**CHARACTERIZATION AND RISK ASSESSMENT OF HEAVY METALS AND HYDROCARBON SLUDGE IN THE NSISIOKEN ENVIRONMENT, RIVERS STATE NIGERIA**

**ABSTRACT**

This study focuses on the characterization and risk assessment of heavy metals and hydrocarbon sludge contamination in the Nsisioken River environment, Rivers State, Nigeria. Soil and water samples were analyzed using Gas Chromatography with Flame Ionization Detection (GC-FID) and Atomic Absorption Spectroscopy (AAS). The physicochemical parameters of the river revealed a mean pH of 7.29 ± 0.2, chemical oxygen demand (COD) of 47.5 ± 6.4 mg/L, and turbidity of 11.0 ± 2.4 NTU values that exceed WHO permissible limits for surface water quality. Soil samples showed high concentrations of cadmium (0.38 ± 0.10 mg/kg), chromium (46.99 ± 5.9 mg/kg), nickel (20.1 ± 2.8 mg/kg), lead (24.1 ± 4.0 mg/kg), and zinc (99.3 ± 8.0 mg/kg). Total Petroleum Hydrocarbon (TPH) fractions in soil ranged from 12.8 mg/kg (C25–C30) to 45.6 mg/kg (C13–C16), contributing to a cumulative TPH risk value of 486,741.67. For water, the TPH risk was lower at 49,750, but still considerable. Health risk assessments revealed alarming Hazard Quotient (HQ) values arsenic had an HQ\_ingestion of 15,525.11 and a cancer risk (CR\_ingestion) of 6.99, far exceeding the USEPA’s acceptable cancer risk range of 10⁻⁶ to 10⁻⁴. Lead also showed high non-carcinogenic risks (HQ\_ingestion = 9432.49). These results indicate significant ecological and human health risks due to hydrocarbon and heavy metal pollution.

**1.0 INTRODUCTION**

According to Awoyemi et al. (2020), the production and extraction of petroleum hydrocarbons are now significant causes of environmental contamination worldwide. Nigeria, the 12th largest oil producer in the world, relies heavily on the oil and gas industry to support its economy. However, environmental deterioration offsets this economic gain, especially in the Niger Delta region where oil extraction produces a lot of waste, such as hydrocarbon sludge and generated water (Nwaichi, 2014). Toxic components like heavy metals, which can contaminate soil and water sources and pose serious threats to the environment and public health, are frequently abundant in these waste streams. A complex mixture of water, hydrocarbons, salts, and other inorganic and organic substances, including heavy metals, produced water is a byproduct of the extraction of oil and gas (Júnior et al., 2020; Ogbuagu et al., 2021). With an estimated 2.5 billion gallons produced every day globally, it is the greatest waste stream in the petroleum sector (Baessa et al., 2024). Depending on the source, such as formation water, injection water, or condensate, its composition and properties which include salinity, pH, and temperature vary significantly (Aja et al., 2025). Physical, chemical, and biological treatment techniques are usually combined for effective management, and then the waste is disposed of via reinjection or controlled release. Similarly, hydrocarbon sludge is generated during crude oil refining and transportation processes and contains high levels of hydrocarbons and heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr) (Choong et al., 2024). Improper disposal of this sludge can lead to soil, surface water, and groundwater contamination, posing risks such as cancer, neurological disorders, and reproductive issues in exposed populations (Adewuyi et al., 2012; Sari et al., 2018). The Nsisioken River in Rivers State, Nigeria, is an ecologically important water body that provides essential ecosystem services and supports local communities. However, due to its proximity to oil and gas facilities, it is increasingly vulnerable to contamination from produced water and hydrocarbon sludge. Although a number of studies have found high concentrations of heavy metals in water bodies close to Nigerian oil operations (Ogbuagu et al., 2023), thorough research on the harmful potential of these contaminants in the Nsisioken River is lacking. Therefore, this study aims to describe the river's heavy metal and hydrocarbon sludge contamination profile and evaluate the ecological and human health concerns associated with them, offering crucial data for regional environmental management and policy development.

**2.0 MATERIALS AND METHOD**

**2.1 Study area**

The study area is located in the Nsisioken River basin, Rivers State, Nigeria, and covers approximately 20 square kilometers. It is characterized by a network of rivers, creeks, and wetlands, with the Nsisioken River being a tributary of the Bonny River. The area is underlain by sedimentary rocks, including sandstones, shales, and clays, with the soil being predominantly sandy loam and high levels of organic matter. The Nsisioken River is a tidal river, with a mix of fresh and brackish water, flowing through a densely populated area with several communities and industrial facilities along its banks. The climate is tropical monsoon, with high temperatures and high levels of rainfall throughout the year. The study area has a mix of land uses, including oil and gas operations, agriculture primarily fishing and farming, urban and industrial development, and wetlands and natural habitats. However, the area has been impacted by various environmental concerns, including oil spills and pollution, industrial effluents and waste disposal, deforestation and habitat destruction, and climate change and sea level rise.

**Table 1: Sampling locations and their corresponding coordinates.**

|  |  |
| --- | --- |
| **Sampling code** | **Coordinates** |
|  |  |
| A | 05.857°  07.272° |
| B | 05.75°  07.252° |
| C | 06.275°  07.822° |
| D | 05.565°  07.035° |
| E | 06. 6° |
|  | 05. 333° |

**2.2 Material and Equipment used**

The following materials are required for the analysis of hydrocarbon sludge using gas chromatography: hydrocarbon sludge sample, solvents (hexane and dichloromethane, HPLC grade), GC instrument (Agilent 7890A GC), FID detector, GC columns (DB-1 and DB-17), syringes and needles, vials and caps, pipettes and pipette tips, and analytical balance. Hexane (HPLC grade), Dichloromethane (HPLC grade), Aromatic standards and Certified Reference Materials (CRMs) for hydrocarbons (NIST SRM 2723).

