Total Petroleum Hydrocarbon Content in Surface Water and Sediment of Qua-Iboe River, Ibeno, Akwa-Ibom State, Nigeria

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ABSTRACT: The total petroleum hydrocarbon content in surface water and sediment of Qua Iboe River, Akwa Ibom State, Nigeria was assessed by randomly collecting samples from five sampling points of the study area and from a control site. The samples were extracted with dichloromethane (DCM) by liquid-liquid partition for water and Soxhlet extraction for sediments followed by subsequent clean up on column chromatography and analyzed by gas chromatography-flame ionization detection (GC-FID) for the determination of total petroleum hydrocarbons (TPH). The results showed variation of total petroleum hydrocarbon (TPH) content from 90 to 250 µg/L in the water and 270 to 830 mg/kg in the sediments, with mean value of 168.33±59.29 µg/L and 606.83±229.48 mg/kg respectively. The average amount of TPH in the water samples collected from all the sampling points was generally lower than the EU standard limit of 300 µg/L. However, the levels in the sediments exceeded the EGASPIN target value (50 mg/kg) for mineral oil but were below the intervention value (5,000 mg/kg), this indicates a serious impact of oil industrial activities on the area. Hence, our findings have indicated evidence that Qua Iboe River is under pollution threat and underscore the need for early remediation if adverse health defects are to be prevented.

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Keywords: Total petroleum hydrocarbon, GC-FID, surface water, sediments

Nigeria has been exploring and exploiting crude oil for decades and the consequences on the oil producing and processing areas have become highly problematic in the onshore and offshore installations (Atunbi, 2011). The unpleasant and environmentally undesirable pollution effects of the waste from these explorations calls for best practicable technology in conversion process involved in obtaining petroleum and petrochemical products from crude oil which generate various types wastes (Uzoekwe and Oghosanine, 2011). The wastes can be generally classified into oily materials, spent catalyst, spent chemicals and other residuals which found their ways into the environment due to incessant release. The increased oil activities have resulted in extensive environmental pollution by oil spills involving blowouts, leakages from tanks or tanker trucks and dumping of waste petroleum products into the environment. The aftermaths of these activities have been documented (Adeniyi and Afolabi, 2002). Crude oil, when refined contains a wide range of components such as hydrocarbons, heavy metals, dye additives, antioxidants, and corrosion inhibitors (Akpordio, 2008). The refined products show higher toxicity compared to crude oil since metal speciation is altered and new metals added to the matrix during the refining processes (Commendatore and Esteves, 2004).

Total petroleum hydrocarbons (TPH) are a large family of several hundred chemical compounds that originally come from crude oil. They are found in the range of $C_6$ through $C_{35}$ as mixture containing hundreds to thousands of hydrocarbons including aliphatic (straight carbon chain) and aromatic (carbon ring) compounds. Some hydrocarbon mixtures may also contain priority pollutants including volatile organic compounds (VOCs), semi-volatile compounds (SVOCs) and metals, each of which have their own specific toxicity information (ATSDR, 1999). The presence of chemical contaminants in the coastal environments from many anthropogenic sources is a major threat to the marine water (Charriau et al., 2009). Large amounts of these contaminants through sewage, petroleum spills, municipal and industrial discharges, automobile wastes and vehicular emission due to incomplete combustion of fossil fuels are possibly carried by river runoffs through their estuaries into the sea (Kachel, 2008). Petroleum hydrocarbons are one of the major pollutants which are frequently discharged into the coastal water, though not usually regulated as hazardous wastes (ATSDR, 1999). Although they are naturally present in very low concentration in the marine sediments, but larger amount comes from petrogenic and pyrogenic sources. Thus, the bottom sediment being the habitat of many aquatic organisms is recognized as reservoir...
of petroleum hydrocarbons in the marine environments with high risk of bioaccumulation (Filho et al., 2013). In this study we report the total petroleum hydrocarbon contents in surface water and sediments of Qua Iboe River located in Ibeno Local Government Area of Akwa Ibom State, Nigeria, with a view on the pollution status.

MATERIALS AND METHODS

Sampling sites: Qua Iboe River is located in Ibeno Local Government Area of Akwa Ibom State in Niger Delta of southern Nigeria (Fig 1). Ibeno has a land mass of 1200 Km² and lies between latitudes 4° 32’N and 5°33’N and longitudes of 7°25’E and 8°25’E. The Local Government Area is the host community to Mobil Producing Nigeria Unlimited. The control site for the study is Etinan Local Government Area, because it is free from oil exploration and other kinds of marine commercial activities.

