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*Original paper*

# Environmental Risk Analysis of Aged Soil in an Environment Impacted by Nigerian Crude Oil

**F. Omoruwou[1*], K.O. Obahiagbon[2], N.A. Amenaghawon[2] and M.O. Daramola[3]**

[1]Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Nigeria
[2]Department of Chemical Engineering, University of Benin, Nigeria
[3]Department of Chemical Engineering, University of Pretoria, Pretoria 0002, Gauteng Province, South Africa.
Corresponding Author Email: omoruwou.felix@fupre.edu.ng

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**ABSTRACT:** This investigation focuses on the degree of pollution brought on by the prospecting and extraction of crude oil, with a focus on some heavy metals (lead, chromium, copper, nickel, and arsenic), their associated ecological effects on the environment (soil), and the potential risks these heavy metals pose to both human health and the environment. The soil collected from five crude oil-polluted sites in the Eastern and Western oil operation blocs in the Niger Delta was preserved, transported, and stored using the standard scientific method. These samples were further digested for heavy metals by the acidification method, followed by the sonication approach. To assess the digested samples both qualitatively and quantitatively, the inductively coupled plasma optical emission spectrometry (ICP-OES) device was used. The results obtained from the analysis revealed that some classified heavy metals were discovered to be over the detection thresholds, except for zinc (Zn), cadmium (Cd), and vanadium (V). The metals and metalloids under study which were evaluated for their ecological risk that constitutes an environmental menace in the crude oil-impacted soil are lead (Pb) and arsenic (As). Therefore, this shows a high risk of using such land for food production, as these metals and metalloids could find their way into the food networks, putting animals, people, and benthic organisms at serious risk. Hence, it is necessary to carry out proper remediation on the soil to mitigate the metals and metalloids to an acceptable or permissible level before any farming or agricultural activities.

**Keywords:** Niger Delta, Heavy metal, Crude oil, Human health, Pollution

## INTRODUCTION

The environment is a system of intricate factors that include soil, water, and air. The basis for humans' existence among other living things is their beneficial relationship (Kalavathy, 2004; Selvi *et al*., 2019). The Niger Delta environment and region are currently threatened by the pollutants produced by a variety of oil and gas-related installations, including oil wellheads, flow stations, loading ports, and refining facilities (Emoyan, 2010). The pollution occasioned by petroleum operations in the upstream, midstream, and downstream sectors has grave consequences. According to Ugochukwu and Ertel (2008), the local environment and biodiversity are negatively impacted by all phases of oil and gas exploration and utilization. They further suggested that there is a need for a comprehensive environmental impact assessment to be carried out before any search for, or extraction of, petroleum and natural gas activity is undertaken to mitigate these negative effects. The body responsible for oil spill detection and response in Nigeria (NOSDRA) reported above 1,300 incidents of oil spills in various parts of the country between 2018 and 2019 (Punch, 2020). The contaminants resulting from these oil spills end up either on land, in the marine environment, or the atmosphere, with dire consequences for humans, plants, and animals. Heavy metals are one such contaminant present in crude petroleum (Oti, 2016). Heavy metals possess metallic characteristics with an atomic weight greater than 20 and densities at least five times that of water (Tchounwou *et al*., 2012). Their quantities in soils devoid of human influence are typically modest and offer no dangers to the environment (de Almeida Júnior *et al*., 2016; Lu *et al*., 2012). Interestingly, most of these metallic contaminants are deposited in the earth's crust. Soil serves as a universal sink for all pollutants, purifies groundwater, and is the primary carbon reservoir in the universe (Hakeem *et al*., 2016). The soil is the best gift that nature offers to humanity. It is a significant part of the biosphere that forms an interface between the atmosphere, the lithosphere, and the hydrosphere (White, 2006). It is the natural habitat of virtually all natural resources, supports plants' growth and development, is a medium for the biogeochemical cycling of nutrients, provides natural habitation to micro and macro organisms, and is the transformation system that provides means for homeostatic interactions between living organisms and non-living things (Chokor, 2019). Because of the support system it offers, every man's activity directly depends on and affects the soil. Soil pollution is principally and necessarily a negative consequence of anthropogenic origin. The support system offered by soil includes food production, water filtration, and carbon storage, making it crucial for human survival. Therefore, it is essential to take measures to prevent soil pollution and preserve the health of our planet.

For people and other creatures, excessive metallic buildup in soils is fatal. This is because these metallic substances through plants and animals can infiltrate the food network, leading to bioaccumulation, which can lead to serious well-being problems such as cancer, diseases of the nervous system, and developmental abnormalities. Therefore, It is essential to monitor and regulate metallic component levels in the soil to ensure a safe environment for all living organisms (Heavy Metal Soil Contamination, n.d.).

Due to food chain transmission, exposure to heavy metals is typically chronic (over a long period). Heavy metals rarely cause acute (instant) poisoning through ingestion or skin contact, but it is conceivable. Long-term exposure to heavy metals is related to serious health issues like:

1. Lead – short-term memory failure
2. Cadmium – has an impact on the digestive system, the renal system, and the liver.
3. Arsenic – poisons the skin and the central nervous system (CNS) as well as the kidneys.

Mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese are the most common cationic metals that cause issues (metallic elements that exist as positively charged cations in soil, such as $Pb^{2+}$). The four elements that react with oxygen to generate negatively charged anionic compounds most frequently found in soil are arsenic, molybdenum, selenium, and boron(*Heavy Metal Soil Contamination*, n.d.). They are regarded as the most harmful environmental contaminants due to their highly harmful effects, widespread distribution, and ease of plant uptake (Jordán *et al*., 2016; Rosen & Chen, 2014; Soriano-Disla et al., 2014).Similar to how heavy metals cause food contamination and endanger both human and animal health, they enter food chains from contaminated land, water, and air. Governments, scientists, and communities must work together to address the global issue of heavy metal contamination. Governmental rules are essential for pollution treatment and source control(He *et al*., 2015). Therefore, this research seeks to provide scientific evidence of heavy metal accumulation in soil impacted by crude oil and, with provided data, assist in policy formulation on how to mitigate crude oil pollution. The heavy metals considered in the evaluation of contamination/pollution levels are arsenic, copper, chromium, lead, and nickel. Their choice was based on the Russian standard- GOST 17.4.102-83 which classified them as high-hazard and medium-hazard heavy metals/metalloids (Chinedu & Chukwuemeka, 2018).

## MATERIALS AND METHODS

### Area of study

The soil sampling conducted in this study was within the Nigerian geopolitical zone called the Niger Delta. The Niger Delta's name originated from the geographical location it covers. Figure 1 depicts the catchments of the Niger River as it joins the Atlantic Ocean as a delta (Usen *et al*., 2016). Other rivers include the Qua Iboe River, Cross River, Sambreiro, Brass, Bonny, and River Imo to the east and Rivers Forcados and Ethiope to the west, and River Nun as the significant direct tributaries with which It discharges into the Gulf of Guinea. From north to south, it covers around two hundred and forty kilometres, while the length of the coastline is roughly three hundred and twenty kilometres, covering a region of thirty-six thousand square km. The area roughly straddles two latitudes of4°30' and 6°30' north of the equator and longitudes 4°59 and 8°51' east of the Meridian. Thus, the result is an equatorial climate with heavy rainfall almost all year long, reaching a maximum output of 3785 mm at Brass near Port Harcourt (Ituen & Alonge, 2009). The locations of the sampling sites were specifically chosen

