

ECOLOGICAL AND HUMAN HEALTH RISKS ASSOCIATED WITH SOIL POLLUTION BY PAHS AND HEAVY METALS IN THE NIGER DELTA

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Abstract: Despite the prevalence of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) in Niger Delta's crude oil regions, comprehensive research on their concentrations and combined risks in crude oil-contaminated soils is lacking. Our study focused on examining the concentration, source, spatial distribution, and health risk of 16 PAHs and 9 different HMs in soils across a gradient of Niger Delta area Nigeria. The objective was to gain a comprehensive understanding of the HMs and PAHs' behavior in the environment and their potential impact on human health. The mean total concentrations of 16 PAHs ($\Sigma_{16}\text{PAHs}$) were 779.58 ng/g for upland area, 749.46 ng/g for mid-slope area, and 679.37 ng g⁻¹ for Low-land. The concentration of the HMs followed the order of Cu > Cd > Ni > Pb > Cr > Fe > Mn > Zn > Co, with Cu, Cd, Ni, and Pb exceeding the permissible levels. The study areas displayed varying concentrations of NO₃⁻, PO₄²⁻, SO₄²⁻, Ca, Na, and K, with some levels exceeding acceptable values, possibly influenced by crude oil contamination and the use of fertilizers. In the Niger Delta regions, the primary sources of soil PAH contamination include crude oil spills, natural crude oil seepage, and coal combustion. With this, the government of Nigeria should strengthen soil contamination monitoring, enforce spill regulations and promote eco-friendly farming.

Keywords: Health Risk, HMs, Niger Delta, Soil, PAHs.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) are prevalent pollutants found in crude oil and urban environments (Sankar et al., 2023). PAHs, which are widespread contaminants, have been identified as human carcinogens, teratogens, and mutagens (Peng et al., 2021). These pollutants primarily result from human activities, including oil spills, coal tar emissions, vehicle exhaust, petroleum refining, and the combustion of fossil fuels. HMs also present health risks to both humans and the environment, particularly when found in elevated concentrations (Ali et al., 2021; Koolivand et al., 2020). They are known to cause various health problems, including neurological and developmental issues (Wan et al., 2018).

In the Niger Delta region, the history of oil production dates back several decades, with extensive extraction activities conducted by multinational oil companies (UNEP, 2021). Unfortunately, this has led to severe environmental degradation, including crude oil spills and gas flaring. The potential sources of PAHs and HMs pollution in the area are primarily linked to these oil-related activities, including oil spills, gas flaring emissions, and improper disposal of oil industry waste (Kariyawasam et al., 2022). These contaminants have infiltrated the region's waterways and ecosystems, posing significant health risks to the local population. Efforts to mitigate pollution and protect human health remain critical in this region (Asagba et al., 2018).

The issue of crude oil contamination of soil can be traced back to the early days of oil exploration and

production (CCME, 2002; Geng et al., 2020; Adeyemi et al., 2019). Crude oil pollution remains a major global environmental problem, with severe implications for soil, water, and air quality (Dong et al., 2021; Han et al., 2021). According to Alawadhi et al. (2018), oil spills are a significant contributor to soil contamination, with ecological and public health consequences. Crude oil spills can lead to soil pollution through direct oil contact or exposure to volatile organic compounds (VOCs) emitted during oil spills (Geng et al., 2020) and can have a synergic effect on the level of heavy metals contribution. PAHs and HMs are prevalent pollutants commonly found in urban settings (Han et al., 2020; Abdallah et al., 2020; Liu et al., 2019). PAHs are pervasive contaminants known for their detrimental effects on human health as they are classified as human carcinogens, teratogens, and mutagens (Chunhui et al., 2015; Wang et al., 2020b; Bussotti et al., 2019). These pollutants can remain in soil for extended periods, resulting in long-term soil degradation and reduced soil fertility (Alawadhi et al., 2018; Al-Mutairi et al., 2019). Furthermore, crude oil contains high levels of heavy metals, such as lead and mercury, which are toxic to both humans and plants (Odu et al., 2018; Uzun et al., 2017). The negative effects of crude oil pollution on soil fertility and plant growth have been extensively researched (Han et al., 2019; Hong et al., 2020). In a study by Iwegbue et al. (2018), it was found that crude oil-contaminated soil had significantly lower pH and organic matter content compared to non-contaminated soil, which can result in poor plant growth and reduced crop yields. Furthermore, crude oil pollutants in the soil can lead to toxic compound accumulation in plants, causing a reduction in food safety and quality (Mishra et al., 2020). HMs and PAHs can be released into the soil due to crude oil spills and leaks, negatively affecting soil health and potentially contaminating crops (UNEP, 2021; Azeez et al., 2019). The persistent nature of these pollutants makes it difficult to restore the soil to its pre-contamination state (Wang et al., 2020b; Al-Abed et al., 2019; Suresh et al., 2020; Amaeze et al., 2021; Huang et al., 2017).

In Delta State, Nigeria, Asagba et al. (2018), found that soil samples from oil-contaminated sites had elevated levels of lead, cadmium, and nickel, which exceeded the Nigerian National Environmental Standards and Regulations Enforcement Agency (NESREA) limits. The study also revealed that sites closer to the oil spills had higher concentrations of HMs than those farther away. HMs are a significant concern in crude oil-polluted soil as they can accumulate in plants and animals, causing severe health effects. Efe et al. (2020), found that heavy metals such as lead, cadmium, and mercury can accumulate in crops, leading to reduced crop yields and food insecurity. Exposure to these metals can cause developmental issues,

neurological disorders, and other health problems in humans and animals.