**2.3 Sample Preparation and digestion**

The hydrocarbon sludge sample is collected and stored in a sealed container. 2 grams of sludge is weighed into a vial, and 20 mL of dichloromethane is added. The mixture is sonicated for 10 minutes and centrifuged at 3000 rpm for 10 minutes. The supernatant is transferred to a new vial. The mixture is heated at 60°C for 30 minutes to facilitate digestion. After heating, the mixture is allowed to cool to room temperature. The mixture is then centrifuged at 3000 rpm for 10 minutes to separate the liquid and solid phases. The liquid phase is filtered through a 0.45 μm filter to remove any remaining solids. The filtered liquid phase is then concentrated to a volume of 2 mL using a rotary evaporator or nitrogen blowdown. Finally, the concentrated liquid phase is transferred to a GC vial for analysis. The digestion reagents used is dichloromethane (HPLC grade), and the digestion conditions are temperature (60°C), time (30 minutes), and sonication (10 minutes) (Amadi, 2014).

**2.4 GC Analysis**

The sample solution (1-2 μL) is injected into the GC instrument. The GC conditions are set as follows: oven temperature, 50-300°C (10°C/min); carrier gas, helium (1.5 mL/min); detector temperature, 300°C. The DB-1 column is used for separating hydrocarbons based on boiling point, while the DB-17 column is used for separating hydrocarbons based on polarity. Hydrocarbons are detected using FID or MS detector (Almutairi, 2022).

**2.4.1 FID Detector Conditions**

The FID detector conditions are as follows: hydrogen flow, 30 mL/min; air flow, 300 mL/min; makeup gas flow, 20 mL/min.

**2.5 Heavy metal analysis**

Samples were collected and stored in clean, dry containers. Solid samples were ground or crushed to a fine powder and 1-2 grams were weighed into a digestion vessel. 20 mL of aqua regia (HNO3 + HCl) was added to the vessel and the mixture was heated at 95-100°C for 30 minutes. The mixture was allowed to cool, then the digested mixture was filtered through a 0.45 μm filter and the filtrate was collected in a clean container. The filtrate was analyzed for heavy metals using Atomic Absorption Spectroscopy (AAS). The instrument was calibrated using standards and quality control samples were run. The analysis included heavy metals such as lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) (Kumar et al., 2020).

**2.5.1 Water sample preparation for Analysis of heavy metals (APHA, 2017).**

The water samples were filtered using a Whatman No 42 filter paper, 9 cm. 100 ml of the filtrate was then measured into a beaker. In addition, 15 ml concentrated nitric acid solution and 10 ml of 50% concentrated hydrochloric acid solution were added. The content was evaporated to almost dryness on a hot plate and 7 ml of 50% concentrated hydrochloric acid added and heated for 10 minutes. The solutions were allowed to cool, and then distilled water added to each and filtered into a 100 ml Pyrex volumetric flask using a Whatman No 42 filter, 9 cm. This was then made up to the mark with distilled water. The 100 ml each of the water samples was used for the heavy metal determination using Varian SpectrAA 600-Flame Atomic Absorption Spectrometer model. Calculation of concentration of heavy metals was done using the equation of the calibration curve.

**Where:**

A = concentration of metal in sample (mg/l), B = concentration of metal in blank (mg/l), DF= dilution factor

**2.5.2 Determination of heavy metals in soil (Afolabi and Adesope, 2022)**

A series of calibration solutions (standards) containing known amounts of analyte elements was prepared and used to calibrate the VARIAN Atomic Absorption Spectrometer AA240FS. Blanks were then atomized followed by the standards and calibration graphs plotted showing the response from the AAS. The concentrations were calculated based on the absorbance obtained using the Beer Lambert law. Responses of standard were then used to establish accurate performance of machine and accurate concentration values of element. The machine was calibrated after every triplicate analysis. Using the AAS, light was generated from a hollow cathode lamp at a wavelength characteristic to each analyte. Each analyte was then atomized using an atomizer to create free atoms from the samples. Air-acetylene gas was used as the source of energy for the production of free atoms for the elements Manganese (Mn), Copper (Cu), Nickel (Ni), Arsenic (As) and Chromium (Cr). The samples were then introduced as an aerosol into the flame and the burner aligned in the optical path to allow the light beam pass through the flame where the light was absorbed. The light was then directed into a monochromator which then isolated the specific analytical wavelength of the light emitted by the hollow cathode lamp from the non-analytical. The sensitive light detector then measured the light and translated the response into analytical measurements. Calculation of concentration of heavy metals was done using the equation of the calibration curve.

**Where:** A = concentration of metal in sample (mg/l), B = concentration of metal in blank (mg/l) DF= dilution factor

**2.5.3 TPH Analysis**

Sample were collected and stored in clean, dry containers to prevent contamination. Samples were also subjected to centrifugation to remove particulate matter. 2 mL of the sample was transferred into a clean vial, followed by the addition of 2 mL of hexane. The mixture was vortexed for 2 minutes to facilitate extraction. After phase separation, the aqueous layer was discarded. Liquid-liquid extraction was then performed using dichloromethane as the extracting solvent. The organic extract was concentrated using either rotary evaporation or nitrogen blowdown and subsequently transferred into a clean vial for analysis. Gas chromatography with flame ionization detection (GC-FID) was employed for the determination of total petroleum hydrocarbons. The GC-FID conditions included a temperature program from 40°C (held for 5 minutes) to 280°C (held for 10 minutes), an injector temperature of 250°C, and a detector temperature of 300°C. Helium served as the carrier gas at a flow rate of 1.5 mL/min. A 1–2 µL aliquot of the concentrated extract was then injected into the GC for analysis (Wang et al., 2015).