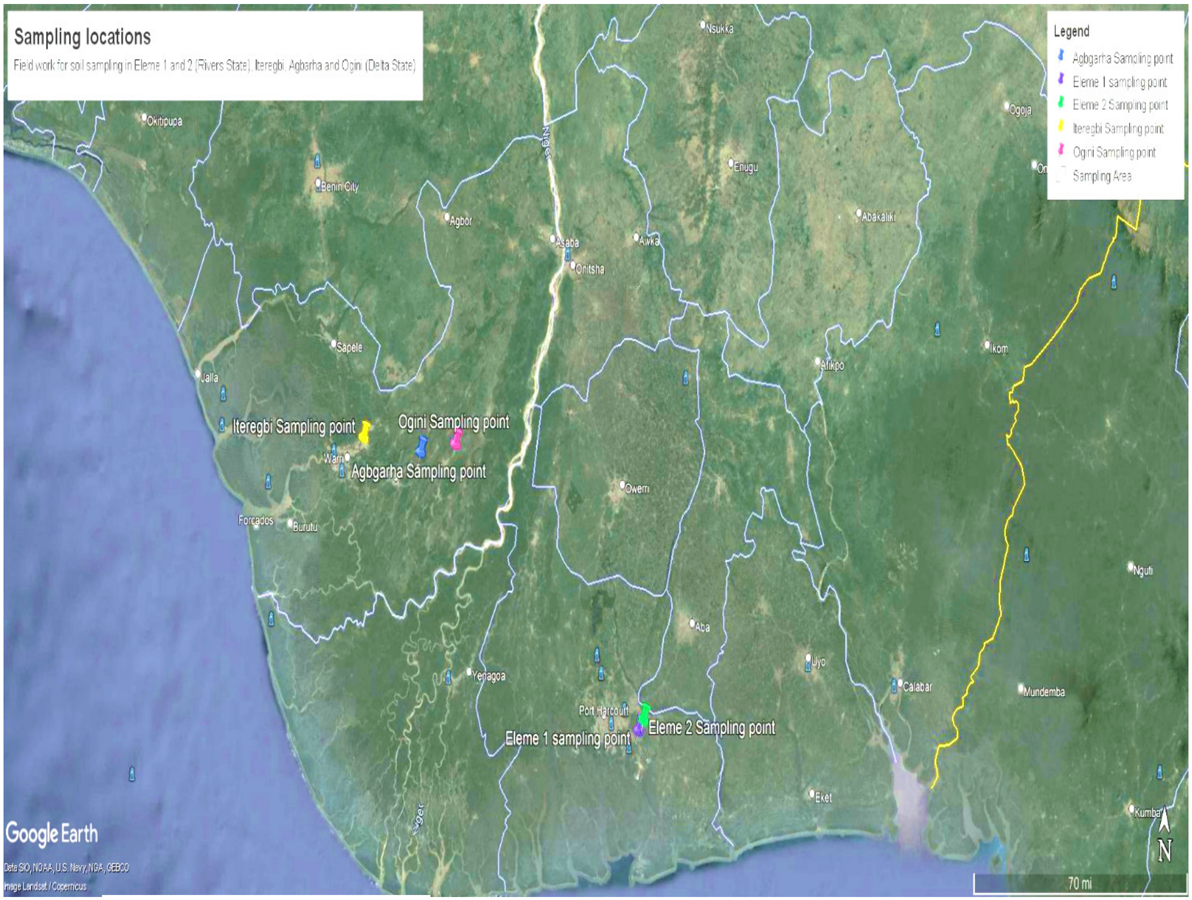

**Figure 1:** Map of Niger Delta region, Nigeria

based on previous instances of crude oil spillage at those sites. Two of the five locations are in Eleme in the present-day Rivers State, while the other three locations (Ogini, Agbarha and Ugbomro) are in Delta State.

## Soil sampling and pre-treatment

In the Delta and Rivers States of Nigeria, five different soil samples were taken from areas that had previously been contaminated by crude oil at a depth of 0 to 20 cm below the surface of the soil. The oil spillage in the five locations was a minimum of four years old when the experimentation was carried out. They were preserved in sterile polythene bags and tightly packed. They were air-dried to reduce moisture content, sieved through a 500-micrometre pore-size standard mesh sieve (no. 35) to remove debris, and kept in the laboratory before use. To give baseline metal levels, the global mean of shale and soil is frequently employed (Nowrouzi & Pourkhabbaz, 2014). Alternatively, the background values can be estimated from soil samples collected from a geologically similar and uncontaminated area either carried out by the researcher or from literature. In this investigation, therefore, the background content of the heavy metals was obtained from the work of Ololade, whose work was done on a similar geological environment and uncontaminated soil (Ololade, 2014).

## Procedures standard management

Through the research, the management of standard procedures was given top priority. This was achieved by ensuring that all glassware and apparatus used were washed with detergent, dried in an oven, and further rinsed with 10% nitric acid to avoid probable impurities. All instruments were calibrated before every use, and extraction and blanks were carried out in duplicates with the same techniques. The analysis of extracts was done in triplicates to ensure the repeatability of the experiment. The results presented are the statistical mean values of all the duplicates.

### Extraction of Metals

The modified Uddin *et al.* (2016) approach was used to identify the metals in the soil. An Erlenmeyer vessel containing 5 g of soil samples was filled with 50 mL of a 1M solution of nitric acid ($HNO_3$) at a weight-to-volume ratio of 1 to 10. The vessels were placed on a magneticelectric burner with the temperature set at 100°C. Stirring was done continuously using a magnetic stirrer. The heating continued until the evolution of the brownish fume stopped. The mixture was cooled, and 5 mL of concentrated nitric acid was introduced to the mixture. Further heating of the mixture was carried out to reduce the final quantity to about 5 mL.

Furthermore, the mixture was cooled to room temperature, and 45 mL of deionised water was added, mixed thoroughly, and filtered with Whatman filter paper no 40. In addition, the filtrates were filtered with a 0.22 µm point-of-use cartridge nitrocellulose membrane filter. The filtrates were collected and stored in a refrigerator at 4°C until they were taken for analysis utilizing optically emitted spectrometry with inductively coupled plasma (ICP-OES).

### Instrumentation

The estimation of the soil-targeted metallic and metalloid components ($Fe^{2+}$, $Cu^{2+}$, $Zn^{+}$, $Pb^{2+}$, $Cr^{6+}$, $Cd^{2+}$, $As^{3+}$, and $Ni^{2+}$) was done using the ICP-OES. The instrument was set up, calibrated, and operated in a manner that was fully following the manufacturer's instructions. Analytical grade metal standard stock solutions (1000 ppm) were applied to the instrument's calibration.

### Pollution/contamination assessment indicators

Markers and metrics of environmental quality are effective tools for managing, assessing, and disseminating unprocessed environmental parameters to policy-making bodies and the public at large (Yahaya *et al.*, 2021). They are essential resources for keeping tabs on environmental advancement, assisting with policy evaluation, and updating the public on recent developments (Gould, 2014). In recent years, a variety of techniques and strategies have been used to evaluate the presence of heavy metals in soil, sediments, and water. The degree of heavy metal present in the chosen sites or regions with a history of crude oil spillage was assessed using the Geoaccumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index, and Enrichment Factor (EF).

### Geoaccumulation Index ($I_{geo}$)

In this study, heavy metal contamination of the soils from the crude oil spillage encountered at the sites and areas under consideration was measured using the geo-accumulation index (Igeo). Muller (1969) made the initial suggestion and utilized it to determine the pollution in soil/sediments by comparing the current metal concentration with levels before industrialization. It is calculated as follows:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \qquad (1)$$

In soil or sediment, Cn is the measured concentration of metal n, Bn is the metal n's geochemical baseline value or target value, and 1.5 is the baseline matrix scaling factor resulting from lithogenic influences. According to the (Table 1), the geo-accumulation index is divided into seven different levels.

