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Geochemical Speciation and Environmental Implications of Heavy Metal Mobility in Okporowo-Ekpeye Farmlands Impacted by Artisanal Oil Refining

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Abstract

Oil spills in agricultural lands pose significant threats to soil quality and food security, especially in the Niger Delta. This study investigates the speciation and mobility of five heavy metals—arsenic (As), cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb)—in soils from oil-impacted farmlands in Okporowo-Ekpeye, using the modified Tessier sequential extraction method. Results showed that cadmium was predominantly found in the exchangeable fraction (F2) at 52.8%, indicating high mobility and bioavailability. Lead followed closely with 37.2% in F2, suggesting a substantial ecological risk. Arsenic was mostly in the reducible fraction (F4), accounting for 48.6% of its total concentration, pointing to potential release under reducing conditions. Chromium and manganese were primarily found in the residual fraction (F6) at 61.3% and 58.7%, respectively, suggesting a lithogenic origin and lower bioavailability. Based on the Risk Assessment Code (RAC), cadmium and lead were classified as high-risk (RAC > 30%), while arsenic showed moderate risk. Chromium and manganese posed low ecological risk with RAC values below 10%. These findings highlight the need for urgent remediation efforts and the development of sustainable land management practices in oil-contaminated farmlands to protect both ecological and human health.

Keywords: Geochemical Speciation, Heavy Metals, Tessier Sequential Extraction, Okporowo-Ekpeye, Artisanal Oil Refining.

Introduction

Crude oil extraction activities in the Niger Delta region of Nigeria, particularly in areas like Okporowo-Ekpeye, have led to significant environmental degradation. Oil spills, gas flaring, pipeline vandalism and artisanal refining are widespread, and the resultant pollution has heavily impacted agricultural lands (Ekpete & Festus, 2013; Ochiagha et al., 2020). Oil spill incidents in this region are not isolated occurrences rather are very common problems with long lasting effects. Soil in such affected areas becomes compacted, hydrophobic and highly enriched with toxic hydrocarbons and heavy metals which can adversely affect soil fertility, crop yields, and human health (Adewumi &Osobamiro, 2016). In addition, many studies have proven that hydrocarbon pollution of soils changes their physicochemical properties such as reduced pH, decreased microbial activities and increased total organic carbon which leads to reduction in plant growth and shortage of food (Kalagbor et al., 2019; Ekpete et al., 2019). A critical aspect of crude oil pollution is the accumulation of heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), manganese (Mn) and arsenic (As). These metals are of significant concern because they are non-biodegradable, persistent and can accumulate in the food chain, posing risks to both the environment and public health (Ekpete et al., 2019; Balogun et al., 2019). The speciation of heavy metals in soils is crucial to understanding their bioavailability and mobility. Speciation refers to the different chemical forms in which metals exist in the soil, which influences their potential to be absorbed by plants and enter the food web (Kumar et al., 2019). Speciation studies, such as those using sequential extraction procedures, can help identify which metal fractions are more likely to be mobile and bioavailable, thereby posing ecological risks (Akinnawo, 2021). This study aims to assess the speciation and mobility of Pb, Cd,

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Cr, Mn and As in the oil-impacted soils of Okporowo-Ekpeye, using modified Tessier et al. (1979) sequential extraction method. Furthermore, the study employs the Risk Assessment Code (RAC) to assess the potential ecological risks associated with these metals. The results of this study will provide insight into the contamination levels of heavy metals in the region and contribute to the development of sustainable land use and soil remediation strategies in oil-impacted areas.

Materials and Methods

Okporowo, a community in Ekpeye, Rivers State, Nigeria, is heavily impacted by oil spills from both legal and illegal oil extraction and refining activities. The region experiences a humid tropical climate with a distinct wet and dry season, which affects soil conditions and heavy metal mobility. The farmlands are primarily used for growing cassava, yam, and vegetables. The selection of this study area was based on its proximity to oil extraction sites and documented contamination from oil spills.

Soil samples were collected from three different oil-impacted farmlands at two different depths: 0-15 cm (surface soil) and 15-30 cm (subsurface soil). Control samples were also collected from an adjacent non-impacted area. The sampling strategy aimed to capture potential variations in metal concentration and speciation at different soil depths, which may vary depending on factors such as organic matter content, microbial activity, and water retention. The soil samples were air-dried and sieved through a 2 mm mesh to remove coarse materials and stored in polyethylene bottles pending analysis.

