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Assessment Of Heavy Metals And Total Petroleum Hydrocarbon Content Of Soil From A Farm Near A Petroleum Filling Station In Effurun, Delta State

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Abstract*: This project assessed the heavy metals and total petroleum hydrocarbon content of soil from farm near petrol filling station in Effurun, Delta State. This research was conducted to determine the concentration of heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon as well as pollution levels. Approximately 300g of composite soil samples was collected at a depth 0cm - 20cm based on proximity to the grid points. Findings revealed that farms around petrol filling stations where moderately polluted with manganese and petroleum hydrocarbon posing effects of soil degradation and potential harm to groundwater, affecting ecosystems and human health. Also, farms were unpolluted with chromium and nickel. While these values may not immediately pose significant threats based on common environmental standards, the accumulation of heavy metals and petroleum hydrocarbons in soil can have long-term implications, especially as it regards Lead. Continuous exposure to even low levels of heavy metals and TPH can degrade soil quality, disrupt plant growth, and pose a risk to groundwater through leaching. In conclusion, heavy metals and Total Petroleum Hydrocarbon (TPH) levels of soil near petrol filling stations are moderately polluted. Statistical analysis showed that concentration levels are similar across all farms.*

ASSESSMENT OF HEAVY METALS AND TOTAL PETROLEUM HYDROCARBON CONTENT OF SOIL FROM A FARM NEAR A PETROLEUM FILLING STATION IN EFFURUN, DELTA STATE

BY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF HIGHER NATIONAL DIPLOMA IN SCIENCE LABORATORY TECHNOLOGY

PETROLUEM TRAINING INSTITUTE
PMB 20, EFFURUN,
DELTA STATE
NIGERIA

NOVEMBER, 2024

CERTIFICATION

This is to certify that this project work "ASSESSMENT OF HEAVY METALS AND TOTAL PETROLEUM HYDROCARBON CONTENT OF SOIL FROM A FARM NEAR PETROLEUM FILLING STATION IN EFFURUN, DELTA STATE" was carried out by TOBORE AKPEVWE (M.22/HND/SLT/11425) the DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY and all literatures used in the course of this research were correctly acknowledged, cited and fully referenced.

Sign: ______________________ __________________

MRS. MFON OTITE - DOUGLAS **Date**
(Project Supervisor)

Sign: ____________________ __________________

DR. D. N. OLOWOYO **Date**
(Head of Department)

DEDICATION

I dedicate this project work to Almighty God for His guidance, support and care throughout my stay in petroleum Training Institute, Effurun. I acknowledge all praise to the Almighty God for bestowing upon me the ability to complete this project.

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ABSTRACT

This project assessed the heavy metals and total petroleum hydrocarbon content of soil from farm near petrol filling station in Effurun, Delta State. This research was conducted to determine the concentration of heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon as well as pollution levels. Approximately 300g of composite soil samples was collected at a depth 0cm - 20cm based on proximity to the grid points. Findings revealed that farms around petrol filling stations where moderately polluted with manganese and petroleum hydrocarbon posing effects of soil degradation and potential harm to groundwater, affecting ecosystems and human health. Also, farms were unpolluted with chromium and nickel. While these values may not immediately pose significant threats based on common environmental standards, the accumulation of heavy metals and petroleum hydrocarbons in soil can have long-term implications, especially as it regards Lead. Continuous exposure to even low levels of heavy metals and TPH can degrade soil quality, disrupt plant growth, and pose a risk to groundwater through leaching. In conclusion, heavy metals and Total Petroleum Hydrocarbon (TPH) levels of soil near petrol filling stations are moderately polluted. Statistical analysis showed that concentration levels are similar across all farms.

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CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

For the past decades, Nigeria has been actively involved in the exploration and exploitation of petroleum. These activities have elevated the growth of the petroleum industry and subsequently associated environmental degradation events including vandalism, blowouts, leakages from tanker trucks, spills amongst others (Adewuyi, Etchie and Etchie, 2012). The aftermath of these events is now clearly seen in many regions around the southern part of the country where these activities are imminent (Adewuyi, Etchie and Ademoyegun, 2011).

As recorded by the Nigerian Oil Spill Monitor (2023) over 50,000barrels of crude oil has been released into the environment in Nigeria within the past twenty (20) years hence causing irreversible and irreparable damage to nature and the environment. These is characterized essentially by high levels of hydrocarbons which is composed of a variety of components such as heavy metals, suspended solid and persistent organic pollutants. According to Bouafa *et al.,* (2023) these components are resistant to environmental degradation, difficult to metabolize, and have the potential to build-up in the food chains of humans or ecosystems through ingestion.

Contamination of the environment by petroleum hydrocarbon and heavy metals can become a serious issue even to the marine environment as some harmful elements can get to the marine environment via sediment contamination and transportation (Ashiru and Ogundare, 2019). These substances become persistent pollutants which are toxic to plants due to their detrimental effects on seed germination, effects on microbial bioavailability and health effects on man such as carcinogenicity (Useh, Etuk-Udo and Dauda, 2015).