**Table 1:** The range of geo-accumulation index and interpretation (Abdullateef *et al.*, 2020; Muller, 1969; Ololade, 2014).

| Range | Interpretation |
|---|---|
| $I_{geo}<0$ | Literally uncontaminated |
| $0< I_{geo}<1$ | Uncontaminated to fairly uncontaminated |
| $1< I_{geo}<2$ | Fairly contaminated |
| $2< I_{geo}<3$ | Fairly to highly contaminated |
| $3< I_{geo}<4$ | Highly contaminated |
| $4< I_{geo}<5$ | highly to extremely contaminated |
| $I_{geo}>5$ | extremely contaminated |

### Contamination Index/Degree of Contamination

In determining the degree of contamination, the contamination factor is evaluated because it serves as a precursor for the degree of contamination estimation. The contamination factor was calculated using the contamination index as defined by Lacatusu (1998).

$$CF = \frac{C_n}{B_n} \qquad (2)$$

$C_n$ =the amount of heavy metal in the soil sample, while $B_n$is the pre-industrial level of the particular metal n, otherwise known as the reference, target, background, or lithogenic concentration. The contamination level, $C_d$ is estimated by applying the formula (3) below;

$$C_d = \sum_{i=1}^{n} CF^i \qquad (3)$$

In this technique, the contamination factor $(CF)$, accounts for the contamination of individual heavy metal (element) based on the required level of concentration, and a $(C_d)$, the value that accounts for the total heavy metals concentration in the soil or sediment pollution within the site under consideration. In the same vein, the following categorization defines the level of contamination factor of a metal in a given location: CF less than 1 is termed low contamination; CF greater than or equal to 1 but less than 3 is considered moderate contamination; when CF is greater than or equal to 3 but less than 6, it is regarded as a high contamination factor; and CF equal to or greater than 6 indicates very high contamination.

## Pollution Load Index (PLI)

The pollution load index (PLI) measures the ratio of the amount of heavy metal in a given soil sample to the background (lithogenic) quantity of that metal. As a result, it might make it easier to comprehend and portray the overall risk of HM toxicity in soil (Rahmanian & Safari, 2020). It was mathematically defined and represented by Tomlinson et al. (1980) as the nth root of the products of all the contamination factors, thus;

$$PLI_{site} = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \dots\dots\dots\dots \times CF_N} \quad (4)$$

Equation 4 is an expression to evaluate the level of HM pollution for a site. This equation can also be adapted for a zone or an estuary with the following expressions;

$$PLI_{zone} = \sqrt[n]{Site_1 \times Site_2 \times Site_3 \dots\dots\dots\dots \times Site_n} \quad (5)$$

$$PLI_{estuary} = \sqrt[n]{Zone_1 \times Zone_2 \times Zone_3 \dots\dots\dots\dots \times Zone_n} \quad (6)$$

Therefore, this work estimated the pollution load metrics for the individual crude oil-polluted sites and zone (Niger Delta). Several CF estimations were developed for individual metals at each location, and a location pollution index was estimated by taking the 5 highest CFs and estimating the fifth root of the products of the 5 factors. PLI greater than 1 shows metal-polluted soil, and PLI less than 1 means there is no metal pollution (Rahmanian & Safari, 2020).

## Enrichment Factor (EF)

The enrichment factor (EF), similar to the geoaccumulation index ($I_{geo}$), is a metric that is applied in the evaluation of the existence and amount of anthropogenically deposited impurities in soil.Its estimation is carried out by comparing the concentration of the reference element to the concentration of one metal in the topsoil. Its main application is to compare the effects of human-induced and nature-induced activities on the input of heavy metallic substances into the environment (Ololade, 2014; Valdés *et al*., n.d.). According to Mohiuddin *et al*.(2010), the enrichment factor is the ratio of the targeted sample to the global background value. A reference element is considered to be an element that is characteristically vertically immobile and void of degradability (Ackermann, 1980; Barbieri, 2016). Aluminium (Al), Iron (Fe), Manganese (Mn), and Rubidium (Rb) have been used by many researchers. However, Iron (Fe) was chosen as the reference element in this investigation due to its global lithogenic abundance, particularly in marine and estuarine environments (Ackermann, 1980; Barbieri, 2016; Chakravarty & Patgiri, 2009; Ogunmodede *et al*., 2015), worldwide application and comparative low pollution potential in the environment(Sutherland, 2000). Equation 7 given below is the expression for estimating EF,

$$EF = \frac{Metal_{sample} / RE_{sample}}{Metal_{background} / RE_{background}} \quad (7)$$

Iron (Fe) was chosen as the study's reference element since it has the highest RE value of any metal. The numerical results imply various amounts of contamination. EF values in the range of 0.5 to 1.5 show that only natural weathering processes may be responsible for the trace metal concentration. EF greater than 1.5, on the other hand, implies that a sizable portion of the metal comes from non-lithogenic sources. Table 2 shows the different classified degrees of enrichment (Barbieri, 2016; Zhang & Liu, 2002).

**Table 2:** Classification of different degrees of enrichment factor.

| Value | Soil Quality |
|---|---|
| EF less than 2 | Insufficiency to low enrichment |
| EF less than 5 but greater than 2 | mild enrichment |
| EF less than 20 but greater than 5 | Significant Enrichment |
| EF less than 40 but greater than 20 | Very high enrichment |
| EF greater than 40 | Extremely high enrichment |

## RESULTS AND DISCUSSION

### The physicochemical parameters and fertility status of the soil

Table 3 presents the physical and chemical parameters of the soil samples obtained from the crude oil-impacted soil in the locations in the study location. The mean temperature of the resulting soil solution used in estimating the pH was 23.93°C at a laboratory condition of 21°C. The soil pH ranged between 4.18±0.025 and 6.16±0.1. These pH values suggest highly to moderately acidic soil. pH is a critical factor in the adsorption and desorption of heavy metals in soil (Elliott *et al*., 1986). Also, most plant nutrients are optimally available to

**Table 3: Site coordinates and soil sample physicochemical parameters.**

| Sample code | Coordinates | | pH | EC(µS) | Soil Fertility Status (mg/kg) | | | MC (%) | TOM (%) | TOC (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Lat. | Long. | $\bar{x} \pm \varepsilon$ | $\bar{x} \pm \varepsilon$ | N | P | K | | | |
| Ugb | 5.573387 | 5.843818 | 6.10 ±0.06 | 212.67±1.45 | 1630.00 | 8.91 | 13.05 | 2.73 | 3.52 | 3.47 |
| Elem 1 | 4.783473 | 7.147542 | 4.38±0.04 | 85.60±1.41 | 920.00 | 32.55 | 7.92 | 6.60 | 2.53 | 2.97 |
| Ogi | 5.566138 | 6.268965 | 5.41±0.04 | 74.27±0.80 | 1190.00 | <4.50 | 10.59 | 2.94 | 3.54 | 3.48 |
| Agb | 5.528374 | 6.075856 | 5.16±0.1 | 164.63±2.14 | 1970.00 | <4.69 | 5.92 | 1.87 | 7.62 | 5.53 |
| Elem 2 | 4.783901 | 7.148508 | 4.19±0.01 | 102.20±1.01 | 1210.00 | 7.36 | 7.07 | 1.50 | 2.03 | 2.72 |

EC: Electrical conductivity; MC: Moisture content; TOM: Total organic matter; TOC: Total organic carbon

plants within the slightly acidic and slightly alkaline (6.5 to 7.5) pH range and are generally very well-suited to plant root growth (Fazal-Ur-Rehman, n.d.). Metals typically form insoluble metal mineral phosphates and carbonate at elevated pH levels, but they are more bioavailable at low pH levels, where they are more likely to exist as unbound ionic molecules or soluble organometals (Egbenda et al., 2015; Olaniran et al., 2013; Osakwe & Okolie, 2016).This is why the pH of a soil or water system can greatly affect the mobility and toxicity of metals. Understanding the relationship between pH and metal speciation is crucial in assessing the environmental risks associated with metal contamination. The acidic state of the soil could be due to the presence of organic acids resulting from the crude oil (Samanta *et al*., 2011) or due to microbial metabolism (Osuji *et al*., 2006). Acidic soil adsorption of metallic ions follows this sequential order; Pb > Cu > Zn > Cd (Elliott *et al*., 1986). A critical look at (Table 3) justifies this order of metallic ions adsorption in the soil.

Specifically, in soil Ugb, the concentration of $Pb^{2+}$ is 139.19 and $Cu^{2+}$ 4.96, while $Zn^{+}$ and $Cr^{6+}$ are below the limits of detection (LoD). The same findings were observed in other samples except that $Pb^{2+}$ is the only ion detected at higher concentrations with the other three metals concentration below their limits of detections (LoD). The oil spillage could be responsible for this high concentration of $Pb^{2+}$as it is one of the identified heavy metals in crude oil (Chinedu & Chukwuemeka, 2018). Also, according to Oti (2016), lead (Pb) has the highest concentration in Bonny Light crude oil obtained from the Niger Delta, Nigeria.