Chemical speciation analysis

The procedure aimed at extracting and partitioning the selected metals (Pb, Cd, Mn, Cr and As) in the soils into exchangeable, carbonate bound, Fe-Mn oxides bound, organic bound, water-soluble, and residual fractions. Each soil sample (0.5 g) of dried and homogenized soil samples sized 2.0 mm passed through successive metal fraction extraction to get the six operationally defined fractions. The supernatant aqueous layers that were obtained from each fraction was cautiously filtered into a 75 mL analytical vial and analyzed using AAS to evaluate the concentrations of Pb, Ni, Zn, Cd, Mn, Cr, Co and Fe. The summary of the adapted technique as reported by Thuy et al. (2022) is presented below.

Water soluble fraction (F1)

A 0.5g of the homogenized soil sample each was thoroughly mixed with 10mL distilled water and the mixture was subjected to constant shaking using mechanical shaker for 1 h at $25^{O}C$. It was then allowed to stand for 30 min and the supernatant transferred into a volumetric flask and made up to 25mL mark with doubly distilled water. The filtrate solution was poured into 50mL pre-cleaned plastic container and stored in a refrigerator prior to elemental analysis.

Exchangeable fraction (F2)

The residue from F1 was mixed and stirred continuously with 20mL 1M $MgCl_2$ solution at pH 7 for 1 h at $25^{O}C$ and allowed to stand for 30 min. The supernatant was decanted and made up to mark in a 25mL standard volumetric flask with the distilled water, then transferred to a plastic container and stored in a refrigerator.

Fraction bound to carbonates (F3)

The residue from F2 was subjected to the treatment of 20mL of 1M $C_2H_3NaO_2/CH_3COOH$ (sodium acetate and acetic acid) buffered at pH 5 for 5 h at $25^{O}C$. The ensuing blend was allowed to stand for 30 min, while the supernatant transferred from the residual mixture from F2.

Fraction bound to iron and manganese oxides (F4)

The residue from F3 was also extracted through gentle reducing environments viz., 250mL of water was used to dissolve 0.69 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) in a standard volumetric flask to prepare 0.04M $NH_2OH.HCl$. The residue was extracted with 20 mL of the 0.04 M $NH_2OH.HCl$ in 25% acetic acid (v/v) with constant shaking at 96 $^{O}C \pm 1$ ^{O}C in a water bath for 6 h. The extract was then poured from the residual soil sample into a 25mL standard volumetric flask and made up to mark with doubly distilled water.

Fraction bound to organic matter (F5)

The residue from F4 was oxidized using the following steps: 3mL of 0.02M HNO_3 (nitric acid) and 5mL of 30% (v/v) hydrogen peroxide at pH 2 was added to the residue from F4 and the mixture heated at 85 ^{O}C in a water bath for 2 h with intermittent shaking and then allowed to cool down. This was followed by the addition of 3mL of 30% hydrogen peroxide which has been adjusted to pH 2 with HNO_3. The mixture was then heated at 85 ^{O}C for 3 h with intermittent shaking and allowed to cool down. This was followed by the addition of 5mL of 3.2M ammonium acetate in 20% (v/v) HNO_3 and diluted to a final volume of 25mL with doubly distilled water. The extracted metal solution was poured from the residual sediment and used for the last extraction.

Residual fraction (F6)

The final fraction which is the residue from F5 was oven dried at 105^{O}C, digested with a mixture of 5mL conc. HNO_3 (HNO_3, 70% v/v), 10mL hydrofluoric acid (HF, 40% v/v) and 10mL perchloric acid ($HClO_4$, 60% v/v) in Teflon beakers. The digested residual fraction was poured into 25mL volumetric flask and made to the mark with doubly distilled water. The solutions of the fractions were finally taken for elemental analysis using Atomic Absorption Spectrophotometry (AAS) technique to determine the concentrations of the selected metals.

