American Journal of Multidisciplinary Research in Africa American Journal of Multidisciplinary Research in Africa Vol. 3(1), pp. 1-11, March, 2023 Copyright©2023 Author(s) retain the copyright of this article ISSN: 2769-0504 https://www.mprijournals.com/

Full Length Research

Review of Determination of Heavy Metals and Total Petroleum Hydrocarbon Concentrations in Remediated Crude Oil Contaminated Soil

JOSEPH Ahmadu Adamu

Department of Chemical Sciences (Industrial Chemistry),

Federal University Wukari,

Taraba State, Nigeria

Corresponding Author: joseadamsons@gmail.com

Accepted 15th March, 2023

Abstract: The discharge of crude oil products to the environment (soil, water and air) has great negative impacts on the organisms living therein. Most of these effects are from heavy metals, total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAH) among others. This research adopts an extensive review of literatures such as conference papers, journal articles, internet sources, books to find out the amount of total metal concentrations and the total petroleum hydrocarbons (TPH) that are likely to be found on crude oil contaminated soil even after remediation or cleanup activities have been carried out. The driving force behind this research is the fact that the people living in most petroleum-contaminated areas such as the Niger Delta Region of Nigeria still experience some negative effects (such as health and agricultural effects) associated with the crude oil pollutants even after remediation. The study concludes that even though heavy metals were still present in the remediated soil, they are not bioavailable for plants uptake; hence their presence is negligible harmless. On the other hand, the total petroleum hydrocarbons (TPH) that remains after cleanup is still well above the background level. As such, it would impose negative impacts on the inhabitants of such areas. The study further recommends that more effective methods of remediation should be carried out, or a combination of more than one method should be adopted in other to obtain absolute cleanup of the polluted area.

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

Cite This Article As: Joseph, A. A. (2023). Review of Determination of Heavy Metals and Total Petroleum Hydrocarbon Concentrations in Remediated Crude Oil Contaminated Soil. American Journal of Multidisciplinary Research in Africa, 3(1): 1-11.

1.0 Introduction of the Study

Soil is the thin layer of organic and inorganic materials that envelopes the Earth's surface. 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 & Maranho, 2018; Egan & Bamfo-Agyei, 2023). 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 loosed top layer of the Earth's surface, consisting of rock and particles mixed with decayed organic matter (humus), and capable of retaining water, providing nutrients for plants, and supporting a wide range of biotic communities (Ihejirika et *al*., 2019). The chemistry of a soil determines its ability to supply available plant nutrients and affects its physical properties and the health of its living population. In addition, a 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.

Abdulkadir et al. (2022) posited that a colloid is a small, insoluble particle ranging in size from 1 nanometer to 1 micrometer, thus small enough to remain suspended by Brownian motion in a fluid medium without settling. Most soils contain organic colloidal particles called humus as well as the inorganic colloidal particles of clay. The very high specific surface area of colloids and their net electrical charges give soil its ability to hold and release ions. Negatively charged sites on colloids attract and release cations in what is referred to as cation exchange. Cation-exchange capacity (CEC) is the amount of exchangeable cations per unit weight of dry soil and is expressed in terms of milliequivalents of positively charged ions per 100 grams of soil (or centimoles of positive charge per kilogram of soil; cmole/kg). Similarly, positively charged sites on colloids can attract and release anions in the soil giving the soil anion exchange capacity (Houghton, 2011). Man's activities in the environment have led to the pollution of soil mostly by chemical contaminants (Nwankwoala, 2018).

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%-3% sulfur, 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.

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. The crude oil so entered the soil can improve soil content of some nutrient elements including Mg^{2+} , K⁺, P, Na⁺ and exhibit a highly significant effect of reducing the chemical composition of soil (Sutton et al., 2013: Abdulkadir et al., 2022).Crop germination is delayed, the chlorophyll content is poor, and some crops perish when grown in high petroleum-contaminated soil. Furthermore, pollutants can enter the human body by breathing, contact with the skin and consumption of pollutantcontaminated animals (Agbogidi *et al.,* 2007).

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 Ogoniland. 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).

2.0 Review of Related Literature

2.1: Crude Oil Pollutant Remediation

Crude oil utilization has improved our living standard, but it has also threatened the aquatic and terrestrial environment with its harmful effects. 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).

2.1.1: Chemical Methods: 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).

2.1.2: Physical Methods: 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).

2.1.3: Thermal Methods: 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 ecofriendly. 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 the environment pollution (Smith, 2017).