Ohaji Egbema is a region located in the Niger Delta area of Nigeria, known for its significant crude oil reserves (Nwachukwu et al., 2020; Kour et al., 2021). Situated in Imo State, Ohaji Egbema is an important hub for oil exploration, production, and distribution in the country (Nwachukwu et al., 2020; Ihenetu et al., 2017). Crude oil plays a vital role in the economic development of Ohaji Egbema and the surrounding communities (Folorunso et al., 2019; Ambade et al., 2023). The region's crude oil reserves have attracted major oil companies, leading to the establishment of oil fields, drilling rigs, and refineries (Ihenetu et al., 2017). However, the presence of crude oil has also brought about various environmental and socio-economic challenges to Ohaji Egbema and in the other hand, endangering the plants and inhabitants of the area (Nwachukwu et al., 2020). Efforts have been made to address these challenges and mitigate the negative impacts of crude oil operations in Ohaji Egbema. The presence of HMs can influence the fate, transport, and toxicity of PAHs, and vice versa. Interactions between PAHs and HMs can lead to synergistic or additive effects, potentially exacerbating their individual toxicities and posing greater risks to ecosystems and human health. Therefore, understanding the relationship between PAHs and HMs is crucial for effective environmental management and pollution control strategies (EPA, 2021; El-Naggar, 2019). Figure 1 below shows the evacuation of crude oil polluted site in drilling company in Ohaji Egbema. Evacuation of crude oil polluted sites involves the removal and relocation of contaminated materials to prevent further environmental damage. Treatment methods are then employed to remediate the polluted areas, which may include physical, chemical, or biological processes but due to leaching, some amount of these PAHs and HMs can still find their way to the ground water body before the remediation process (Wang et al., 2020; Nobili et al., 2020; Ambade & Sethi, 2021). Soil of these ecosystems constitute the final deposit of many substances present in the water column (Botello et al., 2022).

The novelty in this study lies in its comprehensive exploration of the ecological and health risks associated with PAHs and HMs in the context of crude oil contamination, specifically within the Ohaji Egbema region of the Niger Delta. The study addresses a critical scientific problem, considering the presence of these pollutants in an important agricultural area. The significance is underscored by the lack of prior in-depth research in this region, leaving a notable knowledge gap. This study offers crucial insights for farmers, agricultural stakeholders, and researchers by analyzing soil samples to measure the presence of PAHs and HMs,

sedimentary formations, including shale, sandstone, and limestone, as well as volcanic rocks such as basalt and andesite, which could potentially serve as sources for trace elements like Cu, Cd, and Ni. Cu, Cd, and Ni can potentially be derived from both andesite and basalt rocks in the study area of Ohaji Egbema, Imo State, where crude oil drilling takes place. The dry season runs from November to March, while the rainy season runs from April to October. The area has high annual rainfall, ranging from 2,000 to 3,000 mm. One of the significant festivals celebrated in Ohaji Egbema is the Iri Ji Festival, which takes place annually to commemorate the new yam harvest. In recent years, the area has witnessed an influx of investors in the oil and gas sector. Some of the notable oil and gas companies in the area include Shell Petroleum Development Company, Chevron, and Total (Ohaji Egbema, 2017).

2.2 Sample Collection and Processing

Three locations were selected for this study in Ohaji in Niger Delta area, these locations covered the distance from the upland (UL) to the mid-slope (MS) and low-land (LL) over a distance of 30 km (10 km between each location), and were considered as the representative areas for assessment. We selected 75 soil sampling points for the study, and it was done from May 2021 to June 2022. When sampling, 5 sub samples (4 corners and 1 center) from the divided sampling areas (0-5 m²) were taken and mixed to form one composite sample. At each location, twenty-five soil sub samples (0– 15 cm) were collected, each location was split into 5 sampling areas and the means of each area was used for the study, making it total samples of 75. Five 5×5 m soil sampling plots were selected at the sampling site, and one soil sample at 0–15 cm depth was taken using a shovel at each plot. Subsequently, the samples were carefully examined to remove any remaining roots, stones, or other debris. All the soil samples were mixed sufficiently and air-dried naturally and sieved through a 200-mesh sieve for analysis of soil properties and batch experiments.

2.3 Soil analysis

2.3.1 Physicochemical analysis

The pH was measured using Hanna model HI991300, it was standardized using buffer 4 and buffer 7 according to the method used by Ihenetu *et al.*, (2018). Cadmium reduction method was used to measure the nitrate within 48h using Hanna HI 83200 multi parameter bench photometer at 525nm. Hanna HI83200 multi parameter bench photometer at 466nm was used to determine for sulfate using turbidimetric

method. Hanna HI8320 multi parameter bench photometer at 525nm was used to determine for phosphate on the samples by amino acid method, according to Ihenetu *et al.*, (2018).

2.3.2 HMs analysis

The HMs were analyzed according to the methods used by Chunhui *et al.* (2019). First, concentrated hydrochloric acid and nitric acid were added in sequence into a Teflon beaker containing a small amount of the sample. The sample mixture was heated at 150°C, and then a mixture of HF, HNO₃, and HClO₄ was added. The temperature was further increased to 200°C to facilitate digestion. After digestion, the solutions were allowed to cool. The cooled solutions were evaporated until they reached near dryness. Dissolution in Each sample was dissolved in 2.5 ml of aqua regia, resulting in the formation of a solution. These solutions were then transferred to 25-ml volumetric polypropylene tubes. The levels of HMs were measured using inductively coupled plasma mass spectrometry (ICP-MS) following the procedure outlined by Chen *et al.* (2018b).

2.3.3. PAHs analysis

The analysis of the concentrations of 16 PAHs was conducted according to Chunhui *et al.*, (2015) and is as follows: Each soil sample was extracted using a high-performance liquid chromatography-grade organic solvent, specifically a mixture of n-hexane and dichloromethane in a volume ratio of 1:1. The extracted samples were concentrated, and the solvent was changed to n-hexane. Silica gel column chromatography was employed to purify the concentrated extracts, ensuring the removal of impurities and contaminants. Elution of the column was carried out using a mixed solvent composed of n-hexane and dichloromethane in a volume ratio of 3:2. The eluted mixture was concentrated, and the solvent was changed back to n-hexane in preparation for gas chromatography-mass spectrometry measurement. The measurement of the PAH concentrations was performed using gas chromatography-mass spectrometry. Electron impact mode was utilized for ionization, and selective ion monitoring mode was employed for data acquisition. The external reference method was employed to test the target compounds, ensuring accurate identification and quantification. The mean recoveries of all PAHs based on matrix-spiked samples were found to be acceptable. Additionally, during testing, a blank sample and matrix blank were measured for each batch of six samples to account for background and matrix effects.