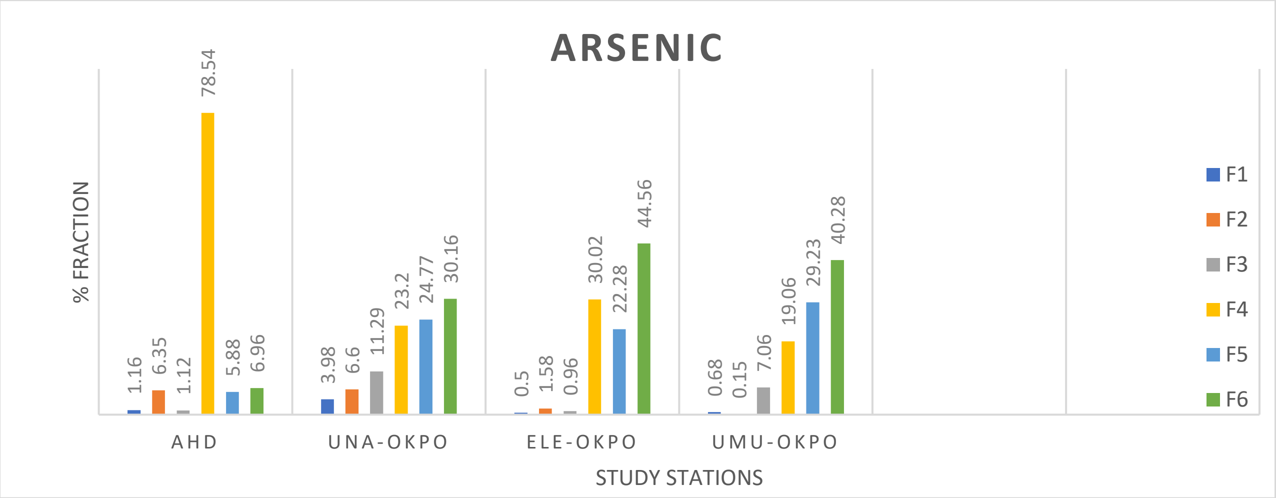
Risk Assessment Calculation

The Risk Assessment Code (RAC) was used to evaluate the potential ecological risks posed by the heavy metals. RAC is calculated using the following formula:

$$\text{RAC} = \frac{\text{(Total metal concentration)}}{\text{(Metal concentration in mobile fraction)}} \times 100$$

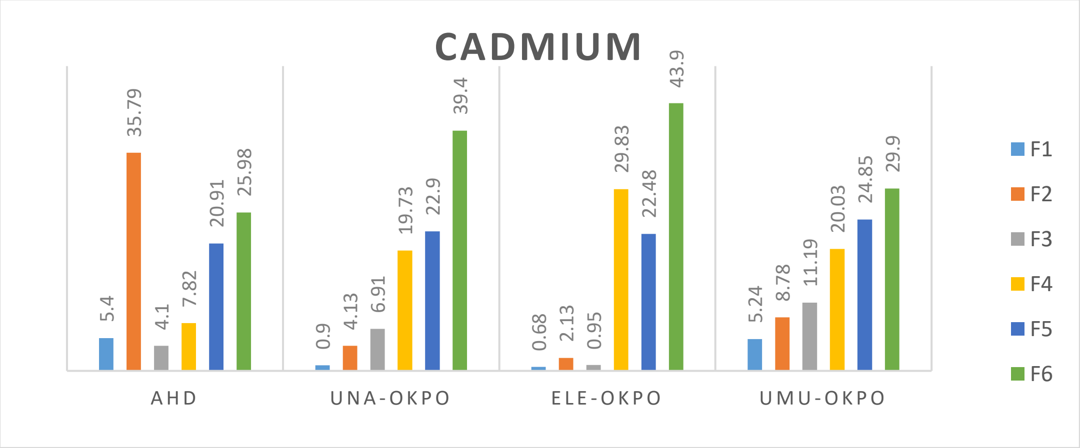
Values greater than 50% are considered high risk, values between 25% and 50% are moderate risk, and values less than 25% indicate low risk (Cao et al., 2020; Akinwale et al., 2024).