2.1. 4 Biological Methods: 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 depended on hydrocarbon concentration, soil characteristics and composition of pollutants (Gentry *et al*., 2004).

2.2: Microbe Assisted Remediation

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).

2.2.1 Phytoremediation: 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)

2.2.2 Rhizoremediation: Rhizoremediation 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).

2.3: Metal Speciation

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 $(Hg^{2+}_{(aq)})$ and methyl mercury chloride $(CH₃HgCl_(aa)$ 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 $CrO₄^{2–}$ 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 complexed 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 species.

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, $SnF₂$ is a common additive of toothpaste. However, many organotin compounds, which are predominantly created by human industrial processes, are highly toxic (ATSDR, 2005). Tributylin tin, 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.

2.4: Bioavailability Concepts

The term *bioavailability* is used to address the potential for a substance to interact with an organism. With the use of this term now widespread among many disciplines, confusion sometimes develops as specific meanings emerge from a particular context, discipline, or method of study. An example is the meaning of bioavailability shared by the toxicology and pharmacology fields, where it refers specifically to the fraction of an administered dose that is absorbed into the organism's circulatory system or into the organ where an effect occurs (Ruby *et al*. 1999; NRC, 2003). The reason for such a restricted definition is clear upon consideration of the methodologies typically employed to evaluate efficiency of uptake of a drug or a toxicant. For example, a study might involve assays of blood levels of a given toxicant to identify peak plasma concentration and half-

life resulting from specific oral dosages. Even this definition of bioavailability could find disfavor, since substances absorbed through the gastrointestinal tract of humans first circulate through the liver, where metabolism may limit the amount released to general systemic circulation.

This view of bioavailability is of little value to the soil geochemist examining the fraction of a metal in a soil that becomes soluble and mobile during a sequential extraction procedure. In fact, there may be no universally acceptable definition of bioavailability, a prospect that may be most evident where operational definitions are desired (Ehlers & Luthy, 2003). Bioavailability processes can be defined as "the individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments. While a process-oriented view will be intuitive for many geochemists, the defined concept is purposely limited on the organism side to exclude processes following transport of a substance across the biological membrane. Because of the context relating to soil and sediment contaminants, it places emphasis on those factors and processes that make the substance "available" to the organism, that is, in a form that can be transported across the organism's biological membrane. This is most commonly interpreted to be a soluble form. However, it is also possible that very small solids or colloidal particles could be transported across some membranes, such as the linings of lungs (Ruby *et al*., 1996, 1999).

2.5: Metal Speciation and Total Petroleum Hydrocarbons (TPH)

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);

Enrichment Factor (EF) = Concentration of metals in non-remediated site …………….(ii) Concentration of metals from remediated site

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). **%Removal of TPH** = X1-X2 x100 …………………………………………… (iv) X1

Where X1is 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.

2.6: Role of Metals in Human Health and Metal Toxicity Concepts

The human body requires the uptake of several essential metals for its proper function. The roles of some of the essential heavy metals such as vanadium and Tungsten are not fully known (Ayua et al., 2023: Abdulkadir & Ajagba, 2022). For others, including Arsenic and Tin, essential roles have been suggested, but not demonstrated. Some metals play a role in active centers of metalloenzymes. In fact, for metals such as Cobalt this may represent the dominant "species" in the human body. Other metals, such as Chromium (III) and Vanadium, are metabolized within the body to form low molecular weight compounds that play a role in glucose metabolism. For some metals, a deficiency may be expressed as a specific disease. For example, Chromium is important in the human metabolic system. A lack of Chromium disrupts glucose metabolism and can lead to obesity,

diabetes, and cardiovascular disease, as well as the impairment of the reproductive system. It is important to note that deficiency in a metal may be caused by several factors. A diet lacking an essential metal is a common cause. For example, in China outbreaks of Keshan disease, a type of heart disease, are restricted to well define geographic regions (Fordyce, 2005). The occurrence of this disease is associated with a lack of dietary Selenium. It is within this context that speciation is important.

Crops grown on soil must be able to extract the Selenium from the soils. Within Zhangjiakou District, Hebei Province, China, Keshan Disease has a high prevalence despite the fact that there is significant total Selenium in the soil. In fact, a study in this region showed that the prevalence of the disease is not correlated with a lack of Selenium in the soil as might be expected (Johnson *et al*., 2000). Rather, the cause for the Selenium deficiency in the diet is a result of the fact that the soil-bound Selenium is not in a form that is available to the plants. Soils in affected areas are rich in organic matter, and it is hypothesized that Selenium is strongly bound with the organic fraction (Johnson et al. 2000). Alternatively, the organic matter may promote reduction of selenate to selenite, the latter commonly being more strongly sorbed to iron hydroxides in soils (Hartikainen, 2005). While geological factors have been shown to contribute to diseases, such as Keshan Disease, additional confounding factors can lead to complex patterns in the prevalence of a disease. The interaction between metals (or metalloids) is one of the confounding factors.

