sequential extraction procedure (SEP) in accordance to the five geochemical forms of metals through a careful choice of extractants was used; a method used by Yebpella *et al.*, (2020) was adopted. The exchangeable fractions was extracted by shaking about 1.0 g soil sample in 20 cm<sup>3</sup> of a 1M MgCl<sub>2</sub> solution and adjusted to the pH of 7.0 using mechanical shaker for 1hour at 20 °C in a polyethylene bottle. The mixture was filtered into a 50 cm<sup>3</sup> volumetric flask and made up to 50 cm<sup>3</sup> with deionized water. The carbonate fractions was extracted with 20 cm<sup>3</sup> of a 1M CH<sub>3</sub>COONa solution and adjusted to a pH of 5.0 with CH<sub>3</sub>COOH and mechanically shaking for 4 hours at room temperature in a polyethylene bottle. The mixture was filtered and the filtrate made up to 50 cm<sup>3</sup> volume with deionized water. The metals bound to iron and manganese oxides reducible fractions was extracted by pouring 50 cm<sup>3</sup> of a 0.04M NH<sub>2</sub>OH.HCl and 10 cm<sup>3</sup> of 25 % CH<sub>3</sub>COOH onto the residue form in a polythene bottle and then heated for 6

hours at 96 °C in a water bath. The mixture was filtered and the filtrate made up to 50 cm<sup>3</sup> volumetric flask with deionized water. Metals bound to organic matter (oxidizable fraction) were extracted by pouring 15 cm<sup>3</sup> of a 0.02M HNO<sub>3</sub> and 25 cm<sup>3</sup> of a 30 % H<sub>2</sub>O<sub>2</sub> onto the residue formed. The pH was adjusted to 2.0 with CH<sub>3</sub>COOH and then heated for 5 hours at 85 °C in a water bath. After cooling, 25 cm<sup>3</sup> mixture of 3.2M NH<sub>4</sub>OAc and 20 % HNO<sub>3</sub> in the ratio of 3:4 was added, followed by continuous shaking for 30 minutes at room temperature. The mixture was filtered and the filtrate made up to 50cm<sup>3</sup> volumetric flask with de-ionized water. The residual fractions, the residue formed were quantitatively transferred into 250 cm<sup>3</sup> beaker followed by the addition of 10 cm<sup>3</sup> mixture of analytical grade acids HNO<sub>3</sub>:HClO<sub>4</sub> in the ratio 5:1. The digestion was performed at a temperature of about 190 °C for 1.5 hours in a fume cupboard. After cooling, it was filtered and the solution was made up to a final volume (50 cm<sup>3</sup>) with deionized water in a volumetric flask. Microwave Plasma Atomic Emission Spectrophotometer (MY 17380004) was used to determine the metal concentrations for all the filtrates. Triplicate determinations were made. All chemicals and reagents used for this research work were of analytical grade from sigma and BDH Company.

### 2.3 Determination of Total petroleum hydrocarbon (TPH)

Ten grams (10g) of the soil sample was weighed into extraction bottle and 20mL of extraction mixture (DCM: Hexane) in ratio 2:2 were added. The mixture was shaking for 1hr and the organic aqueous layer was decanted. Extracted organic phase was dried using anhydrous sodium sulphate salt and the extract decanted into a 1.0 mL vial for TPH analyzer. Buck Model HC-404 Total Hydrocarbon Analyzer was used for the TPH analysis. It is a self contained machine with fixed infra-red analyzer design for rapid, accurate analysis to total petroleum hydrocarbons in water, soil and sludge samples.

### 3.0 Results of the Study

Table 3.1: Total Metals concentrations (mg/kg) in Soil from Eleme; Nkeloeken Remediated and Non Remediated Soil.

