Quantification and Distribution of Polynuclear Aromatic Hydrocarbons (PNAs) in Surface Waters in the Vicinity of Kokori Oil Field, Nigeria

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ABSTRACT: The distribution pattern and sources of sixteen PANs listed as priority pollutants were investigated in eight composite water samples using Gas Chromatography (GC) with a Hewlett-Packard model 6890 with 30m x 0.28 capillary column. Analytical observation of the percentage distribution of PNAs concentration in the study area show that SSy(20.12%)>SSx(16.75%)>SSz(16.01%)>SSa(14.43%)>SSb(13.24%)>SSc(12.06%)>SSd(6.84%)>SSe(0.55%). The observed distribution of genotoxic (Gen.) and carcinogenic (Car.) PNAs and other PNAs in the study area show that the Gen. and Car PNAs recorded 29.58% over other PNAs with 70.42%. The percentage distribution of low PNAs/high PNAs and ratio analysis show that these sources are petrogenic and pyrogenic but dominated with petrogenic PNAs.

Polynuclear aromatic hydrocarbons (PNAs) are fused-ring compounds that enter natural waters via wastewater effluents from coke and petroleum refining industries, accidental spills and leakage, rainwater runoff from highway or from intentional refining industries, accidental spills and leakage, wastewater effluents from coke and petroleum fused-ring compounds that enter natural waters via polynuclear aromatic hydrocarbons (PNAs) are ubiquitous in the environment being present in air, smoke, asphalt road and roofing operations, (Berko, 1999). PNAs exhibit toxic characteristic at low concentrations and several have been listed as priority pollutants to be monitored in industrial effluents, natural waters, (Watts, 1997). PNAs are generally insoluble in water but can be readily solubilised in organic acids. They are therefore adsorbed on particulates and any oil contaminant that may be present in water, sediment and soil because of their lipophilic, high boiling point and hydrophobic properties (Lundstedt, et al., 2003). Their effects and fate in nature are of great environmental and human health concern due to their widespread occurrence, persistence in aquatic ecosystem and carcinogenic properties as well as having cardiovascular, bone marrow and liver toxicity, (IPCS, 1998 and Muller, 1997). PNAs are ubiquitous in the environment being present in air (Berko, 1999), soil (Wcislo 1998), water (WHO) and food such as cereals, grains, flour, bread, vegetable, fruits, fish, meat, processed or picked food and contaminated cow and human breast milk, (FSA, 2002; Falco, et al., 2003 and Azza, 2006). The need to monitor PNAs concentrations in aquatic environment around oil installation is imperative because there are no data on PNAs status around oil installations and the attendant human and environmental effect of these persistent and organic pollutants (POPs).

MATERIALS AND METHODS

Study area
The study area falls within the Kokori oil-field and is located between latitude 6° 02’ to 6° 05’N and longitude 5° 36’ – 5° 42’E. The oil wells have been in operations for over 30 years. The study area covers an approximate area of 2km² with access road made of asphalt connecting various oil well head. Well 13, 34, 35 and 13 are in a fenced land measuring about 200 sq feet. Also, well 14 36 37 in a fenced land measuring 200sq feet. Anthropogenic activities in the area include: oil/gas extraction (with oil well-heads and flow station), and peasant agriculture. According to UNDP (2006), the rainfall pattern is the characteristics of the rainforest zone with mean annual rainfall of 3000mm. Temperature are high and fairly constant throughout the year. Average monthly temperature for the warmest months (February to April) ranged from 28°C to 33°C while the average monthly temperature for the coolest months (June – September) ranged between 21°C and 23°C.

Sampling
Samples were collected in the month of June 2007. All sample containers were thoroughly washed with laboratory grade phosphate detergent and then rinsed with deionized water. The containers were then heated for about 30 minutes until dryness. Samples were collected in a litre amber glass bottle with Teflon-lined screw-cap, 5ml of 1:1 HCl acid was added. Samples were transferred from sample station in container with ice chest and stored at ≤ 4°C for 5 days before extraction and analysis as recommended by OIEWG (1999) and APHA, 1998.

Analysis
Samples for PNAs analysis were extracted with methylene chloride, dried with anhydrous Na₂SO₄ and solvent exchanged into hexane. Clean up and fractionation was done using silica gel permeation chromatography. Final extracts after concentration using a rotary evaporator was packed in 2mL GC vials and analysed with a gas chromatograph (GC), Hewlett-Packard model 6890 with a 30m x 0.25mm capillary column (Crosslinked 50% pH siloxane) and a flame ionization detector. GC column conditions: Column made up of 5% pims (100/120
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mesh) coated with 3% OV-17 packed in a 1.8 + 2mm 10 glass column with Helium carrier gas at 40mL/min. flow rate. Column temperature held at 100°C for 4min, there programmed at 8°C/min to a final hold at 280°C. H₂ and Air gas were used to light up the fid. PnAs levels was accomplished using a seven-point external standard (APHA, 1998). The standard curves were linear, with correlative confluent for the investigated PnAs ranging between 0.997 and 0.999, no external standards were employed in the qualification using the GC. The analysis was done at Thermostell laboratory, Effurun Warri.