2.3.4 Risk Assessment

PAH and HM polluted soils could influence the health of the residents by ingestion and dermal absorption of soil pollutants (USEPA, 2021). In this research, we employed the toxic risk assessment via ingestion and dermal absorption, we calculated the hazard quotient and carcinogenic risk assessment. We employed the toxicity equivalence factor to evaluate the potential risk of the studied pollutants.

2.3.5 Quality assurance and quality control

The reagents utilized in the experiments were of top-notch analytical grade, which were bought from BDH Chemical Ltd, UK, and Sigma-Aldrich Chemie GmbH, Germany. Detergents and deionized water were utilized to wash the dishes and sample bottles. They were soaked for the time being with a solution of 10% HNO₃ in a 1 % HCl solution, trailed by washing with deionized water. Also, the reagents that were utilized for the assurance of anion concentrations with the Hanna Hi 83,200 Instrument were gotten from Hanna Instruments. The instrument (Agilent 240FS AA) utilized for the assurance of the concentrations of metallic elements in the samples has high sensitivity—regularly > 0.9 absorbance with a precision of < 0.5 % RSD from ten-second integrations for 5 mg/L Cu standard. The soil samples and different reagents were weighed with Shimadzu AW 320 analytical balance (Shimadzu, Japan). After extraction, the concentrations of the target compounds were measured and compared to the concentrations of the same selected soil samples without PAH standards. The limit of detection (LOD) was determined by calculating three times the noise level of the chromatogram obtained from the blank sample. The sample size used for analysis was 5 g, and the final volume of the extracted solution was 1 ml.

2.3.6 Data analysis

Statistical analysis (parametric and nonparametric tests) of the obtained results were

performed using SPSS software (Version 25.0, IBM Inc. US) and Microsoft office excel (Microsoft Inc. US), the results were considered significance at p-value < 0.05. The figures were plotted using R programming software (R 1386, 4.1.0) was used for data plotting.

3. RESULTS AND DISCUSSION

3.1 Textual and Physicochemical Characteristics of Soil samples

For the visual characteristics of the soil samples, each location is associated with specific attributes such as color (UL samples are more of reddish-brown, while MS and LL represent brown and reddish yellow respectively), moisture content of the samples are moist during the dry season and wet during the rainy season. The reaction with hydrochloric acid ranging from weak to strong in all the sampling areas. These visual characteristics provide valuable insights into the physical and chemical properties of the soil samples across different locations, which can be crucial for various agricultural, environmental, or geological assessments and analyses. Table 1 presents the soil characteristics in the study locations, the pH values across all three locations fall within the acceptable range of 6.5-8.5, as recommended by the World Health Organization (WHO, 2021). These slightly alkaline conditions, with the lowest mean pH observed in the LL area, can influence the availability of nutrients and the microbial activity in the soil. The study areas show relatively low NO₃⁻ concentrations, with mean values ranging from 8.85 to 11.51. However, in the context of crude oil-contaminated soil, PAHs can affect microbial populations responsible for nitrification processes, potentially influencing nitrate availability (Iwegbue et al., 2018). The PO₄²⁻ concentrations appear to be higher than the acceptable value, ranging from 1.96 to 2.91. These elevated levels indicate the presence of PO₄²⁻, which are important

Table 1: Mean physiochemical characteristics

	UL				MS				LL				
Parameters	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Bv (WHO, 2021)
pH	6.52	7.52	7.02	0.252	6.33	7.12	6.7	0.315	5.98	6.33	6.12	0.136	6.5-8.5
NO ₃ ⁻	10.65	13.24	11.51	0.861	10.25	12.95	11.3	1.016	7.98	9.65	8.85	0.617	50
PO ₄ ²⁻	1.96	2.41	2.1	0.196	1.41	2.95	1.96	0.619	2.11	3.66	2.91	0.58	1
SO ₄ ²⁻	2.31	4.32	3.14	0.714	2.35	3.52	2.88	0.488	2.14	3.02	2.56	0.336	250
Ca	7.62	10.32	9.33	1.07	8.64	9.62	8.82	0.39	7.66	9.21	8.22	0.619	75
Na	0.21	0.36	0.28	0.057	0.32	0.96	0.65	0.247	0.24	0.45	0.35	0.086	200
K	4.65	5.86	5.05	0.472	4.01	5.03	4.51	0.417	4.96	6.32	5.44	0.527	20
Σ ions	33.92	44.03	38.43	3.622	33.31	42.15	36.82	3.492	31.07	38.64	34.45	2.901	

Key: Min = minimum, Max: maximum, SD = standard deviation, BV = background value, Number of samples = 5

nutrients for plant growth. The higher phosphate concentrations may be associated with the application of nitrogen, phosphorus, and potassium (NPK) fertilizers used to remediate the soil or enhance plant growth. However, the presence of PAHs can influence the microbial activity responsible for PO_4^{2-} availability and nutrient cycling (Chen et al., 2018a; Lehmann-Konera et al., 2020). SO_4^{2-} concentrations fall within acceptable limits, with mean values ranging from 2.56 to 3.14. The presence of PO_4^{2-} in the study area can have implications for soil fertility and water quality. In crude oil-contaminated soil, PAHs can interact with sulfate-reducing bacteria, potentially affecting sulfur transformations and the availability of sulfates. Ca concentrations show moderate levels, with mean values ranging from 8.22 to 9.33. Ca is an essential nutrient for plants and plays a crucial role in soil structure and nutrient availability. However, in the presence of PAHs from crude oil contamination, Ca availability can be influenced by interactions with organic matter and microbial activity. Na concentrations are relatively low, with mean values ranging from 0.28 to 0.65. These levels indicate a limited presence of Na, which is beneficial for soil quality. K concentrations are within acceptable ranges, with mean values ranging from 4.51 to 5.44. Adequate K availability is crucial for plant growth, but in the presence of PAHs from crude oil contamination, interactions between PAHs and soil components can affect K availability and nutrient uptake by plants.