Additionally, such contamination tends to harden or change the texture of the soil and limit microbiological activities. This is because sequestration of petroleum hydrocarbons in soil may result in limited bioavailability (Useh *et al.,* 2015). To fight against these pollution problems, several solutions have been put forward by researchers. While these solutions have proved effective, they are rarely applied in several areas hence increasing environmental risk seen residents have to rely on self-purification (natural attenuation) process of the environment (Bouafa *et al.,* 2023). It has been shown that microorganisms native to the contaminated sites can degrade pollutants by their natural metabolism.

It is conceivable that the devastating effects of petroleum activities has impacted communities in Delta state. However, there are limited data on the existing level of pollutants in the environment which could serve as a baseline data to aid in a rapid response to such environmental mishaps (Uwem and Sunday, 2018). It is therefore necessary to conduct this study.

1.2 Aim of the Study

The aim of the study is to assess the heavy metals and total petroleum hydrocarbon content of soil from farms near petrol filling stations in Effurun, Delta State.

1.3 Objectives of the Study

The objectives of the study are;

I. To determine the concentration of heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon in farm near petroleum filling station.

II. To ascertain the spatial distribution of heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon around the study area and its pollution index values.

III. To compare with concentrations of heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon in control soil.

1.4 Significance of the Study

This study shows the spatial distribution of heavy metal and total petroleum hydrocarbons in soil around petrol filling stations as well as indicating the influence of these facilities on soil quality. It will also portray the environmental risk to which residents are exposed to as it regards soil contamination and help in developing measures to minimize contamination. It will help to create a base for further study in a similar area and aid in determining areas requiring urgent attentions.

1.5 Scope of the Study

This study is limited in scope to the assessment of the heavy metals (Lead, Cadmium, Manganese, Nickel) and total petroleum hydrocarbon content of soil from farms near petrol filling stations in Effurun, Delta State.

CHAPTER TWO

LITERATURE REVIEW

2.1 Soil

Soil is a major component of the world's ecosystem and consisting of both biotic and abiotic factors necessary for the development of living organisms (Idibie and Idibie, 2021). Ayodele (2019) categorizes it as a heterogeneous mixture of inorganic solids, organic (humic) solids gases, and liquids formed from the decomposition of rock and organic matter overtime. Soil is composed of several chemical elements occurring naturally like nitrogen and oxygen that play an essential role for plant growth.

The physical, chemical and biological properties of soil make it an excellent medium for plant growth and other functions. However, soil contaminations which may be natural or human induced have weaken soil properties including influencing plant root development, soil water absorption by plant, biotoxicity soil structure, water stress and nutrients deficiencies (Idibie and Idibie, 2021). According to Uqetan *et al.* (2017) variety of contaminants affect topsoil and subsoil leading to soil pollutions especially in farm lands and hence requiring enhanced ploughing and harrowing for effective cultivation.

2.2 Soil Pollution and Sources

Soil pollution is the occurrence in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease-causing agents, which have adverse effects on plant growth and animal health (Ewetola, 2013). The pollution of the environment (mainly terrestrial and aquatic) by petroleum is the most common occurrence destroying soil structure, increasing soil bulk density, soil reducing soil porosity, aeration and nutrients availability (Uquetan *et al.,* 2017). This could also be caused by industrial activities, agricultural chemicals, or inappropriate disposal of waste. Soil is most often contaminated with heavy metals and petroleum products (Albuquerque *et al.,* 2017).

Soil pollution can also lead to water pollution if toxic chemicals leach into groundwater, or if contaminated runoff reaches streams, lakes, or oceans. According to Food and Agriculture Organization (FAO) (2018) soil pollution comes from both point and diffused sources.

2.2.1 Points Sources: Point sources contamination is one caused by a specific event or a series of events within a particular area in which contaminants are released to the soil, and the source and identity of the pollution is easily identified. Examples include former factory sites, inadequate waste and wastewater disposal, uncontrolled landfills, excessive application of agrochemicals, spills of many types, and many others. Point-source pollution is very common in urban areas. Soils near roads have high levels of heavy metals, polycyclic aromatichydrocarbons, and other pollutants (Kim *et al.,* 2017).

2.2.2 Diffused Sources: Diffuse pollution is pollution that is spread over very wide areas, accumulates in soil, and does not have a single or easily identified source. Diffuse pollution occurs where emission, transformation and dilution of contaminants in other media have occurred prior to their transfer to soil (FAO and ITPS, 2015). Examples of diffuse pollution are numerous and can include sources from nuclear power and weapons activities, uncontrolled waste disposal and contaminated effluents released in and near catchments, land application of sewage sludge, the agricultural use of pesticides and fertilizers which also add heavy metals, persistent organic pollutants, excess nutrients and agrochemicals that are transported downstream by surface runoff, flood events and atmospheric transport and deposition.