Electrical conductivity (EC) is a measured parameter that indicates the presence of ions that can permit the flow of electrons through the medium (Enyoh *et al*., 2017; Osuji et al., 2006; Verla *et al*., 2017). The mean electrical conductivity measured for the five oil spill-impacted locations ranged between 73.47 and 214.12 µS. The significant variation in value can be explained by the differences in the length of time the oil could have stayed in the different locations hence varying degrees of chemical transformation that may have taken place. The variations in soil particulate distribution and levels of the organic substance are other factors that could exist, determining the amount of adsorbed ions on the soil particles. Also, the higher the EC, the more probable the presence of heavy metal ions associated with the oil spillage experienced in these sites (Osuji *et al*., 2006). The soil fertility status shows the range of Total Nitrogen to be 920mg/kg to 1970mg/kg, Phosphorus 7.36mg/kg to 32.55mg/kg, and potassium 7.07mg/kg to 13.05mg/kg. These values indicate low fertility soil possibly resulting from the oil spillage effect; hence cannot be used for any meaningful agricultural purpose (Abii & Nwosu, 2009; Ayeni & Adeleye, 2014; Essien & John, 2010).

Other essential soil parameters evaluated in this study are the soil moisture content (MC), total organic matter (TOM), and total organic carbon (TOC), as shown in (Table 3). These are indicators that determine soil productivity potential. They play a significant role in conserving the sustainability of plants by improving soil's physical, chemical, and biological properties (Fageria, 2012). Heavy metallic ions and soil organic matter have a strong affinity for one another and can form stable complexes, which helps to lessen soil contamination (Ashraf *et al*., 2013).

It suggests that the building of complexes with metals is increased and that the availability of heavy metals decreases as organic carbon levels rise. The loss-on-ignition approach was used to calculate the TOC and TOM in this investigation as proposed by Nelson and Sommers (Blume et al., 1990; Schumacher, 2002). The TOM and the TOC have a range of 2.03-7.62 % and 2.72-5.53%, respectively. These low values in TOM and TOC are indicators of soil with very low fertility and could be adjudged as low-quality soil that cannot sustain crop growth adequately (Fageria, 2012; Wander & Traina, 1996). Generally, the physical and chemical parameters of the sampled soil from the five sites under study indicate low fertility, which is probably due to the oil spillage effect.

## The level of heavy metal in the soil

The distributions of the target heavy metals across the selected crude oil impacted sites are shown in (Table 4, Figures 1a and 1b). Table 4 summarizes the minimum, maximum, mean, and standard deviation of the metal

**Table 4**: The heavy metal concentrations in the soil across the crude oil-impacted sites and background concentrations.

| | **Soil (mg/kg dry weight)** | | | | | | | | **Source** |
|---|---|---|---|---|---|---|---|---|---|
| **Location/Site** | **$Fe^{2+}$** | **$Cu^{2+}$** | **$Zn^{+}$** | **$Pb^{2+}$** | **$Cr^{6+}$** | **$Cd^{2+}$** | **$As^{3+}$** | **$Ni^{2+}$** | |
| Ugb | 138.25 | 19.63 | nd | 139.19 | 5.32 | nd | 13.91 | 4.59 | **This study** |
| Elem 1 | 457.72 | 19.70 | nd | 456.67 | 1.64 | nd | 10.33 | 4.56 | ,, |
| Ogi | 251.27 | 19.60 | nd | 247.27 | 1.02 | nd | 10.23 | 4.59 | ,, |
| Agb | 244.69 | 19.69 | nd | 240.64 | 1.12 | nd | 10.23 | 4.58 | ,, |
| Elem 2 | 231.28 | 19.55 | nd | 225.9 | 1.09 | nd | 10.22 | 4.61 | ,, |
| Sum | 1323.21 | 98.17 | - | 1308.67 | 10.19 | - | 54.91 | 22.93 | ,, |
| Mean | 264.64 | 19.63 | - | 261.73 | 2.04 | - | 10.98 | 4.59 | ,, |
| StDev | 117.20 | 0.06 | - | 117.48 | 1.85 | - | 1.64 | 0.02 | ,, |
| Min | 138.25 | 19.55 | - | 139.19 | 1.02 | - | 10.22 | 4.56 | ,, |
| Max | 457.72 | 19.70 | - | 456.67 | 5.32 | - | 13.91 | 4.61 | ,, |
| Background | 221.95 | 127.85 | na | 10.25 | 8.2 | 1.65 | na | 13.2 | (Ololade, 2014) |

na: not available; nd: Not detected

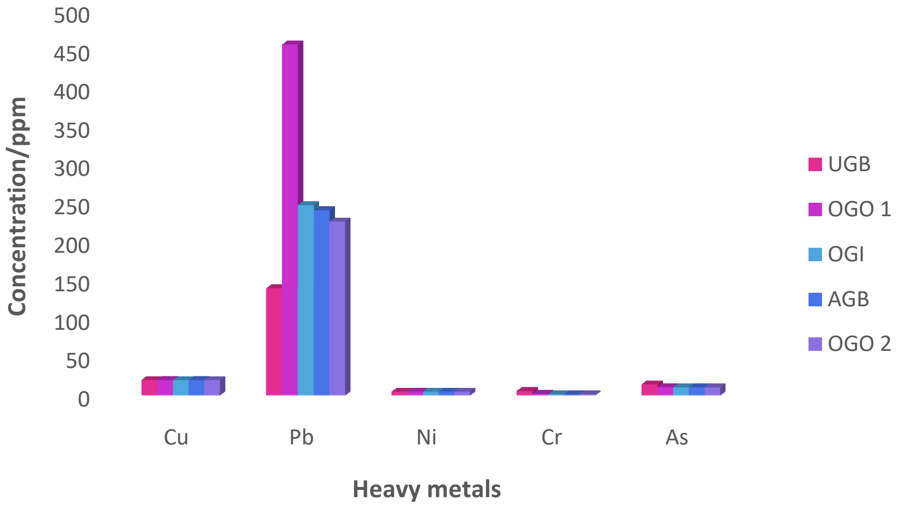

**Figure 1a:** Heavy metals distribution in the crude oil-impacted sites

concentration in the different sites. A close examination of (Table 4) reveals that $Fe^{2+}$, $Pb^{2+}$, $Cr^{6+}$, and $As^{3+}$ concentration in some sites varies markedly with the mean value. It is a pointer that such metal is a pollutant in those sites. Also, comparing the mean values with their individual background concentration shows that they are anthropogenically deposited in the sites except for $Cu^{2+}$and $Cr^{6+}$. Also, viewing the table against the background knowledge of heavy metals present in crude oil, it could be inferred that the high concentration of $Pb^{2+}$ far above its lithogenic concentration results from the crude oil spillage. This assertion is clearly demonstrated in (Figures 1a and 1b). $Pb^{2+}$ is more than all other contaminants, including $Fe^{2+}$, a relatively abundant heavy metal. These findings are also in consonance with the work of Oti (2016). $Fe^{2+}$ and $Pb^{2+}$ had the highest concentrations across all sampling locations, and their combined totals fell within a similar range, while $Cr^{6+}$ on its part showed the least concentration except in Ugb location. The high amount can be justified by comparing it with its background values. In (Figure 1b), the target heavy metals distribution pattern in each site is similar, which could be explained because they all experienced crude oil spillage, probably with closely related chemical properties or similar assays. The concentration of each heavy metal varies only slightly depending on the region.