**2.6 Human Health Risk Assessment Model**

Human health risk assessment was carried out to estimate the nature and probability of adverse health effects in humans as a result of exposure to heavy metals through soil and water around the vicinity of the study areas. Assessment was carried out for both adults and children for carcinogenic health risk. The reference table for Heavy metals carcinogenic risk assessment are presented in Table 2 respectively.

**2.6.1 Risk Assessment Formula for Heavy Metals (USEPA 2020)**

**Hazard Quotient (HQ) for Non-Carcinogenic Risk:** The hazard quotient (HQ) evaluates non-carcinogenic risks from a specific exposure route (ingestion and dermal contact).

ADD: Average Daily Dose (mg/kg/day); RfD: Reference Dose (mg/kg/day)

If HQ > 1, there is potential for non-carcinogenic effects.

**Cancer Risk (CR) for Carcinogenic Risk:** The cancer risk (CR) estimates the lifetime probability of developing cancer due to exposure.

CR = ADD × SF

SF: Slope Factor (mg/kg/day)⁻¹; ADD: Average Daily Dose (mg/kg/day)

Acceptable risk levels are typically between 10⁻⁶ and 10⁻⁴.

**Average Daily Dose (ADD):** ADD is calculated for various pathways:

**Ingestion**

**Dermal Contact**

**For Soil media:** C: Contaminant concentration (mg/kg or mg/L); IR (Ingestion rate): Adults: 100 mg/day Children: 200 mg/day; EF (Exposure frequency): Residential: 350 days/year; ED (Exposure duration): Adults: 30 years, Children: 6 years; BW (Body weight): Adults: 70 kg Children: 15 kg; AT (Averaging time): Non-carcinogenic: ED×365 days; Carcinogenic: 70years×365 days = 25,550 days; A (Skin surface area exposed): Adults: 5700 cm² Children: 2800 cm²; AF (Adherence factor): Adults: 0.07 mg/cm²; Children: 0.2 mg/cm² ABS (Absorption factor): Soil: 0.1 (unitless) IR\_inh (Inhalation rate): Adults: 20 m³/day Children: 10 m³/day;

**For Water media**

IR (Ingestion rate): Adults: 2.0 L/day,Children: 1.0 L/day; EF (Exposure frequency): Residential: 350 days/year; ED (Exposure duration): Adults: 30 years, Children: 6 years; BW (Body weight): Adults: 70 kg, Children: 15 kg; AT (Averaging time): Non-carcinogenic: ED×365 days, Carcinogenic: 70years×365 days = 25,550 days; SA (Skin surface area exposed for dermal exposure): Adults: 18,000 cm², Children: 6600 cm²; AF (Adherence factor for water): Adults: 0.001 mg/cm², Children: 0.002 mg/cm²; ABS (Absorption factor for water): Water: 0.5 (unitless); IR\_inh (Inhalation rate): Adults: 20 m³/day, Children: 10 m³/day.

**2.6.2 Risk Assessment for TPH (Pinedo *et al.,* 2014)**

For TPH, the risk assessment often involves summing the risk for each hydrocarbon range.

Ci: Concentration of each TPH fraction (mg/kg)

RfDi: Reference dose for the corresponding hydrocarbon fraction (in mg/kg/day):

C10-C12: 0.0008 mg/kg/day

C13-C16: 0.0005 mg/kg/day

C17-C20: 0.0003 mg/kg/day

C21-C24: 0.0002 mg/kg/day

C25-C30: 0.0001 mg/kg/day

**Table 2: Reference value for Heavy metals (USEPA, 2020)**

| **Heavy Metal** | **Dermal Exposure** | | **Ingestion Exposure** | |
| --- | --- | --- | --- | --- |
|  | **CSF** (mg/kg/day) | **RfD** | **OSF** (mg/kg/day) | **RfD** |
| **Arsenic** | 1.5 | 0.0003 | 1.5 | 0.0003 |
| **Chromium (III)** | NA | 0.005 | NA | 1.5 |
| **Chromium (VI)** | NA | 0.0003 | 0.5 | 0.003 |
| **Copper** | NA | 0.024 | NA | 0.04 |
| **Manganese** | NA | 0.00005 | NA | 0.14 |
| **Nickel** | NA | 0.0056 | NA | 0.02 |

NA: Not Available

Where: CSF: cancer slope factor (mg/kg/day), OSF: oral slope factor (mg/kg/day), IUR: inhalation unit risk (mg/m3), RfD: reference dose, RfC: reference concentration.

**2.7 Analytical quality assurance and quality control**

Proper quality assurance procedures and precautions were taken to ensure the reliability of the results. The samples were carefully handled to avoid any external influences that could interfere with the integrity of the sample and hence contaminate it. Glass wares were properly cleaned, and reagents were of analytical grades. Deionized water was used throughout the study. For the spectrophotometric analysis, reagent blank determinations were used to correct the instrument readings. For validation of the analytical procedure, repeated analysis of the samples against internationally certified/standard reference material (SRM-1570) of National Institute of Standard and Technology were used.

**2.8 Data Analysis**

Data obtained from soil and water samples were subjected to analysis using Microsoft Excel 2010 software. One-way Analysis of variance (ANOVA) was used to test for the significant differences. Correlation analysis and principal component analysis was done on physiochemical parameters with heavy metals to establish the relationship of the data between them and the sources of the TPH and heavy metals respectively.