2.3 Petroleum Industries and Operations in Nigeria

According to Uqueta *et al.* (2017), the petroleum industry both significantly contributes to land degradation in Nigeria's Niger-Delta region and serves as the primary engine of the country's economy. Since its discovery, the nation has continued to explore for and develop its oil resources, particularly in areas rich in oil. However, the environment continues to be adversely affected by oil exploitation at every level (Bello and Anobeme, 2015). This is because the contaminants present in petroleum oil's impacts negatively the physical, chemical, and microbiological characteristics, which in turn impaired agricultural seed germination and hindered the growth of farmed crops.

Currently, several communities in Nigeria are impacted by petroleum related activities and products especially around petrol filling stations.

2.4 Petrol Filling Station

Petrol filing station is a facility where fuel and other petroleum products including Premium Motor Spirit (PMS), Liquefied petroleum gas, Automated Gas Oil and Dual Purpose Kerosene are sold for automobiles use (Afolabi, Olajide and Omotayo, 2011). These fuels are vapours that carry hazardous potential and highly to result in hazardous events such as fire in the case of mishandling. Petrol filling stations present health and safety concerns, especially to soil based on its constituents.

Petrol filling station often comprise of underground tank farms that exist for storage of petroleum products. Operation of petrol filling stations serve as a medium for solving fuel scarcity in Nigeria and has overtime continued to show great relevance to the Nigeria power system (Ships and Port, 2016). However, poorly constructed underground tanks within these stations may cause hazards to communities such as fire outbreak, soil deterioration, atmospheric pollution and others.

According to Ulakpa *et al.* (2022) the use of underground storage tanks and inappropriate disposal of petroleum wastes in and around petrol filling station causes environment contamination by increasing the concentration of petroleum hydrocarbons and heavy metals in soil. Additionally, fuel reports on the potential impact on the environment, including soil degradation, air pollution, and water contamination is well documented. Alharbi *et al.* (2018)

study on the application of underground storage tanks found that thirty-five VOCs were identified in the water samples collected from petrol filling stations including, Methylene chloride, tribromomethane, toluene, chlorobenzene, dibromochloromethane, and benzene. The measured petroleum hydrocarbon levels were clearly indicative of subsoil contamination and subsequent accumulation in soil over time,

2.4.1 Soil Contamination from Spills and Leakages of Petroleum Products

In Nigeria, most of the terrestrial ecosystems and shoreline in oil-producing areas are important agricultural lands. However, contact with petroleum and/or refined petroleum products, causes damage to the soil conditions of these agricultural lands, which culminates in loss of soil fertility. This fertility is reduced due to the constituents within the oil such as monocyclic aromatic hydrocarbons, PAHs and trace metals. Overtime, petroleum product spills and leakages have led to unfavourably effects on inorganic levels of soils (Oyem and Oyem, 2013).

Consequently, many heavy metals in petroleum products are basically a reflection of those carried over during movement of the source rock to the reservoir rock. Metals in crude oil also come from the use of drilling mud during crude oil extraction. These substances, when further added to the crude oil, act as toxins in the soil. These heavy metals in the crude dispense themselves into the petroleum fractions after fractionation and refining thus giving rise to their presence in petroleum products. Generally, refined products will produce more toxic effects than crude oil and the relative toxicity of oil is directly correlated with the proportion of PAHs. Levels of monocyclic aromatic compounds in soil increases majorly due to soil contamination from refined petroleum products as seen in previous studies by Ubong and Edwin (2018) on their research of petroleum products effect on soil around truck park areas in Nigeria.

2.4.2 Types and Effects of Soil Contaminants from Petroleum Products

In considering the types and effects of soil contaminants from petroleum products, it is important to consider the types of contaminants that could be present in soils, it is important to consider the chemicals that offer the greatest threat to human health. Contaminants that pose major risk to soil are usually those chemicals in nature than biological. Examples of these contaminants include heavy metals, asbestos, dioxins and persistent organic pollutants (Science Communication Unit, 2013).

2.4.2.1 Heavy Metals: Soil acts as a repository for many heavy metals that human activity releases into the environment. This may protect the wider environment to some extent by 'locking away' heavy metals and preventing them reaching other parts of the environment, such as water supplies. However, the soil itself may then present a risk to those who live or eat crops grown on it (Morgan, 2013). Various heavy metals include Arsenic (As), Lead (Pb), Cadmium (Cd), Chromium (Cr) (although only the form Cr(VI) is toxic, Copper (Cu), Mercury (Hg), Nickel (Ni) and Zinc (Zn). The concentrations of heavy metals in soils are varied according to the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the soils (Bashir *et al.,* 2014).