To determine the extent and quantify the potential impact or scale of contamination of heavy metal concentrations arising from natural or human-caused sources, the pollution load index (PLI) and enrichment factor (EF) evaluation results were applied. The study's PLI and EF results were both less than 1. The amounts of Cr, Cu, Pb,

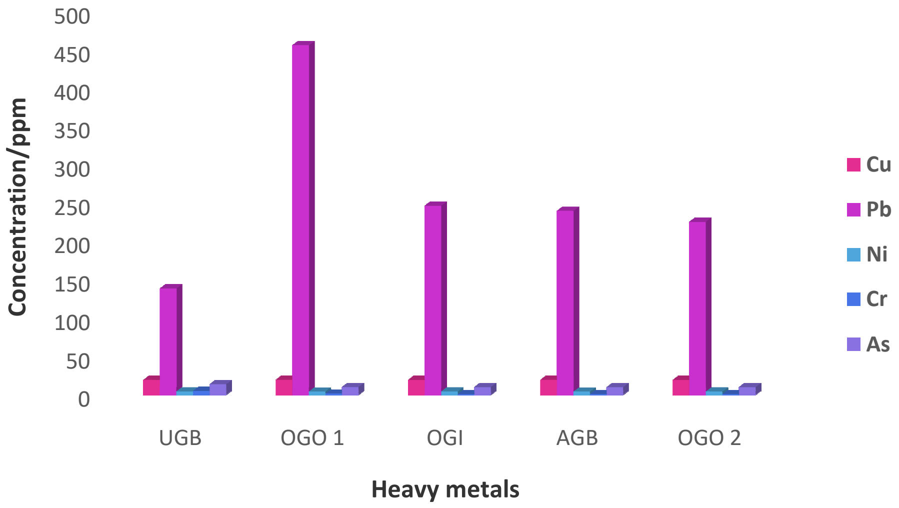

**Figure 1b:** Heavy metals present on a site basis.

**Table 5:** Heavy metal contamination in soil: maximum allowable limits in some organizations and countries.

| Country/Organization | Metal/ ppm | | | | | | | Source |
|---|---|---|---|---|---|---|---|---|
| | $Cu^{2+}$ | $Zn^{+}$ | $Pb^{2+}$ | $Cr^{6+}$ | $Cd^{2+}$ | As | $Ni^{2+}$ | |
| WHO | 36 | 50 | 85 | 100 | 0.8 | na | 35 | (Ogundele et al., 2015; WHO, 1996) |
| DPR | 36 | 140 | 85 | 100 | 0.8 | na | 35 | (Ololade, 2014) |
| Australia | 100 | 200 | 300 | 50 | 3 | 20 | 60 | (He et al., 2015) |
| Canada | 150 | 500 | 200 | 250 | 3 | 20 | 100 | „ |
| China | 50-200 | 200-300 | 80 | 150-300 | 0.3-0.6 | 20-40 | 40-60 | „ |
| Germany | 200 | 600 | 1000 | 500 | 5 | 50 | 200 | „ |
| Tanzania | 200 | 150 | 200 | 100 | 1 | 1 | 100 | „ |
| Netherlands | 190 | 720 | 530 | 180 | 13 | 76 | 100 | „ |
| New Zealand | $>10^4$ | na | 160 | 290 | 3 | 17 | na | „ |
| UK | na | na | na | na | 1.8 | 43 | 230 | „ |
| USA | 270 | 1100 | 200 | 11 | 0.48 | 0.11 | 72 | „ |
| Indian | 135-270 | 300-600 | 250-500 | - | 3-6 | | 75-150 | (Srivastava et al., 2017) |

and Zn exhibited no enrichment, indicating that the soil pollution may have been of natural origin.

## Distribution and enrichment of metals

The Igeo and EF for the heavy metals in the research locations are displayed in (Table 5) and (Figures 2 and 4). The resulting EF suggests that only lead (Pb) is the enriched metal among the five metals in the locations under consideration. Its concentration demonstrates a very high level of enrichment in the five locations. Conversely, the EF for copper, nickel, and chromium isan indication that they were not enriched in the soil of all the locations. The enrichment of the soil by Pb can best be explained by the fact that it is the metal with the highest concentration in Niger Delta crude, as reported by Oti, (2016).Lead, copper, nickel, and vanadium are the individual heavy metal levels given in decreasing order. Therefore, it can be inferred that Pb is the only metal enriched by the oil spillage effect while Cu, Ni, and Cr detected are through lithogenic deposits, and As could not be determined because there was insufficient information to quantify it. The negative values of the geoaccumulation index for copper, nickel, and chromium in all the locations under study imply that these three metals did not contaminate the soil above their background values $B_n$. On the other hand, lead (Pb) and arsenic (As) values ($3<I_{geo}<4$) are indicative of strongly polluted soil with these metals. This aligns with the enrichment factors results.

## Pollution Load Index (PLI), Contamination Factor (CF), and Degree of Contamination (Cd)

In this study, the data for the estimated contamination factor (CF), degree of contamination (CD), and pollution load index (PLI) are depicted in (Table 6). The CD for the five locations with a history of crude oil spillage ranged