Nutritional status is known to affect toxicity. For example, anemia—low iron status—promotes the uptake of Nickel and Manganese. Hence, individuals affected by anemia are at a higher risk for adverse effects of Nickel and Manganese uptake compared to healthy individuals exposed to the same Nickel and manganese levels. Conversely, exposure to methylmercury has been shown to inhibit uptake of selenium, an antioxidant (Norling *et al*., 2004). A second major confounding factor is genetic predisposition. Genetic disorders that disrupt the uptake or transport of essential metals or formation of antioxidants are more difficult to diagnose and remedy (Zhou *et al*., 2001). Exposure and uptake of toxic metals, or even essential metals at levels in excess of the optimal range, can lead to adverse health effects. Exposure history is an important factor in evaluating the toxicity of a metal. Toxicologists distinguish between acute and chronic toxicity. Acute toxicity is that associated with short-term exposure to a toxicant, sometimes in lethal doses. Chronic toxicity is that associated with long-term exposure, and is usually the type most relevant to environmental toxicants.

2.7: Economic Effects of Crude Oil Spillage

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 (Essien & Antai, 2005; Abu & Chikere, 2006; Cohen, 2008; Essien & Antai, 2009).

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.

3.0 Methodology of the Study

The study adopts an extensive review of literature such as conference papers, journal articles, internet sources, books to determine the effectiveness of remediation activities that have been carried on crude oil contaminated soil in Niger Delta Region of Nigeria. This particular approach was chosen in order to review previous articles and articulate the degree of each heavy metal present on remediated soil, as well as total petroleum hydrocarbons (TPH) in other studies and make suggestions to future researchers who may decide to adopt an empirical method to validate the findings identified in this study.

4.0: Conclusion of the Study

Remediation activities are usually carried out with the purpose of complete removal of total petroleum hydrocarbons (TPH), heavy metals and other pollutants or eliminating at least 90-99% of them 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. With regards to the total concentration of the heavy metals in the remediated and non-remediated soil, percentage bioavailability analysis showed that metals in the remediated soil are nonbioavailable for plant uptake. This implies that most of the metal species after remediation were associated with the organic and residual fractions. 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%, I hereby suggest that plants grown on the remediated soil should be study 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 I still recommend the growing of plants on the remediated soil to verify its viability for agricultural purposes.

5.0: Acknowledgement: With a grateful heart, I wish to acknowledge my supervisor; Dr. B.N Hikon, for his kindness, guidance and support all through the period of this research work. My profound gratitude goes to the great scholar, Dr. Akintunde Ajagbe; the Publisher and Editor in Chief, Maryland Publishing and Research Institute, Inc. USA, for his mentorship, kindness and patience that resulted to the success of this work. His great contribution (funding, corrections, and advice) is accepted and appreciated with an immeasurably high esteem.

6.0 References of the Study

Abbaspour, A., Zohrabi, F., Dorostkar, V., Faz, A. & Acosta, J. (2020). Remediation of an Oil Contaminated Soil by Two Native Plants Treated With Biochar and Mycorrhizae. *J. Environ. Manag. 254*, 109755.

Adekola, F., Abdus-Salam, N., Bale, R. & Oladeji, I. (2010). "Sequential Extraction of Trace Metals and Particle Size Distribution Studies of Kainji Lake Sediment, Nigeria. *Chem. Spec. Bioavailab.* 22(1): 43- 49.

Ayua, G. T., Magomya, A. M. & Etim, E. E. (2023). A Technical Report of Student Industrial Work Experience Scheme (SIWES) on Oracle Business Conglomerate Feeds Proximate Analysis Lab. *American Journal of Multidisciplinary Research in Africa*, 3(1): 1-12. DOI: https://doi.org/10.58314/2667TYO

Abdulkadir, B. & Ajagba, G. C. (2022). Cassava Grating Machines, Designs and Fabrication: A Review of Related Literature. American Journal of Multidisciplinary Research in Africa, 3(1): 1-11. DOI: https://doi.org/10.58314/908876

Agbogidi, M., Eruotor, G. & Akparobi, O. (2005). Effects of Crude Oil Levels on the Growth of Maize (Zea Mys L.). *American Journal of Food Technology,* 2(6): 66-77. DOI:10.3923/ajft.2007.529.535.