Samples	Cd	V	Ba	Ni	Pb	Cr
RSENA	1.04	1017.38	11.53	1.28	2.43	1.47
RSENB	1.24	1382.23	9.86	1.36	2.29	1.43
RSENC	1.07	1168.37	6.91	1.26	2.27	1.40
Mean	1.12±0.12	1189.33±183.33	9.43±2.34	1.30±0.05	2.33±0.09	1.43±0.04
<b>Non Remediated Sites.</b>						
NRSENx	2.62	2332.45	228.52	ND	3.57	20.74
NRSENY	3.58	2128.95	221.40	ND	3.84	198.76
NRSENz	5.27	2165.62	221.66	ND	2.33	28.84
Mean±SD	3.82±1.34	2209.01±108.47	223.86±4.04	ND	3.25±0.81	82.78±100.
WHO	0.8	150	9	67.9	0.3	3.8

ND = Non detected

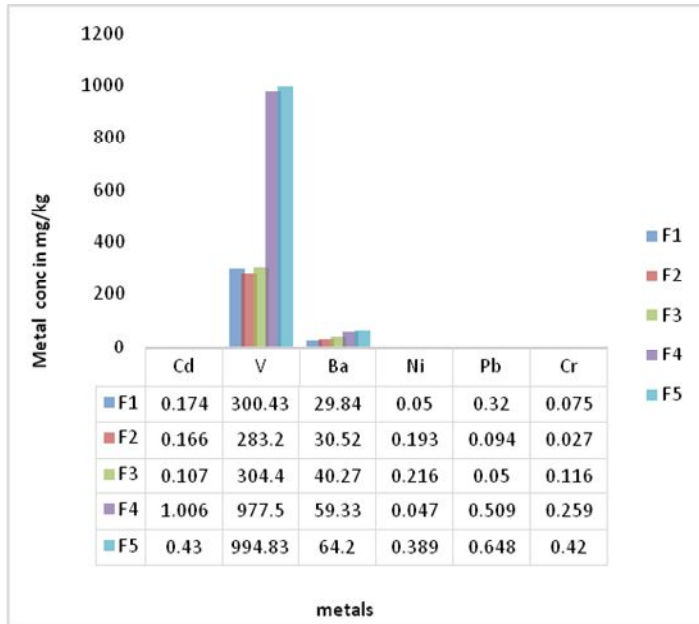


Figure 3.1: Speciation of Metals from Remediated Soil (mg/kg)

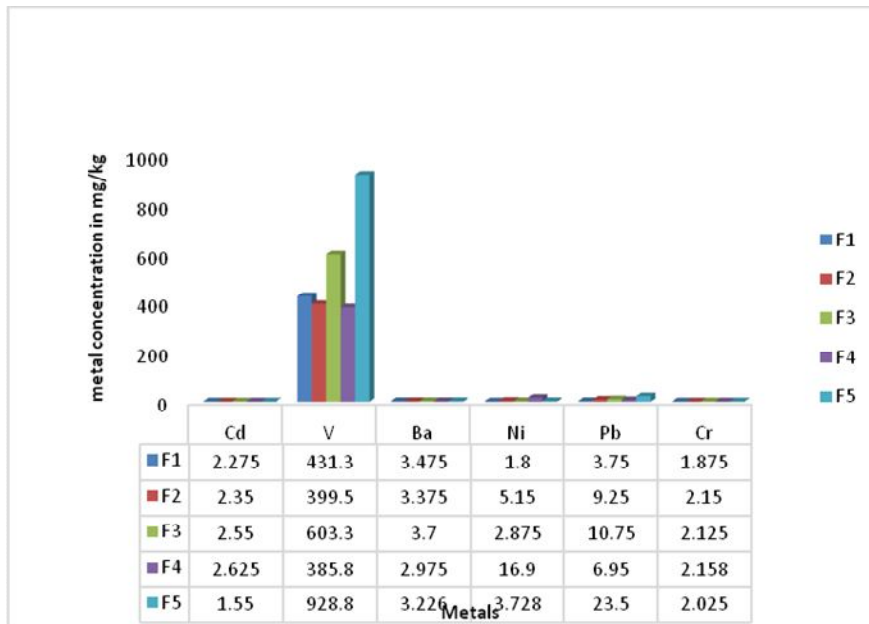


Figure 3.2: Speciation of Metals from Non Remediated Soil (mg/kg)