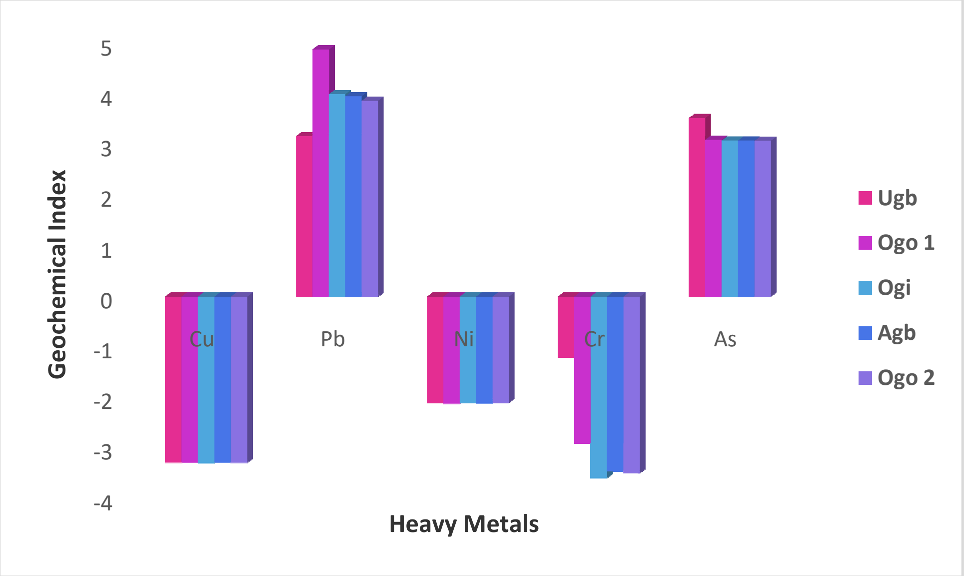

**Figure 2:** The heavy metals Geochemical Indices in the crude oil-impacted sites.

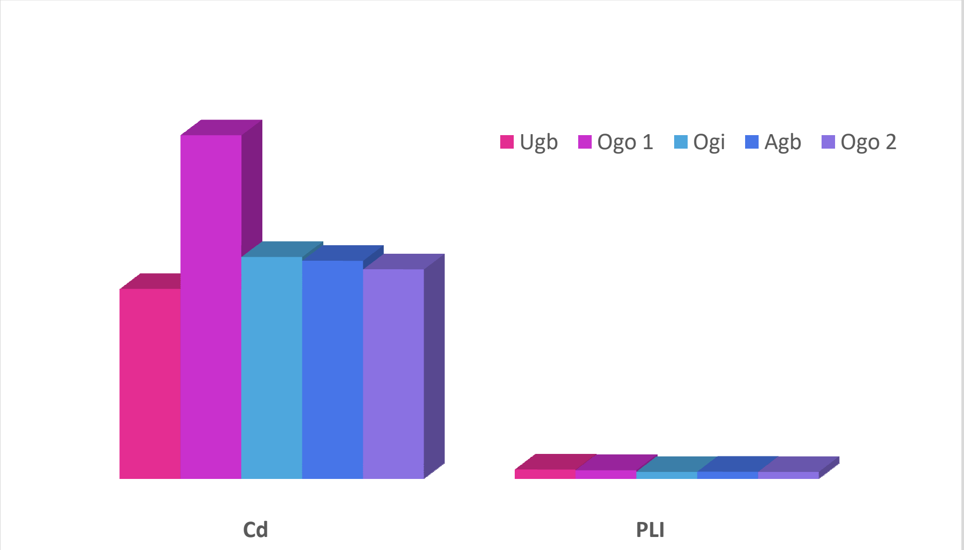

**Figure 3:** Plot showing the degree of contamination and pollution load index in the crude oil-impacted sites.

from 32.1171 to 58.1652. This range of values indicates soil with a very high degree of contamination possibly resulting from anthropogenic activities and, in this case, oil spillage. Also, from Figure 3, the plot shows that the sites did not experience the same degree of contamination. Specifically, the degree of contamination from site to site is in this order; Elem1>Ogi>Agb>Elem2>Ugb. The reasons that could possibly be adduced for the variations in the degree of contamination are; the age of the oil spilled, the nature of the oil, the amount of oil spilt, the geological characteristics of the environments, soil characteristics, and the type of plants in the surrounding. Therefore, the severity of this anthropogenic pollution calls for grave concern as the heavy metals examined are deleterious to the generality of environmental health. In consideration of the individual metals in each site, their contamination factor values revealed the intensity of individual metal concentrations. Lead (Pb2+) has the highest contamination factors in four of the five locations (Figure 1a, 1b, and Table 6), with values ranging from 13.5795 to 44.5532, while copper ($Cu^{2+}$) has the lowest CF values in

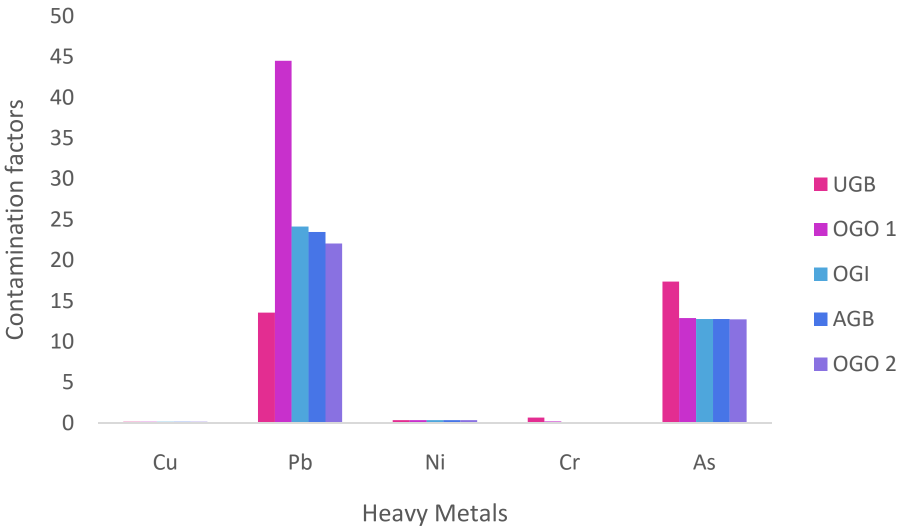

**Figure 4:** The contamination factor of the heavy metals in the locations

**Table 6:** Estimated degree of contamination, geochemical index, pollution load index, and soil enrichment factor.

| Sample | Geochemical Index | | | | | Degree of contamination | Pollution load index | Enrichment factor | | | | | Contamination Factor | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Pb | Ni | Cr | As | | | Cu | Pb | Ni | Cr | As | Cu | Pb | Ni | Cr | As |
| Ugb | -3.2883 | 3.1784 | -2.1089 | -1.2092 | 3.5350 | 32.1171 | 1.5224 | 0.2465 | 21.8009 | 0.5583 | 1.0416 | na | 0.1535 | 13.5795 | 0.3477 | 0.6488 | 17.3875 |
| Elem 1 | -3.2832 | 4.8925 | -2.1184 | -2.9069 | 3.1057 | 58.1652 | 1.4369 | 0.0747 | 21.6040 | 0.1675 | 0.0970 | ,, | 0.1541 | 44.5532 | 0.3455 | 0.2000 | 12.9125 |
| Ogi | -3.2942 | 4.0074 | -2.1089 | -3.5920 | 3.0917 | 37.5364 | 1.1533 | 0.1351 | 21.3090 | 0.3072 | 0.1099 | ,, | 0.1529 | 24.1239 | 0.3477 | 0.1244 | 12.7875 |
| Agb | -3.2839 | 3.9682 | -2.1121 | -3.4571 | 3.0917 | 36.9021 | 1.1699 | 0.1397 | 21.2953 | 0.3147 | 0.1239 | ,, | 0.1540 | 23.4771 | 0.3470 | 0.1366 | 12.7875 |
| Elem 2 | -3.2905 | 3.8770 | -2.1027 | -3.4963 | 3.0889 | 35.4370 | 1.1489 | 0.1471 | 21.1500 | 0.3352 | 0.1276 | ,, | 0.1533 | 22.0390 | 0.3492 | 0.1329 | 12.7625 |

**Table 7: The Geochmical index and Enrichment factor of the selected metals on each sampling location.**

| | | Cu | | Pb | | Ni | | Cr | | As | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **S/N** | **Station** | **$I_{geo}$** | **EF** | **$I_{geo}$** | **EF** | **$I_{geo}$** | **EF** | **$I_{geo}$** | **EF** | **$I_{geo}$** | **EF** |
| 1 | Ugb | -3.2883 | 0.2465 | 3.1784 | 21.8009 | -2.1089 | 0.5583 | -1.2092 | 1.0416 | 3.5350 | - |
| 2 | Elem 1 | -3.2832 | 0.0747 | 4.8925 | 21.6040 | -2.1184 | 0.1675 | -2.9069 | 0.0970 | 3.1057 | - |
| 3 | Ogi | -3.2942 | 0.1351 | 4.0074 | 21.3090 | -2.1089 | 0.3072 | -3.5920 | 0.1099 | 3.0917 | - |
| 4 | Agb | -3.2839 | 0.1397 | 3.9682 | 21.2953 | -2.1121 | 0.3147 | -3.4571 | 0.1239 | 3.0917 | - |
| 5 | Elem 2 | -3.2905 | 0.1471 | 3.8770 | 21.1500 | -2.1027 | 0.3352 | -3.4963 | 0.1276 | 3.0889 | - |
| Mean | - | -3.2880 | 0.1486 | 3.9847 | 21.4318 | -2.1102 | 0.3366 | -2.9323 | 0.3000 | 3.1826 | - |
| Max | - | -3.2832 | 0.2465 | 4.8925 | 21.8009 | -2.1027 | 0.5583 | -1.2092 | 1.0416 | 3.5350 | - |
| Min | - | -3.2942 | 0.0747 | 3.1784 | 21.1500 | -2.1184 | 0.1675 | -3.4963 | 0.0970 | 3.0889 | - |
| SD | - | 0.0046 | 0.0619 | 0.6096 | 0.2641 | 0.0057 | 0.1406 | 0.9998 | 0.4147 | 0.1971 | - |

two of the five locations (Ugb and Elem 1), and chromium (Cr6+) has the lowest values in the remaining three sites (Ogi, Agb, and Elem 2).In each of the five places, the rising sequence of CF is different. However, Ogi, Agb, and Elem 2 share a similar order. The increasing order of CFin these three locations is Cr<Cu<Ni<As<Pb. The soil structural difference and age of spillage could be responsible for the differences in the CF increasing order from one location to another. A critical examination of CF values in (Tables 6 and 7) reflected in (Figure 4) shows that lead (Pb) and arsenic (As) are the primary contaminants that may have resulted from the oil spillage in the 5 locations under consideration. The pollution load index (PLI) data can further buttress this assertion. Specifically, the PLI for the five locations is greater than 1 (>1), meaning the sites are polluted with heavy metals. However, the contamination factor made it clear which heavy metals had readings that were higher than the background levels. Consequently, soils from the crude oil polluted sites (as a representation of other crude oil impacted environments) are considered to be of heavy metals (lead (Pb) and arsenic (As)) pollution concern considering the level of oil spillage that is being experienced consistently over the past years in Niger Delta. Although some metals, including zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni), and iron (Fe), are needed by organisms in trace amounts, their presence in the soil beyond certain permiscible limits is inimical to their survival. Incidentally, the two heavy metals (Pb and As) that are more than the maximum permissible limits belong to a group called metalloids. These classes of metals do not provide any benefit to organisms and are considered the main threat to the environment (Chibuike & Obiora, 2014).