Water collection: Water samples were collected using a glass cup and amber bottle. One liter of water at a depth 5 cm was collected at several points within each site and pooled together to obtain one liter of composite sample and the procedure was repeated for each site. The water samples were filtered and preserved on the site with hydrochloric acid (HCl) and stored in amber bottles at temperature of 4°C extracted within 14 days of collection.

Sediment collection: Sediment samples were collected using a core sediment grab sampler. Several sediments were collected at different sampling locations within each site and pooled together to obtained 300 g of composite sample, the procedure was repeated for each site. The sediment was stored at 4°C and extracted within 14 days of collection.

Sample preparation and extraction: The petroleum hydrocarbons were spiked into the sediment and water by dissolving equal masses of diesel and lubricating oils in acetone-n-hexane (40 mL) and then mixing the solution with 40 g of sediment and 100 mL of water (WSDE, 1997).

Liquid-liquid extraction of water sample: One liter of the water was placed into a separatory funnel with a glass stoppered using 50 mL of dichloromethane (DCM) as the extracting solvent. The separatory funnel was shaken vigorously for at least 10 min and the organic layer was allowed to separate clearly from the aqueous phase for a minimum of 15 min. The lower organic layer was collected into a separate flask bottle. The extraction was repeated three times for each sample. Water residue was expelled from the organic layer by passing the extracts through funnel containing filter paper with sodium sulphate. The extract for each sample was concentrated using rotary evaporator with water bath at 35°C. Concentrated extracts were transferred to a pre-weighed bottle and evaporated to dryness (Manahan, 2003).

Soxhlet extraction of sediment sample: Composite sample (100 g) was weighed and air dried,
homogenized and sieved. The procedure was repeated for all the sample including the control. The sediment sample was wrapped in a filter paper and placed in a thimble, and loaded into the main chamber of the Soxhlet extractor and extracted with dichloromethane (DCM) over a period of 24 hr. The extracts collected was concentrated using a rotary evaporator at 35°C. The concentrated extracts were transferred to pre-weighed sample bottle and evaporated to dryness (Saari et al., 2007). This was followed up by a column chromatography for cleanup.

Silica gel cleanup and separation: The water and sediment extracts were transferred into a 10 mm ID × 30 cm chromatographic column packed with 10 g activated silica gel slurry with about 2 cm anhydrous sulphate layer on top. The column was eluted with 20 mL of n-hexane to obtain the hydrocarbon fraction. The eluates were concentrated to about 2 mL with rotary evaporator at 30°C and evaporate to dryness. The spiked sample was treated the same way as the main sample for quality assurance (Maioli et al., 2011).

Gas Chromatography Analysis: All the cleaned sample extracts were analyzed using Agilient 7820A gas chromatograph (GC) equipped with flame ionization detector and HP-5 fused silica capillary column (30m × 0.32 mm ID x0.25 μm film thickness). The carrier gas was helium at flow rate of 1.75 mL/min and average velocity of 29.47 cm/sec. Exactly 1 μL of the sample extract was injected in splitless mode at 300°C. The column temperature was held at 40°C for 1 min and then increased at 7°C/min to 320°C. The detector temperature was 300°C (Kim et al., 2013). The gas chromatograph was calibrated with petroleum hydrocarbon calibration working standards prepared in the range of 0.05–20 μg/mL using n-hexane as diluent. Calibration curves were plotted, and average response factor was generated with Agilent Chemstation chromatography software for each analyte. The curves were linear with correlation coefficients ranging from 0.9846 to 0.9919. The unresolved peaks were quantified using the response factor of nC-15 in accordance with the method of Luan and Szelewski (2008). TPH was integrated with baseline holding and peak sum slicing and then quantified as the sum of concentrations of the n-alkanes that eluted from nC-9 to nC-36 and UCM. Data analysis was carried out using the Agilent software from which the low molecular n-alkanes/high molecular n-alkanes and unresolved n-alkanes/resolved n-alkanes were obtained (Cortes et al., 2012).

