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Abstract: The aim of this study was to assess the hydrocarbon contamination in addition to other sediment characteristics of a tidal creek in the Niger Delta, Nigeria. Total of seventy six sediment samples were collected in triplicates from four locations (AZ1, AZ2, AZ3- Azuabie creek and OK - Okujagu creek) monthly from July - December 2016. Standard Methods described in APHA were used to analyse conductivity, pH, nitrate, sulphate and phosphate while total organic carbon (%TOC) was determined by the method of Walkley and Black. Gas chromatography was used for the determination of target hydrocarbon analytes after extraction from sediment. Results show mean value ranges thus: pH (4.6-6.7), conductivity (3260.0-15333.3μS/cm), nitrate (1.4-3.9μg/g), sulphate (53.6-493.3μg/g), phosphate (0.14-3.17 μg/g), THC (7.9 -1144.6 μg/g), TPH (5.7-819.5 μg/g) and PAH (0.013-3.9 μg/g). All sediment variables examined showed significant difference (p<0.001) between locations, periods and had significant interaction (p<0.001) between location and period except TOC. TOC and Petroleum hydrocarbon contaminants were high within Azuabie creek compared to the Okujagu creek. The TPH levels exceeded the target value (50μg/g) but below the intervention value (5000 μg/g) of Department of Petroleum Resources (DPR) suggesting serious impact on the environment. PAH values obtained in this study fall within and above sediment quality guidelines (SQG) with regards to effect range low (ERL) for low (552 ng/g) and high (1700 ng/g) molecular weight PAH, effect range medium for low (3160 ng/g) and high (9600ng/g) molecular weight PAH. Principal Component Analysis (PCA) segregated sites within Azuabie creek as hotspots with hydrocarbon contamination particularly at location AZ1 and AZ2. The study concluded that sediment of the study area fall within moderate-high pollution with regards to hydrocarbon contamination traceable to anthropogenic activities in the area. Such level of hydrocarbon in sediments could be toxic to aquatic life.


I. Introduction

Water quality is becoming a major issue in countries affected by hydrocarbon extraction [1, 2, 3, 4, 5]. The petroleum industry, according to [6] contributes greatly to aquatic environmental degradation and pollution. This is a major challenge in the Niger Delta region of Nigeria where water and sediment contamination is on the increase due to human and hydrocarbon related activities. The widespread contamination of the environment by petroleum products is also due to the drive for use of petroleum-based products as gasoline, kerosene, fuel oil, mineral oil and asphalt. Kerosene in particular, is a major energy source to power cooking stoves in the Niger Delta region hence, the increased demand. [3] stated some human- mediated sources of petroleum products into the environment as oil production, marine transportation, atmospheric or aerial depositions from combustion of coal and gas flaring, direct ocean dumping, coastal, municipal and industrial wastes, and runoffs. This is the situation in the Niger Delta region of Nigeria where oil exploration and production, transportation and storage and in recent times, illegal oil refining and bunkering activities has caused substantial pollution along the coast lines, creeks, rivers and estuaries with huge depletion of the sources of livelihood of the people. Petroleum hydrocarbons though not usually regulated as hazardous wastes is one of the major pollutant frequently discharged into the coastal water, [7, 8]. In marine sediments, they are naturally present in low concentrations but larger amount has been reported to come from petrogenic and pyrogenic sources [9, 10, 11]. Bottom sediment is the habitat of many aquatic organisms and known as potential reservoir of petroleum hydrocarbons in marine environments, posing risk of bioaccumulation [12, 8, 13]. [14] reported that hydrocarbon pollution impairs the growth and development of marine organisms, causes fish, crustaceans and mollusks to acquire objectionable odour or flavor which reduces their market value and acceptability, ultimately it leads to death of both flora and
fauna which is common in the Niger Delta [15]. The Azuabie creek on the upper reaches of the Bonny estuary in the Niger Delta is prone to domestic, municipal and industrial waste discharge and in recent times route for transportation of illegally refined petroleum hydrocarbons. This study therefore seeks to assess the hydrocarbon contamination of the sediments obtained from Azuabie creek using an adjacent creek (Okujagu) as control site.

II. Materials And Methods

Study area

The study creek (Azuabie) is used for various kinds of fishing activity and also serves as transportation route for commercial and industrial operations. It is located in the upper reaches of the Bonny estuary, Niger Delta (Fig. 1). Mangrove forests flanking both sides of the creek are gradually being cleared for development purposes. Okujagu creek (control site) has similar fishing and vegetational characteristics but less industrial activities compared to Azuabie creek.