Anyadoh, S. O. & Ibekwe, V. I. (2007). Cleanup of crude oil-contaminated soil. *Terrestrial and Aquatic Environmental Toxicology,* 1(2): 54-59.

Abdulkadir, B., Ajagba, G. C. & Joshua, F. J. (2022). Empirical Investigation on the Design and Fabrication of Cassava Grating Machine of 4.5kw. *American Journal of IT and Applied Sciences Research*, 1(4): 1-10. https://doi.org/10.58314/278975

Barnes, D., Laderach, S. & Showers, C. (2002) Treatment of Petroleum-Contaminated Soil in a Newly Isolated Pseudomonas Sp. Strain from Used Motor Oil-Contaminated Soil. International Biodeterioration & Biodegradation, 122: 128- 140. Cold, Wet, Remote Regions, Missoula: USDA Forest Service.

Hikon, B. N., Egah, G. O., Ngatem, G. S. & Bwede, D. D. (2018). Bioavailability and Plants Uptake of Selected Heavy Metals in Akwana Mining Site and Environs, Wukari, Taraba State, Nigeria. *International Journal of Modern Chemistry,10(2):154-171.*

Chandran, P. & Nlanjana, D. (2011). Microbial Degradation of Petroleum Hydrocarbon Contaminations: An Overview. *Biotechnology International, 2(1); 88-97.*

Chebbi, A., Hentati, D., Zaghden, H., Baccar, N. & Rezgui, F. (2017) Polycyclic Aromatic Hydrocarbon Degradation and Biosurfactant Production by a Newly Isolated Pseudomonas Sp. Strain from Used Motor Oil-Contaminated Soil. *International Biodeterioration & Biodegradation,* 122, 128-140.

Egan, C. A. & Bamfo-Agyei, E. (2023). The Influence of Temperature Control on Labour Productivity on Masonry Work. *American Journal of IT and Applied Sciences Research,* 3(1): 1-13. https://doi.org/10.58314/23456H

Edwin-Wosu, N., Kinako, P., Essien, J. & Antai, S. (2011). Socio-Economic Variables Associated with Poverty in Crude Oil Polluted Crops Farms in Rivers State, Nigeria. *Journal of Applied Sciences,* 1(3): 462- 472.

Ezeji, U., Anyadoh, S. O. & Ibekwe, V. I. (2007). Cleanup of crude oil-contaminated soil. *Terrestrial and Aquatic Environmental Toxicology,* 1(2): 54-59.

Gentry, T. & Pepper, C. (2004). New Approaches for Bioaugmentation as a Remediation Technology. *Critical Reviews in Environmental Science and Technology,* 34(5): 447-494.

Germida, J., Frick, C. & Farrell, R. (2002). Phytoremediation of Oil-Contaminated Soils. *Developments in Soil Science*, 28: 169-186.

Ihejirika, C. E., Iheanacho, C., Okezie, U., Dike, M. U. & Njoku, P. C. (2019) Post-Remediation Assessment of the Quality of Oil Spill Impacted Soils. *J Environ Pollut Manage., 2: -191-203.*

Fagbote, E., & Olanikpekun, E. (2010). Evaluation of the Status of Heavy Metal Pollution of Soil and Plant (hromalaena Odorata) of Agbadu Bitumen Depot Area, Nigeria. *American–Eurasian J Sci Res.,* 5, 241-248.

Gentry, T. & Pepper, C. (2004). New Approaches for Bioaugmentation as a Remediation Technology. *Critical Reviews in Environmental Science and Technology,* 34(5): 447- 494.

Gebeyehu, C., Gedefa, S., Dagne, C. & Garoma, F. (2022). Performance Evaluation of Bread Wheat (Triticum Aestivum L.) Varieties for Grain Yield in BunoBedele, South West Oromia, Ethiopia. *American Journal of IT and Applied Sciences Research*, 1(4): 1-11. https://doi.org/10.58314/467900

Hartkainen, H. (2005). Biochemistry of Selenium, and its Impact on Food Chain Quality and Human Quality and Human Health. *Critical Reviews in Environmental Science and Technology*, 18(4): 309-318.

Johnson, E., RIngo, S. & Dowse, H. (2000). Native and Heterologous Neuropeptides are Cardioactive in Drosophila Melanogaster. *J. Insect Physiol.,* 46(8): 1229-1236.