3.2. Levels of HMs in soils

The results of the concentration of HMs (Table 2) indicate varying concentrations of these metals in the soil samples. Fe concentrations range from 7.166 to 11.056 mg/kg, which shows higher levels of Fe in the soil. Cu concentrations range from 17.130 to 24.544 mg/kg, indicating the presence of Cu in the soil, which can be derived from crude oil spillage, natural sources, or anthropogenic activities. Considering the effects of PAHs, it is known that crude oil contains PAHs, which are organic compounds formed during incomplete combustion or pyrolysis of organic materials (Alawadhi et al., 2018). PAHs can be released into the environment through crude oil spills or anthropogenic activities related to oil extraction, transportation, or refining. PAHs are known to have toxic properties and can persist in the environment for a long time. Cu-based compounds are used in certain oil industry processes and equipment, and their degradation or corrosion can release Cu ions into the environment, including the soil. PAHs present in crude oil can contribute to soil contamination, and the release of Cu from associated equipment can be an

indirect consequence of crude oil pollution. Cd concentrations range from 17.478 to 18.010 mg/kg, indicating the presence of this toxic HM. Co concentrations range from 14.16 to 16.800 mg/kg, and Ni concentrations range from 16.224 to 23.344 mg/kg, suggesting the presence of these metals in the soil, which can originate from natural sources or industrial activities. While Cr concentrations in the study (0.842 to 2.78 mg/kg) are relatively low and within acceptable values, it is noted that higher concentrations of certain forms of Cr can be toxic. Mn concentrations (11.440 to 12.226 mg/kg) indicate the presence of this essential nutrient for plants, and Zn concentrations (116.134 to 125.946 mg/kg) indicate the presence of this essential micronutrient within acceptable ranges for agricultural soils. Lastly, Pb concentrations range from 7.344 to 8.940 mg/kg, indicating the presence of this toxic HMs. Pb is known to have detrimental effects on human health and the environment. Although the concentrations observed in the data are relatively low, the presence of lead highlights the need for monitoring and appropriate management practices. The difference in the levels of HMs in UL, MS and LL were identified using Kruskal-Wallis (H) test. The results inferred that these 3 different locations had similar influences on the accumulation of these pollutants in the surface soil samples ($P > .05$).

3.3 Mean of PAHS concentration in all sampling areas

Table 3 provides experimental data about the mean concentrations of PAHs in the three sampling locations expressed in ng g⁻¹. From the results obtained, NaP shows a mean concentration ranging from 126.39 ng g⁻¹ in LL to 156.28 ng g⁻¹ in MS. DaA exhibits a mean concentration range of 152.71 ng g⁻¹ in MS to 168.82 ng g⁻¹ in LL. Flu displays a mean concentration range of 200.15 ng g⁻¹ in LL to 231.67 ng g⁻¹ in MS. Interestingly, some PAHs demonstrate higher mean concentrations in specific sampling areas. For example, BaP exhibits a higher mean concentration of 40.04 ng g⁻¹ in UL compared to 24.27 ng g⁻¹ in LL. Similarly, Chr has a higher mean concentration of 32.43 ng g⁻¹ in LL compared to 28.93 ng g⁻¹ in MS. This variability might be attributed to various factors, including different emission sources, geographical characteristics, and meteorological conditions in each sampling area. To better understand the data's significance, it is essential to consider the SD values. The SD provides a measure of data dispersion around the mean and helps assess the reliability of the mean values. For instance, NaP has a relatively low SD, indicating that its mean concentration is less

Table 2. Concentration of HMs (mg/kg) for all sampling locations

UL					MS				LL				BV
Metals	Min	Max	Mean	SD	Min	Max	Mean	SD	min	max	mean	SD	
Fe	9.65	13.52	11.056	1.051	6.33	8.52	7.166	0.656	7.65	9.35	8.188	0.596	0.3
Cu	14.62	23.62	20.472	3.133	14.32	20.31	17.130	2.433	23.15	26.52	24.544	1.191	2.0
Cd	13.52	20.21	17.478	2.077	15.32	20.31	17.550	1.821	16.35	19.35	18.010	1.053	0.003
Co	13.25	18.36	15.398	1.905	12.35	16.35	14.16	1.497	15.36	18.52	16.800	1.222	0.5
Ni	16.25	29.35	23.28	5.243	14.52	18.65	16.224	1.694	19.52	25.31	23.344	2.227	0.02
Cr	0.96	9.65	2.78	3.435	0.63	0.99	0.842	0.149	0.92	1.32	1.114	0.171	0.05
Mn	10.52	14.25	12.226	1.251	10.21	15.32	12.24	1.947	10.25	14.25	11.440	1.614	0.4
Zn	98.35	150.32	125.94	21.823	109.2	142.2	119.24	14.15	103.2	132.4	116.13	11.709	3.0
Pb	6.54	9.63	8.94	1.126	6.35	8.35	7.344	0.696	5.96	9.62	7.698	1.480	0.01
Σ HMs	183.66	288.91	237.57	41.044	189.2	251	211.89	25.05	202.36	256.64	227.26	21.263	

Number of samples = 5

Table 3. Mean of PAHS concentration in all sampling locations (ng g⁻¹)