2.4.2.1.1. Lead (Pb): Lead pollution in soil is a serious environmental concern due to its persistent and toxic nature. Lead can accumulate in soils through various sources, such as industrial activities, vehicular emissions, lead-based paints, and contaminated water runoff, often near urban and industrial areas. Once in the soil, lead does not readily degrade and can remain for extended periods, posing a risk to both human health and ecosystems.

2.4.2.1.2. Chromium (Cr): Chromium is a less seen element and occurs naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite ($FeCr_2O_4$). Major sources of chromium contamination include releases from electroplating processes and the disposal of Cr containing wastes. Chromium (VI) is the form of chromium commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Chromium (VI) is the dominant form of chromium in shallow aquifers where aerobic conditions exist (Raymond and Felix, 2011).

2.4.2.1.3. Arsenic (Ar): Arsenic is a metalloid that occurs in a wide variety of minerals, mainly as As_2O_3, and can be recovered from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. It is also present in ashes from coal combustion. In aerobic environments, Arsenic is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states. Arsenate and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Alysson and Fabio, 2014). Since arsenic is often present in anionic form, it does not form complexes with simple anions such as chlorine ion (Cl^-) and sulhpur (IV) oxides (SO_4^{2-}).

2.4.2.1.4. Zinc (Zn): Zinc is added during industrial activities, such as mining of coal, waste combustion and steel processing. Industrial sources or toxic waste sites may cause the concentrations of Zn to reach levels that can cause health problems (Alysson and Fabio, 2014). Zinc shortages can cause birth defects (Wuana and Okieimen, 2011). A consequence is that Zn polluted sludge is continually being deposited by rivers on their banks.

2.4.2.1.5. Cadmium (Cd): Cadmium with mercury (Hg) and Lead (Pb), Cd is one of the big three heavy metal poisons and is not known for any essential biological function (Raymond and Felix, 2011). In its compounds, Cd occurs as the divalent Cd (II) ion.

2.4.2.1.6. Nickel (N_i): Nickel pollution in soil poses significant environmental and health risks due to the element's toxic nature at elevated levels. Nickel can enter the soil from various sources, including industrial emissions, mining activities, waste disposal, and the use of nickel-containing fertilizers and pesticides. Nickel-contaminated soil can also affect water quality, as it may leach into groundwater, further spreading its impact on ecosystems and public health.

2.4.2.1.7. Iron (Fe): Iron pollution in soil often originates from industrial activities such as mining, smelting, and the disposal of iron-rich waste. While iron is a naturally occurring element essential for plant and animal life, excessive amounts in soil can alter the soil's pH, affecting its structure and fertility. Elevated iron levels can also disrupt the availability of other essential nutrients, potentially stunting plant growth and affecting crop quality.

2.4.2.2. Asbestos: According to Science Communication Unit, (2013) asbestos contamination in the soil is of concern in many locations, because it can be released to the air by the wind or by human disturbance. Asbestos has long-term health consequences if it is inhaled, with increased mortality from lung cancer and mesothelioma. Disturbing contaminated soil can pose an inhalation risk. Studies have shown asbestos concentrations of health concern may be released from soils that contain only low levels (less than 1%) asbestos contamination.

2.4.2.3. Dioxins: Dioxins are a group of chemically-related compounds that are persistent organic pollutants (POPs). Highly toxic, dioxins accumulate up the food chain, with the highest levels found in animals at the top of the food chain. The largest source of dioxin in human is through application of herbicides on agricultural soils. Waste incineration, industrial processes and deposition onto soils from atmospheric fallout are also significant sources. When dioxins enter soils, they remain in the very top layer (the top 0.1 cm) with a half-life (time taken for concentration to halve) of 9-15 years. At deeper soil levels, dioxins can persist for 25-100 years (Science Communication Unit, 2013).

2.4.2.4. Persistent Organic Pollutants: Organic (carbon-based) pollutants include pesticides. Those that were once released into air or water will end up in soils, with the exception of those that are deposited at the bottom of oceans. Among organic pollutants some are referred to as 'POPs,' or persistent organic pollutants, which do not break down quickly in the environment. They can be found to emanate from petroleum products and they include**;**

Polychlorinated biphenyls (PCBs)

Polycyclic aromatic hydrocarbons (PAHs)

Organic fuels (gasoline, diesel)

2.4.2.5. Total Petroleum Hydrocarbon: Petroleum hydrocarbons in the environment at many contaminated sites all over Nigeria and in other developing countries has been reported. Hydrocarbon concentrations are elevated by aliphatic and aromatic hydrocarbons such as phenol, naphthalene, benzo (a) anthracene, benzo (a) pyrene, and fluoranthene. The present-day petroleum-based and non-petroleum produced chemical compounds mainly blended by employing base oils composed of hydrocarbons (organic compounds containing carbon and hydrogen exclusively) (Ayodeji *et al.,* 2019). Their introduction into soil increases pollution index of soil.