Kong, F., Sun, G. & Liu, K. (2018). Degradation of Polycyclic Aromatic Hydrocarbons in Soil Mesocosms by microbial/Plant Bioaugmentation: Performance and Mechanism.Chemosphere198:83- 91.Irispublishers

Maurizio, B. (2016). *The Importance of Enrichment factor (EF) and Geoaccumulation Index n (Igeo) to Evaluate the Soil Contamination.* Department of Earth Science, Sapienza University of Rome, P.le Aldo Moro5-00185 Rome, Italy.

Oluwatson, G., Adeyolanu, O., Dauda, T. & Akinbola, G. (2008). Levels and Geochemical Fractions of Cd, Pb and Zn in Valley Bottom Soils of some Urban Cities in South-Western Nigeria. *African J Biotech.,* 7(19): 3455-3465.

Olusesi, A. & Joshua, F. J. (2022). An Empirical Investigation of Automatic Streets Lighting Systems Design and Implementation for Crime Prevention in Residential Areas. *American Journal of IT and Applied Sciences Research*, 1(4): 1-10. https://doi.org/10.58314/262690

Owhe-Ureghe, U. B., Okorie, E. C., Olunaike, J. H. & Okhani, P. (2022). Empirical Analysis of Enteric Pathogens in Raw Milk Sold at Aduwawa, Agbor, Asaba, Auchi and Warri, Nigeria. *American Journal of IT and Applied Sciences Research,* 1(3): 1-12. https://doi.org/10.58314/235509

Plumlee, G. & Ziegler, T. (2006). The Toxicological Geochemistry of Earth Materials: An Overview of Processes and the Interdisciplinary Methods Used to Understand Them. *Rev Mineral Geochem*, 63:xxxx-xxxx

Raju, M., Mallavarapu, M., Kadiyala, V. & Kuppusamy, S. (2020). Ecological Impacts of Total Petroleum Hydrocarbons. *Critical Reviews in Environmental Science and Technology*, 8(2): 109-123. DOI: 10. 1007/978- 3-030-24035-6_5

Rashed, N. & Han, B. (2021). Heavy Metals in the Environment, C*oastal Zone Management, Science Direct; CR2022.*

Ruby, M., Schoof, R., Brattin, W., Goldade, M., Post, G. & Harnois, M. (1999). Advances in Evaluatin the Oral Bioavailability of Onorganics in Soil for Use in Human Health Risk Assessment. Arsenic, Bioavailability, Metals. Environmental Science and Technology. *American Chemistry Society*, 4(4): 45-67. https://doi/10.1021es1990479z.

Seitinger, P., Baumgarbner, A. & Schindlbauer, H. (1994). The Behaviour of Oil Spills in Soils and Groundwater. *National Resources and Development*, 40: 69-84.

Thomas, F. (2013). What is the Limit of Total Petroleum Hydrocarbons in Soil?. Researchgate.net/520e433d11b8d3bef9b94/citation/download

Ukonu, C. U., Lasisi, H. O., Adewole, E. A. & Olunaike, J. H. (2022). Empirical Analysis of Hydrogen Cyanide in Streams used for Commercial Fermentation of Cassava. *American Journal of IT and Applied Sciences Research*, 1(3): 1-9. https://doi.org/10.58314/456890

Yerima, E. A., Hikon, B. N., Ogbodo, C.V., Ataitiya, H. & Ani, J. D. (2019). Chemical Speciation and Mobility of Heavy Metals in Soils Around Nasarawa Sack and Packaging Company Akwanga, Nigeria. *Journal of Advances in Chemistry, 5(16): 21-32.*

Yabpella, G., Hikon, B., Magomya, A., Josua, Y. & Paninga, M. (2020). Influence of Soil Properties on Metal Availability; A Case Study of Arufuand Akwana Mine, Taraba State, Nigeria. *Department of Chemical* Sciences, Federal University Wukari, PMB 1020 Wukari Taraba State. Asian Journal of Biochemistry ISSBN 1815-9923.

Yusuf, K. (2007). Sequential Extraction of Lead, Copper, Cadmium and ZINC in Soils near Ojota Waste Site. *J Agronomy,* 6(2): 331-337.

Zhang, J. & Liu, C. L. (2002). Riverine Composition and Estuarine Geochemistry of Particular Metals in China-Weathering Features, Anthropogenic Impact and Chemical Fluxes. *Estuar Coast Shelf Sci*., 54: 1051- 1070.