Statistical Analysis: All determinations were replicated four times and the results were reported as mean ± standard deviation. Student’s t-test was used for the comparison between the two means. ANOVA was used for more than two means. A difference was considered statistically significant when P<0.05

RESULTS AND DISCUSSION

Levels of Total Petroleum Hydrocarbons in the Water Samples: Total petroleum hydrocarbons (TPH) in the surface water were evaluated in all the sampling points. The results are summarized in Table 1. The TPH concentration in the study area varied widely across the five sampling locations from 2.50-250.00 μg/L. The highest concentration was observed at site WS2, followed by WS5 and WS4 as shown in Figure 2. Sites WS2 and WS5 are creeks that receive sewage from oil industries operating in the area, and improper clean up after oil spillage could also account for the higher concentration of TPH in the site. However, the TPH concentration in WS4 may be attributed to commercial activities such as fishing with speed boat whose engine might be discharging engine oil or lubricating oil into the water. But the WS3 and WS1 exhibited low concentration of TPH due to less anthropogenic activities and less commercial activities. Generally, the TPH concentration was lower in the control site compared to the study area. The spatial distribution of petroleum hydrocarbons in the water matrix is depicted in Figure 2. The total mean concentration of TPH (168.33μg/L) from all sample sites was lower than the European Union Environmental Protection Agency (EUEPA, 2009) acceptable standard limit for petroleum hydrocarbons (300 μg/L) in river and basin water.

The level of water TPH from this study (168.33 μg/L) was significantly lower (P<0.05) compared to values reported in Niger Delta region. The levels of TPH was reported for groundwater samples (1352–12,110 μg/L) collected from some communities in Niger Delta, Nigeria were found to be high (Alinnor et al., 2014) while surface water from Ubeji in Warri, Nigeria contain 73,500 μg/L of TPH (Adewuyi et al., 2011). Other regions around the world including Strait of Johor, in Peninsular, Malaysia reported 25-2,795 μg/L (Suratman, 2013) and Deepwater Horizon, Gulf of Mexico contains 60,000–260,000 μg/L of TPH (Sammarco et al., 2013). However, other studies have reported lower values of TPH than obtained in this study, these include water samples from Dungun River basin water, Malaysia was 12–41 μg/L (Suratman, 2013) and Levantine Basin, Israeli Coastline was 19–88 μg/L (SOGRLI, 2014).
Total Petroleum Hydrocarbon Content in Surface.....

Table 1: Total Petroleum Hydrocarbons (TPH) in Qua Iboe River Water (μg/L)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Study Area Sampling Site</th>
<th>Total Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WS 1</td>
<td>WS 2</td>
<td>WS 3</td>
</tr>
<tr>
<td>Total n-alkanes</td>
<td>63.52</td>
<td>183.25</td>
<td>91.34</td>
</tr>
<tr>
<td>UCM</td>
<td>29.32</td>
<td>64.38</td>
<td>42.83</td>
</tr>
<tr>
<td>TPH</td>
<td>92.84</td>
<td>247.63</td>
<td>134.17</td>
</tr>
<tr>
<td>C15-C19</td>
<td>ND</td>
<td>0.91</td>
<td>ND</td>
</tr>
<tr>
<td>C18-C22</td>
<td>0.03</td>
<td>2.56</td>
<td>5.20</td>
</tr>
<tr>
<td>C25-C35</td>
<td>33.86</td>
<td>11.61</td>
<td>21.70</td>
</tr>
<tr>
<td>C31/C19</td>
<td>ND</td>
<td>0.53</td>
<td>ND</td>
</tr>
<tr>
<td>U/R</td>
<td>0.21</td>
<td>0.48</td>
<td>0.11</td>
</tr>
</tbody>
</table>


Levels of Total Petroleum Hydrocarbons in the Sediment Samples: Sediments are soil particles found at the bottom of water and are regarded as most common river pollutant. In this study, the concentrations of TPH in Qua Iboe River sediments are presented in Table 2. The values ranged from 5.0-827 mg/kg, with site SS2 indicating the highest concentration of TPH, followed by site SS5 while the lowest concentration of TPH was obtained from site SS1, which could possibly be related to low exploration of oil in the area. There was no doubt that larger contribution of hydrocarbon pollutants in the sediment of Qua Iboe River water was from discharge, as well as the introduction of the industrial effluents and leachates from oil companies since this is the main hydrocarbon related activities. Notwithstanding, there is statistically significant difference (P<0.05) in the levels of TPH determined between the sampling stations.