## Conclusion

This research provides useful and significant scientific data about the condition of the soil in the Niger Delta region of Nigeria, which is currently experiencing a massive crude oil spill. It does this by estimating the level of five heavy metals and metalloids (lead, copper, nickel, chromium, and arsenic, as well as their possible sources and ecological risk). Five (5) different locations were randomly chosen with a history of crude oil spillage in the region's western and eastern oil blocs, where crude oil exploration and exploitation is a constant daily affair coupled with illegal activities resulting in oil spillage. Inductively coupled plasma optical emission spectrometry equipment was utilized to analyze the heavy metal contamination in soil samples from the five (5) locations. Several pollution and environmental susceptibility metrics were employed to assess the results. Lead and arsenic are the metals of major concern in all of the sites, according to the research. Although lead is the sole metal with a concentration over the maximum allowed limit (MPL), the pollution indices reveal that arsenic is still unacceptably toxic even when its concentration is below the MPL. The geochemical index in all the locations under study suggests strong arsenic pollution and strong to extreme lead pollution with the other three metals (chromium, copper, and nickel) being practically unpolluted in the soil. These findings show that the lead and arsenic found in the soil are from anthropogenic sources, while the copper, nickel, and chromium are of lithogenic origin. However, the enrichment factor (EF) shows that only lead was highly enriched in all the soil studied, confirming that its source is crude oil. The geochemical index and enrichment factor evaluation of the site agrees with the pollution load index. Specifically, the PLI for the five sites is greater than 1, which connotes significant metal pollution. It is interesting to note that the main metal contaminant in this study, lead, has no biological function and may be hazardous to microorganisms. It is known to cause damage to DNA, enzymes, and cell membranes in microorganisms. The presence of these pollutants in the soil can have adverse effects on the environment and human health. Therefore, it is important to implement effective remediation strategies to mitigate their impact.

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## REFERENCES

Abdullateef, J., Edith B, A., Victor O, A., & Mustapha A, F. (2020). Application of Pollution Load Indices, Enrichment Factors, Contamination Factor and Health Risk Assessment of Heavy Metals Pollution of Soils of Welding Workshops at Old Panteka Market, Kaduna-Nigeria. *Open Journal of Analytical and Bioanalytical Chemistry*, *4*, 011–019. https://doi.org/10.17352/ojabc.000019

Abii, T., & Nwosu, P. (2009). The Effect of Oil-Spillage on the Soil of Eleme in Rivers State of the Niger-Delta Area of Nigeria. *Research Journal of Environmental Sciences*, *3*(3), 316–320. https://doi.org/10.3923/rjes.2009.316.320

Ackermann, F. (1980). A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. *Environmental Technology Letters*, *1*(11), 518–527. https://doi.org/10.1080/09593338009384008

Ashraf, M. A., Maah, M. J., & Yusoff, I. (2013). Soil Contamination, Risk Assessment and Remediation Muhammad. In *Intech* (Vol. 32, Issue July, pp. 137–144). https://doi.org/10.5772/57287 1.

Ayeni, L. S., & Adeleye, O. E. (2014). Mineralization Rates of Soil Forms of Nitrogen, Phosphorus, and Potassium as Affected by Organomineral Fertilizer in Sandy Loam. *Advances in Agriculture*, *2014*, 1–5. https://doi.org/10.1155/2014/149209

Barbieri, M. (2016). The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. *Journal of Geology & Geophysics*, *5*(1), 1–4. https://doi.org/10.4172/2381-8719.1000237

Blume, L. J., Schumacker, B. A., Shaffer, P. W., Cappo, K. A., Papp, M. L., van Remortel, R. D., Coffey, D. S., Johnson, M. G., & Chaloud, D. J. (1990). Handbook of methods for acid deposition studies laboratory analysis for soil chemistry. In *Epa/: Vol. 600/* (pp. 4-90/023).

Chakravarty, M., & Patgiri, A. D. (2009). Metal Pollution Assessment in Sediments of the Dikrong River, N.E. India. *Journal of Human Ecology*, *27*(1), 63–67.

Chibuike, G. U., & Obiora, S. C. (2014). *Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods*. https://doi.org/10.1155/2014/752708

Chinedu, & Chukwuemeka. (2018). Oil Spillage in the Niger Delta, Nigeria. In *Journal of Health & Pollution* (Vol. 8, Issue 19).

Chokor, A. A. (2019). *Chemical Assessment of Heavy Metals Contaminated Soil : A Review of Evaluation Indices*. *7*(2), 34–40. https://doi.org/10.12691/env-7-2-1

de Almeida Júnior, A. B., do Nascimento, C. W. A., Biondi, C. M., de Souza, A. P., & Barros, F. M. do R. (2016). Background and reference values of metals in soils from Paraíba state, Brazil. *Revista Brasileira de Ciencia Do Solo*, *40*, 1–13. https://doi.org/10.1590/18069657rbcs20150122

Elliott, H. A., Liberati, M. R., & Huang, C. P. (1986). Competitive Adsorption of Heavy Metals by Soils. *J. Environs. Qual.*, *15*, 214–219.

Emoyan, O. (2010). The Oil and Gas Industry and the Niger Delta: Implications for the Environment. *Journal of Applied Sciences and*

*Environmental Management*, *12*(3). https://doi.org/10.4314/jasem.v12i3.55488

Enyoh, C. E., Ihionu, E. A., Verla, A. W., & Ebosie, P. N. (2017). Physicochemical Parameter of Palm Oil and Soil from Ihube Community, Okigwe, Imo State Nigeria. *International Letters of Natural Sciences*, *62*, 35–43. https://doi.org/10.18052/www.scipress.com/ilns.62.35

Essien, O., & John, I. (2011). Impact of Crude-Oil Spillage Pollution and Chemical Remediation on Agricultural Soil Properties and Crop Growth. *Journal of Applied Sciences and Environmental Management*, *14*(4). https://doi.org/10.4314/jasem.v14i4.63304

Fageria, N. K. (2012). Role of Soil Organic Matter in Maintaining Sustainability of Cropping Systems. *Communications in Soil Science and Plant Analysis*, *43*(16), 2063–2113. https://doi.org/10.1080/00103624.2012.697234

Fazal-Ur-Rehman, M. (n.d.). *Course Code-CHEM 2041 For BS Chemistry (4-Years).*

Gould, H. R. (2014). Environmental Indicators—A Key to the Stratigraphic Record. In Recognition of Ancient Sedimentary Environments. In *SEPM Society for Sedimentary Geology*. (Vol. 25, Issue 0, p. 38). https://doi.org/10.2110/pec.72.02.0001

Hakeem, K. R., Akhtar, J., & Sabir, M. (2016). *Soil science: agricultural and environmental prospectives.* Springer, International Publishing AG Switzerland.

He, Z., Shentu, Yang, X., Baligar, Zhang, T., & Stoffella, &. (2015). Heavy Metal Contamination of Soils: Sources, Indicators, and Assessment. *Journal of Environmental Indicators*, *9*, 17–18.

Ituen, E. U. U., & Alonge, A. F. (2009). Niger Delta region of Nigeria, climate change and the way forward. *ASABE - Bioenergy Engineering Conference 2009*, *April 2015*, 229–238. https://doi.org/10.13031/2013.29162

Jordán, M. M., Rincón-Mora, B., & Almendro-Candel, M. B. (2016). Heavy metal distribution and electrical conductivity measurements in biosolid pellets. *Journal of Soils and Sediments*, *16*(4), 1176–1182. https://doi.org/10.1007/s11368-014-1021-2

Kalavathy, S. (2004). The Multidisciplinary nature of environmental studies. *Environ. Stud.*, *1*, 1–13.

