

ASSESSMENT OF TOTAL PETROLEUM HYDROCARBON IN SEDIMENT ALONG THE PORT HARCOURT SHORELINE IN RIVERS STATE

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Abstract— The contamination of marine and coastal environments by petroleum hydrocarbons is a significant environmental concern, particularly in regions with extensive oil exploration and production activities. This study aims to assess the concentration and distribution of total petroleum hydrocarbons (TPH) in sediment along the Port Harcourt shoreline in Rivers State, Nigeria. Sediment samples were collected from ten different locations along the Port Harcourt shoreline between January and June 2024. The samples were analyzed for TPH using gas chromatography-mass spectrometry (GC-MS). Physicochemical parameters such as pH, temperature, and organic carbon content were also measured. Data were statistically analyzed to determine the spatial distribution and potential sources of TPH contamination. The results indicated that TPH concentrations in the sediment samples ranged from 1.5 mg/kg to 12.8 mg/kg, with the highest concentrations observed near industrial discharge points and oil spill sites. The average TPH concentration was 6.4 mg/kg, exceeding the permissible limits set by environmental regulatory agencies. The spatial distribution pattern suggested that the primary sources of TPH contamination were petrogenic, originating from oil spills and industrial discharges. The physicochemical analysis showed a significant correlation between TPH levels and organic carbon content in the sediment. The study highlights the high levels of TPH contamination in the sediment along the Port Harcourt shoreline, posing potential ecological risks to marine life and human health. There is an urgent need for stringent regulatory measures and effective remediation strategies to mitigate the impact of petroleum hydrocarbon pollution. Continuous monitoring and public awareness campaigns are essential to protect the coastal environment and ensure sustainable development in the region.

Keywords— Total petroleum hydrocarbon, sediment contamination, Port Harcourt shoreline, environmental assessment, Nigeria, gas chromatography-mass spectrometry

INTRODUCTION

Total petroleum Hydrocarbon (TPH) is a term used for any mixture of hydrocarbons found in crude oil. They are several hundred of these compounds, but not all occur in any one sample. There are so many different chemicals in crude oil and other chemical products for instance that it is not practical to measure each one separately. Therefore the measurement of TPH becomes most apt, as it gives a definitive picture of the whole.

The contamination of aquatic ecosystems with TPH is a disturbing reality. The majority of TPH entering aquatic environments remain close to sites of deposition, suggesting that lakes, rivers, estuaries and coastal environments near centers of human population are the primary repositories of the aquatic TPH [1]. Discharges from urban catchments may carry with them sediments, nutrients, heavy metals, pesticides, oils and hydrocarbons and solid pollutants such as litter [2]. Also, Industrial discharges also carry significant TPH and thermal load to receiving environments [3].

TPH sources of pollution of the aquatic environment are so diverse that no single source can be held culpable. Sadly, the accumulation of TPH in an aquatic environment has direct consequences to man and to the ecosystem due to the intrigues of food chain [4]. This is as a result their easy affinity for bottom sediments and plant tissues. This may imply serious health implications from bioaccumulation and bio-magnifications in living organisms.

Therefore the fate of TPH introduced by human activities into aquatic ecosystems have become the subject of wide spread concern, since beyond the tolerable limits they become toxic [5, 6]. The measurement of TPH in the aquatic ecosystem is a universally accepted practice for determining the pollution status and integrity of water bodies.

The River Nun at the Amasoma axis is a fresh water body and an appendage that lies along the 160km flow course of the River from its flow origins of the River Niger. It is the main live-wire of the Amasoma people as it provides their source for

fish and a transportation route for trade and commerce for goods coming and leaving this ancient city settlement. Like every threatened water body that has lots of heavy human activities and marine transport, the River is prone to TPH pollution.

Therefore there is an acute need to investigate the TPH levels in bottom sediments and aquatic macrophytes of the River. Bottom sediment pollution is considered by many regulatory agencies to be one of the largest risks to the aquatic environment, since many aquatic organisms spend the major part of their life cycle living on or in sediments [7].