	UL				MS				LL			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
PAHs												
Naphthalene (NaP)	135.21	164.32	146.94	10.586	146.20	163.30	156.28	5.674	119.61	135.32	126.39	6.112
Dibenzyl (a-h) anthracene (DbA)	163.52	175.32	168.82	4.644	135.23	163.30	152.71	10.351	145.52	163.52	155.83	5.880
Fluorene (Flu)	215.30	253.21	231.67	14.019	198.35	231.20	215.67	13.465	193.20	210.51	200.15	6.157
acenaphthene (Ace)	11.20	18.32	15.88	2.737	10.52	16.21	13.05	2.385	13.22	16.35	14.89	1.220
Benz[a]anthracene (BzA)	16.35	19.65	17.98	1.441	14.52	19.65	16.43	2.138	11.32	16.32	14.11	2.184
Benzo[a]pyrene (BaP)	32.98	45.25	40.04	5.059	25.52	36.52	31.48	4.570	16.32	33.21	24.27	7.502
Chrysene (Chr)	29.65	36.25	31.76	2.717	24.52	33.23	28.93	3.361	29.36	36.25	32.43	2.853
Benzo[b]fluoranthene (BgP)	39.52	49.52	43.43	4.127	49.31	58.12	52.42	3.515	19.65	56.32	46.89	17.737
Benzo[k]fluoranthene (Bkf)	8.65	11.32	10.26	0.956	6.31	9.65	7.01	1.714	5.32	7.65	6.07	0.954
Acenaphthoquinone (Acy)	19.65	23.52	21.66	1.437	22.31	36.25	29.55	5.574	19.35	23.32	20.14	1.377
Pyrene (Pyr)	13.52	17.32	15.13	1.735	15.32	19.52	17.15	1.526	11.25	14.32	12.09	1.187
Phenanthrene (Phe)	9.54	17.52	13.24	3.212	8.65	14.32	10.76	2.266	6.32	9.36	7.65	1.363
Fluoranthene (Flo)	19.52	27.25	22.77	3.113	15.20	20.32	18.02	2.115	17.35	19.65	18.46	0.836
Σ ₁₃ PAHs	714.61	858.77	779.58	55.783	671.96	821.59	749.46	58.654	607.79	742.1	679.37	55.362

Number of samples = 5

variable across the sampling location. On the other hand, BgP has a higher SD, suggesting greater variability in its mean concentrations between the sampling areas.

3.4. Health risk assessment of soil HMs

ADI_{ING/DERM} for heavy metals in all sampling areas

The provided data in Figure 2 presents a result of the concentration of various metals (Fe, Cu, Cd, Co, Ni, Cr, Mn, Zn, Pb) in different exposure pathways which include ingestion exposure (Exp_{ing}) and dermal exposure (Exp_{derm}). In terms of Exp_{ing}, Zn stands out with the highest concentration levels among the metals assessed. It exhibits significantly higher values compared to the other metals. Cu, and Ni also show relatively high concentrations in Exp_{ing}, although lower than Zn. On the other hand, Fe, Cd, Co, Mn, and Pb display comparatively lower concentration levels in Exp_{derm}, with Cr exhibiting the lowest concentration among all the metals. In dermal exposure (Exp_{derm}), a similar pattern emerges. Zn maintains the highest concentration levels, followed by Cu and Ni. Fe, Cd, Co, Mn, and Pb exhibit lower

concentration levels in dermal exposure compared to Zn, Cu, and Ni. Cr has the lowest concentration level among all the metals in dermal exposure.

In analyzing the Hazard quotient Exp_{ing} data as seen in Figure 3, we can observe that Cd and Co have the highest concentration levels among the metals assessed. They exhibit significantly higher values compared to the other metals. Pb also displays relatively high concentration levels in Exp_{ing}. Cu, Ni, and Cr show lower concentration levels compared to Cr, Co, and Pb. Fe, Mn, and Zn exhibit the lowest concentration levels among the metals in Exp_{ing}. Moving on to dermal exposure (Exp_{derm}), Cd and Co continue to have the highest concentration levels among the metals assessed, similar to Exp_{derm}. Pb also maintains relatively high concentration levels in Exp_{derm}. Cu, Ni, and Cr show lower concentration levels compared to Cd, Co, and Pb. Fe, Mn, and Zn exhibit the lowest concentration levels among the metals in Exp_{derm}. When comparing the concentration levels of each metal and exposure across the three different locations, variations occurred in LL with higher concentration of HQ_{ing} for Co, in collaboration with other location for Co.

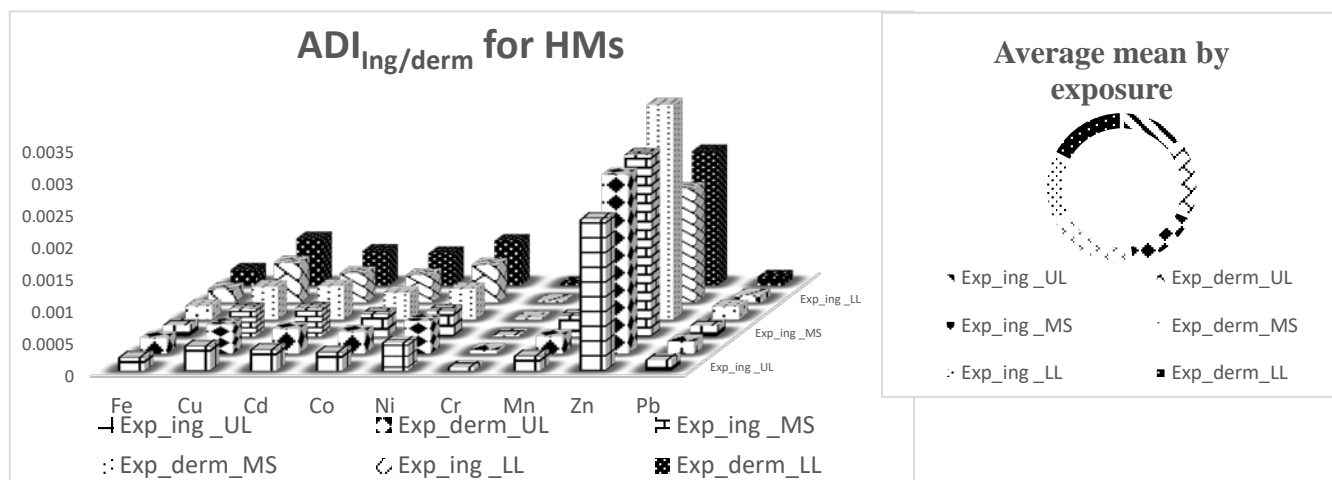


Figure 2. ADI_{ing/derm} for HMs in all sampling areas and average mean of HMs by sites