RESULTS AND DISCUSSION

Analyses of result show that, there is high concentration of PANs in the study area with mean values ranging from 0.2309 to 1.0468mgL⁻¹ as shown in Table 1. The cumulative results also indicated that the total concentration of PnAs in the various sample station is in the order of SSY > SSX > SSZ > SS T > SS W > SS U > SS V > SS A. The results further reveal that SSXYZ has 52.88% of the total concentration in the study area while SS UVW has 32.14% with SS T and SS A having 14.43% and 0.55% respectively. This shows that well- head 14, 36 and 37 contributed more to the release of these contaminates in the study area. The mean concentration distribution of the sixteen PnAs listed as priority pollutant show that the 2 membered ring occupied the lowest % (9.7%) from the total PnAs concentration of 9.491mgL⁻¹. Similarly, the 5 and 6 membered ring accounted for 9.70% and 12.46% respectively. While the 4 membered ring having 22.34%, the 3 membered ring accounted for the highest % (46.40%).

Investigation into the sources of PnAs have used the molecular ratio of some specific hydrocarbons (Soclo et al., 2000; Yunker et al., 2002; Lin, et al.; 2005 and Emoyan et al., 2008). From the computed Ant/178 ratio of 0.004, flt/flt + pyr of 0.57; flu/pyr of 2.13 and phe/Ant of 1.03 reveal that petrogenic and pyrogenic source contributed to the distribution of these priority contaminant in the study area. However, the results show that low molecular weight hydrocarbon (LPnAs) accounted for 55.5% while high molecular weight hydrocarbon (HPnAs) recorded 44.5%, which is an indication that the sources of PnAs concentration in the study area is of petroganic dominance.

Table 1:

<table>
<thead>
<tr>
<th>PnAs</th>
<th>Mean Concentration level at the study area</th>
<th>Canadian Guidelines CCME, 2008</th>
<th>Netherlands MPC Guideline CCME, 2008</th>
<th>NA</th>
<th>MPC</th>
<th>Guideline</th>
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<tbody>
<tr>
<td>Nap</td>
<td>0.8634</td>
<td>0.000011</td>
<td>NA</td>
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<tr>
<td>Ace</td>
<td>0.7428</td>
<td>0.000058</td>
<td>0.0012</td>
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<tr>
<td>Flu</td>
<td>1.0468</td>
<td>0.0003</td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ant</td>
<td>0.8421</td>
<td>0.000012</td>
<td>0.00007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phe</td>
<td>0.8714</td>
<td>0.0004</td>
<td>0.0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fla</td>
<td>0.6594</td>
<td>0.000004</td>
<td>0.0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyr</td>
<td>0.4918</td>
<td>0.000025</td>
<td>NA</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Chr</td>
<td>0.4745</td>
<td>NA</td>
<td>0.0003</td>
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<tr>
<td>B[a]A</td>
<td>0.4950</td>
<td>0.000018</td>
<td>0.00001</td>
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<td></td>
</tr>
<tr>
<td>B[a]P</td>
<td>0.2309</td>
<td>0.000015</td>
<td>0.00005</td>
<td></td>
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</tr>
<tr>
<td>B[k]</td>
<td>0.3938</td>
<td>NA</td>
<td>0.00004</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>B[ghi]P</td>
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<td>NA</td>
<td>0.000033</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA: Not Available</td>
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</table>

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Comparing the mean concentration values of some selected PNAs in the study area with International guidelines for the protection of aquatic lives as shown in Table II, show that the concentration ratio of the observed PNAs with these guidelines is well above 1:100. Result screening show that the oil well-head and the flare site recorded 99.45% of the total concentration while the control point accounted for 0.55%.

**Conclusion:** Analyses of results show that, there is high percentage of PNAs in the study area when compared with International guidelines for the protection of aquatic ecosystem. The sources of these POPs are of patrogenic dominance as shown in the results.

**REFERENCES**


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Falco, G; Domingo J.L; Lobet J. M; Teixido A; Casas C; Muller L. (2003). PAHs in foods: Human Exposure through the Diet in Catalonia, Spain, J. Food Protection, 66, 2325-231.

(FSA), Food Standard Agency of UK (2002). PAHs in the UK diet: 2000 Total Diet Study Samples. Food Survey Information Sheet No 31/02. UK. FSA.