2.5 Bioremediation Technologies for Petroleum Based Soil Contaminants

Biotechnology refers to a set of scientific techniques that utilize living organisms (which could be plants or animals) or parts of organisms to make, modify or improve products. It is also the development of specific organisms for specific application or purpose and may include the use of novel technologies such as recombinant DNA, cell fusion and other new bioprocesses. It is usually applied for environmental pollution control or remediation. There exist various types of biotechnologies which can be used for crude oil spill remediation for soil. These technologies include bioremediation (Adams *et al.* 2018) and phytoremediation.

Bioremediation Technology: Bioremediation is a technology that exploits the abilities of microorganisms and other natural habitat of the biosphere to improve environmental quality for all species, including man. As cited by Adams *et al.* (2015) the presence of microorganisms with the appropriate metabolic capabilities is the most important requirement for crude oil spill bioremediation The development of innovative bioremediation technology as a functional tool in clean-up of crude oil polluted environment has depended so much on the basic knowledge of the physiology and ecology of the natural bacterial populations found in such polluted sites. There exist various bioremediation technologies such as bioaugmentation (addition of oil-degrading microorganisms to supplement the indigenous populations of microorganism), biostimulation (modification of the environment to stimulate existing bacteria capable of bioremediation. This can be done by addition of various forms of limiting nutrients and electron acceptors, such as phosphorus, nitrogen, oxygen, or carbon) and others (biosparing, bioventing) (Adams *et al.,* 2015).

Phytoremediation Technology: Phytoremediation can be defined as the process or method in which plants are used in clean-up of contaminated environments. It is a remediating technology that promises effective, inexpensive, and less intrusive clean up and restoration of oil-contaminated environments. Phytoremediation involves plant that aid in the restoration of contaminated ecosystem. For example, salt marsh plants are able to take up hydrocarbons from oil-contaminated sediment and increase the hydrocarbon or total lipid fraction of the aerial portions of plants. There exist three established mechanisms by which plants decontaminate oil polluted sites and they include;

I. direct uptake of petroleum hydrocarbons into their tissues;
II. release of enzymes and exudates that stimulate the activity of hydrocarbonoclastic microbes and direct biochemical transformation (enzymes) of petroleum hydrocarbons;
III. enhancement in the degradation of the contaminants in the rhizosphere due to mycorrhizal fungi and the activity of soil microbial consortia.

CHAPTER THREE

Materials and Methods

This study followed a similar approached used by Ashiru and Ogundare, (2019) in assessing the total petroleum hydrocarbon and trace metal concentration in Effurun Delta State.

3.1 Materials

The following materials were used for the study;

Table 3.1: Materials Used for the Study

Material	Manufacturer
Beaker	Pyrex
Stirring Rod	Pyrex
Sulphuric Acid	H_2SO_4
Concentrated Nitric Acid	HNO_3
Atomic Absorption Spectrophotometer	

3.2 Collection of Samples (ASTM D6911-15)

The study area was gridded and approximately 300g of composite soil samples was collected at a depth 0cm - 20cm based on proximity to the grid points. These sampling was done with the use of a soil auger from different points and homogenized into a polythene bag for analysis.

3.3 Sample Preparation

A composite sample was drawn from each polythene bag. The composite sample was air dried and allowed to pass through a 2mm sieve to remain large stones and debris prior to analysis.

3.4 Digestion/Heavy Metal Determination:

- Two grams(2g) of soil sample was weighed into a 200ml conical flask.
- 20ml digestion mixture was added into the soil sample.
- The sample was heated for 15mins until a milky white coloration is formed.
- Sample was cooled before the 20ml of distilled water would be added.
- A filter paper was used to filter into a 100ml volumetric flask making it up to mark.
- Finally, sample was poured into a heavy metal can.
- The digestion sample was analyzed for heavy metals of interest using the Atomic Absorption Spectrophometer at different wavelength.

3.5 Determination of TPH

- 5g of soil sample was weighed into 250ml beaker
- To the soil sample, 50ml of pure xylene solution was added.
- The mixture was spined in the magnetic stirrer for 15mins.
- The mixture was allowed to settle and filtered to drain off solvent phase.
- Absorbance was recorded at 420-425nanameters wavelength.

3.6 Pollution Index

$$I - geo = Log_2\left(\frac{Cn}{1.5Bn}\right)$$

Where;

C_n is the concentration of the heavy metal in the polluted sample

B_n is the concentration of the metal in the unpolluted (control) samples.