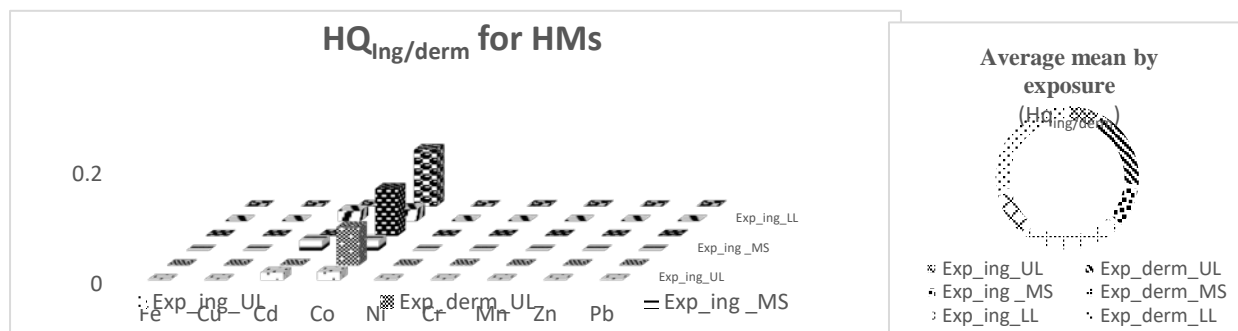


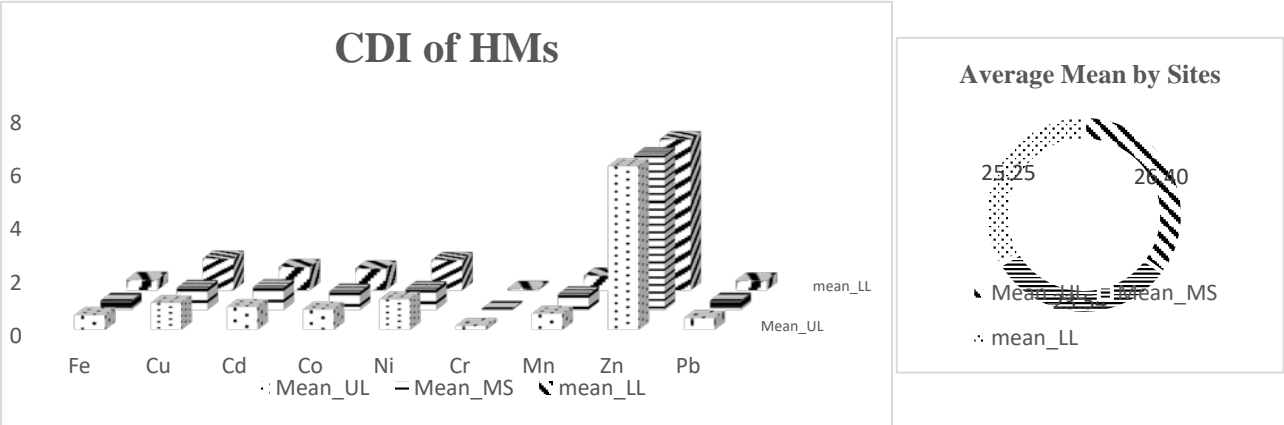
Figure 3. HQ_{ing/derm} for heavy metals and the average mean of HMs by sites

From the results obtained from the CDI as shown in Figure 4, the CDI values for Fe range from 0.348 to 0.537 across the sampling locations. These values suggest a moderate level of contamination for Fe. Cu shows varying levels of contamination, with CDI values ranging from 0.830 to 1.186. These values indicate a moderate to high level of contamination for Cu. Cd displays consistent CDI values across the sampling areas, ranging from 0.847 to 0.872. These values suggest a moderate level of contamination for Cd. Similarly, Co exhibits relatively consistent CDI values ranging from 0.688 to 0.812, indicating a moderate level of contamination for Co. Ni demonstrates varying levels of contamination, with CDI values ranging from 0.787 to 1.130. This suggests a moderate to high level of contamination for Ni. Cr displays relatively low CDI values across all sampling locations, ranging from 0.041 to 0.134, indicating a low level of contamination for Cr. Mn shows consistent CDI values ranging from 0.551 to 0.591 across the sampling areas, indicating a moderate level of contamination. Zn exhibits high levels of contamination with CDI values ranging from

5.645 to 6.104, indicating a high level of contamination for Zn. Finally, Pb displays consistent CDI values ranging from 0.352 to 0.429, indicating a moderate level of contamination for Pb.

The carcinogenic risks of HMs were calculated and displayed in Figure 5, the Cr_{ing} values for Cr ranges from 0.0168 to 0.0553 across the sampling locations. These values suggest a relatively narrow concentration range for Cr, indicating a consistent level of its presence in the sampled areas. Cd exhibits a wider range of concentrations, with Cr_{ing} values ranging from 0.0348 to 0.1018. This indicates a broader distribution of Cd concentrations across the sampling location. Pb also displays a wide range of concentrations, with Cr_{ing} values ranging from 0.0506 to 0.1416. This suggests a significant variation in Pb concentrations within the sampled location.

Figure 6 presents the toxic equivalent concentration (BaPeq) of PAHs in soils, measured in ng g⁻¹, across three sampling locations. The BaPeq is a metric that allows for the comparison of the toxic potency of different PAH compounds by converting their concentrations into an equivalent concentration