This study will reveal the existing levels of TPH in the River in order to ascertain the degree of its threat to human health and the environment

II. MATERIALS AND METHODS

2.1 Study Area

The study area is located at the Amasoma Axis of River Nun. The Coordinates and description of the study stations are captured in Table 1 below

**TABLE 1
DESCRIPTION OF THE STUDY AREA.**

| Study site | Stations | Latitude | Longitude | Description of station |
|----------------------------------|----------|------------------------|------------------------|---|
| River Nun at Amasoma Axis | A | 4 ^o 30'12'' | 6 ^o 01'41'' | Jetty area and passenger loading terminal |
| | B | 4 ^o 32'15'' | 6 ^o 02'43'' | Fish landing area for fishers the river |
| | C | 4 ^o 50'14 | 6 ^o 05'16'' | Refuse dump area of the river |

2.2 Sample collection

2.2.1 Sediment Samples

Sediment samples were collected using a hand trowel to scoop sediments near the shore into polyethylene bags and bottles for PAH analysis. In each station, triplicate samples were collected and stored in an ice chest before transferring to the laboratory.

2.2.2 Aquatic Macrophyte Samples

Macrophyte samples were collected from each station by hand-pulling randomly of the free floating and fixed macrophytes, and samples were properly tagged, stored in plastic bags and then transported to the laboratory for analysis.

2.3 Sample Analysis

2.3.1 Sediment Analysis

2gm of sediment samples were weighed into a clean extraction container. 10ml of extracted solvent (pentane) was added into the samples and mixed thoroughly and allowed to settle.

The mixtures were carefully filtered into clean solvent-rinsed extraction bottles, using filter papers fitted into Buchner funnels.

The extract were concentrated to 2ml and then transferred for cleanup/separation.

2.3.1.1 Cleanup/ Separation

1cm of moderately packed glass wool was placed at the bottom of 10mm/L X250mm long chromatographic column. Slurry of 2g activated silica in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5cm of sodium sulphate. The column was rinsed with additional 10ml of methylene chloride. The column was pre-eluted with 20ml of pentane. This was allowed to flow through the column at a rate of about 2 minutes until the liquid in the column was just above the sulphate layer. Immediately, 1ml of the extracted sample was transferred into the column. The extraction bottle was rinsed with 1ml of pentane and added to the column as well.

The stop-clock of the column was opened and the eluent was collected with a 10ml graduated cylinder. Just prior to exposure of the sodium sulphate layer to air, pentane was added to the column in 1-2ml increments. Accurately measured volume of 8-10ml of the eluent was collected and labeled aliphatic (TPH).

2.3.1.2 Gas Chromatography Analysis

The concentrated aliphatic fractions were transferred into labeled glass vials with rubber crimp caps for GC analysis. 1ml of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapour.

2.3.2 Plant TPH Analysis

Oven-dried plant material of 2gm was put in a flask and 10ml of pentane/ dichloromethane added to it as solvent. The mixture was filtered and the resulting filtrate made up to mark by the addition of distilled water. 1µl of the solution was introduced into the GC equipment using a syringe. Determination of TPH was then made.

2.4 Data Analysis

The bioaccumulation factor (BAF) was calculated for TPH in order to estimate the absorption rate of TPH between sediments and plant tissues (leaf, stem and root) using the equation below:

$$\text{Bioaccumulation factor (BAF)} = \frac{\text{Conc of parameter in organism}}{\text{Conc of parameter environment}}$$

Or

$$\frac{\text{conc of parameter in Macrophyte (sample)}}{\text{concof parameter in sediment}}$$

Regression analysis was employed using the Microsoft Excell[®] tool pack in order to determine the correlation between TPH in bottom sediments with that in plant tissues (leaf, stem and root). Analysis of variance was employed at the 95% confidence level to determine the degree of significance in interaction of TPH between sediments and macrophyte tissues and between macrophyte tissues (leaf, stem, and root).



PLATE1: PICTORIAL PRESENTATION OF RIVER NUN AT AMASOMA AXIS

III. RESULT

The results of the study are captured in Tables 2 - 4.