The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the soil

Farm A

$$I - geo\ (Pb) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{0.01}{1.5\ (18.45)}\right) = -11.4$$

$$I - geo\ (Mn) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{22}{1.5\ (37.75)}\right) = -1.4$$

Farm B

$$I - geo\ (Pb) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{10.75}{1.5\ (18.45)}\right) = -1.4$$

$$I - geo\ (Mn) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{71.5}{1.5\ (37.75)}\right) = 0.3$$

Farm C

$$I - geo\ (Pb) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{11.6}{1.5\ (18.45)}\right) = -1.2$$

$$I - geo\ (Mn) = Log_2\left(\frac{Cn}{1.5Bn}\right) = Log_2\left(\frac{45.15}{1.5\ (37.75)}\right) = -0.3$$

Class	Value of Soil Quality
<0	Unpolluted
0-1	Unpolluted to moderately polluted
1-2	Moderately polluted
2-3	Moderately polluted to highly polluted
3-4	Highly polluted
4-5	Highly polluted to very highly polluted
>5	very Highly polluted

CHAPTER FOUR

Results and Discussions

4.1 Results

The Result of heavy metal concentration in farms around petrol filling stations in Effurun is represented below;

Table 4.1: Heavy metals of Farms near Petrol Filling Station in Effurun

Parameters	**Methods**	**Farm A**	**Farm B**	**Farm C**	**Control**	**US.EPA**
Lead (Pb -mg/kg)	SM-3500	<0.01	10.75	11.63	18.45	420
Chromium (Cr – mg/kg)	SM-3500	<0.01	<0.01	<0.01	<0.01	3000
Nickel (Ni – mg/kg)	SM-3500	<0.01	<0.01	<0.01	<0.01	75
Manganese (Mn – mg/kg)	SM-3500	22.00	71.25	45.15	37.75	-

Table 4.2: Total Petroleum Hydrocarbon of Soil from Farms near Petrol Filling Station in Effurun

Parameters	Methods	Farm A	Farm B	Farm C	Control	US.EPA
Total Petroleum Hydrocarbon (TPH – mg/kg)	API-RP45	3.98	4.12	4.01	1.89	-

NESREA: National Environmental Standard and Regulations Enforcement Agency

Table 4.3: Statistical Analysis on Variance in Heavy Metals and TPH

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	364.5823	3	121.5274	0.29312	0.829768	3.238872
Within Groups	6633.588	16	414.5992			
Total	6998.17	19				

From table 4.3, there is no significant difference in concentration values observed in farms and control

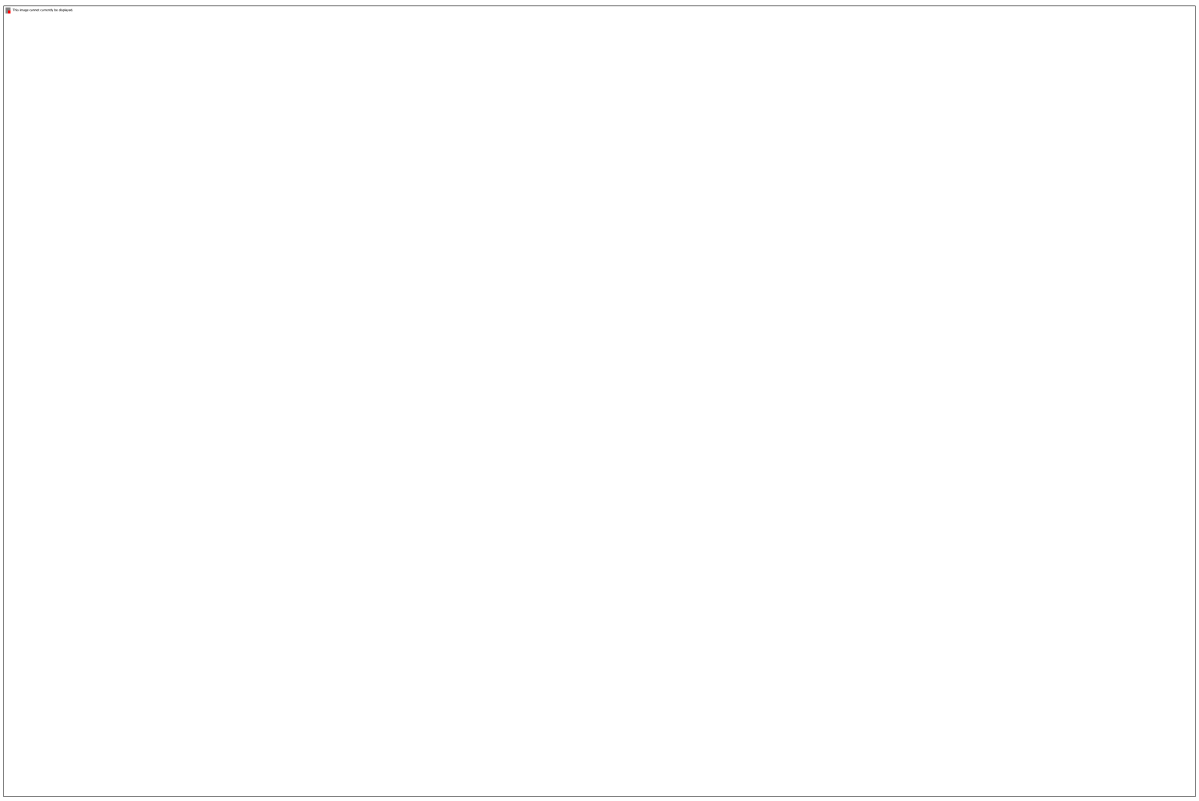

Figure 4.1: Geographical Map of Sample Point

The pollution index of the selected heavy metals examined in the study is shown in table 4.4