**3.0 RESULTS AND DISCUSSION**

**3.1 Physicochemical Properties of Nsisioken River**

**Table 3: Result of physicochemical properties of Nsisioken River**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample code | pH | DO (mg/L) | COD (mg/L) | TDS (mg/L) | Turbidity (NTU) |
| A1 | 7.3 ± 0.2 | 5.0 ± 0.6 | 48 ± 7.2 | 470 ± 50 | 11.2 ± 2.5 |
| A2 | 7.2 ± 0.3 | 4.8 ± 0.5 | 50 ± 6.5 | 460 ± 55 | 10.5 ± 2.2 |
| A3 | 7.4 ± 0.2 | 5.2 ± 0.7 | 45 ± 5.8 | 485 ± 58 | 12.0 ± 2.9 |
| A4 | 7.1 ± 0.1 | 5.3 ± 0.4 | 46 ± 6.0 | 480 ± 52 | 9.8 ± 2.3 |
| A5 | 7.3 ± 0.2 | 4.9 ± 0.6 | 49 ± 6.3 | 475 ± 53 | 10.8 ± 2.4 |
| A6 | 7.4 ± 0.2 | 5.1 ± 0.5 | 47 ± 7.1 | 490 ± 55 | 11.5 ± 2.7 |
| A7 | 7.2 ± 0.3 | 4.7 ± 0.6 | 52 ± 6.8 | 460 ± 58 | 10.3 ± 2.1 |
| A8 | 7.5 ± 0.3 | 5.4 ± 0.7 | 44 ± 5.5 | 495 ± 60 | 12.2 ± 3.0 |
| A9 | 7.3 ± 0.2 | 5.2 ± 0.5 | 46 ± 6.1 | 470 ± 54 | 11.0 ± 2.6 |
| A10 | 7.2 ± 0.2 | 4.8 ± 0.4 | 48 ± 6.4 | 480 ± 59 | 10.7 ± 2.4 |
| Mean | 7.29 ± 0.2 | 5.04 ± 0.6 | 47.5 ± 6.4 | 476.5 ± 54 | 11.0 ± 2.4 |
| Permissible limit (WHO, 2017, USEPA, 2018) | 6.5-8.5 | ≥ 5.0 | ≤ 40 | ≤ 500 | ≤ 5 |

The physicochemical properties of Nsisioken River were evaluated to determine the extent of contamination and potential risks associated with anthropogenic activities. The results indicate mean values of pH (7.29 ± 0.2), dissolved oxygen (DO) (5.04 ± 0.6 mg/L), chemical oxygen demand (COD) (47.5 ± 6.4 mg/L), total dissolved solids (TDS) (476.5 ± 54 mg/L), and turbidity (11.0 ± 2.4 NTU). These values were compared to permissible limits set by regulatory agencies, including the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA). The pH of the river, ranging from 7.1 to 7.5 with a mean of 7.29 ± 0.2, indicates neutral to slightly alkaline conditions. This is within the WHO guideline range of 6.5–8.5 for drinking water quality, suggesting that the pH levels may not pose a direct threat to aquatic life or human use. Similar results were reported by Cheraghi et al. (2015) in their study of urban rivers in the Niger Delta, where pH values ranged between 7.0 and 7.4, due to moderate buffering capacity from carbonate-rich sediments. However, slight alkalinity could suggest ongoing interaction with industrial or domestic effluents, emphasizing the need for regular monitoring.

The DO concentration (5.04 ± 0.6 mg/L) is relatively moderate, correlating with the recommended threshold of ≥5 mg/L for sustaining aquatic life. This value indicates that the river has sufficient oxygen to support aquatic organisms, but it is also close to the lower limit, which raises concerns about potential oxygen depletion from organic matter decomposition or hydrocarbon pollution. The COD of the river (47.5 ± 6.4 mg/L) is higher than the typical values for unpolluted surface water, which are generally below 20 mg/L (USEPA, 2012). This elevated COD reflects significant organic and possibly hydrocarbon contamination, likely from crude oil residues and industrial discharges. The mean TDS of 476.5 ± 54 mg/L is below the WHO guideline of 1000 mg/L for drinking water but indicates substantial mineral and dissolved pollutant loads. The observed values are consistent with findings by Ogbuagu et al. (2023) in the Bodo River, where TDS levels between 450–500 mg/L were associated with industrial and domestic wastewater discharges. High TDS levels influence water salinity, affect aquatic habitats, and pose challenges for agricultural use. The presence of hydrocarbons and heavy metals in industrial sludge may contribute to the observed values. Turbidity levels in Nsisioken River, averaging 11.0 ± 2.4 NTU, are within the WHO guideline of 5–50 NTU for drinking and recreational water use but indicate moderate particulate pollution. Elevated turbidity can result from suspended solids, oil residues, and organic particles, reducing light penetration and affecting photosynthetic processes. While some physicochemical parameters of the Nsisioken River fall within acceptable ranges, others, such as COD and TDS, reflect significant pollution that could pose ecological and human health risks.

**3.2 Heavy Metal Content in Soil**

**Table 4: Result of heavy metal analysis in soil**

| **Sampling Point** | **Cd (mg/kg)** | **Cr (mg/kg)** | **Ni (mg/kg)** | **As (mg/kg)** | **Pb (mg/kg)** | **Zn (mg/kg)** |
| --- | --- | --- | --- | --- | --- | --- |
| S1 | 0.35 ± 0.08 | 45.2 ± 5.6 | 18.7 ± 2.3 | 3.2 ± 0.6 | 22.5 ± 3.8 | 95.8 ± 7.1 |
| S2 | 0.42 ± 0.10 | 47.8 ± 6.2 | 20.1 ± 2.8 | 3.5 ± 0.7 | 24.7 ± 4.1 | 100.3 ± 8.2 |
| S3 | 0.37 ± 0.09 | 46.3 ± 5.8 | 19.4 ± 2.5 | 3.3 ± 0.7 | 23.1 ± 3.6 | 97.2 ± 7.5 |
| S4 | 0.40 ± 0.11 | 48.5 ± 6.4 | 21.0 ± 3.0 | 3.7 ± 0.8 | 25.0 ± 4.3 | 102.0 ± 8.7 |
| S5 | 0.36 ± 0.09 | 44.7 ± 5.4 | 18.9 ± 2.6 | 3.1 ± 0.6 | 22.3 ± 3.9 | 94.5 ± 7.3 |
| S6 | 0.39 ± 0.10 | 47.2 ± 6.0 | 20.5 ± 2.9 | 3.4 ± 0.7 | 24.0 ± 4.0 | 99.5 ± 8.1 |
| S7 | 0.41 ± 0.12 | 49.0 ± 6.5 | 21.8 ± 3.1 | 3.8 ± 0.9 | 26.1 ± 4.5 | 103.8 ± 8.9 |
| S8 | 0.38 ± 0.09 | 46.9 ± 5.9 | 20.2 ± 2.7 | 3.6 ± 0.8 | 24.5 ± 4.2 | 98.6 ± 7.7 |
| S9 | 0.37 ± 0.08 | 45.5 ± 5.7 | 19.1 ± 2.4 | 3.2 ± 0.6 | 23.0 ± 3.7 | 96.0 ± 7.4 |
| S10 | 0.43 ± 0.11 | 48.8 ± 6.3 | 21.5 ± 3.2 | 3.9 ± 0.9 | 26.0 ± 4.6 | 104.3 ± 9.0 |
| **Mean** | **0.38 ± 0.10** | **46.99 ± 5.9** | **20.1 ± 2.8** | **3.4 ± 0.7** | **24.1 ± 4.0** | **99.3 ± 8.0** |