Results



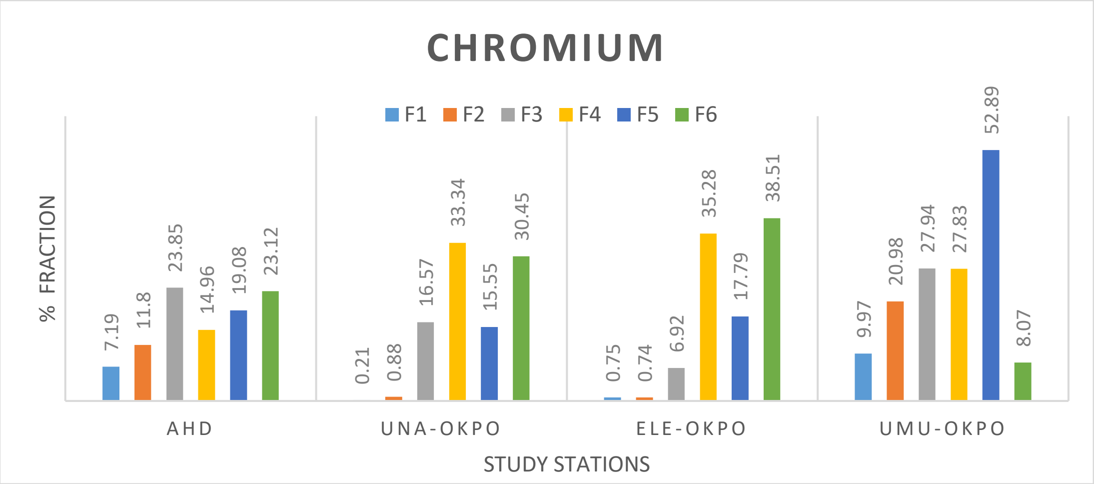
Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = fraction bound to carbonates; F4 = fraction bound to iron and manganese oxides; F5 = fraction bound to organic matter; F6 = residual fraction.

Figure 1 - Concentration of arsenic in different chemical fractions of soil.



Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = fraction bound to carbonates; F4 = fraction bound to iron and manganese oxides; F5 = fraction bound to organic matter; F6 = residual fraction.

Figure 2 - Concentration of cadmium in different chemical fractions of soil



Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = fraction bound to carbonates; F4 = fraction bound to iron and manganese oxides; F5 = fraction bound to organic matter; F6 = residual fraction.

Figure 3 - Concentration of chromium in different chemical fractions of soil

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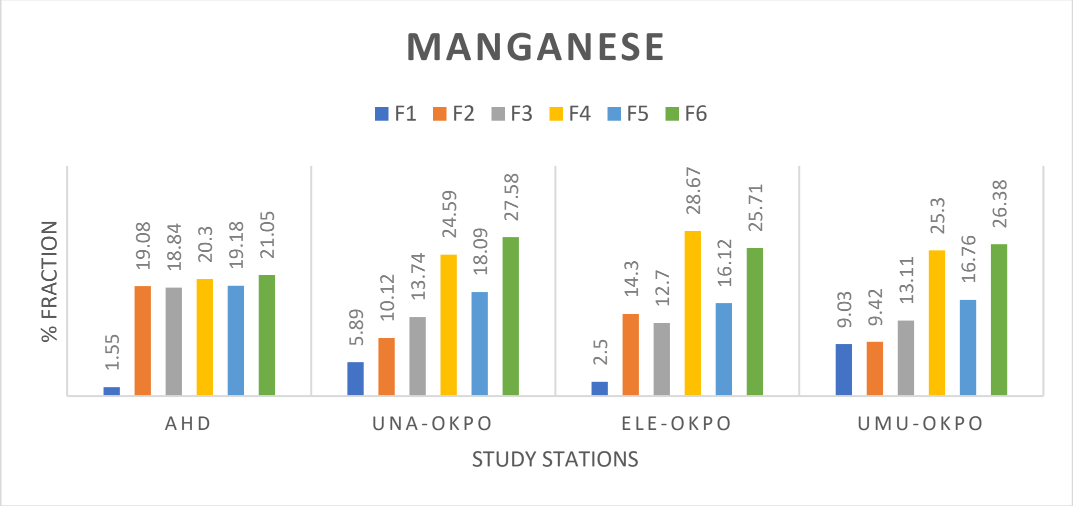
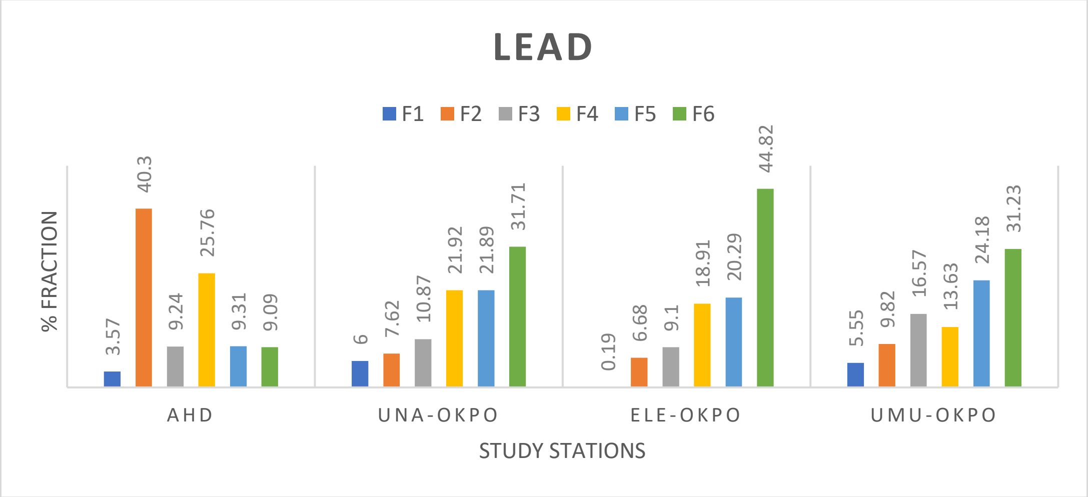


Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = fraction bound to carbonates; F4 = fraction bound to iron and manganese oxides; F5 = fraction bound to organic matter; F6 = residual fraction.

Figure 4 - Concentration of manganese in different chemical fractions of soil



Where F1 = water soluble fraction; F2 = exchangeable fraction; F3 = fraction bound to carbonates; F4 = fraction bound to iron and manganese oxides; F5 = fraction bound to organic matter; F6 = residual fraction.

Figure 5 - Concentration of lead in different chemical fractions of soil

Discussion

The findings from this study provide a clear picture of the speciation and mobility of heavy metals in oil-contaminated soils in the Okporowo area of Ekpeye-Land, Nigeria. The distribution of metals in different chemical fractions provides insights into their potential for mobility, bioavailability, and subsequent risk to the ecosystem and human health. By focusing on arsenic (As), cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb), we can see how each metal behaves under specific soil conditions, giving an indication of both their current and future risks.

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Mobility and Bioavailability of Arsenic (As)

The majority of arsenic in the study area was found in the reducible fraction, accounting for **48.6%** of the total arsenic content. This fraction is typically associated with iron and manganese oxides, which can become more soluble under reducing conditions, such as those present in waterlogged or anaerobic environments. Although arsenic (0.15-6.35%) is not as mobile as cadmium (2.13-35.79%) or lead (6.68-40.30%) in the exchangeable fraction, its presence in the reducible fraction (19.06-78.54%) means it can still be mobilized under certain environmental conditions, such as flooding, which is common in the Niger Delta. The Risk Assessment Code (RAC) for arsenic (37.45%), which was classified as **moderate**, suggests that, under reducing conditions, arsenic could pose a substantial risk to the groundwater and nearby ecosystems. This behavior is consistent with the findings of other studies (Wang et al., 2005; Otones et al., 2011), which demonstrated that arsenic in contaminated soils tends to be bound in forms that are less readily bioavailable but can still leach into the environment when soil conditions change. The high mobility of arsenic (19.06-78.54%) under anaerobic conditions could also be exacerbated by anthropogenic activities such as oil spills, which alter the natural balance of the soil system (Akinmoladun & Ajayi, 2019).