Table 3.2; Total Petroleum Hydrocarbon

S/No	Sample ID	X1	X2	X3
1	TRSEN1	207.043	206.913	206.978
2	TRSEN2	202.087	193.650	197.868
3	TRSEN3	204.565	200.282	202.423
4	TNRSENa	473.530	472.229	472.880
5	TNRSENb	502.677	418.301	460.489
6	TNRSEnC	488.104	445.265	466.685

## 4.0 Discussion of the Study

### 4.1 Total Metal Concentration in Remediated and Non-remediated Soil (mg/kg)

The result showed that the metal concentration in the remediated soil varied as follows: Cd ( $1.04 \pm 0.03 - 1.24 \pm 0.80$  mg/kg), V ( $1017.38 \pm 115.04 - 13382 \pm 124.3$  Mg/kg), Ba ( $6.91 \pm 0.90 - 11.520 \pm 1.02$  mg/kg), Ni ( $1.26 \pm 0.08 - 1.360 \pm 0.08$  mg/kg), Pb ( $2.29 \pm 0.08 - 2.43 \pm 0.10$  mg/kg), and Cr ( $1.40 \pm 0.06 - 1.47 \pm 0.09$  mg/kg). The result also indicated that the highest concentration of Cd, V and Ni were recorded in sampling point RSEN<sub>B</sub> while that of Pb, and Cr were recorded in sampling RSEN<sub>A</sub>.

However, the mean concentrations of Cd, V, Ba and Pb in the remediated soil were found to be higher than the WHO/FAO permissible limit. While Ni and Cr had mean concentrations lower than the permissible limit. The higher concentration of Cd, V, Ba and Pb could be as a result of the abundance of these metals in crude oil deposit. But the least concentration of Ni, and Cr could be as a result of the remediation work. Consequently the mean concentrations of heavy metals in the non-remediated soil were higher than their corresponding in the remediated soil, and are ten times greater than the permissible limit. Radulescu *et al.*, (2012) in their research work on soil contaminated by crude oil, they revealed that Cd has a mean concentrations of 2.01mg/kg which is lower than 3.820 mg/kg obtained in this study.

The concentration of the heavy metals in both remediated and non-remediated soil decreases in this order: remediated soil; V > Ba > Pb > Cr > Ni > Cd. Non-remediated soil: V > Ba > Cr > Cd > Pb > Ni. The high concentration of V and Ba in both soil samples indicated that they are the chief or major constituent metals in crude oils (Duyck *et al*, 2002).

Vanadium (V) is the 22nd most abundant metal on the earth crust, found in combined form in coal, petroleum and other minerals. Even after remediation, its concentration is still found to be over 9 times, 7 times and 6 times in RSEN<sub>B</sub>, RSEN<sub>C</sub> and RSEN<sub>A</sub> corresponding to the concentration of 11382.23, 1168.37 and 1017 mg/kg respectively which is higher than its permissible limit. Probably this is the reason why V is often referred to as the hazardous heavy element in the soil. In comparison with the non-remediated soil, part of Vanadium was successfully eliminated from the soil. However, since its concentration is still above the background limit (permissible limit), it is likely that the effects associated with high amount of Vanadium, such as decrease in stems length, poor fruits and roots in plants will occur. Also, health impacts such as liver and kidney damage could result from bioaccumulation when plants with high Vanadium cont are consumed over time.

#### 4.2 Metal Enrichment Factor (EF)

The metal enrichment factor (equation ii), is the ratio of the concentration of metals in non-remediated soil to the concentration of metals in remediated soil (Hikon *et al.*, 2018).  $0.5 \leq EF \leq 1.5$  suggests that the trace metals in the soil may come entirely from natural weathering processes (Zhang, *et al.*, 2002). However, an  $EF > 1.5$  indicates that a significant portion of the heavy metals were delivered from non-crustal materials so, these metals were released from other sources, like point and non-point pollution and biota (Maurizio, 2016). From Table 4.6 above, it can be seen that the only metal that follows the trend discussed above is Pb in SEN1 with  $EF < 1.5$  ( $EF = 1.47$ ). The rest of the metals, including Lead from the remaining two sites can be concluded as being delivered by other sources such as petroleum activities.