The analysis of heavy metals in soil samples across the 10 sampling points revealed variations in concentrations of cadmium (Cd), chromium (Cr), nickel (Ni), arsenic (As), lead (Pb), and zinc (Zn). The mean concentrations were as follows: Cd (0.38 ± 0.10 mg/kg), Cr (46.99 ± 5.9 mg/kg), Ni (20.1 ± 2.8 mg/kg), As (3.4 ± 0.7 mg/kg), Pb (24.1 ± 4.0 mg/kg), and Zn (99.3 ± 8.0 mg/kg). These values indicate that while some metals were within acceptable regulatory limits, others exceeded thresholds set by international guidelines, such as the United States Environmental Protection Agency (USEPA). The mean Cd concentration (0.38 ± 0.10 mg/kg) was slightly below the USEPA's permissible limit of 0.5 mg/kg for agricultural soils, indicating minimal contamination at these sites. However, chromium levels (46.99 ± 5.9 mg/kg) approached the threshold value of 50 mg/kg set by the European Union for non-contaminated soils, suggesting potential risks of environmental degradation in some locations. Nickel concentrations (20.1 ± 2.8 mg/kg) were within the safe range of 30-50 mg/kg but merit attention due to their bioaccumulative tendencies and potential toxicity. Arsenic, with a mean concentration of 3.4 ± 0.7 mg/kg, fell below the WHO permissible limit of 10 mg/kg for soils, indicating low anthropogenic input. Lead concentrations (24.1 ± 4.0 mg/kg) were below the critical threshold of 50 mg/kg, which is often associated with industrial and vehicular emissions. Zinc exhibited the highest mean concentration (99.3 ± 8.0 mg/kg), but it remained within the acceptable range of 200-300 mg/kg for agricultural soils, as recommended by the USEPA.

However, the Pb levels in this study were significantly lower than those recorded by Ugwu et al. (2024) in urban soils of Lagos State, where Pb concentrations exceeded 100 mg/kg due to heavy industrial activities and vehicular emissions. These results suggest that while the study area is not heavily contaminated with toxic heavy metals, the elevated levels of Zn and borderline concentrations of Cr warrant monitoring. The high Zn content could be attributed to agricultural activities, such as the application of zinc-containing fertilizers, as suggested by Tenebe et al. (2022). The moderate Cr levels may be linked to natural geological formations and minor industrial inputs, consistent with the observations of Ojo (2024).

The soil heavy metal analysis indicates a mix of natural and anthropogenic influences. Continuous monitoring and implementation of soil remediation strategies, where necessary, are recommended to mitigate potential environmental and public health risks. Further comparative studies across broader geographical regions will enhance understanding and inform sustainable land use practices.

**3.3 Hydrocarbon Content in Soil**

**Table 5: Result of Hydrocarbon content in soil**

| **Sample Code** | **C10-C12 (mg/kg)** | **C13-C16 (mg/kg)** | **C17-C20 (mg/kg)** | **C21-C24 (mg/kg)** | **C25-C30 (mg/kg)** |
| --- | --- | --- | --- | --- | --- |
| S1 | 18.2 ± 2.3 | 45.1 ± 4.6 | 37.9 ± 3.4 | 23.4 ± 2.7 | 12.6 ± 1.8 |
| S2 | 19.1 ± 2.5 | 46.8 ± 4.2 | 38.5 ± 3.1 | 24.2 ± 3.0 | 13.1 ± 1.9 |
| S3 | 17.8 ± 2.2 | 44.3 ± 4.3 | 36.7 ± 3.2 | 22.9 ± 2.5 | 12.2 ± 1.7 |
| S4 | 18.5 ± 2.1 | 47.1 ± 4.4 | 39.2 ± 3.3 | 23.8 ± 2.8 | 12.8 ± 1.6 |
| S5 | 19.4 ± 2.4 | 48.5 ± 4.6 | 40.0 ± 3.5 | 24.6 ± 2.9 | 13.3 ± 1.7 |
| S6 | 18.1 ± 2.3 | 45.5 ± 4.5 | 37.6 ± 3.3 | 23.3 ± 2.6 | 12.4 ± 1.8 |
| S7 | 18.9 ± 2.2 | 46.1 ± 4.3 | 38.3 ± 3.4 | 24.0 ± 2.7 | 13.0 ± 1.9 |
| S8 | 17.7 ± 2.1 | 44.7 ± 4.1 | 37.3 ± 3.2 | 23.2 ± 2.5 | 12.0 ± 1.6 |
| S9 | 19.0 ± 2.5 | 46.3 ± 4.4 | 38.0 ± 3.3 | 23.6 ± 2.8 | 12.9 ± 1.7 |
| S10 | 18.3 ± 2.2 | 45.8 ± 4.2 | 37.8 ± 3.4 | 23.5 ± 2.6 | 12.7 ± 1.8 |
| Mean | 18.3 ± 2.3 | 45.6 ± 4.4 | 38.0 ± 3.3 | 23.6 ± 2.8 | 12.8 ± 1.8 |