Fig. 1: Map showing study area

Sample Collection and Analysis

Total of seventy six sediment samples were collected in triplicates from four locations (AZ1, AZ2, AZ3- Azuabie creek and OK- Okujagu creek) on a monthly basis from July - December 2016 using an Ekman grab. July - September represent wet season while October - December represent dry season period. Samples were wrapped in properly labeled aluminum foils and put in ice coolers before taken to the laboratory for analysis. Procedures described in Standard Methods for the examination of water and waste water analysis [16] were adopted in the analyses of pH, conductivity, nitrate, phosphate while the total organic carbon (TOC) in percentage was determined by the method of [17]. Hydrocarbons (total hydrocarbon content -THC, total petroleum hydrocarbon - TPH and polycyclic aromatic hydrocarbon - PAH) were extracted from sediment with 100 ml analar grade of methyl isobutyl ketone. The extracts were centrifuged for 5 minutes and later decanted. Supernatants were reduced to 5 ml using a rotary evaporator maintained at 20°C as used by [18]. Gas
Hydrocarbon Contamination of Sediments in the Niger Delta Region: a case study of the Azuabie.

Data Analysis

Two-way analysis of variance (General linear model) after log (x+1) transformation of data was used to detect significant difference between locations, periods and interaction of location with period. Post-hoc analysis using Tukey test indicated where actual significant difference occurred either for location or period. Principal component analysis (PCA) after normalization of data was used for site discrimination based on sediment variables. The softwares Ms Excel, Minitab R16 and Primer 6 were used in data analysis.

III. RESULTS

The spatial and temporal characteristics of the sediment is presented in Fig.2a - j: Mean pH value was lowest (4.6) at location OK and highest (6.7) at AZ2 while mean conductivity was lowest (3260.0 µS/cm) and highest (15333.3 µS/cm) at the same location (OK). Nitrate, phosphate and sulphate also varied in space and time with sulphate values generally higher. Mean THC values ranged from 7.9 - 1144.6 µg/g while mean TPH values ranged from 5.7 - 819.5 µg/g and mean PAH values ranged thus 0.013 - 3.9 µg/g. The hydrocarbons showed the same trend in space and period but TOC was observed to be lowest (1.04%) at AZ3 and highest (4.6%) at AZ1. Sediments obtained from Azuabie creek generally had higher concentrations of key contaminants (THC, TPH and PAH) compared to the control creek (Okujagu). PCA showed the four locations discretely positioned based on their sediment characteristics. All sediment variables examined showed significant difference (p<0.001) between locations, periods and had significant interaction (p<0.001) between location and period except TOC (Table 1) suggesting that the concentration of TOC in sediments was regardless of the interplay of location and period. The significant differences in space and time occurred thus for the following parameters examined.

Table 1: ANOVA Table with F-values sediment variables.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Location (F-values)</th>
<th>Period (F-values)</th>
<th>Location interaction Months (F-values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13.24***</td>
<td>8.64***</td>
<td>9.95***</td>
</tr>
<tr>
<td>Conductivity(µS/cm)</td>
<td>30.82***</td>
<td>69.21***</td>
<td>10.68***</td>
</tr>
<tr>
<td>Nitrate(µg/g)</td>
<td>488.04***</td>
<td>534.45***</td>
<td>511.71***</td>
</tr>
<tr>
<td>Sulphate(µg/g)</td>
<td>8.13***</td>
<td>57.04***</td>
<td>14.13***</td>
</tr>
<tr>
<td>Phosphate(µg/g)</td>
<td>3.80*</td>
<td>77.15***</td>
<td>13.87***</td>
</tr>
<tr>
<td>THC(µg/g)</td>
<td>112.10***</td>
<td>352.32***</td>
<td>40.63***</td>
</tr>
<tr>
<td>TPH(µg/g)</td>
<td>43.57***</td>
<td>265.13***</td>
<td>32.85***</td>
</tr>
<tr>
<td>PAH (µg/g)</td>
<td>50.14***</td>
<td>128.51***</td>
<td>34.71***</td>
</tr>
<tr>
<td>TOC (%)</td>
<td>3.26*</td>
<td>1.98ns</td>
<td>1.62ns</td>
</tr>
</tbody>
</table>