Vanadium from site SEN2 with EF 1.54 is approximately equal to 1.5, hence the source could be thought of as from natural weathering while the remaining two sites (SEN3 and SEN1) are from both point source and non-point sources; including crude oils. Chromium at site SEN2 is seen to have the highest EF value of 138.99, indicating how rich it is in the soil as well as other metals. Nickel shows no EF value. This shows that its amount on the soil is too negligible to be detected by the TPH analyzer, hence it can be concluded that Ni is not so rich in the soil, and any little amount found will likely be from natural process of weathering of rocks (from point source).

#### 4.3 Pollution Load Index (PLI)

The estimated values of pollution load index (PLI) indicate the degree of pollution based on potential contribution of all elements in a particular location (Rashed, 2019). For  $PLI < 1$  implies that there is no contamination on the soil by the metals. On the other hand,  $PLI > 1$  shows that the soil is contaminated. Chromium and Nickel found in the remediated soil as shown on the table above have PLI values less than 1, indicating that the soil was no more contaminated by these two metals as compared to the non-remediated soil where their PLI values are far greater than one (ranging from 2.6 – 12.8 mg/kg for Pb and 5.46 to 51.5 mg/kg for Cr).

Barium in remediated soil RSENC shows 0.77 PLI, which is less than one. Hence that particular location has been freed from the contamination of Ba while the remaining two remediated sites are still contaminated with Barium, even after treatment (with PLI value ranging from 1.1 - 1.28). This implies that there are either recontamination as a result of smokes from illegal refinery or surface run off of water, or the initial contamination resulting from crude oil spillage during drilling, transportation and other means are still retained. The main contaminants or pollutants of the soil from the findings are Cd, V and Pb which have PLI values far above 1 as seen on the table above.

#### 4.4 Speciation of Heavy Metals in Remediated and Non-remediated Soil

The different metal species in the soil were exchangeable fraction, Carbonate fraction, reducible fraction, organic fraction), inert fraction. The bioavailability and bioaccessibility, as well as the transfer factors of the metals depend on the amount that is bounded to F1, F2 and F3. If the amount of metals bounded to F4 – F5 are greater than those bonded to F1 to F3, the metal will not be available to be absorbed by plants, hence the term non-bioavailability is used. The reverse is the case when the concentrations of F1-F3 are greater (Garey *et al.*, 2015).

In sample site RSEN<sub>A</sub>, the concentration of Cd varies as follows; F1 –F3 have the concentrations of  $0.171 \pm 0.001$ ,  $0.180 \pm 0.010$  mg/kg and  $0.121 \pm 0.003$  mg/kg; with F2 having the highest concentration of  $0.180 \pm 0.010$ . The concentration of F4 and F5 were  $0.320 \pm 0.008$  and  $0.401 \pm 0.020$ . It can be seen that the amount of Cd bounded to F4 and F5 are greater than the F1 - F3 fractions. This implies that even if a large

amount of metal pollutants are present in the soil, since the larger portions are in the F4 and F5 fractions, they will not be readily released for the plants to absorb. Cd decreases in the following order: in RSEN<sub>A</sub>, F5>F4>F2>F1>F3. In RSEN<sub>B</sub>, F5>F4>F2>F1>F3, and RSEN<sub>C</sub> gives F5>F4>F1>F2>F3. The metal speciation results gotten in soils around Nasarawa sack and packaging bags Akwanga, Nigeria Yerima, (Yerima et al., 2019) shows that most of the heavy metals in their controlled sample followed the same trend of being bounded F5 and F4, while only lower fractions were held by F1-F3. However, the reverse was the case for the non-controlled or polluted soil. Sample site RSEN<sub>B</sub> and RSEN<sub>C</sub> recorded the highest concentrations in F4 and F5 (0.403±0.01 and 0.474±0.004 for RSEN<sub>B</sub>, and 0.305±0.004 and 0.415±0.010 for RSEN<sub>C</sub>), indicating non-bioavailability.