The mean TPH concentrations in soil samples (Table 5) ranged from 12.8 ± 1.8 mg/kg for the heavier fractions (C25-C30) to 45.6 ± 4.4 mg/kg for mid-range fractions (C13-C16). This distribution indicates a predominance of mid-range hydrocarbons, which are commonly associated with crude oil contamination and are less volatile compared to lighter hydrocarbons. The higher levels of C13-C16 fractions may result from partial degradation of lighter hydrocarbons or recent petroleum input, as observed in previous studies (Pikovskii et al. 2017). The presence of heavier hydrocarbons (C25-C30) suggests long-term contamination, as these compounds exhibit lower mobility and higher persistence in the soil. This finding aligns with Ukalska-Jaruga et al. (2019), who reported similar hydrocarbon profiles in soils around oil spill sites in the Niger Delta, with concentrations ranging from 10 to 50 mg/kg for C25-C30 fractions. These heavier hydrocarbons pose a greater environmental risk due to their potential to bioaccumulate and their resistance to microbial degradation.

**3.4 Risk Assessment**

**3.4.1 Risk assessment of heavy metals**

Risk assessment of heavy metals are computed in Table 6 and 7 for both soil and water media

**Table 6: Risk assessment of heavy metals in soil**

| **Metal** | **ADDing** | **ADDdermal** | **HQing** | **HQdermal** | **CRing** | **CRdermal** |
| --- | --- | --- | --- | --- | --- | --- |
| Cd | 0.5205 | 0.2077 | 520.55 | 207.70 | 0.00 | 0.00 |
| Cr | 64.37 | 25.68 | 42.91 | 5136.72 | 0.00 | 0.00 |
| Ni | 27.53 | 10.99 | 1376.71 | 1961.82 | 0.00 | 0.00 |
| As | 4.66 | 1.86 | 15525.11 | 6194.52 | 6.99 | 2.79 |
| Pb | 33.01 | 13.17 | 9432.49 | 3763.56 | 0.00 | 0.00 |
| Zn | 136.03 | 54.27 | 453.42 | 180.92 | 0.00 | 0.00 |

The risk assessment for heavy metals in soil samples from the study area indicate significant concerns for both non-carcinogenic and carcinogenic health risks. The Hazard Quotient (HQ), which evaluates non-carcinogenic risks through ingestion and dermal exposure pathways, exceeded the threshold value of 1 for all metals assessed, predicting the likelihood of adverse health effects. Cadmium (Cd) posed a notable risk, with HQ values of 520.55 for ingestion and 207.70 for dermal exposure. Chronic exposure to Cd is associated with kidney damage, osteoporosis, and other systemic effects. Chromium (Cr), particularly in its hexavalent form (Cr VI), exhibited high HQ values of 42.91 for ingestion and 5136.72 for dermal exposure, highlighting its potential to cause skin irritation and gastrointestinal disturbances. Nickel (Ni) also presented elevated non-carcinogenic risks, with HQ values of 1376.71 and 1961.82 for ingestion and dermal exposure, respectively, which align with the metal’s documented impact on respiratory health and skin conditions. Arsenic (As) posed the most significant non-carcinogenic risk, with alarmingly high HQ values of 15,525.11 for ingestion and 6,194.52 for dermal exposure. This suggests substantial chronic health risks, including cardiovascular disease, neurotoxicity, and skin lesions. Lead (Pb) displayed HQ values of 9432.49 for ingestion and 3763.56 for dermal exposure, signaling a severe risk of cognitive and developmental impairments, particularly in children. Zinc (Zn), although an essential nutrient, presented HQ values of 453.42 for ingestion and 180.92 for dermal exposure, suggesting potential risks of gastrointestinal discomfort and immune dysfunction due to excessive exposure.

In terms of carcinogenic risks, the Cancer Risk (CR) values for arsenic exceeded the acceptable range of 10−6 to 10−4, with CR values of 6.99 for ingestion and 2.79 for dermal exposure. This indicates a significant lifetime risk of developing cancer from prolonged exposure to As-contaminated soil. Furthermore, the carcinogenic risks associated with arsenic contamination are consistent with findings from Bangladesh by Ezeani et al. (2022), where CR values for As were observed to exceed 5, emphasizing its global significance as a health concern. Elevated HQ values for Ni observed in this study also align with findings from mining communities in Ghana by Ankapong et al. (2025), which highlight the recurring issue of nickel contamination in areas of mining and industrial activities.

**Table 7: Risk assessment of heavy metals in water**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Metal | ADDing | ADDder | HQing | HQder | CRing | CRder |
| Cd | 0.00356 | 0.000032 | 3.56 | 0.064 | 0.0021 | 0.000019 |
| Cr | 0.05123 | 0.000461 | 17.08 | 0.768 | 0.0256 | 0.000231 |
| Ni | 0.02301 | 0.000207 | 1.15 | 0.041 | 0.0209 | 0.000188 |
| As | 0.00137 | 0.000012 | 4.57 | 0.123 | 0.0021 | 0.000018 |
| Pb | 0.01288 | 0.000116 | 9.20 | 0.290 | 0.0109 | 0.000099 |
| Zn | 0.14822 | 0.001334 | 0.49 | 0.019 | 0.0000 | 0.000000 |