Key * = P < 0.05; ** = P < 0.01; *** = P < 0.001; ns (not significant)
Sediment characteristics showed significant variations in space and time with both factors also having significant interactions. This suggests discrete effect of human activities on the aquatic system with an overlap of the effect of time and space on the entire creek. The pH of the sediment was moderately acidic and comparable to values obtained in the upper Bonny estuary [20, 21]. Locational differences could be due to sediment composition and respective microbial activities within the sediment coupled with the influence of seasons in the area. Freshwater and saline water intrusion from both ends of the creek played key role in the spatial difference.
observed in the conductivity of the sediment. Dilution effect due to rainfall could cause the observed seasonal influence. Conductivity values obtained in this study also match with the documentations of [22] in the study area. No particular trend was observed in the nitrate concentration in sediment but values observed within Azuabie creek was significantly different from those got from the control station. Phosphate levels generally increased towards the wet season period traceable to increased run-offs from nearby abattoir and other human activities. Significant differences in sulphate, nitrate and phosphate values obtained in the study area could also be due to environmental differences and such values match the reports of [23, 22]. Total hydrocarbon (THC) was generally high within Azuabie creek with significant differences observed in time and space. Elevated concentrations of THC observed coincided with periods of oil spill from bunkering operations as thick films of oil was conspicuously observed during sampling. THC level in sediments of this study was lower compared to the values (1.403±0.61 – 3.755±113.14 µg/g) documented by [24] and 400 – 6205 µg/g by [25] in other tidal creeks in the Niger Delta. Studies of the New Calabar River showed THC values ranging from 112.30±17.07 – 657.30±95.14 µg/g [26] accommodating the range observed in this study. Locations within the Azuabie creek shored similar hydrocarbon levels except at AZ3 that closely related to the control point (OK). All months of study had significant differences (p<0.001) in THC except in October and November that had the lowest concentration possibly due to reduced inflow from land based sources. TPH is of environmental interest because they are toxic to human system and animals. Some of the TPH compounds are carcinogenic and poses health hazards [27]. Values of TPH obtained in this study were however lower than mean values (1242.3 - 5199.5 µg/g) obtained by [27] but in top soils within the Niger Delta area. TPH values obtained in this study is also comparable to the range of 18.01 ±0.04 - 210.23 ±1.18 µg/g (epipelagic sediment) and 5.00 ±0.82 - 232.00 ±3.23 µg/g (benthic sediment) documented by [18] in the Niger Delta. The TPH value of the current study also falls within the range (12.59 - 1.100 µg/g) reported by [28] in an estuary in South Africa. The TPH levels in this study however, exceeded the target value (50 µg/g) but below the intervention value (5000 µg/g) of [29] suggesting serious impact of anthropogenic activities. [30] stated that majority of the sediment samples collected from the Niger Delta rivers does not pose a serious threat to the ecosystem except for two locations, Imo river and Oginni canal where PAH-contaminated sediments were likely to be acutely toxic to certain sediment dwellers. The PAH concentrations in the current study was generally higher compared to the 65 - 331 ng/g reported in sediments and 24 - 120 ng/g in soils of the Niger Delta region [30]. Values of PAH reported in sediment elsewhere around the world are thus: nd –102,000 ng/g [31] 6-8,400 ng/g [32] 31–133 ng/g [33]. The PAH values obtained in this study were within and above sediment quality guidelines (SQG) with regards to effect range low (ERL) for low (552 ng/g) and high (1700 ng/g) molecular weight PAH, effect range medium for low (3160 ng/g) and high (9600ng/g) molecular weight PAH taken from [34] and [35]. The elevated PAH concentration in this study is traceable to pyrogenic and pyrogenic origin due to the operations of marine boat combustion engines and huge spills of petroleum hydrocarbon from bunkering activities. Such levels of PAH could cause severe biological harm and tainting to biota and seafood within the aquatic system of the study area. In general, sediments are classified into three classes: low, moderate and high, with respect to their hydrocarbon content [36]. Based on the findings of this study, the hydrocarbon content of sediments of Azuabie creek could be rated as moderate- high pollution status. High concentrations of petroleum hydrocarbons have been reported in sediments of estuaries, harbours, bays and in coastal areas receiving industrial and urban discharges [37,38, 39]. Multivariate analysis showed sampling sites AZ1 and AZ2 were clearly discriminated based on hydrocarbon concentrations indicating sites as hotspots within the creek. TOC was also high at AZ1 within the creek. The TOC values obtained in sediments of this study compared favourably with values (1.03 - 6.38%) reported within the Niger Delta [30]. [40,41] have reported linear relationship between TOC and PAH in sediment but it also depends on factors such as temperature and composition of organic matter which affects the level of PAHs formed during incomplete combustion of organic matter or during its thermal maturation [42]. In this study, correlation between TOC and PAH was not significant (r=0.27, P=0.05)) indicating that PAH may be of recent origin and had not fully incorporated into organic matter but may have acute toxicity on aquatic life.

V. Conclusion

In conclusion, examination of the sediment of Azuabie creek showed that pH was generally acidic with no obvious trend while conductivity increased toward the saline end of the creek showing seasonal influence. The nutrient parameters (nitrate, phosphate and sulphate) also varied in time and space with sulphate having higher values. THC, TPH and PAH within the Azuabie creek were generally high and followed a particular trend with significant difference in space and period. TOC was also high within the creek traceable to wastes from nearby waste dumps and city abattoir. PCA discriminated sites within the Azuabie creek as hotspots with hydrocarbon contamination. The study concluded that sediment of the study area could be rated as moderate-high pollution vis-à-vis hydrocarbon contamination that may be toxic to aquatic biota.
Hydrocarbon Contamination of Sediments in the Niger Delta Region: a case study of the Azuabie ...

Reference

[14] W.B. Dambo, Tolerance of the Periwrinkles Pachymelania aurita(Muller) and Tymanotonus fuscatu (Linne) to refined oils, Environmental Pollution (79), 1992, 293–296.