Lacatusu, R. office for official publications of the E. C. L. (1998). *Appraising levels of soil contamination and pollution with heavy metals In Heinike HJ, Eckselman W, Thomasson AJ, et al. Land information systems for planning the sustainable use of land resources. European Soil Bureau Research Report No. 4. O, office for.*

Lu, Z., Cai, M., Wang, J., Yang, H., & He, J. (2012). Baseline Values for Metals in Soils on Fildes Peninsula, King George Island, Antarctica: The Extent of Anthropogenic Pollution. *Environ Monit Assess*, *184*, 7013–7021.

Mohiuddin, K. M., Zakir, H. M., Otomo, K., Sharmin, S., & Shikazono, N. (2010). Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. *International Journal of Environmental Science and Technology*, *7*(1), 17–28. https://doi.org/10.1007/BF03326113

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geol. J*, *2*, 108–118.

Nowrouzi, M., & Pourkhabbaz, A. (2014). Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere Reserve, Iran. *Chemical Speciation and Bioavailability*, *26*(2), 99–105. https://doi.org/10.3184/095422914X13951584546986

Ogundele, D. T., Adio, A. A., & Oludele, O. E. (2015). Heavy Metal Concentrations in Plants and Soil along Heavy Traffic Roads in North Central Nigeria. *Journal of Environmental & Analytical Toxicology*, *05*(06), 6–10. https://doi.org/10.4172/2161-0525.1000334.

Ogunmodede, O. T., Adewole, E., & Ojo, A. A. (2015). *Quantitative Evaluation of Soil Properties Pollution Hazards in Urban Solid Waste Dump Sites in Nigeria*. *5*(1), 5–15. https://doi.org/10.5829/idosi.wjep.2015.5.1.9367

Ololade, I. A. (2014). An Assessment of Heavy-Metal Contamination in Soils within Auto-Mechanic Workshops Using Enrichment and Contamination Factors with Geoaccumulation Indexes. *Journal of Environmental Protection*, *05*(11), 970–982. https://doi.org/10.4236/jep.2014.511098

Olaniran, A. O., Balgobind, A., & Pillay, B. (2013). Bioavailability of heavy metals in soil: Impact on microbial biodegradation of organic compounds and possible improvement strategies. *International Journal of Molecular Sciences*, *14*(5), 10197–10228. https://doi.org/10.3390/ijms140510197

Osakwe, S. A., & Okolie, L. P. (2016). Physicochemical Characteristics and Heavy Metals Contents in Soils and Cassava Plants from Farmlands along A Major Highway in Delta State, Nigeria. *Journal of Applied Sciences and Environmental Management*, *19*(4), 695. https://doi.org/10.4314/jasem.v19i4.18

Osuji, L. C., Idung, I. D., & Ojinnaka, C. M. (2006). Preliminary Investigation on Mgbede-20 Oil-Polluted Site in Niger Delta, Nigeria. *CHEMISTRY & BIODIVERSITY* , *3*, 568–577.

Oti, W. J. O. (2016). Levels of Heavy Metal in Bonny Light Crude Oil. *IOSR Journal of Applied Chemistry (IOSR-JAC*, *9*(7), 86–88. https://doi.org/10.9790/5736-0907018688

Punch. (2020, June). Nigeria records 1,300 oil spills in two years. *Punch Newspaper*.

Rahmanian, M., & Safari, Y. (2020). Contamination factor and pollution load index to estimate source apportionment of selected heavy metals in soils around a cement factory, SW Iran. *Archives of Agronomy and Soil Science*, 1–12. https://doi.org/10.1080/03650340.2020.1861252

Rosen, V., & Chen, Y. (2014). The influence of compost addition on heavy metal distribution between operationally defined geochemical fractions and on metal accumulation in plant. *Journal of Soils and Sediments*, *14*(4), 713–720. https://doi.org/10.1007/s11368-013-0819-7

Samanta, A., Ojha, K., & Mandal, A. (2011). Interactions between Acidic Crude Oil and Alkali and Their Effects on Enhanced Oil Recovery.*25*, 1642–1649. https://doi.org/10.1021/ef101729f

Schumacher, B. A. (2002). Methods for the Determination of Total Organic Carbon (Toc) in Soils and Sediments *Brian* (Vol. 20, Issue 4).

Selvi, A., Rajasekar, A., Theerthagiri, J., Ananthaselvam, A., Sathishkumar, K., Madhavan, J., & Rahman, P. K. S. M. (2019). Integrated remediation processes toward heavy metal removal/recovery from various environments-A review. *Frontiers in Environmental Science*, *7*(May). https://doi.org/10.3389/fenvs.2019.00066

Soriano-Disla, J. M., Gómez I., & Jordán M.M. (2014). The transfer of heavy metals to barley plants from soils amended with sewage sludge with different heavy metals burdens. *J Soils Sediments*, *14*, 667–696.

Srivastava, V., Sarkar, A., Singh, S., Singh, P., de Araujo, A. S. F., & Singh, R. P. (2017). Agroecological responses of heavy metal pollution with special emphasis on soil health and plant performances. *Frontiers in Environmental Science*, *5*(OCT), 1–19. https://doi.org/10.3389/fenvs.2017.00064

Sutherland, R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, *39*(6), 611–627. https://doi.org/10.1007/s002540050473

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. In *EXS* (Vol. 101, pp. 133–164). https://doi.org/10.1007/978-3-7643-8340-4_6

Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen*, *33*(1–4), 566–575. https://doi.org/10.1007/BF02414780

Uddin, A. H., Khalid, R. S., Alaama, M., Abdualkader, A. M., Kasmuri, A., & Abbas, S. A. (2016). Comparative study of three digestion methods for elemental analysis in traditional medicine products using atomic absorption spectrometry. *Journal of Analytical Science and Technology*, *7*(1). https://doi.org/10.1186/s40543-016-0085-6

Ugochukwu, C. N. C., & Ertel, J. (2008). Negative impacts of oil exploration on biodiversity management in the Niger De area of Nigeria. *Impact Assessment and Project Appraisal*, *26*(2), 139–147.

https://doi.org/10.3152/146155108X316397A

Usen, S. A., Eneh, G. A., & Udom, I. E. (2016). *Journal of Education and Practice www.iiste.org ISSN* (Vol. 7, Issue 17). Online. www.iiste.org

Valdés, J., Vargas, G., Sifeddine, A., Ortlieb, L., & Guiñ Ez, M. (n.d.). *Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), Northern Chile: Geochemical and statistical approach*.

Verla, E. N., Andrew, W., Enyoh, C. E., & Verla, A. W. (2017). Pollution assessment models of surface soils in Port Harcourt city, Rivers State, Nigeria Phytoremediation of organics-polluted water with cana lily in a hydropoenic system. View project Environmental pollution View project Pollution assessment models of surface soils in Port Harcourt city, Rivers State, Nigeria. *WNOFNS*, *12*, 1–20. www.worldnewsnaturalsciences.com

Wander, M. M., & Traina, S. J. (1996). Organic matter fractions from organically and conventionally managed soils, II: Characterisation of Composition. *Soil Science Society of America Journal*, *60*(4), 1087–1094.

White, R. E. (2006). Principles and Practice of Soil Science -The Soil as a Natural Resource. In *Kōkūbyō Gakkai zasshi. The Journal of the Stomatological Society, Japan* (4th Editio). Blackwell publishing. https://doi.org/10.5357/koubyou.55.153.

WHO. (1996). *Permissible limits of heavy metals in soil and plants*.

Yahaya, S. M., Abubakar, F., & Abdu, N. (2021). Ecological risk assessment of heavy metal-contaminated soils of selected villages in Zamfara State, Nigeria. *SN Applied Sciences*, *3*(2). https://doi.org/10.1007/s42452-021-04175-6

Zhang, J., & Liu, C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China - Weathering features, anthropogenic impact and chemical fluxes. *Estuarine, Coastal and Shelf Science*, *54*(6), 1051–1070. https://doi.org/10.1006/ecss.2001.0879.