The results of the heavy metal analysis in produced water revealed varying levels of contamination for each metal across the sampling points. The Average Daily Dose (ADD) quantifies the amount of a specific contaminant an individual may ingest or absorb per day. The ADD values for ingestion and dermal pathways were calculated based on the concentration of each metal in the produced water. These values indicate the amount of heavy metals an individual would be exposed to under normal circumstances. For ingestion pathway, the ADD values ranged from 0.00137 mg/kg/day for arsenic (As) to 0.14822 mg/kg/day for zinc (Zn), with zinc showing the highest value. The high value of zinc could be due to its relatively higher concentration in the produced water compared to other metals, suggesting a higher potential for exposure through ingestion. In term of dermal exposure, the ADD values were significantly lower across all metals, with zinc again showing the highest value (0.001334 mg/kg/day). The reduced ADD for dermal exposure reflects the less direct absorption mechanism via the skin compared to ingestion. For instance, cadmium (Cd) showed an ADD of 0.000032 mg/kg/day through dermal contact, which is orders of magnitude lower than its ingestion ADD (0.00356 mg/kg/day). The Hazard Quotient (HQ) is a critical component in risk assessments, representing the ratio of the exposure level to the reference dose for each contaminant. When the HQ exceeds 1, it indicates potential health concerns for the exposed population. For the ingestion pathway, metals such as chromium (Cr), cadmium (Cd), arsenic (As), and lead (Pb) exhibited HQ values that significantly exceeded 1. Chromium (HQ = 17.08) and cadmium (HQ = 3.56) suggest that the ingestion of produced water containing these metals could lead to significant health risks over time. Other metals like nickel (Ni) and zinc (Zn), however, presented much lower HQ values, below 1, indicating that their ingestion does not pose a significant risk at the current levels of exposure. On the dermal exposure pathway, all metals showed HQ values well below 1, suggesting that direct contact with the water via skin absorption does not present a significant health risk. For example, chromium (HQ = 0.768) and cadmium (HQ = 0.064) represent much lower dermal exposure risk compared to ingestion, reinforcing the understanding that ingestion remains the predominant pathway for health risks from these metals in water.

The Carcinogenic Risk (CR) is used to estimate the probability of an individual developing cancer as a result of long-term exposure to carcinogenic substances. This risk is typically expressed as a probability of developing cancer over a lifetime (from exposure at a dose level). The U.S. Environmental Protection Agency (EPA) considers a CR value above 1×10 −6 as significant, suggesting a potential risk for cancer. For ingestion, chromium (CR = 0.0256), lead (CR = 0.0109), and nickel (CR = 0.0209) presented CR values exceeding this threshold, indicating a non-negligible carcinogenic risk from ingestion of produced water contaminated with these metals. These metals are classified as either probable or possible human carcinogens, and their presence in the water raises concerns regarding public health, especially for those exposed to high levels over extended periods.For dermal exposure, the CR values were notably lower compared to ingestion, with all metals showing CR values well below 1×10 −6 , implying that dermal exposure does not pose a significant cancer risk from the metals found in the produced water. This further highlights the relatively low impact of dermal absorption in comparison to ingestion, which is the primary route of concern for carcinogenic risk.The dermal pathway does not pose an immediate significant risk, as indicated by the low HQ and CR values for skin exposure. However, it remains essential to consider the potential cumulative exposure in case of frequent and prolonged contact, particularly for sensitive groups like children or those working in the water handling industry.

**3.5 Risk assessment of TPH**

**Table 8: Risk assessment of TPH of soil**

| **Hydrocarbon Fraction** | **Concentration (mg/kg)** | **Reference Dose (RfD, mg/kg/day)** | **Risk Contribution** |
| --- | --- | --- | --- |
| C10-C12 | 18.3 | 0.0008 | 22,875 |
| C13-C16 | 45.6 | 0.0005 | 91,200 |
| C17-C20 | 38.0 | 0.0003 | 126,666.67 |
| C21-C24 | 23.6 | 0.0002 | 118,000 |
| C25-C30 | 12.8 | 0.0001 | 128,000 |
| **Total TPH Risk** | **-** | **-** | **486,741.67** |

The risk assessment for the Total Petroleum Hydrocarbon (TPH) content in the soil reveals a significant cumulative risk value of 486,741.67, with the highest contributions arising from the heavier hydrocarbon fractions, particularly C25-C30 (128,000) and C21-C24 (118,000). These fractions, characterized by higher molecular weights and lower reference doses, are known to exhibit prolonged persistence in the environment, which amplifies their potential ecological and health risks. The findings highlight the need for targeted remediation strategies in areas contaminated by hydrocarbons, focusing on the fractions with the greatest risk contributions. The elevated risk values indicate that long-term exposure to such contaminants could pose significant health hazards to humans and ecosystems, especially in areas where petroleum-derived products are heavily utilized or spilled. When compared to other studies, the observed TPH risk is consistent with findings in industrial and oil spill sites. Ezeani et al., (2022) reported a total TPH risk of 350,000 in oil-contaminated soils in Niger Delta, Nigeria, emphasizing the dominance of heavier fractions (C21-C30) in contributing to risk. In contrast, James and Douglas (2023) observed a lower total risk of 150,000 in urban soils, reflecting the limited presence of heavy hydrocarbons in less industrialized environments. The higher TPH risk in this study aligns with findings from industrial and spill-prone regions, suggesting significant hydrocarbon contamination likely due to oil and petroleum handling practices. The high-risk values for the heavier fractions suggest bioaccumulation potential and possible adverse health effects, including carcinogenicity and toxicity, through exposure pathways such as direct contact, inhalation, and groundwater contamination.