4. CDI of HMs in all sampling locations and the average mean of CDI HMs

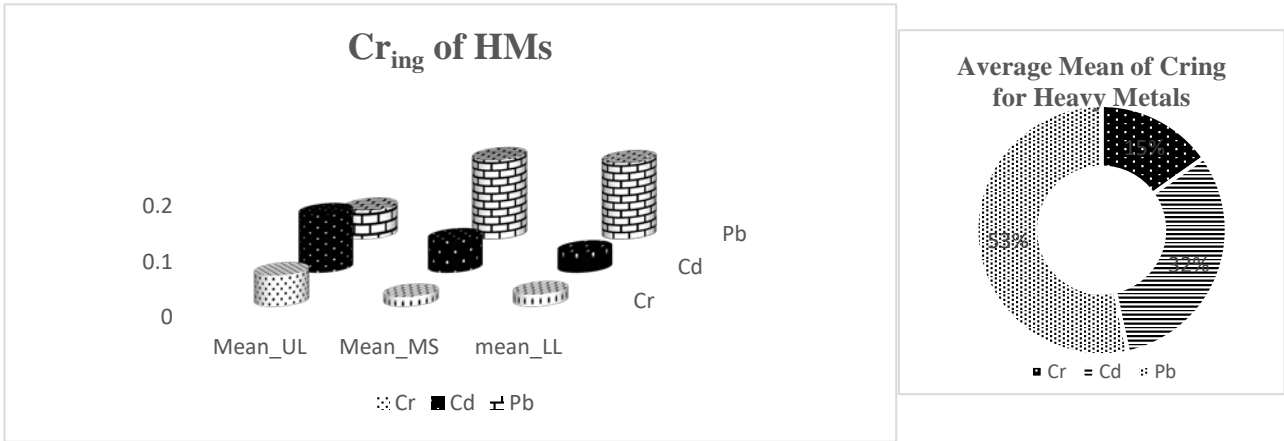


Figure 5. Cr_{ing} of HMs in all sampling areas

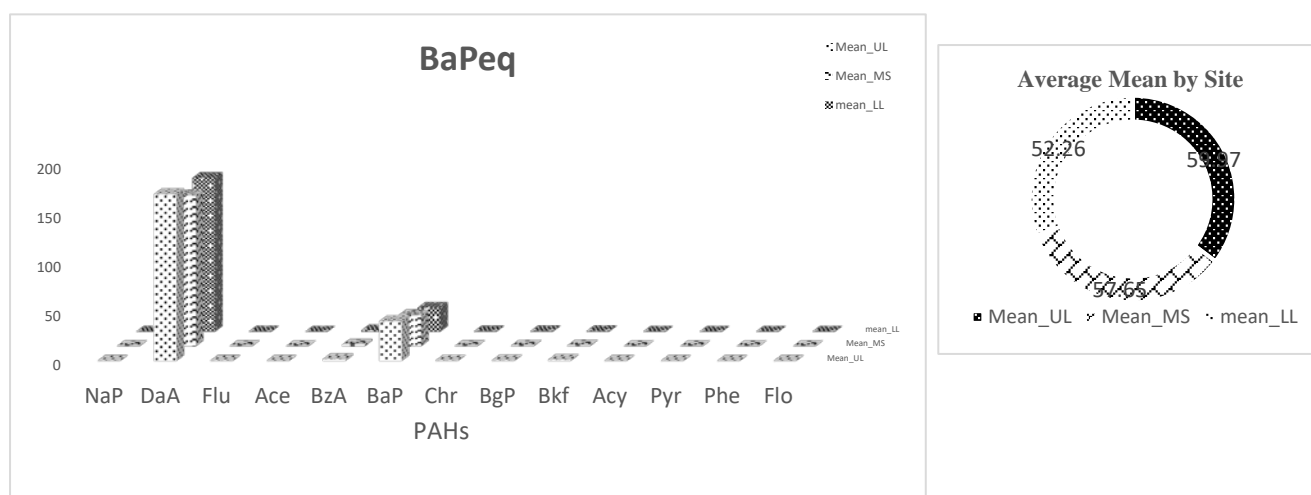


Figure 6. Toxic equivalent concentration (BaPeq) (ng g⁻¹) of PAHs in soils

of BaP, a known carcinogenic PAH. Analyzing the data, we observe varying BaPeq concentrations of different PAHs in the sampled soils. From the results, NaP shows BaPeq concentrations ranging from 0.12639 ng g⁻¹ in LL to 0.15628 ng g⁻¹ in MS. DbA exhibits BaPeq concentrations ranging from 152.71 ng g⁻¹ in MS to 168.82 ng g⁻¹ in UL. Flu displays BaPeq concentrations ranging from 0.20015 ng g⁻¹ in LL to 0.23167 ng g⁻¹ in MS. It is important to note that the BaPeq values provide an estimation of the overall toxic potential of PAH mixtures present in the soils. Higher BaPeq concentrations indicate a higher overall toxicity of the PAH mixture. Consequently, it is crucial to assess these concentrations in relation to regulatory standards or guidelines to evaluate potential risks to human health and the environment. The variations in BaPeq concentrations among the sampling areas may be attributed to several factors, including differences in pollution sources, environmental conditions, and human activities. It is

important to identify the specific PAH compounds contributing to the BaPeq concentrations to better understand the potential sources and develop appropriate remediation strategies if necessary.

3.5. Factor analysis of PAHs and HMs

The given loading plot in Figure 7 represents the results of factor analysis for PAHs and HMs. The loading plot shows the correlation between the chemical elements (PAHs and HMs) and the underlying factors derived from the data. To interpret the loading plot, the values of the loadings range from -1 to 1, where positive values indicate a positive correlation with the factor, and negative values indicate a negative correlation. Elements with higher absolute loading values (closer to 1) have a stronger association with the corresponding factor. Elements with loadings close to 0 are less correlated with the factor and may not contribute significantly to it. Mn