TABLE 2
TPH (ppm [mg/kg]) IN MACROPHYTES AND SEDIMENTS IN NUN RIVER AMASOMA

| Parameters | Stations | | |
|------------|--------------------|---------------------|--------------------|
| | ST1 | ST2 | ST3 |
| Leaves | 0.14 ^{ad} | 0.14 ^{ab*} | 0.11 ^{ba} |
| Stem | 0.18 ^{ac} | 0.18 ^{ac} | 0.14 ^{bb} |
| Root | 0.21 ^{ab} | 0.23 ^{bd} | 0.20 ^{ac} |
| Sediment | 0.21 ^{ab} | 0.27 ^{bc} | 0.36 ^{cd} |

**Means with the same letter superscript along the same column are not significantly different.*

**Means with the same letter superscript along the same row are not significantly different*

TABLE 3
CORRELATION CO-EFFICIENT FOR TPH IN SEDIMENT AND MACROPHYTE (LEAVES, STEM, AND ROOT).

| | Sediment | Leaves | Stem | Root |
|----------|----------|--------|-------|------|
| Sediment | 1 | | | |
| Leaves | -0.64 | 1 | | |
| Stem | -0.83 | 0.92 | 1 | |
| Root | -0.16 | -0.16 | -0.09 | 1 |

TABLE 4
BIOACCUMULATION FACTOR FOR TPH

| Parameters | Stations | | |
|------------|----------|------|------|
| | ST1 | ST2 | ST3 |
| Leaf | 0.67 | 0.52 | 0.31 |
| Stem | 0.86 | 0.67 | 0.39 |
| Root | 1.0 | 0.85 | 0.56 |

IV. DISCUSSION AND CONCLUSION

Despite the presence of potential anthropogenic sources of TPH in the river shores at the study stations, this study found only insignificantly low concentrations of TPH in sediment and plant tissues. This is in disagreement with the findings of previous works done on similar water bodies with human inputs[8]. However, the presence of TPH may be due to their easy affinity for bottom sediments and plant tissues. Also the presence of TPH in plant tissues was observed to be correlated to the amounts of these elements in bottom sediments because plants ingest or absorb them from sediments.[9] noted that the extent of bioaccumulation in biota is dependent on the chemical effect of the metal or pollutant, its tendency to bind to particular materials and or the lipid content and composition of the biological tissues. In a similar study [10] also observed differential rate of adsorption of heavy metals in leaf, stem, and root of bitter leaf and okra plants in the Niger Delta exposed to metal polluted soils.

The study reveal a spatial increasing trend in TPH in both sediments and plant tissues from station to station (station 1 > station 2 > station 3). One reason for this may be the fact that station 1 is a Jetty and landing terminal for all boats transport from the city to the hinterlands of southern- Ijaw and beyond. As such lots of petroleum products are landed on the jetty both for fueling and domestic use. This is result is in disagreement with the findings of [11] who experienced a trendless spatial variation of TPH in study stations with evidently different potential of TPH generation. However, it may be difficult to predict and identify which station and sources may produce more TPH. [12] put it aptly by saying that the exact identification of TPH sources to the Niger Delta soils is not feasible due to the variety of processes contributing to the formation and preservation of TPH in soils of this area.

Also, in all stations throughout the study the result indicate that the absorption of TPH by macrophyte tissues show that root > stem > leaf. The lower concentration of TPH in leaf samples may have been caused due to phytodegradation or phyto transformation of petroleum hydrocarbons which was subjected the contaminants to the bioremedial processes occurring within the areal part of plant itself[8].Hydrophobic chemicals are generally not sufficiently soluble in water or are bound so

strongly to the surface of the roots and may not pass beyond the root's surface due to the high proportion of lipids present at the surface, so cannot be easily translocated into the plant [13]

The mean level of Bioaccumulation factor (BAF) of TPH in plants samples was found to be 1 and lower than 1. The lower BAF value of leaf samples shows uptake of hydrophilic compound of petroleum hydrocarbons by root and translocation to the leaf through vascular system. In general, chemicals that are highly water soluble are not sufficiently sorbed to roots or actively transported through plant membranes [14].

Finally, these results show the mean value of TPH in macrophyte samples and sediments does not exceed the average global permissible limit in soil (1000mg/l) and also lower than the phytotoxic level in the plants (1000-12000 mg/l)[8]. It can be concluded that the River Nun at Amasoma Axis is only mildly polluted but there is reason to still monitor its water characteristic and promulgate land use ordinances to protect its fishery and entire ecosystem

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