Vanadium, Barium, Nickel and Lead followed the same trend, showing that they are not bioavailable. However, there is an exception with Chromium on the remediated soil. In sample site RSEN<sub>A</sub>, the highest concentration was found in F5 (0.453±0.01), followed by F3 (0.370±0.005) while F4 (0.250±0.001), F1 (0.080±0.001), and F2 (0.040±0.002) being the least in concentrations. In RSEN<sub>B</sub>, Cr occurs highest in F5 and F3 (0.422±0.005 and 0.350±0.004 mg/kg), whereas F2 with the concentration of 0.041±0.004 mg/kg.

The result showed that the soil from non-remediated sites had greater values of metal species compared to the remediated site. Also, most of the highest values of metal concentrations were found bounded to F1, F2 and F3 (that is the exchangeable fraction, carbonate fraction, the reducible or Iron-Manganese fraction. The implication of this is that the metals in the non polluted soil are bioavailable for plant absorption. In sample site NRSEN<sub>X</sub> for example, Cd occurred most in F3 (3.80±0.05 mg/kg)>F4 (3.75±0.02 mg/kg), with the least occurring as follows F2>F1>F5. The abundance of Ba in NRSEN<sub>Y</sub> soil sample decreases in the order of F5>F1>F4>F2>F3, corresponding to the concentration 3.45±0.08, 3.10±0.20, 2.75±0.20, 2.65±0.32, 2.55±0.02 mg/kg.

#### 4.5 Total Petroleum Hydrocarbon (TPH)

The total petroleum hydrocarbon (TPH) content of the soil was determined, and the result obtained was presented on table 3.2 above. The background limit for TPH in the soil is 100 -300 mg/kg adopted from Thomas (2013). The remediated soil has a total petroleum hydrocarbon ranged from 193.65 to 207.04 mg/kg. In comparison to the permissible limit stated above, the concentration of TPH obtained falls at the threshold level, hence is considered safe for the environment. On the other hand, the non remediated soil showed a higher amount of TPH compared to the ones obtained from the remediated sites. In fact a range of 298.677 mg/kg (502.677mg/kg - 204.556 mg/kg) and 224.65 mg/kg (418.301mg/kg -193.65) implying that a very high percentage of TPH was removed during the remediation process.

Similar research was carried out on topsoil and subsoil samples from Onitsha North, Anambra state, Nigeria by Nwakwoala and Ememu (Nwakwoala & Ememu, 2018) and came out with results that fell on the same range with the on shown above; their concentrations of TPH range from 109.43 to 2112 mg/kg and 105.57 – 1747.82 mg/kg in topsoil and subsoil respectively. However, the lower range of their results indicated unpolluted whereas the upper values (from 300 mg/kg and above) are above the WHO background level, showing that the soil on those respective locations were polluted by TPH.

Since the TPH content of the remediated soil is still up to 100 and above (100-300b mg/kg), it is very likely that this amount will keep rising with time. The gradual increase will be as a result of recontamination or other negligible sources such as those released from cyclist and others. As such, it is advisable that phytoremediation; which involves the growing of plants that selectively absorb the toxic TPH should be carried out in order to maintain a balance.