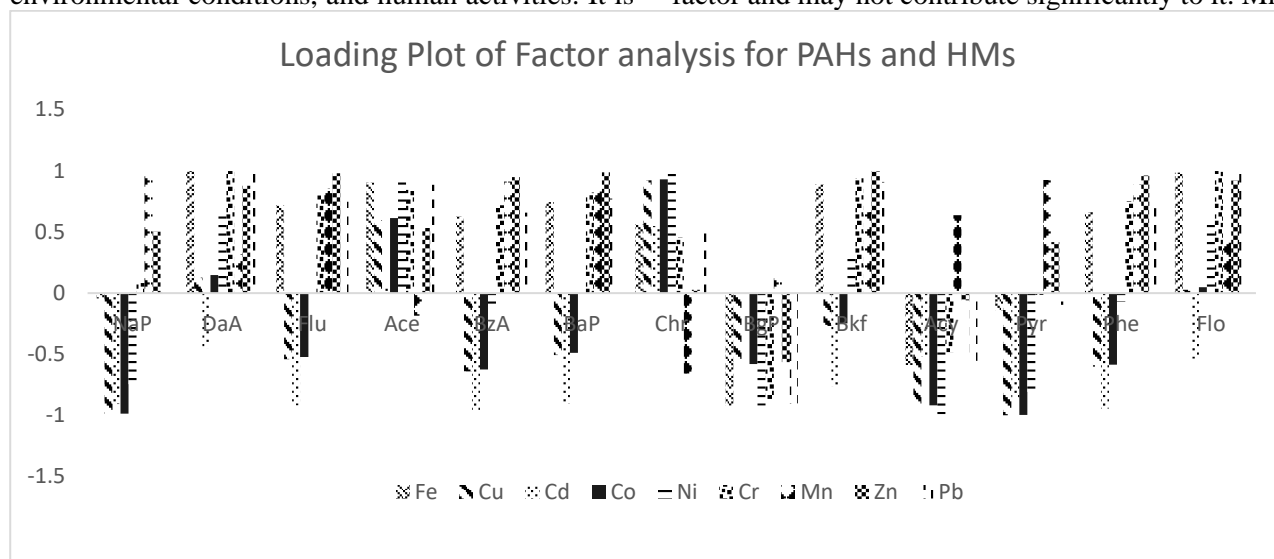


Figure 7. Factor analysis of PAHs and HMs in soils

has a high positive loading on Factor 1 (approximately 0.957). Cu shows a positive loading of approximately 0.6438 on Factor 2, and Phe exhibits a positive loading of about 0.6639 on Factor 3. This suggests that Cu and Phe are positively correlated and may share similar sources or environmental behaviors. Zn demonstrates a positive loading of approximately 0.9801 on Factor 3, while Flo has a positive loading of around 0.9628 on the same factor. This indicates a positive correlation between Zn and Flo, implying common factors influencing their presence in the environment. Cr exhibits a positive loading of approximately 0.9986 on Factor 2, and BaP shows a positive loading of about 0.823 on the same factor. This suggests a positive correlation between Cr and BaP, indicating potential co-occurrence or similar sources. Mn demonstrates a positive loading of approximately 0.8898 on Factor 2, while Flo has a positive loading of around 0.4175 on Factor 3. This indicates a positive correlation between Mn and Flo, suggesting potential associations in the environment. Cu shows a negative loading of approximately -0.9878 on Factor 1, while Cd exhibits a negative loading of around -0.9067 on the same factor. This indicates a negative correlation between Cu and Cd, suggesting different sources or behaviors in the environment. Cu exhibits a negative loading of approximately -0.9983 on Factor 2, while Ni shows a negative loading of around -0.8071 on the same factor. This suggests a negative correlation between Cu and Ni, implying potential differences in their distribution and behavior. Ni demonstrates a negative loading of approximately -0.9898 on Factor 2, while Bkf has a negative loading of around -0.9968 on the same factor. This indicates a negative correlation between Ni and Bkf, suggesting different associations in the environment.

4. CONCLUSIONS

The levels and health risk analysis of PAHs and HMs in soil from Niger Delta Area Nigeria were assessed. The concentrations of Σ HMs in upland were in the range of 183.66 to 288.91 mg/kg with a mean of 237.57 mg/kg. In mid-slope soils, the concentration of Σ HMs were 189.2 to 251 with a mean of 211.89 mg/kg while the concentration in low-land soil ranges from 202.64 to 256.64 with the mean of 227.26 mg/kg, respectively. The mean concentration of Σ ₁₆PAHs in upland, mid-slope and low-land were 779.58, 749.46 and 679.37 respectively. The slightly alkaline conditions observed in the soil can influence nutrient availability and microbial activity. The study areas displayed varying concentrations of NO_3^- , PO_4^{2-} , SO_4^{2-} , Ca, Na,

and K, with some levels exceeding acceptable values, possibly influenced by crude oil contamination and the use of fertilizers. Fe, Cu, Cd, Co, Ni, Mn, and Zn were detected, with some levels suggesting moderate to high contamination. Cr and Pb showed relatively low concentrations. PAHs were also present, with different mean concentrations among the sampling areas. The variability in PAH concentrations could be attributed to various factors, including emission sources and geographical characteristics. The health risk assessment of soil HMs revealed that Cd, Co, and Pb displayed the highest hazard quotients (HQ) in exposure pathways. The chronic daily intake (CDI) calculations for various HMs indicated moderate contamination levels, with Zn showing a high level of contamination. The carcinogenic risks of Cr and Cd indicated relatively narrow concentration ranges, while Pb showed significant variations. The toxic equivalent concentration (BaPeq) of PAHs demonstrated varying levels of toxicity potential in the sampled soils. The given loading plot represents the results of factor analysis for PAHs and HMs, showing the correlation between the chemical elements and underlying factors. PAHs and HMs in the Niger Delta region, heavily impacted by crude oil pollution, poses significant health risks. PAHs are carcinogenic and can lead to respiratory issues, while HMs such as lead and mercury can cause neurological and developmental problems. To reduce pollution, comprehensive measures must be taken, including stringent regulations on oil extraction and transportation, improved spill response and cleanup procedures, investment in clean energy alternatives, and community education on proper waste disposal and the dangers of contamination. Collaborative efforts involving government, industry, and local communities are essential for mitigating the health hazards posed by PAHs and HMs in this environmentally sensitive region. Reducing PAHs and HMs pollution in the Niger Delta region is fraught with complexities, primarily due to a history of extensive oil production, inadequate environmental regulations, and the lack of transparent accountability. This challenge has significant implications for both environmental sustainability and social justice. Environmental sustainability requires bolstering regulatory frameworks, engaging local communities, adopting cleaner technologies, and investing in healthcare and education. However, the study may have limitations concerning data availability and scope, potentially not fully capturing pollution sources and their socio-economic factors. Addressing these challenges is pivotal for mitigating adverse health effects, reducing environmental degradation, and promoting social equity in the

region. The findings from this study highlight the presence of HMs and PAHs in the soil, which may have implications for environmental contamination and potential health risks. Understanding the distribution and levels of these contaminants is essential for effective soil management and remediation strategies. Further research and ongoing monitoring are crucial to assessing long-term impacts and implementing appropriate measures to protect both human health and the environment. The results provide valuable insights that can inform policy decisions and actions to safeguard soil quality and promote sustainable environmental practices.

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Conflicts of Interest

The authors confirm that there are no known financial or personal relationships that could have influenced the research presented in this study.

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