Table 4.4: Pollution Index of Soil around Petrol Filling Station

S/N	Parameters	PI(A)	Level	PI(B)	Level	PI(C)	Level
1	Pb	-11.4	Unpolluted	-1.4	Unpolluted	-1.2	Unpolluted
2	Cr	-0.6	Unpolluted	-0.6	Unpolluted	-0.6	Unpolluted
3	Ni	-0.6	Unpolluted	-0.6	Unpolluted	-0.6	Unpolluted
4	Mn	-1.4	Unpolluted	0.3	Moderately Polluted	-0.3	Moderately Polluted
5	TPH	0.5	Moderately Polluted	0.5	Moderately Polluted	0.5	Moderately Polluted

4.2 Discussion of Results

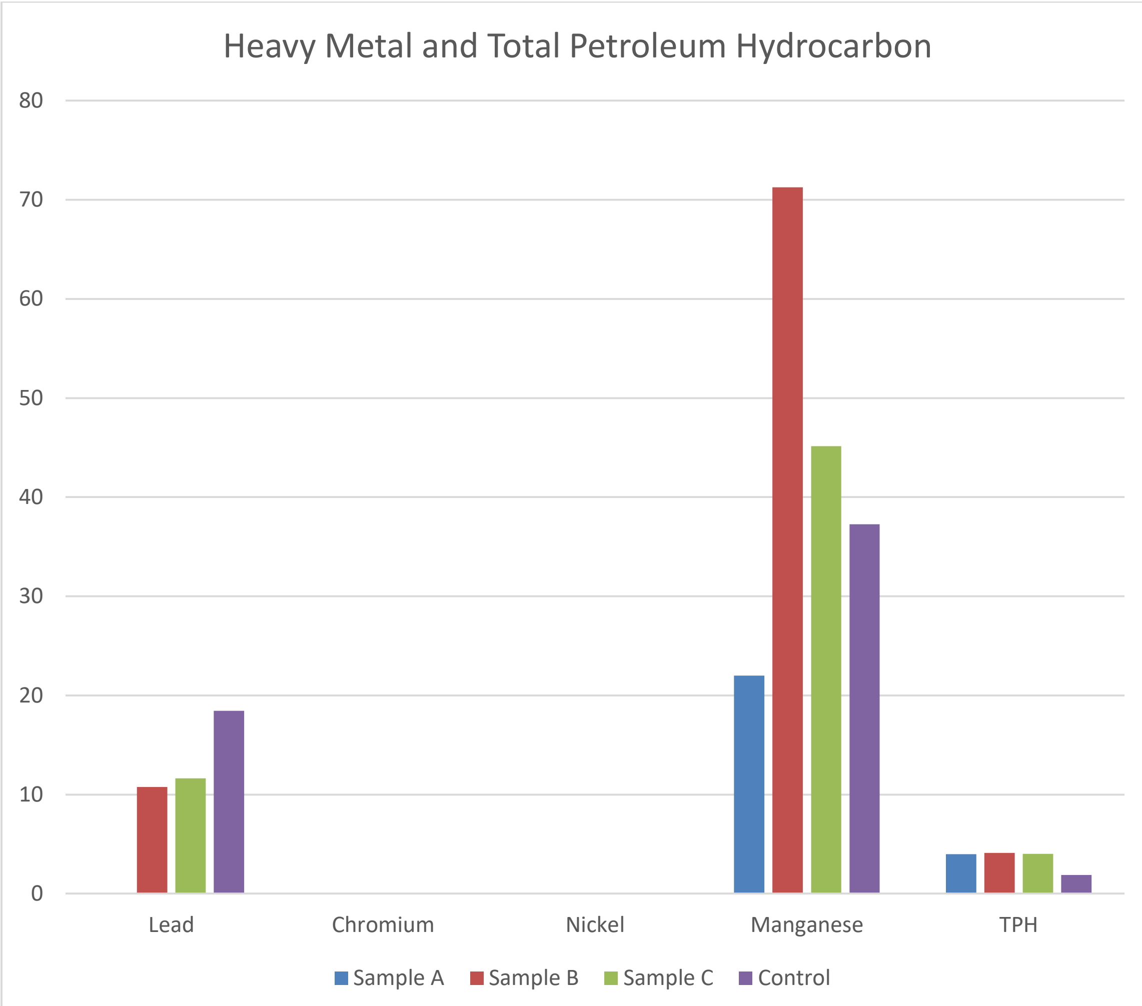

Figure 4.2: Heavy Metals and TPH Concentration

The study indicated heavy metal pollution of farm near Petrol filling stations in Effurun with a view to study the possible contamination threat of filling stations products on farm practices. Study have reported that these occurrences is associated with oil spills, vandalism and leakage from petroleum tankers amongst others (Adewuyi *et al.,* 2012). From table 4.1, Lead was observed in soil around petrol filling stations B and control site, although in concentrations less than allowable limits. The concentrations of