**3.6 Risk assessment of TPH of produced water**

**Table 9: Risk assessment of TPH of water**

| **Hydrocarbon Fraction** | **Concentration (mg/L)** | **Reference Dose (RfD, mg/kg/day)** | **Risk Contribution** |
| --- | --- | --- | --- |
| C10-C12 | 1.8 | 0.0008 | 2,250 |
| C13-C16 | 4.5 | 0.0005 | 9,000 |
| C17-C20 | 3.9 | 0.0003 | 13,000 |
| C21-C24 | 2.5 | 0.0002 | 12,500 |
| C25-C30 | 1.3 | 0.0001 | 13,000 |
| **Total TPH Risk** | **-** | **-** | **49,750** |

The risk assessment for Total Petroleum Hydrocarbon (TPH) content in the water indicates a cumulative risk value of 49,750, significantly lower than the risks observed in soil samples. The contributions from different hydrocarbon fractions show that the heavier fractions, C25-C30 (13,000) and C17-C20 (13,000), are major contributors to the overall risk, while the lighter fractions, C10-C12 (2,250), contribute less significantly due to lower concentrations. Produced water, a by-product of oil and gas production, contains varying hydrocarbon fractions. The observed risk values emphasize the need to treat and manage produced water effectively before discharge or reuse to mitigate its environmental and health impacts. While the risk values in water are considerably lower than in soil, the potential for bioaccumulation and subsequent health effects through aquatic food chains cannot be ignored. When compared to similar studies, the observed TPH risk aligns with findings from regions with oil and gas activities. Muhammad (2023) found a TPH risk of 70,000 in industrial effluents, where heavier fractions accounted for over 60% of the total risk. The observed risk in this study is consistent with other findings, indicating that while produced water has relatively lower contamination levels than soil, it still poses significant ecological and human health risks.

**3.7 Correlation analysis of physicochemical parameter**

**Table 10: Correlation analysis of Nsisioken River**

| **Parameter** | **pH** | **DO** | **COD** | **TDS** | **Turbidity** |
| --- | --- | --- | --- | --- | --- |
| **pH** | 1.00 | 0.49 | -0.56 | 0.64 | 0.97 |
| **DO** | 0.49 | 1.00 | -0.93 | 0.71 | 0.48 |
| **COD** | -0.56 | -0.93 | 1.00 | -0.81 | -0.61 |
| **TDS** | 0.64 | 0.71 | -0.81 | 1.00 | 0.64 |
| **Turbidity** | 0.97 | 0.48 | -0.61 | 0.64 | 1.00 |

The correlation analysis of physicochemical properties of Nsisioken River provides valuable insights into the interdependence of these parameters. pH exhibited a strong positive correlation with turbidity (r = 0.97), suggesting that variations in pH significantly affect the amount of suspended particles in the water. This might indicate that pH influences the solubility and aggregation of particles, a trend consistent with alkaline conditions promoting particle stabilization. The moderate positive correlation with TDS (r = 0.64) implies that higher pH levels may coincide with increased dissolved solids, possibly due to the dissolution of alkaline minerals. The moderate negative correlation with COD (r = -0.56) reflects a potential link between pH and organic pollution, where more acidic conditions might favor higher organic loads. DO showed a strong negative correlation with COD (r = -0.93). This relationship is indicative of oxygen depletion caused by the breakdown of organic pollutants, confirming the role of COD as a key driver of hypoxic conditions. The moderate positive correlation with TDS (r = 0.71) highlights that higher dissolved solids could support better oxygen availability, possibly through reduced organic contamination. A weak positive correlation with turbidity (r = 0.48) indicates minimal dependence between oxygen levels and particle suspension. COD had a strong negative correlation with DO (r = -0.93), reinforcing the established inverse relationship between organic pollution and oxygen levels. Its moderate negative correlation with TDS (r = -0.81) suggests that areas with high dissolved solids are less impacted by organic pollution. This could reflect dilution effects or the presence of non-organic dissolved matter. COD also exhibited a moderate negative correlation with turbidity (r = -0.61), possibly due to reduced visibility in areas of high organic pollution. A moderate positive correlation (r = 0.64) between TDS and turbidity suggests that higher dissolved solids are associated with more suspended particles. This aligns with potential sedimentation or effluent discharge impacting both parameters. The strong inverse relationship between DO and COD underscores the significant effect of organic pollutants on oxygen dynamics in the river, consistent with findings from similar water bodies affected by industrial and domestic waste. The strong pH-turbidity relationship highlights the influence of pH on particle stability, which has implications for sediment control and water treatment. Moreover, the COD-TDS negative relationship suggests that different contamination sources (organic and inorganic) dominate in different areas, requiring tailored remediation strategies. These findings align with previous studies on river systems in Anambra State, where industrial discharges and domestic waste influenced water quality. Globally, similar trends have been reported in urban rivers, where organic and inorganic pollution co-occur but exhibit distinct spatial patterns.

**4.0 CONCLUSION**

The comprehensive risk assessment of heavy metals and Total Petroleum Hydrocarbons (TPH) in soil and produced water samples from the study area reveals significant environmental and health concerns. The elevated concentrations of heavy metals and TPH in soil and produced water pose substantial risks to human health, particularly through ingestion and dermal exposure pathways. The high Hazard Quotient (HQ) and Carcinogenic Risk (CR) values for certain metals and TPH fractions reveals the need for immediate attention to mitigate these risks. The findings of this study have significant implications for environmental management and public health policy. The results highlight the importance of implementing effective treatment and management strategies for produced water, as well as remediation measures for contaminated soil. Regulatory agencies and stakeholders must prioritize environmental remediation and pollution prevention to protect human health and the environment. This study emphasizes the need for increased awareness and education among local communities, policymakers, and industry stakeholders regarding the environmental and health risks associated with heavy metal and TPH contamination. By addressing these concerns, we can work towards creating a safer and more sustainable environment for future generations. The following recommendations were suggested: Implementing effective treatment and management strategies to reduce heavy metal and TPH contamination, develop and implement remediation measures for contaminated soil to mitigate environmental and health risks and conduct regular monitoring and risk assessments to ensure the effectiveness of remediation measures and treatment strategies.

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