#### 4.7 Percentage Removal of Total Petroleum Hydrocarbon Pollutants from the Soil

Percentage removal as presented on the table above shows that 56.277% of TPH was successfully eliminated from the contaminated soil of TNRSEN<sub>A</sub>. 58.09% was removed from polluted site TNRSEN<sub>C</sub> and at most, 59.798% from location TNRSEN<sub>B</sub>. It should be known that TPH above the back ground level can be lethal. Some of the common effects associated with TPH are; neurotoxicity, mutagenic and carcinogenic to humans (Raju *et al.*, 2020). The amount of total petroleum hydrocarbons (TPH) in percentage that was successfully removed from the crude oil contaminated soil from Nkeleoken community of Rivers state was determined using equation (iv) in chapter two. This was gotten by dividing the difference between the TPH of non-remediated soil and that of remediated soil by TPH of the non-remediated soil. It was found that 56.28% of TPH was removed from the first sample location; NRSEN<sub>A</sub>. While 43.72% remained in the soil. In the second location (NRSEN<sub>B</sub>), only 59.80% was eliminated from the soil leaving 40.20% in the soil as pollutants. Location NRSEN<sub>C</sub> had it that just 58.09% was removed.

On average, 58.06% of TPH was successfully removed from Nkeleoken community in Rivers state during the remediation carried out, leaving 41.94% in the soil. The aim of the remediation was to obtain either 100% or at least 90-99% TPH removal from the crude oil contaminated soil. It was shown that the mean TPH value of  $1633.56 \pm 1271.76$  mg/kg was obtained from crude oil contaminated soil of a different location (Ihejirika, 2019). This result is comparatively high compared the mean TPH obtained from the remediated soil on this research ( $202.09 \pm 30.04$  mg/kg) confirming that much TPH was removed during remediation. According to Agency for Toxic Substance and Disease Registry (ATSDR), the compounds in some TPH fractions can also affect the blood, immune system, liver, spleen, kidney, developing foetus and lungs. Certain TPH compounds can be irritating to the skin and eyes (Tochukwu *et al.*, 2020). One TPH compound (Benzene) has been shown to cause cancer (Paul *et al.*, 2018). Some other TPH compounds or petroleum products such as; benzo(a)pyrene and gasoline are considered to be probably and possibly carcinogenic to humans based on cancer studies in people and animals (Tony *et al.*, 2019).

One TPH compound (n-hexane) can affect the central nervous system in a different way, causing a nerve disorder called “peripheral neuropathy” characterized by numbness in the feet and legs, and in severe cases, paralysis swallowing. Some petroleum products such as gasoline and kerosene cause irritation of the throat and stomach, central nervous system, depression, difficulty in breathing and pneumonia from breathing liquid into the lungs. However, for the fact that some TPH fractions are persistent pollutants and are present in water and soil, signifies the sure intake of the substances through the roots of plants and presence in the fruits of the plants with higher tendencies for bioaccumulation in aquatic biota spells serious concern. The presence of TPH in the soil serves as a reservoir for PAHs leached into the ground water and as runoff into surface water. Its presence indicates the exposure of humans to health problems (Okezie, 2021).

#### 5.0 Conclusion of the Study

The purpose of Remediation is to totally remove the total petroleum hydrocarbons (TPH) or to eliminate at least 90-99% from the soil. And the research carried out shows that the concentrations of TPH at the remediated sites were below WHO permissible limit for soil. It would still be a challenge only if the amount of TPH left after remediation were higher than the background limit (based on WHO standard). Since there is a relationship between the obtained result and other’s similar work, it can be inferred that the work is of standard. With regards to the total concentration of the heavy metals in the remediated and non-remediated soil, speciation results showed that the remaining metals in the remediated soil are non-mobile, hence cannot be taken up by plant. This implies that most of the metal species after remediation were associated with the organic (F4) and residual fractions (F5). This is also an indication that the soil is safe in terms of heavy metal despite high pollution load index (PLI) values. Since the percentage removal of the total petroleum

hydrocarbon is not up to 100%, the study suggests that plants grown on the remediated soil should be investigated for bioaccumulation and transfer factor assessment. With regards to heavy metals concentration, it has been shown by the speciation result that the remediation was able to reduce most of the metals concentrations thereby making them immobile (non-bioavailable). Hence, this study recommends the growing of plants on the remediated soil to verify its viability for agricultural purposes.

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