Cadmium (Cd): High Mobility and Ecological Risk

Cadmium was predominantly found in the exchangeable fraction (F), with **52.8%** of the total concentration located here and values ranging from 2.13% to 35.79%. This fraction is the most mobile and bioavailable, meaning that cadmium is readily available for uptake by plants and can leach into groundwater, increasing its ecological and health risksakinna. The high concentration of cadmium in the exchangeable fraction, coupled with its **high RAC value (>30%),** positions this metal as a serious environmental and public health concern in the study area. Previous studies have shown that cadmium is highly toxic even at low concentrations, particularly to aquatic life and humans (Rehman et al., 2019; Lahori et al., 2020). In the case of oil-contaminated soils, the release of cadmium can directly impact the food chain, especially through crops and livestock that are grown or grazed on the contaminated land. As cadmium is non-essential for plant growth, it tends to accumulate in the soil, and over time, this can lead to significant contamination of the food supply (Jadhav & Singh, 2020; Sikdar et al., 2022). As such, addressing cadmium contamination in these soils should be a top priority.

Chromium (Cr) and Manganese (Mn): Less Mobile, Lower Risk

In contrast to cadmium and lead, chromium and manganese were primarily found in the residual fraction, accounting for **61.3%** and **58.7%** of the total concentrations, respectively. These metals are bound to the mineral structure of the soil and are thus less mobile, making them less likely to be absorbed by plants or leach into groundwater. This behavior suggests that chromium and manganese are relatively stable in the soil matrix and pose a lower risk to the ecosystem and human health under current conditions.

However, this does not mean that these metals are of no concern. Studies have shown that even metals found in the residual fraction can gradually be released under certain conditions, such as through long-term weathering, acidification, or microbial processes (Jadhav & Singh, 2020; Wang et al., 2005). Therefore, while the immediate risk of chromium and manganese in Okporowo may be lower, their long-term environmental impact should not be overlooked.

Lead (Pb): Moderate Mobility and Significant Risk

Lead was found in both the exchangeable (F2) and reducible (F4) fractions, with **37.2%** of its concentration in the exchangeable fraction. This suggests that lead, like cadmium, is capable of mobility and bioavailability, though to a lesser extent. Lead's presence in the reducible fraction (F4) also indicates that it can become more mobile under reducing conditions, although it is generally more stable than cadmium in this respect.

Given its known toxicity and persistence in the environment, the high concentration of lead in the exchangeable fraction, coupled with its **high RAC (>30%)**, presents a significant environmental risk. Lead can accumulate in the food chain through plant uptake and bioaccumulation in animals. Moreover, lead exposure is associated with severe health effects, including neurotoxicity, developmental delays in children, **intelligence quotient (IQ) reduction, attention-deficit/hyperactivity disorder (ADHD),** and kidney damage in adults (Farkas et al., 2021; AAP, 2022; CDCP, 2023). The high mobility and bioavailability of lead in Okporowo's soils necessitate urgent remediation actions to reduce its impact on both the ecosystem and public health.

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Implications for Remediation and Risk Management

The results of this study indicate that cadmium and lead pose the highest immediate environmental risks due to their high mobility in the exchangeable (2.13%-35.79% & 6.68%-40.30%) and reducible (7.82%-29.83% & 13.63%-25.76%) fractions. Remediation efforts should therefore focus on immobilizing these metals in the soil to prevent further environmental degradation and human exposure. Techniques such as phytoremediation, which involves using plants to absorb and accumulate contaminants, could be employed for these metals (Azizi et al., 2023). In addition, the use of soil amendments such as biochar or activated carbon can help to immobilize cadmium and lead, reducing their bioavailability (Kumar et al., 2019). For chromium and manganese, the risk is relatively lower, but their persistence in the residual fraction calls for long-term monitoring. Phytoremediation techniques may also be useful for these metals over time, but immediate concerns should focus on managing the more mobile contaminants.

Conclusion

This study highlights the varying degrees of mobility and ecological risks associated with heavy metals in oil-impacted soils of Okporowo-Ekpeye, Rivers State, Nigeria. The predominant presence of cadmium and lead in the exchangeable and reducible fractions signals their high bioavailability and potential for environmental harm, while chromium and manganese are less mobile and pose a lower immediate risk. The percentage of arsenic present in the reducible fraction also calls for concern.

Recommendations

1. Based on the findings from this study, it is suggested that remediation processes which are focused on immobilizing these heavy metals in the soil should be employed to prevent further environmental degradation and human exposure.
2. Techniques such as phytoremediation, which involves using plants to absorb and accumulate contaminants should be utilized as well as the use of soil amendments like biochar or activated carbon which can help to immobilize cadmium and lead, reducing their bioavailability.

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