Lead indicated the possibility of gasoline spills and/or leakage since Lead alkyes are commonly as gasoline additives and may be found in tanks that may have Lead-based coatings or materials. The result obtained in this study is slightly higher than those obtained by Ashiru and Ogundare (2019) in which Lead (0.036 – 0.403mg/kg) was identified as the second highest heavy metals in petroleum contaminated soil, and Emmanuel *et al.* (2014) in which lead in soil near petrol filling station ranged from 4.93 – 74.2mg/kg. The variation in concentration can be attributed to the degree of pollution.

The presence of chromium and nickel in soil around petrol filling stations can be of concern due to its potential environmental and health risk. From table 4.1, the concentrations of chromium and nickel were below detectable levels of 0.01mg/kg. A concentration of chromium and nickel in soil around a petrol filling station reported as <0.01 suggests that the area is currently safe from significant chromium contamination. This may be due to the fact petrol stations don't usually involve processes that directly use or emit chromium and nickel. Also, chromium and nickel are not traditionally major additive in fuel formulations. Geo-pollution effects also revealed that the soil was unpolluted with chromium and nickel. The result is against those reported by Kadili *et al.,* (2021) and Ayodele *et al.* (2019) which showed the presence of chromium and nickel in high concentration and can be attributed to soil contamination with crude oil, as compared to petrol filling stations which only have the presence of refined petroleum products.

From table 4.1, the concentration of manganese varied from 22 – 71.25mg/kg for contaminated soil around petrol filling station. Manganese is a naturally occurring element found in soil, but elevated levels can result from human activities. Geo-pollution index revealed that soil around some petrol filling station is moderately polluted with manganese which may be due to contaminated effect from petrol filling stations. Manganese has been found to be used as an additive in fuels, primarily in the form of methylcyclopentadienyl manganese tricarbonyl (MMT). This compound is often used to increase the octane rating of gasoline. Study by Ahmed *et al.* (2020) revealed a similar result with manganese observed in concentrations between 24.5-29.1mg/kg.

Total Petroleum Hydrocarbon (TPH) levels near petrol filling stations are crucial indicators of potential contamination from petroleum-related activities. The concentrations provided farm A (3.98 mg/kg), farm B (4.12 mg/kg) and farm C(4.01mg/kg) fall under relatively low contamination levels. These TPH levels may not immediately pose severe risks, but persistent contamination over time can lead to soil degradation and potential harm to groundwater, affecting ecosystems and human health. Also, comparing these values to control soil showed moderate pollution and indicates that TPH levels should still be monitored to prevent further accumulation. Prolonged exposure to even low levels of TPH can result in adverse ecological impacts, such as reduced soil fertility and potential uptake of hydrocarbons by plants. Additionally, TPH contamination can affect air quality through the volatilization of lighter hydrocarbon compounds. The results are consistent with those reported by Adewuyi *et al.* (2012) in which TPH values for control soil was 1mg/kg and elevated up to 26mg/kg. however, comparison of contamination with this published study showed that contamination in area persisted over a long time as compared to our results.

CHAPTER FIVE

Conclusion and Recommendations

5.1 Conclusion

In conclusion, the heavy metals and Total Petroleum Hydrocarbon (TPH) levels near petrol filling station, as observed in the provided concentration revealed that farm around petrol filling station was moderately polluted with manganese and petroleum hydrocarbon posing effects of soil degradation and potential harm to groundwater, affecting ecosystems and human health. Also, farm was unpolluted with chromium and nickel. While these values may not immediately pose significant threats based on common environmental standards, the accumulation of heavy metals and petroleum hydrocarbons in soil can have long-term implications, especially as it regards Lead. Continuous exposure to even low levels of heavy metals and TPH can degrade soil quality, disrupt plant growth, and pose a risk to groundwater through leaching. This highlights the importance of proper handling of petroleum products, regular soil monitoring, and immediate response to spills to prevent buildup and its associated risks to human health and the environment.

5.2 Recommendations

It is recommended that;

i. Phytoremediation should be applied in soil around petrol filling stations to serve as hyperaccumulators which can absorb and store heavy metals from contaminated soils.

ii. Immobilization techniques should be applied to bind heavy metals in the soil, reducing its mobility and the potential for groundwater contamination.

iii. Regular monitoring should be conducted to prevent increase in concentrations of pollutants in soil.

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