Table 2: Total Petroleum Hydrocarbon (TPH) in Qua Iboe River Sediments (mg/Kg)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Study Area Sampling Site</th>
<th>Total Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS 1</td>
<td>SS 2</td>
<td>SS 3</td>
</tr>
<tr>
<td>Total n-alkanes</td>
<td>89.41</td>
<td>286.71</td>
<td>169.32</td>
</tr>
<tr>
<td>UCM</td>
<td>183.65</td>
<td>539.51</td>
<td>216.37</td>
</tr>
<tr>
<td>TPH</td>
<td>273.06</td>
<td>826.62</td>
<td>385.69</td>
</tr>
<tr>
<td>C15-C19</td>
<td>1.85</td>
<td>3.67</td>
<td>0.93</td>
</tr>
<tr>
<td>C18-C22</td>
<td>2.14</td>
<td>6.40</td>
<td>4.31</td>
</tr>
<tr>
<td>C25-C35</td>
<td>42.87</td>
<td>68.92</td>
<td>48.19</td>
</tr>
<tr>
<td>L/H</td>
<td>0.34</td>
<td>0.96</td>
<td>0.58</td>
</tr>
<tr>
<td>C31/C19</td>
<td>26.40</td>
<td>22.82</td>
<td>18.24</td>
</tr>
<tr>
<td>U/R</td>
<td>1.33</td>
<td>4.85</td>
<td>2.42</td>
</tr>
<tr>
<td>CPI</td>
<td>0.88</td>
<td>3.40</td>
<td>1.90</td>
</tr>
<tr>
<td>ACL</td>
<td>29.37</td>
<td>30.65</td>
<td>29.81</td>
</tr>
</tbody>
</table>

SS: Sediment Sample; UCM: unresolved complex mixture; TPH: total petroleum hydrocarbon; L/H: low molecular n-alkanes/high molecular n-alkanes; U/R: unresolved n-alkanes/resolved n-alkanes; CPI: carbon preference index; ACL: average carbon chain length, ND: Not Detected.
Petroleum hydrocarbons in the sediments of the study area were found to be significantly higher with mean concentration of 606.83 mg/kg than in control site (5.0 mg/kg) due to the onshore and offshore activities by the operating oil companies. Other activities like bunkery and improper cleanup after oil spillage may be responsible for the high TPH. Although no sediment guideline is in place for the TPH, nevertheless, four levels of total petroleum hydrocarbon (TPH) pollution were suggested as reported by Ritchie et al. (2001) These are unpolluted (10–15 mg/kg), slightly polluted (15–50 mg/kg), moderately polluted (50–200 mg/kg) and heavily polluted statuses (>200 mg/kg).

This classification is not entirely different from the respective target and intervention values of 50 mg/kg and 5,000 mg/kg set as environmental guidelines and standards for the petroleum industry in Nigeria (EGASPIN) for soil and sediment TPH by the Department of Petroleum Resources, Nigeria (DPR, 2002). Considering our findings, the TPH concentrations of Qua Iboe River sediments are significantly lower (P<0.05) than the intervention level across the study area. However, the TPH are higher than target level, which is the level that requires attention when TPH are above standard limits (Olajire et al., 2007). The mean TPH levels in the sediment compartment of the study area (606.83 mg/kg) were found to be comparatively lower than those reported (496–6972 mg/kg) for sediments from Ceuta harbour, North Africa (Guerra-Gracia et al., 2005). But soil in communities in Niger Delta region of Nigeria are reported to have higher TPH of 1242-5,200 mg/kg (Alinnor et al., 2014) and Bizerte Lagoon, Tunisia is reported to be 0.05–20 mg/kg (Mzoughi et al., 2005). Non-polluted sediments reported in some studies include those from coastal area of Putatan and Papar-Sabah, Main Outfall Drain in Al-Nassiriya City, Southern Iraq, and coastline and mangroves of the northern Persian Gulf.

**Conclusion:** The total petroleum hydrocarbon contents from Qua Iboe river surface water and sediment were determined using GC-FID and reported for the first time. Our findings have indicated evidence of crude oil contamination of the river. The TPH pollution levels may have serious health implications, so epidemiological studies on the indigenous people of the area is imperative. It is recommended that oil fingerprinting should be carried out to identify pollution sources with a view to providing cost-effective remediation measures if adverse health defects are to be prevented.

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